TECHNICAL ASSISTANCE DOCUMENT
FOR THE
NATIONAL AIR TOXICS TRENDS STATIONS PROGRAM

Revision 4

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# ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>ADQ</td>
<td>audit of data quality</td>
</tr>
<tr>
<td>AIRS</td>
<td>Aerometric Information Retrieval System</td>
</tr>
<tr>
<td>amu</td>
<td>atomic mass unit</td>
</tr>
<tr>
<td>ANP</td>
<td>annual network plan</td>
</tr>
<tr>
<td>ANSI</td>
<td>American National Standards Institute</td>
</tr>
<tr>
<td>AQS</td>
<td>Air Quality System</td>
</tr>
<tr>
<td>ASE</td>
<td>accelerated solvent extraction</td>
</tr>
<tr>
<td>ASL</td>
<td>analytical support laboratory</td>
</tr>
<tr>
<td>ASQ</td>
<td>American Society for Quality</td>
</tr>
<tr>
<td>ato</td>
<td>atmosphere absolute</td>
</tr>
<tr>
<td>BFB</td>
<td>bromofluorobenzene</td>
</tr>
<tr>
<td>BP</td>
<td>boiling point</td>
</tr>
<tr>
<td>CAA</td>
<td>Clean Air Act</td>
</tr>
<tr>
<td>CAR</td>
<td>corrective action report</td>
</tr>
<tr>
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<td>California Air Resources Board</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts Service</td>
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</tr>
<tr>
<td>CCV</td>
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<td>CDCF</td>
<td>canister dilution correction factor</td>
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<td>chromatography data system</td>
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<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
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<td>CL</td>
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<td>CSN</td>
<td>Chemical Speciation Network</td>
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<td>CV</td>
<td>coefficient of variance</td>
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<td>DART</td>
<td>Data Analysis and Reporting Tool</td>
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<td>2,4-dinitrophenylhydrazine</td>
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<td>DOC</td>
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<tr>
<td>DQI</td>
<td>data quality indicator</td>
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<td>Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs</td>
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<td>DQO</td>
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<td>EI</td>
<td>electron impact</td>
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<td>United States Environmental Protection Agency</td>
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ESMB extraction solvent method blank
EtO ethylene oxide
eV electron volt

FAA flame atomic absorption
FAEM flexible approaches to environmental measurement
FB field blank
FEM federal equivalent method
FID flame ionization detector
FRM federal reference method

g gram(s)
GC gas chromatograph
GC/MS gas chromatograph/mass spectrometry
GFAA graphite furnace atomic absorption spectrometry
GPRA Government Performance Results Act
GPS global positioning system

HAP hazardous air pollutant
HCF hydrocarbon-free
HCl hydrochloric acid
HEPA high efficiency particulate air
HF hydrofluoric acid
Hg mercury
HNO3 nitric acid
HPLC high performance liquid chromatograph
HQ hazard quotient
HR high resolution
HVAC heating, ventilation, and air conditioning

IB instrument blank
ICAL initial calibration
ICB initial calibration blank
ICP/AES inductively coupled plasma/atomic emission spectroscopy
ICP/MS inductively coupled plasma/mass spectrometer
ICP/OES inductively coupled plasma/optical emission spectroscopy
ICS interference check standard
ICV initial calibration verification
ID identifier
I.D. inner diameter
IDCF instrument dilution correction factor
IDL instrument detection limit
IS internal standard

K-D Kuderna-Danish
KI potassium iodide
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<tr>
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<td>National Air Toxics Trends Station</td>
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<td>nm</td>
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<td>O₃</td>
<td>ozone molecule</td>
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<td>Definition</td>
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<td>Office of Air Quality Planning and Standards (EPA)</td>
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<td>polycyclic aromatic hydrocarbon</td>
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<td>Photochemical Assessment Monitoring Stations</td>
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<td>PCB</td>
<td>polychlorinated biphenyl</td>
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<td>photodiode array</td>
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<td>polydimethylsiloxane</td>
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<tr>
<td>PE</td>
<td>performance evaluation</td>
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<tr>
<td>PFTBA</td>
<td>perfluorotributylamine</td>
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<tr>
<td>PM</td>
<td>particulate matter</td>
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<td>PM₂ₛ₅</td>
<td>particulate matter with aerodynamic diameter ≤ 2.5 microns</td>
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<tr>
<td>PM₁₀</td>
<td>particulate matter with aerodynamic diameter ≤ 10 microns</td>
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<td>POC</td>
<td>parameter occurrence code</td>
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<td>POM</td>
<td>polycyclic organic matter</td>
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<td>ppb</td>
<td>part(s) per billion</td>
</tr>
<tr>
<td>ppbv</td>
<td>part(s) per billion by volume</td>
</tr>
<tr>
<td>PPE</td>
<td>personal protective equipment</td>
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<td>part(s) per million</td>
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<td>ppmv</td>
<td>part(s) per million by volume</td>
</tr>
<tr>
<td>ppt</td>
<td>part(s) per trillion</td>
</tr>
<tr>
<td>pptv</td>
<td>part(s) per trillion by volume</td>
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<td>psi</td>
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<td>psia</td>
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<tr>
<td>psig</td>
<td>pound(s) per square inch gauge</td>
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<td>PT</td>
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<td>PTFE</td>
<td>polytetrafluoroethylene</td>
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<tr>
<td>PUF</td>
<td>polyurethane foam</td>
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<td>QA</td>
<td>quality assurance</td>
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<td>QAPP</td>
<td>quality assurance project plan</td>
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<td>QC</td>
<td>quality control</td>
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<td>QFF</td>
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<td>QMP</td>
<td>quality management plan</td>
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<td>QSA</td>
<td>quality systems audit</td>
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<td>r</td>
<td>correlation coefficient</td>
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<td>RB</td>
<td>reagent blank</td>
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<tr>
<td>RBS</td>
<td>reagent blank spike</td>
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<td>RH</td>
<td>relative humidity</td>
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<td>RRF</td>
<td>relative response factor</td>
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<td>RRT</td>
<td>relative retention time</td>
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<td>RSD</td>
<td>relative standard deviation</td>
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<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>RT</td>
<td>retention time</td>
</tr>
<tr>
<td>SB</td>
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<tr>
<td>SIM</td>
<td>selective ion monitoring</td>
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<tr>
<td>SLT</td>
<td>state, local, or tribal agency</td>
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<td>SMB</td>
<td>solvent method blank</td>
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<td>SOP</td>
<td>standard operating procedure</td>
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<td>sample quantitation limit</td>
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<td>SRM</td>
<td>standard reference material</td>
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<td>SSCV</td>
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<td>SSI</td>
<td>size-selective inlet</td>
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<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
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<tr>
<td>SVOC</td>
<td>semi-volatile organic compound</td>
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<td>TAD</td>
<td>technical assistance document</td>
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<td>trip blank</td>
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<td>TC</td>
<td>to contain</td>
</tr>
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<td>TIC</td>
<td>total ion chromatogram</td>
</tr>
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<td>TOF</td>
<td>time of flight</td>
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<td>TSA</td>
<td>technical systems audit</td>
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<td>TSP</td>
<td>total suspended particulate</td>
</tr>
<tr>
<td>TTP</td>
<td>through the probe</td>
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<tr>
<td>UATS</td>
<td>urban air toxics strategy</td>
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<td>UHPLC</td>
<td>ultra high performance liquid chromatography</td>
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<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>VOC</td>
<td>volatile organic compound</td>
</tr>
<tr>
<td>v/v</td>
<td>volume per volume</td>
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1.0: INTRODUCTION

1.1 Background

Hazardous air pollutants (HAPs), or air toxics, are regulated under the Clean Air Act (CAA) as amended in 1990 and currently include a list of 188 toxic pollutants associated with adverse health effects (https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications). Such HAPs are emitted by numerous stationary and mobile sources. The U.S. Environmental Protection Agency (EPA) Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels to significantly reduce the potential for human health risk.

The National Air Toxics Trends Station (NATTS) Program was developed to fulfill the need for long-term ambient air toxics monitoring data required to assess attainment of GPRA commitments. The NATTS network was designed to generate data of a known, consistent, and standardized quality sufficient to enable the identification of spatial, and, more importantly, long-term temporal trends in the concentrations of air toxics. This technical assistance document (TAD) presents best practices and sets forth requirements for the collection and reporting of NATTS network air toxics measurement data and is intended as an aid to the agencies responsible for implementing the NATTS Program. EPA recognizes that the partnership between the EPA and state and local air monitoring agencies is intrinsic to attaining the goal of the NATTS Program to generate high quality data needed to accomplish the end goal of trends detection. This TAD includes information on the implementation and maintenance of the necessary quality system, on the collection and analysis of air samples, on the data handling and validation, and on the reporting of results to EPA’s Air Quality System (AQS) database.

1.2 Target Analytes: Analytes of Critical Concern/Risk Drivers

While it is impractical to measure all HAPs at all monitoring sites, HAPs have been assigned by analytic class to a tiered system according to their relative toxicity. The 1990 CAA amendments required EPA to develop a subset of the 188 toxic pollutants identified in Section 112 that have the greatest impact on the public and the environment in urban areas. The resulting subset of air toxics consisted of 33 HAPs which are identified in the Integrated Urban Air Toxics Strategy (UATS)\(^1\), commonly referred to as the Urban HAP List. This subset of 33 HAPs covers a variety of inhalation exposure periods (acute/chronic), exposure pathways (inhalation, dermal, ingestion), and associated adverse health effects (cancer/non-cancer). However, the NATTS Program is primarily concerned with traditional inhalation pathway exposures of more ubiquitous HAPs, and is focused on measuring HAPs which have available and cost-effective measurement methods. As such, 18 of the 33 UATS HAPs were selected as core HAPs for the NATTS Program. HAPs omitted from the UATS list include those for which analysis methods are less cost-efficient or less reliable and those HAPs deemed to have a lesser impact on inhalation exposure relative to their greater impact on the welfare of watersheds and water bodies through airborne deposition. Also omitted from the NATTS program were those HAPs which are categorized as persistent bio-accumulative compounds (PBTs) such as pesticides, mercury, polychlorinated biphenyls (PCBs), and dioxins.\(^2\)
Hexavalent chromium was removed from the list of NATTS core HAPs in June 2013 due to it being a local source-driven pollutant (and not ubiquitous) and due to the preponderance of non-detect results on a national scale which provided little useful data. Sites are not required to, but may elect to, collect and report hexavalent chromium measurement data. With the removal of hexavalent chromium, the 17 remaining UATS HAPs included polycyclic organic matter (POM), which was added later (in 2007) as speciated polycyclic aromatic hydrocarbons (PAHs). The replacement of POM with naphthalene and benzo(a)pyrene brought the list of required NATTS core HAPs to 18. Further, following the 2014 National Air Toxics Assessment (NATA) report which employed the updated cancer risk data from 2016, EPA added ethylene oxide (EtO) to the list of required HAPs in 2019.

Sixty-two of the 188 HAPs have been selected as “Analytes of Principle Interest” for the NATTS Program; these 62 belong to one of four different analyte classes according to the method by which they are typically measured, i.e., volatile organic compounds (VOCs), carbonyls, metals, and PAHs. These 62 “Analytes of Principle Interest” include 18 (19 when replacing POM with naphthalene and benzo(a)pyrene) of the UATS HAPs (mentioned previously) and are listed in Table 1.2-1 along with their analyte classes and concentrations corresponding to a 10^{-6} cancer risk and a noncancer risk at a hazard quotient (HQ) of 0.1. Of these 62 HAPs, 19 have been identified as major risk drivers based on a relative ranking performed by EPA and have been designated NATTS Core, or Tier I, analytes; these pollutants must be measured and reported at all NATTS sites. The remaining 42 Tier II HAPs are highly desired and should be measured and reported. EPA recognizes that additional resources are required to provide quality-assured data for the additional Tier II analytes; however, given that these methods are already conducted to measure the Tier I Core analytes, data for many of Tier II analytes can be reported with modest additional resource input.
# Table 1.2-1. Analytes of Principle Interest for the NATTS Program

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<th>HAP</th>
<th>Analyte Class and Collection and Analysis Method</th>
<th>Tier</th>
<th>10^6 Cancer Risk Concentration (µg/m³)</th>
<th>Noncancer Risk [Hazard Quotient = 0.1] Concentration (µg/m³)</th>
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<td>VOC by TO-15A</td>
<td>I (UATS)</td>
<td>NA</td>
<td>0.002</td>
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<td>4 a</td>
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<tr>
<td>acetonitrile</td>
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<td>II</td>
<td>NA</td>
<td>6</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.015</td>
<td>2</td>
</tr>
<tr>
<td>bromoform</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.91</td>
<td>NA</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>70</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>chloroprene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>0.7</td>
</tr>
<tr>
<td>p-dichlorobenzene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.091</td>
<td>80</td>
</tr>
<tr>
<td>cis-1,3-dichloropropene</td>
<td>VOC by TO-15A</td>
<td>II (UATS)</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>trans-1,3-dichloropropene</td>
<td>VOC by TO-15A</td>
<td>II (UATS)</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>ethyl acrylate</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.071</td>
<td>NA</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>100</td>
</tr>
<tr>
<td>ethylene oxide</td>
<td>VOC by TO-15A</td>
<td>I</td>
<td>0.0002</td>
<td>NA</td>
</tr>
<tr>
<td>hexachloro-1,3-butadiene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.0022</td>
<td>9</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>500</td>
</tr>
<tr>
<td>methyl isobutyl ketone</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>300</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>70</td>
</tr>
<tr>
<td>methyl tert-butyl ether</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>3.8</td>
<td>300</td>
</tr>
<tr>
<td>methylene chloride</td>
<td>VOC by TO-15A</td>
<td>II (UATS)</td>
<td>2.1</td>
<td>100</td>
</tr>
<tr>
<td>styrene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>100</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>VOC by TO-15A</td>
<td>II (UATS)</td>
<td>0.017</td>
<td>NA</td>
</tr>
<tr>
<td>toluene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>40</td>
</tr>
<tr>
<td>1,1,2-trichloroethane</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>0.063</td>
<td>40</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td>m&amp;p-xylenes</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>o-xylene</td>
<td>VOC by TO-15A</td>
<td>II</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>formaldehyde</td>
<td>carbonyl by TO-11A</td>
<td>I (UATS)</td>
<td>0.08 a</td>
<td>0.98 a</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>carbonyl by TO-11A</td>
<td>I (UATS)</td>
<td>0.45</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Table 1.2-1. Analytes of Principle Interest for the NATTS Program (Continued)

<table>
<thead>
<tr>
<th>HAP</th>
<th>Analyte Class and Collection and Analysis Method</th>
<th>Tier</th>
<th>$10^{-6}$ Cancer Risk Concentration ($\mu g/m^3$)</th>
<th>Noncancer Risk [Hazard Quotient = 0.1] Concentration ($\mu g/m^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nickel</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>0.0021</td>
<td>0.009</td>
</tr>
<tr>
<td>arsenic</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>0.00023</td>
<td>0.003</td>
</tr>
<tr>
<td>cadmium</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>0.00056</td>
<td>0.001</td>
</tr>
<tr>
<td>manganese</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>NA</td>
<td>0.03</td>
</tr>
<tr>
<td>beryllium</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>0.00042</td>
<td>0.002</td>
</tr>
<tr>
<td>lead</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>I (UATS)</td>
<td>NA</td>
<td>0.015</td>
</tr>
<tr>
<td>antimony</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>II</td>
<td>NA</td>
<td>0.02</td>
</tr>
<tr>
<td>chromium</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>II (UATS)</td>
<td>0.00008</td>
<td>0.01</td>
</tr>
<tr>
<td>cobalt</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>II</td>
<td>NA</td>
<td>0.01</td>
</tr>
<tr>
<td>selenium</td>
<td>metal by IO-3.1 and IO-3.5</td>
<td>II</td>
<td>NA</td>
<td>2</td>
</tr>
<tr>
<td>naphthalene</td>
<td>PAH by TO-13A</td>
<td>I (UATS $^b$)</td>
<td>0.029</td>
<td>0.4</td>
</tr>
<tr>
<td>benzo(a)pyrene</td>
<td>PAH by TO-13A</td>
<td>I (UATS $^b$)</td>
<td>0.00057</td>
<td>NA</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>anthracene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>benz(a)anthracene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.0091</td>
<td>0.3</td>
</tr>
<tr>
<td>benzo(b)fluoranthene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.0091</td>
<td>0.3</td>
</tr>
<tr>
<td>benzo(e)pyrene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>benzo(k)fluoranthene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.0091</td>
<td>0.3</td>
</tr>
<tr>
<td>chrysene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.091</td>
<td>0.3</td>
</tr>
<tr>
<td>dibenz(a,h)anthracene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.0091</td>
<td>0.3</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>fluorene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>indeno(1,2,3-cd)pyrene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>0.0091</td>
<td>0.3</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
<tr>
<td>pyrene</td>
<td>PAH by TO-13A</td>
<td>II (UATS $^b$)</td>
<td>NA</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$^a$ These values are per the NATTS Workplan Template, April 2022

$^b$ PAH compounds included in the UATS list as POM

1.3 Importance of Adherence to Guidelines

The overall data quality objective (DQO) of the NATTS Program is to detect trends in HAP concentrations covering rolling three-year periods with uniform certainty across the 26-site
network with a coefficient of variation (CV) not to exceed 15 percent. Stated another way, the DQO is to be able to detect a 15% difference (trend) in non-overlapping three-year periods within acceptable levels of decision error. This is accomplished by generating representative concentration data for the various HAPs with appropriate sensitivity (detectability) within acceptable limits of imprecision and bias. For overall trends to be discernable, concentration data must be generated with methods which meet minimum performance criteria. The DQO, data quality indicators (DQIs), and their associated measurement quality objectives (MQOs), or acceptance criteria, are presented in detail in Sections 2.1 and 3.2. EPA recognizes there is a disconnect in the NATTS bias MQO, which may not exceed 25%, and bias criteria (the allowable tolerance for calibration standard deviation from the established calibration) in individual methods, notably TO-13A and TO-15A, which exceed 25%. For information regarding the determination of the DQO, DQIs, and MQOs, please refer to the following background reports and 2013 DQO reassessment report:

- Analysis, Development, and Update of the National Air Toxics Trends Stations (NATTS) Network Program-Level Data Quality Objective (DQO) and Associated Method Quality Objectives (MQOs), Final Report, June 13, 2013 [https://www.epa.gov/sites/default/files/2021-03/documents/nattsdqo20130613.pdf](https://www.epa.gov/sites/default/files/2021-03/documents/nattsdqo20130613.pdf)

Together, these documents provide a roadmap for determining and verifying the NATTS DQO and supporting MQOs.

A review of data during Phase I of the NATTS pilot project identified that variations in sampling, analysis, data reporting, and quality assurance (QA) resulted in a large degree of data inconsistency. This TAD was developed and revised to increase consistency across the network and facilitate attainment of the NATTS DQO. Failure to attain the prescribed NATTS MQOs limits the ability to detect trends. Trends must be assessed so that EPA, as outlined in the EPA’s Integrated Urban Air Strategy, may verify that the cumulative health risks associated with air toxics are in fact decreasing.

### 1.4 Overview of TAD Sections

This document is organized so as to present guidance and requirements in the likely order in which they are needed when establishing a network site or network sites and analytical support laboratory (ASL), i.e., planning, implementation, data verification and validation, and data reporting to AQS. Background information, the NATTS DQO, and the framework and requirements for quality systems are addressed first, followed by collection and analysis of air samples, with data handling and validation tables completing the document. Each section is briefly described below.
1. Background – Brief overview of the history of the NATTS Program, NATTS analytes, and critical changes from Revision 3
2. Metrics Defining Data Quality for the NATTS Program – Importance of data consistency, NATTS monitoring objectives, quality systems, and siting criteria
3. Quality Assurance and Quality Control – Quality Assurance Project Plan (QAPP) development, QAPP elements including standard operating procedures (SOPs), corrective action, equipment calibration, document control, training, chain of custody (COC), traceability, labeling, control charting, software, records review, and data verification
4. Collection and Analysis Methods – method detection limit (MDL) procedures, VOCs, carbonyls, PM$_{10}$ metals, and PAHs
5. Meteorology – Brief description of required and NATTS-related meteorological measurements
6. Data Handling and Reporting – Procedures and policies for collection, transformation, data validation, data reporting (to AQS), backup, archival, and calculations
7. Data Validation Tables – A series of tables detailing method specific critical criteria

1.5 Critical Changes and Updates from Revision 3 of the NATTS TAD

This revision to the NATTS TAD incorporates changes needed to Revision 3 to address programmatic changes, advancements in technology and refinements to measurement methods, ambiguities and inconsistencies, inclusion of updated measurement and data handling guidance and requirements, and additional information for meteorological measurements.

Specific changes include:
- Addition of EtO as a Tier I required NATTS analyte
- Revision to the MDL determination procedure for harmonization to the revised 40 CFR Part 136 Appendix B procedure
- Clarification of precision acceptance criteria for field and laboratory measurements
- Updating of VOC equipment qualification, sample collection, and sample analysis procedures and acceptance criteria
- Specifying instructions for reporting sampling unit flow verification and audit data to AQS
- Updates to blank acceptance criteria for VOCs (by TO-15A) and PAHs (by TO-13A)
- Clarification on data handling practices

With the removal of hexavalent chromium as a NATTS core HAP in June 2013, guidance for sample collection and analysis for this analyte is not provided within this TAD revision.
1.6 Good Scientific Laboratory Practices

Good scientific practices, including instrument calibration and proper recording of observations, measurements, and instrument conditions, are equally important at both the field monitoring site and in the laboratory. Such practices are necessary to generate data which are consistent, comparable, standardized, traceable, and defensible. Appropriate aspects of good laboratory and field monitoring site practices are to be detailed in each monitoring agency and ASL NATTS quality system. The need for and examples of such practices are given below and in Section 2.

1.6.1 Data Consistency and Traceability. To be able to verify that the NATTS network generates data of quality sufficient to evaluate the main NATTS Program DQO, data collection and generation activities must be traceable to calibrated instruments, certified standards, and to activities conducted by individuals with the appropriate and documented training. Traceability in this case refers to ensuring the existence of a documentation trail which allows reconstruction of the activities performed to collect and analyze a sample and to the certified standards and calibrated instrumentation employed to determine analyte concentrations and necessary calculations or data transformations. To specifically ensure attainment of overall network bias requirements, each reported concentration must be traceable to a measurement of known accuracy, be it from an analytical balance, volumetric flask, gas chromatography/mass spectrometer (GC/MS), mass flow controller (MFC), critical orifice calibration plate, etc. Maintaining this traceability from sample collection to final results reporting assures that NATTS data are credible and defensible, and that the root cause of nonconformances may be found and corrected which thereby enables continuous improvement in NATTS program activities. Instrument calibration specifications and frequencies are provided in Section 3.

1.7 NATTS as the Model for Air Toxics Monitoring

Air toxics monitoring is an important, but often secondary, consideration for many air quality agencies. One reason for such is that there are no national ambient air quality standards (NAAQS) for air toxics for which regulatory compliance efforts would be required. Guidance for conducting air toxics sample collection and analysis is not as widely available as for criteria pollutants and is limited to performance-based compendium methods as compared to Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs). This TAD is intended to primarily provide guidance and delineate requirements for NATTS sites and their ASLs; however, aspects of sampling, analysis, and QA could be applied by agencies conducting air toxics monitoring outside of the NATTS network. This TAD incorporates feedback provided by the air toxics community with vast and varied experience conducting air toxics measurements. Feedback and input provided by the air toxics community were carefully reviewed and considered by a small workgroup of EPA and state/local/tribal (SLT) stakeholders in reviewing and revising this TAD. The NATTS network is a collaboration of SLT monitoring organizations with EPA. With an extensive network of experienced site operators, monitoring program experts, and laboratory staff, the NATTS network strives to be the exemplar of air toxics monitoring.
1.8 References


2.0: IMPORTANCE OF DATA CONSISTENCY

As the main goal of the NATTS Program is to detect long-term trends in ambient air toxics concentrations across the continental United States, sample data collected at each site must be comparable over time and from one site to the next. The ability to detect and evaluate trends on a nationwide basis requires the standardized operation of the NATTS Program based upon four key components:

- Known and specific MQOs for the program;
- Specified measurement (collection and analysis) methods performed in a standardized and consistent manner across the network;
- Known and specific acceptance criteria for various aspects of the specified monitoring methods; and
- Stability of monitoring sites including location and operation over the required period of time.

In short, each site’s concentration data are to meet the MQOs and be generated with standardized methods that are appropriately sensitive, show minimal bias, and are sufficiently precise. Moreover, the collected samples taken together must be representative of the ambient conditions at the site over the course of a year and the annual dataset must be adequately complete. If program MQOs are not attained at each site, the network data will not be consistent across all sites and the ability to detect concentration trends will be compromised. MQOs related to each of the specific DQIs are described in more detail in Section 2.1.

This TAD is written such that requirements are described as “must,” “will,” and “is to/are to” and recommendations are described as “should” or specifically stated as a recommendation. It is expected that monitoring agencies will make good faith efforts to comply with the requirements and adopt recommendations, where feasible. Additionally, monitoring aspects cited as best practices are those activities or procedures which are expected to result in improving or routinely meeting acceptance criteria or improving efficiency.

EPA performs assessment of the NATTS Program data to evaluate the percentage of data meeting MQOs as part of performing trends analysis for DQO evaluation. In recent NATTS assessments, evaluation has determined there was not sufficient data meeting MQOs (A-rated data) to properly perform trends analysis. In short, this means that MQOs for the NATTS measurements did not satisfy the bias, precision, completeness, or sensitivity MQOs and the non-compliant data were excluded from the trends evaluation. EPA adjusted the MQO acceptance metrics for measurement data (B-rated data) to increase the amount of data that could be incorporated into the trends analysis. This compromise to allow additional data of lower quality may provide sufficient network data for trends analysis in certain instances; however, it risks widening the allowable decision error associated with detecting the presence of a trend, and is a last resort to use the collected data for the network’s intended purpose. Monitoring agencies and ASLs cannot assume that such a compromise will be allowed for future NATTS assessments and must make good faith efforts to attain the NATTS MQOs, seeking guidance from EPA Regional...
and Office of Air Quality Planning and Standard (OAQPS) staff as needed for assistance with monitoring logistics, data analysis, and other procedures, as necessary. NATTS monitoring agencies should communicate with EPA Regions and EPA OAQPS when situations arise that risk the attainment of an MQO.

2.1 Data Quality Objectives and Relationship to the Quality Assurance Project Plan

The DQO process ensures that the type, quantity, and quality of data used in decision making are appropriate to evaluate the overall DQO of the NATTS Program. Discussion of the determination of the NATTS DQO is addressed in the NATTS Quality Management Plan (QMP) and is not reproduced here. Background information on the development of the NATTS DQO process is detailed in the initial DQO report and a follow up assessment was completed in 2013 to verify that the DQO and supporting MQOs remained applicable and suitable to attain network goals.

Each monitoring organization and ASL (if not part of the parent monitoring organization) must develop a QAPP that describes the framework of the resources, responsible individuals, and actions to be taken to attain the NATTS DQO. QAPP development is described further in Section 3.3.1.

There is a single main DQO for the NATTS Program, which is:

To be able to detect a 15% difference (trend) between two successive 3-year annual mean concentrations (rolling averages) within acceptable levels of decision error.

This main DQO is directly related to demonstrating a reduction in health-based risk related to air toxics inhalation exposure. To achieve this main DQO, the NATTS Program network was designed to meet the following primary monitoring objectives, which are to:

- Measure concentrations of the NATTS Tier I core analytes and Tier II analytes of interest in ambient air at each NATTS site. These analytes are listed in Table 1.2-1.

- Generate data of sufficiently high and known quality that are nationally consistent. Such requires the implementation and maintenance of a robust and functional quality system, the proper execution of the applicable sampling and analysis methods, and that the specified methods provide sufficient sensitivity to obtain a limit of detection at or lower than that at which adverse health effects have been determined.

- Collect sufficient data to represent the annual average ambient concentrations of air toxics at each NATTS site. Collection of one sample every six days results in 60 or 61 samples per year exclusive of additional quality control (QC) samples such as blanks, collocated samples, duplicates, etc.

In addition to these primary monitoring objectives, the NATTS network was designed to address the following secondary monitoring objectives, which are to:

- Complement existing programs. The NATTS network is integrated with existing programs such as criteria pollutant monitoring, Photochemical Assessment Monitoring Stations (PAMS), National Core (NCore), Chemical Speciation Network (CSN), etc., and to take advantage of efficiencies of scale to the extent that
methodologies and operations are compatible. Establishment of NATTS sites at existing sites leverages the existing resources of experienced operators and infrastructure to achieve program objectives.

- Reflect community-oriented population exposure. Stationary monitors are sited to be representative of average concentrations within a 0.5- to 4-kilometer area (i.e., neighborhood scale). These neighborhood-scale measurements are more reflective of typical population exposure, can be incorporated in the estimation of long-term population risk, and are the primary component of the NATTS Program. Note that some NATTS sites may no longer truly represent neighborhood scale due to source or infrastructure changes. While new near-field sources may impact the measured concentrations, stability of the site location is necessary to detect trends which may still be discernable even when sites are impacted by such sources.

- Represent geographic variability. A truly national network must represent a variety of conditions (topography, altitude, proximity to large bodies of water, etc.) and environments that will allow characterization of different emissions sources and meteorological conditions. The NATTS Program supports population risk characterization and the determination of the relationships between emissions and air quality under different circumstances, and allows for tracking of changes in emissions. National assessments must reflect the differences among cities and between urban and rural areas for selected HAPs, so the network:
  - Includes cities with high population risk (both major metropolitan areas and other cities with high or potentially high anticipated air toxics concentrations);
  - Distinguishes differences within and between geographic regions (to describe characteristics of areas affected by high concentrations (e.g., urban areas or source-impacted areas) versus low concentrations (e.g., rural areas or non-source-impacted areas);
  - Reflects the variability among pollutant patterns across communities; and
  - Includes background monitoring (i.e., sites without localized sources).

The above monitoring objectives are supported by the DQIs as described in the following subsections:

2.1.1 Representativeness. To adequately characterize the ambient air toxics concentrations over the course of a year, sample collection must occur every six days per the national sampling calendar (https://www.epa.gov/amtic/sampling-schedule-calendar) for a 24-hour period beginning and ending at midnight local standard time (without correction for daylight savings time, if applicable). This sample collection duration and frequency provides a sufficient number of data points to ensure that the collected data are representative of the annual average daily concentration at a given site. Collection methods are designed to efficiently capture airborne HAPs over this time period in order to measure concentrations representative of the ambient air during sample collection. Samples must be collected for 24±1 hours (1380 to 1500 minutes) or associated measurement data will be invalidated (NULL Qualifier AG indicating sample time out of limits) when reported to AQS.
2.1.2 Completeness. Comparison of concentration data across sites and over time requires that a minimum number of samples be collected over the course of each calendar year. The MQO for completeness prescribes that ≥ 85% of the annual air samples must be valid, equivalent to 52 of the annual 61 expected samples (51 during years when there are only 60 collection events).

A valid sample is one that was collected, analyzed, and reported to AQS without null data qualifiers. A NULL Data Qualifier in AQS invalidates the sample result for the specific parameter and does not provide concentration information. Only one NULL qualifier can be appended to such invalidated data; therefore, data reported with a NULL code provide only the information associated with that NULL Data Qualifier. If a collected sample is voided or invalidated for any reason, a make-up sample collection should be attempted as soon as practical according to the make-up sampling policy below.

2.1.2.1 Make-up Sample Policy. Samples and sample results may be invalidated for a number of reasons. In all cases, the concentration data are entered in AQS qualified with a Null Data Qualifier indicating the data are invalid and a concentration value is not recorded for the measurement/attempted sample. In order to increase the likelihood of attaining the completeness MQO of ≥ 85%, make-up samples should be scheduled and collected when a sample or sample result is invalidated.

A replacement sample should be collected as close to the original sampling date as possible, and preferably before the next scheduled sampling date. When scheduling make-up sample collection, consideration should be given to minimize bias introduced to the annual concentration average due to differences in concentration from the originally scheduled sample date. Such considerations include concentration differences due to sample collection on a particular day of the week (weekday versus weekend) and potential seasonal effects (e.g., increased PAHs from woodburning smoke in winter). If it is not feasible to collect the make-up sample prior to the next scheduled sampling date, the sample should be collected within 30 days of the missed collection date. In all cases, the make-up sample should be collected within the calendar year averaging period that starts January 1 and ends December 31. Note: For sampling units employing six-day timers, omitting to reset the timer following a make-up sample can result in mistakenly collecting samples on dates that do not follow the national sampling calendar (note such samples collected on a non-scheduled sampling date are not to be invalidated unless critical criteria are not otherwise met).

To summarize, make-up samples should be collected as close to the original sampling date as possible, and should be collected according to the following, in order of most preferable to least preferable:

1. Before the next scheduled sampling date
2. Within 30 days of the missed collection date
3. Within the calendar year.

In order to be temporally representative of the annual concentration at a given site, the sample dates must be as evenly distributed as possible to capture concentrations that fluctuate seasonally.
or according to weather patterns. It is not appropriate to delay make-up sampling until the end of
the calendar year, as this may bias the data to be more seasonally than annually representative.

2.1.3 **Precision.** Reproducibility is a key component of ensuring concentration results at
one site are comparable to those at other sites and are comparable over time. For the NATTS
Program, precision of field and laboratory activities (inclusive of extraction and analysis) may be
assessed by collection of collocated and/or duplicate field samples; the precision of laboratory
handling and analysis may be estimated by the subdivision of a collected sample into preparation
duplicates which are separately taken through all laboratory procedures (digestion or extraction
and analysis) and includes instances in which target analytes may be added to a subsample to
prepare matrix spike duplicates; and analytical precision is assessed by the replicate analysis of a
sample or sample extract/digestate. A summary of possible precision assessments is shown in
Table 2.1-1. Precision sample collection and replicate analysis requirements will be detailed in
each site’s annual NATTS monitoring plan.

<table>
<thead>
<tr>
<th>HAP Class</th>
<th>Collocation *</th>
<th>Duplicate Field Samples *</th>
<th>Preparation (Digestion/Extraction) Duplicate</th>
<th>Laboratory Control Sample Duplicate</th>
<th>Matrix Spike Duplicate</th>
<th>Analysis Replicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>PM$_{10}$ metals – high volume collection</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>PM$_{10}$ metals – low volume collection</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>PAHs</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

*Note: Collection of collocated and duplicate field samples is highly desired, but not required, and will
be detailed in the site’s annual monitoring plan.

The network MQO is based on an evaluation of at least an entire year’s data. In all cases a CV of
≤ 15% must be met. For more information on how the CV is calculated, see the 2011-2012
NATTS Quality Assurance Annual Report. Note that this precision MQO is different than the
precision acceptance criteria for the individual collection and analysis methods; imprecision of
the latter may be permitted to be > 15%; however, it is not inclusive of numerous (N ≥ 3)
discrete measurements. Such method-specific precision requirements apply to comparing
discrete pairs of two measurements (i.e., pairwise) and do not apply to larger (N > 2) sample sets.

2.1.3.1 **Precision Evaluation Calculation.** Previous versions of this TAD prescribed to
calculate a relative percent difference (RPD) for precision pairs (i.e., collocated samples,
duplicate samples, replicate analyses, etc.) when both of the measurements in the precision pair
were above a specified threshold (e.g., 5-fold MDL). This threshold was specified to be a
concentration below which uncertainty is sufficiently high that the precision calculation was
likely to exceed the prescribed method precision criterion. However, by specifying that both
measurements in the precision pair equal or exceed the threshold, it overlooked situations of
obvious poor precision when one measurement was many-fold the threshold and one measurement was less than the threshold.

To address this oversight, the precision pair acceptance determination has been revised for situations where one of the pairwise measurements is above and one is below the threshold. This determination of RPD is solely for assessing precision; the concentrations measured of the precision pair are to be reported to AQS as measured. In summary, pairwise precision is determined according to the following hierarchy:

1. When both of the pairwise measurements are ≥ the threshold, calculate the RPD. When the RPD exceeds the specified precision criterion, associated data are qualified (QA Qualifier LJ indicating the value is an estimate) when input to AQS. Note that qualifiers cannot be added to AQS QA transactions and only raw data (RD) transactions can include qualifiers. For further information on reporting precision data to AQS, refer to Section 3.3.1.3.15.5.

2. When both of the pairwise measurements are < the threshold, the precision evaluation is not meaningful and is not required. Data are not to be qualified if an RPD is calculated and exceeds the acceptance criterion.

3. When one of the pairwise measurements is < the threshold and one is ≥ the threshold, substitute the threshold value for the measurement that is < the threshold and calculate the RPD. This convention assigns a best-case scenario for the measurement of lower magnitude and permits quantifying the imprecision of the pairwise measurements. If the RPD exceeds the precision acceptance criterion, associated data are qualified (QA Qualifier LJ indicating the value is an estimate) when input to AQS.

An example illustrating scenario 3 above follows:

A pair of collocated VOC samples is analyzed. Precision is to be assessed above a threshold concentration of 5-fold MDL where the MDL for benzene is 0.05 part per billion by volume (ppbv), therefore this comparison threshold is 0.25 ppbv. The primary sample measures 0.65 ppbv for benzene and the collocated sample measures 0.15 ppbv. The primary sample is above the threshold and the collocated is less than the threshold, therefore the threshold is substituted for the collocated sample result:

\[
\begin{align*}
\text{MDL:} & \quad 0.05 \text{ ppbv} \\
5x \text{ MDL:} & \quad 0.25 \text{ ppbv} \\
\text{Sample A:} & \quad 0.65 \text{ ppbv} \\
\text{Sample B:} & \quad 0.15 \text{ ppbv}
\end{align*}
\]

\[
\text{RPD} = \frac{|\text{Sample A} - \text{Sample B}|}{\text{average of Sample A and Sample B result}}
\]

\[
\text{RPD} = \frac{|0.65 \text{ ppbv} - 0.25 \text{ ppbv}|}{(0.65 \text{ ppbv} + 0.25 \text{ ppbv})/2} = 88.9\%
\]
The RPD exceeds the pairwise precision criterion of < 25.1%, therefore associated data are qualified (QA Qualifier LJ indicating the value is an estimate) when input to AQS. The ASL should take corrective action to verify sample identifiers are correct and should notify the monitoring agency of the precision criterion exceedance so corrective action investigation can be taken at the field monitoring site.

2.1.3.2 Precision Data Substitution. In the event that data for a sample are invalidated, there may exist valid precision data that could be reported as a substitute (this is common for criteria pollutants). The primary goal for such substitution is to maximize measured pollutant data reporting to AQS and the associated completeness. This situation would apply for precision data generated through the collection and analysis of duplicate samples and the analysis of replicate samples. When duplicate and replicate precision data are invalidated, it is EPA’s strong preference that a make-up precision measurement be conducted to ensure sufficient valid QA precision data are collected and reported.

**Duplicate samples:** If the primary sample result for a duplicate precision pair is invalidated and its corresponding duplicate sample result is valid, the EPA’s strong preference is that the monitoring agency substitutes the valid duplicate sample result when reporting to AQS (as an RD transaction). In this case, the substituted duplicate measurement in the RD transaction is to be qualified (QA Qualifier SS indicating the measurement is a value substituted from a secondary monitor). The monitoring agency would then not report a QA transaction for the invalid precision measurement and instead would report the QA Duplicate transaction to AQS for the subsequent make-up duplicate event. If for any reason the monitoring agency is unable to conduct a make-up duplicate event, the monitoring agency will report the invalid precision pair to AQS using a QA Duplicate transaction for which it will report the valid measurement and -999 for the invalidated measurement. This substitution of -999 is made because AQS QA transactions do not accept addition of qualifiers and this communicates to data users that the measurement was invalid.

**Replicate analysis:** Each analytical methods subsection in Section 4 prescribes performing replicate analysis to evaluate analytical precision with each analysis batch. Replicate analysis is to be performed on a field collected ambient air sample (excluding field QC blank samples, such as field blank, trip blank, etc.). Replicate analysis can therefore be performed on primary samples, collocated samples, and duplicate samples. ASLs typically employ a convention to report the first analysis result for a replicate analysis pair. However, in the event the first analysis result of a replicate analysis pair is invalidated and the second analysis result is valid, the EPA’s strong preference is that the ASL substitutes the valid replicate sample result when reporting to AQS (as an RD transaction). In this case, the substituted replicate measurement in the RD transaction is to be qualified (QA Qualifier SS indicating the measurement is a value substituted from a secondary monitor). The monitoring agency would then not report a QA Replicate transaction for the invalid precision measurement and instead would report the QA Replicate transaction to AQS for the subsequent make-up replicate measurement. If for any reason the monitoring agency is unable to conduct a make-up replicate measurement, the monitoring agency will report the invalid precision pair to AQS using a QA transaction for which it will report the valid measurement and -999 for the invalid measurement. This substitution of -999 is made because AQS QA transactions do not accept addition of qualifiers and this communicates to data users that the measurement was invalid.
2.1.4 Bias. Bias is the difference of a measurement from a true or accepted value and can be negative or positive. As much as possible, bias should be minimized as biased data may result in incorrect conclusions and therefore incorrect decisions. Bias may originate in several places within the sample collection, analysis, and data reduction steps. Sources of sample collection bias include, but are not limited to, incorrectly calibrated flows or out-of-calibration sampling instruments, elevated and unaccounted-for background on collection media and in sampling instruments, poorly maintained (dirty) sampling inlets and flow paths, and poor sample handling techniques resulting in contamination or loss of analyte. Sources of sample analysis bias include, but are not limited to, poor hygiene or technique in sample preparation, incorrectly calibrated or out of tolerance equipment used for standard materials preparation and analysis, and infrequent or inappropriate instrument maintenance leading to enhanced or degraded analyte responses. Data reduction bias can be due to incorrect calculations or application of correction factors resulting in systematic bias in reported data.

2.1.4.1 Assessing Laboratory Bias - Proficiency Testing. Each ASL analyzing samples on behalf of NATTS monitoring sites must participate in the NATTS proficiency testing (PT) program when offered. PT studies are conducted for each of the four sample classes, VOCs, carbonyls, PM$_{10}$ metals, and PAHs, and conducted at a frequency determined by OAQPS, typically twice annually for each class. Participating ASLs are blind to the spiked concentrations and are to analyze the PT samples via methods and procedures identical to those employed for field-collected air samples.

PT target analytes, which include all Tier I analytes, among others, are identified in the following tables in Section 4:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>4.2-1</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>4.3-1</td>
</tr>
<tr>
<td>PM$_{10}$ Metals</td>
<td>4.4-1</td>
</tr>
<tr>
<td>PAHs</td>
<td>4.5-1</td>
</tr>
</tbody>
</table>

Each laboratory’s PT results, on an analyte-by-analyte basis, must be $<\pm 25.1\%$ of the assigned target value, defined as the NATTS laboratory average, excluding statistically determined outliers. In the event the NATTS laboratory average is not a suitable reference value, such as when several ASLs demonstrate a contamination issue, the assigned target value may be referenced to the theoretical nominal concentration or referee laboratory average, as applicable, and will be communicated in the PT results evaluations.

Laboratories which do not meet the bias acceptance criterion on an analyte-by-analyte basis must identify the root cause of the bias for the failed analyte, take corrective action, as appropriate, to eliminate the cause of the bias, and must evaluate the potential for bias in reported field sample data going back to last acceptable PT result for that analyte. In the event of two consecutive failed PTs for a given analyte, measurement data for that analyte(s) are to be qualified when reported to AQS. For results showing an unacceptable bias, measurement data are to be qualified (QA Qualifier LK or LL indicating a high or low bias, respectively). EPA recognizes that the NATTS MQO bias criterion of $\pm 25\%$ established through the DQO process is narrower than the bias criterion (the permitted tolerance for analysis of calibration standards when compared to the
established calibration curve) for some of the analytical methods, namely TO-15A and TO-13A. In order for the main NATTS DQO to be achieved, the bias MQO criterion must be achieved.

2.1.4.2 Assessing Field Bias. Bias in field sampling activities will primarily occur due to two factors, deviation in flow rate calibration from the method-specified tolerance and enhancement (e.g., from contamination) or suppression (e.g., loss due to breakthrough or destruction reactions) from the sample collection process. Additional unknown bias can occur due to leaks in sampling train flow pathways that introduce monitoring shelter air or other undesired atmospheres.

**Flow Rate Bias:** Flow rate bias results in errors in the collected air volume for the associated samples for methods that employ normalization of the measured concentration to the collected air volume: carbonyls, PM$_{10}$ metals, and PAHs. The direction of the flow rate bias in carbonyls, PM$_{10}$ metals, and PAHs samplers is opposite that to the bias introduced in the reported concentrations. That is, flow rates which are biased low (the actual flow rate as measured by a flow transfer standard is higher than the sampling unit reading) result in a smaller collected air volume and therefore an overestimation of air concentrations. Conversely, flow rates which are biased high result in underestimation of air concentrations.

As VOCs collection methods involve collection of whole air into the canister, the flow rate accuracy is of less importance and does not directly correlate to errors in the magnitude of measured concentrations. Rather, it is important that the flow rate into the canister be constant over the entire 24-hour collection period so as to best characterize the average burden of VOCs over the entire sampling duration.

Indicated flow rates for carbonyls and PAHs must be $< \pm 10.1\%$ of both the flow transfer standard and the design flow rate (where applicable). The indicated flow rate for the low volume PM$_{10}$ metals method must be $< \pm 4.1\%$ of the flow transfer standard and $< \pm 5.1\%$ of the design flow rate. The indicated flow rate for the high volume PM$_{10}$ metals method must be $< \pm 7.1\%$ of the transfer standard and $< \pm 10.1\%$ of the design flow rate. Inability to meet these criteria must result in corrective action including, but not limited to, troubleshooting the sampler for leaks or obstructions to flow, and if flow rate bias remains unacceptable, recalibration of the sampling unit flow or resetting of flow linear regression response (adjustment of the slope and intercept), where possible. Sampling units which cannot meet these flow accuracy specifications must not be utilized for sample collection. Additionally, following a failing flow rate calibration or calibration check, agencies must evaluate sample data collected since the last acceptable calibration or calibration check, and such data may be subject to invalidation. Corrective action is recommended to prevent out of tolerance conditions for flow calibration checks which indicate flows approaching, but not exceeding the appropriate flow acceptance criterion. Flow rate calibration verifications must be performed at a minimum quarterly; however, to minimize risk of invalidation of data when flow rate calibration verifications fail acceptance criteria, monthly flow rate calibration verifications are strongly recommended.

**Analyte Enhancement or Suppression:** Collected samples may be subject to analyte enhancement due to contamination within the sampling unit or other source in the sampling process such as passive sampling during sample transport. Conversely, analyte concentration suppression may occur due to analyte losses from breakthrough (i.e., lower collection efficiency
on carbonyls or PAHs collection media) or from destructive reactions or adsorption within the sampling flow path (e.g., particulate residue adsorbing target analytes or exposure of catalytic surfaces the react target analytes). An EPA study on TO-11A demonstrated that aldehyde breakthrough on 2,4-dinitrophenylhydrazine (DNPH) cartridge media was not appreciable at flow rates of ≤ 1.25 L/minute; however, breakthrough of PAHs on polyurethane foam (PUF)/resin sorbent media has not been formally studied.

Limiting of passive sampling (contamination) is discussed within the individual methods sections that follow. Sampling bias due to interactions within the sampling unit for VOCs and carbonyls is evaluated and characterized by performing bias qualification checks on the sampling units prior to field deployment. These qualification activities involve providing humidified analyte-free zero air (zero check) and a known low-concentration standard (known standard check) to the sampling unit and collecting a reference sample upstream of the sampling unit and a challenge sample through the sampling unit. The difference in measured values between the reference and challenge samples is calculated and evaluated for unacceptable enhancement (positive bias) or suppression (negative bias). These zero and known standard qualification checks are described further in Sections 4.2.3.3 and 4.3.7.1.1, for VOCs and carbonyls, respectively.

2.1.5 Sensitivity. Following promulgation of the CAA and its amendments, ambient air toxics concentrations have generally decreased. As concentrations decrease, they become increasingly difficult to measure and, as a result, measurement methods must become increasingly sensitive to measure the target analytes with appropriate bias and precision. Concurrent with decreases in ambient air toxics concentrations, health risk assessments for exposures to air toxics are generally driving health risk-based concentrations lower, which also precipitates a need to improve method sensitivity (i.e., detectability). In order to ensure that methods are sufficiently sensitive, MDL MQOs have been established which prescribe the maximum allowable MDL for each required NATTS Tier I core analyte. As concentrations for HAPs decrease in the ambient atmosphere and are measured closer to the MDL or below the MDL, this results in a decrease in the accuracy (decrease in precision and increase in bias) of the percent change estimate in evaluating a trend.

The MDL and sample quantitation limit ([SQL], defined as 3.18 times the MDL concentration) provide information on the concentration at which both positive identification and accurate quantification is expected, respectively. While all measured concentrations (even those less than the MDL) must be reported to AQS, the confidence associated with each reported concentration is correlated to its relationship to the corresponding MDL and SQL.

The SQL is equivalent to ten-fold the standard deviation of seven measurements of MDL samples, which was defined in draft EPA guidance in 19947 as the minimum level (ML). The 3.18-fold constant term was derived by dividing 10 standard deviations by 3.14 (the Student’s T value for 7 replicates). This 10-fold factor of the standard deviation of the population of spiked samples for determining the MDL represents the concentration range for each method in which the analyte is confidently detected above background and is in a measurement range within or near to that for which the bias criterion for the method applies (i.e., within the useable calibration range of the method). The MDL process in 40 Code of Federal Regulations (CFR) Part 136
Appendix B is protective against reporting false positives such that 99% of the measurements made at the determined MDL value are positively detected above background (determined to be different from the contribution of the method background), but does not attempt to characterize precision or address accuracy at the determined MDL concentration. The SQL concentration provides more confidence to the accuracy of the measurement with well-characterized precision.

MDL MQOs that must be met (as of the publication of this document in July 2022), i.e., not to be exceeded, are given in Table 4.1-1. Further discussion of MDL background, determination, and importance are described in Section 4.1.

2.2 NATTS Workplan Template

Each year the EPA will post a NATTS workplan template for monitoring agencies conducting NATTS Program work covering the grant period from July 1 through June 30 of the following calendar year. This workplan template details the sample collection, sample analysis, and data reporting responsibilities and the associated budget with which each agency will comply. The workplan template briefly describes the NATTS main DQO and associated outputs and outcomes as related to the EPA’s strategic goals. The workplan template will prescribe the quantity of QA sample measurements (e.g., collocated, duplicate, or analysis replicate) to be made at each monitoring site for the grant funding year. The workplan template also specifies the required MDL MQOs for the Tier I Core analytes. NATTS monitoring agencies are expected to detail these requirements in their annual network monitoring plan(s) and in their NATTS QAPP. When applicable to the ASL, pertinent details will be included in the ASL QAPP governing the NATTS Program work. The current NATTS workplan template can be accessed on EPA’s AMTIC: https://www.epa.gov/amtic/air-toxics-ambient-monitoring#natts

2.3 Quality System Development

Eleven quality management specifications are defined in EPA Order CIO 2105.0 (https://www.epa.gov/sites/production/files/2015-09/documents/epa_order_cio_21050.pdf) for all EPA organizations covered by the EPA Quality System. It is EPA policy that each agency conducting NATTS Program work must have a quality system that conforms to the minimum specifications of the American National Standards Institute (ANSI)/American Society for Quality (ASQ) E4 “Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs”. ASQ E4 is based on the general principle that the quality system provides guidelines for QA and QC based on the continuous cycle of planning, implementation, documenting, and assessment. Each agency’s quality system will also comply with the requirements as given in this TAD, which complements the requirements in ASQ E4. The purpose of defining the quality systems requirements in this manner is to provide a single source for developing or revising quality systems for NATTS Program work. Quality systems documents, including QAPPs and SOPs, will reflect the requirements. The quality system and associated functions are described in the plan-do-check-act feedback loop to ensure continuous improvement to ensure NATTS MQOs are met.

Plan: The planning portion of the quality system incorporates development of quality systems documents such as a QMP, QAPP, and SOPs which define the activities to be conducted, who
they are conducted by, when activities are conducted, and how they must be documented. These
documents must adapt and incorporate adjustments to procedures and policies when changes are
needed or when procedures and policies become obsolete. Quality systems documents serve a
dual purpose in that they describe how activities will be conducted and serve to document
policies and procedures for reconstructing past activities.

**Do:** Activities described in the quality systems documents must be implemented and executed as
prescribed and deviations documented and corrective actions taken to correct nonconformances.
Staff training is a necessary element of a functional quality system, ensuring that each individual
conducting activities has the experience and skills required to generate work products of a known
and adequate quality. Appropriate training combined with up-to-date quality systems documents
ensure that staff have both the skills and procedures to conduct activities as required.

**Check:** Assessments are conducted during and after planning and implementation to ensure that
work products meet the objectives and needs of the program as defined during planning.
Additionally, assessments ensure that quality systems documents sufficiently describe the
activities to be performed, that measurements and calculations are accurate, that reported data are
accurate, that staff perform activities per the current quality systems documents, that staff
training is up to date, and that nonconformances are communicated to those ultimately
responsible for the program.

**Act:** Following assessments, root cause analysis is performed and corrective action is taken to
address nonconformances such that the NATTS Program may be continuously improved.

Each agency will develop and maintain a robust and fully-functioning quality system to ensure
that NATTS Program MQOs for the various DQIs are met. A fundamental part of a functional
quality system is the QAPP, which each monitoring agency and associated ASL must develop
and maintain for NATTS program work. Details and specific quality system elements that must
be incorporated in the NATTS QAPP are presented in Section 3.

### 2.4 Siting Considerations

Urban concentration data are needed to address the range of population exposures across and
within urban areas. Conversely, rural concentration data are needed for characterization of
exposures of non-urban populations, to establish non-source impacted concentrations (as
practicable), and to better assess environmental impacts of emissions of air toxics. The NATTS
network at the time of this TAD revision consists of 21 urban sites and 5 rural sites. Twenty-four
of these 26 monitoring sites have been established since 2009, and only modest modifications
involving relocation within a small geographic area have occurred over the past several years for
these 24 sites. Long-term monitoring needed to measure average concentrations over successive
three-year periods requires that sites are maintained at, or in very close proximity to, their current
location. This long-term data generation from each monitoring site is integral to discerning
trends in air toxics concentrations. The current list of NATTS network sites can be found on
EPA’s website (accessed February 2022): [https://www.epa.gov/amtic/list-national-air-toxic-
trends-sites-natts](https://www.epa.gov/amtic/list-national-air-toxic-trends-sites-natts).
For each of the 24 currently operating legacy sites in the NATTS network, sampling unit siting may have changed little, if at all, from when sample collection for the NATTS Program began at the specific site. Nonetheless, site operators should evaluate instrument siting annually to ensure that requirements continue to be met consistently across the network. Siting criteria to consider relate to changes at the site such as tree growth, construction/demolition or development on property near the site, new sources, and other changes which may impact sample collection and the resulting measured concentrations. Particular attention should be paid to vertical placement of inlets, spacing between sampling inlets, proximity to vehicle traffic (especially where traffic levels have increased due to housing or business development or for traffic-related infrastructure such as parking garages), and proximity to obstructions or other interferences. Additionally, monitoring agencies should be aware of changes in sources, population, and neighborhood make-up (businesses, industry, etc.) which may impact sampler siting or sample concentrations.

Monitoring unit inlet placement must conform to the specifications listed in 40 CFR Part 58 Appendix E ¹⁰ and the additional guidance given below. Measurement data for sampling unit inlet siting that is non-compliant will be qualified (QA Qualifier SX indicating does not meeting siting criteria) when reported to AQS.

2.4.1 Sampling Instrument Spacing. Requirements for sampler spacing are relative to the sampling unit inlet (edge) and must conform to the criteria listed in Table 2.4-1.

As an example, per Table 2.4-1, an inlet to a carbonyls sampler must be no less than 2 m and no more than 15 m above the ground and it may be no closer than 2 m to any high volume sampler. Moreover, the inlets of collocated samplers may be no further apart than 4 m in the horizontal direction, and no more than 3 m apart vertically.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Flow Rate</th>
<th>Inlet Above Ground Level Height Requirement a</th>
<th>Horizontal Collocation Requirement b</th>
<th>Vertical Collocation Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>Low volume (&lt; 1000 mL/min)</td>
<td>2-15 m</td>
<td>0-4 m</td>
<td>≤ 3 m</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>Low volume (~ 1 L/min)</td>
<td>2-15 m</td>
<td>0-4 m</td>
<td>≤ 3 m</td>
</tr>
<tr>
<td>PM₁₀ Metals</td>
<td>Low volume d (~16.7 L/min)</td>
<td>2-15 m</td>
<td>1-4 m c</td>
<td>≤ 3 m</td>
</tr>
<tr>
<td>PM₁₀ Metals</td>
<td>High volume e (~ 1.1 m³/min)</td>
<td>2-15 m</td>
<td>2-4 m e</td>
<td>≤ 3 m</td>
</tr>
<tr>
<td>PAHs</td>
<td>High volume e, f (~ 0.139 m³/min)</td>
<td>2-15 m</td>
<td>2-4 m f</td>
<td>≤ 3 m</td>
</tr>
</tbody>
</table>

a Many standalone sampling unit inlets do not meet the minimum height and must be installed on a support structure such as a riser or rooftop to elevate the inlet to the proper height.
b Distance measured from nearest edges of sampling inlets.
c 40 CFR Part 58 Appendix A Section 3.3.4.2(c).
d Low volume PM₁₀ samplers must be ≥ 1 m from other sampling inlets including criteria gas monitors.
e These high volume sampling units must be minimally 2 m from all other sampling inlets.
f 40 CFR Part 58 Appendix E¹⁰ states that high volume sampling units are those with flow > 200 L/minute. However, the regulations are silent on high volume PAHs sampling units, which operate > 139 L/minute; in this TAD they are conservatively being treated as high volume sampling units such that they must minimally be 2 m horizontally from other instrument inlets.
Sampling inlet distances are measured from the nearest edge of the sampling unit inlet where ambient air is ingested and it is not appropriate to measure from the center of the sampler inlet. For example, the required distance of minimally 2 m from a high volume PM$_{10}$ sampler is measured from the edge of the size-selective inlet (SSI) where ambient air is ingested.

Minimum distances from high volume samplers are critical to ensure that scrubbed air is not sampled. High volume samplers include those for total suspended particulate (TSP) sampling for lead (Pb) and PAHs, and are further described below in Section 2.4.2.

Note that for gaseous HAP sampling methods (VOCs and carbonyls), there is no minimum collocation distance as gases are much more homogeneous in the ambient air than particulate matter, and are not likely to influence one another, particularly at the low flow rates utilized.

### 2.4.2 Interferences to Sampling Unit Siting

Interference from other samplers, particularly high volume sampling units for PAHs and PM$_{10}$ metals, must be avoided by ensuring that all inlets are minimally 2 m (meters) from any high volume inlet. Additionally, to eliminate recollection of already sampled “scrubbed” air, exhausts (when so equipped) from high volume sampling units must be directed away from air samplers in the primary downwind direction via hose/tube that terminates minimally 3 m in distance from any sampler. Low-volume PM$_{10}$ samplers must also be minimally 1 m away from other sampling inlets including other PM monitors and gas monitor inlet probes (including criteria gas monitors).

PM$_{10}$ metals sampling units must not be installed in an unpaved area unless covered by vegetation year round, so the impacts of wind-blown dusts are kept to a minimum.¹⁰

Tarred or asphalt roofs should be avoided for locating inlets for carbonyls, VOCs, and PAHs air samplers as these materials may emit target analytes during warmer sampling periods. If sampler installation is performed on such a roof, it is recommended that the tar or asphalt be encapsulated or sufficiently weathered and that collected samples be evaluated for marker compounds indicative of contamination or influence from the tar or asphalt.

### 2.4.3 Obstructions

An inlet of standalone sampling units and inlet probes must be at least 1 meter vertically or horizontally away from any supporting structure, wall, parapet, or other obstruction. If the probe is located near the side of a building, it should be located on the windward side relative to the prevailing wind direction during the season of highest concentration potential.

Inlet probes must have unrestricted airflow (preference is that 360° around the probe is unrestricted; however, minimally an arc of 270° will be unrestricted around the inlet probe and the unrestricted arc will include the predominant wind direction) and be located away from obstacles so that the distance from the obstacle to the inlet is at least twice the height difference the obstacle protrudes above the inlet. Mounting of inlet probes to the side of a building or wall is strongly discouraged and requires approval by the respective EPA Region. For instance, if a monitoring trailer is 4 m above the inlet of a PM$_{10}$ metals sampling unit, the inlet must be minimally 8 m horizontally from the monitoring trailer.
All sampling inlets must be minimally 10 m from the dripline (end of the nearest branch) of any tree.

2.4.4 **Spacing from Roadways.** Sampling unit inlets for VOCs, carbonyls, PM$_{10}$ metals, and PAHs must meet or exceed the minimum distance from roadways according to Table 2.4-2. Note that these distances should also be observed from parking garages and parking lots.

<table>
<thead>
<tr>
<th>Roadway Average Daily Traffic (ADT), Vehicles per Day</th>
<th>Minimum Distance to Inlet (m) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 15,000</td>
<td>15</td>
</tr>
<tr>
<td>20,000</td>
<td>20</td>
</tr>
<tr>
<td>40,000</td>
<td>40</td>
</tr>
<tr>
<td>60,000</td>
<td>60</td>
</tr>
<tr>
<td>80,000</td>
<td>80</td>
</tr>
<tr>
<td>≥ 100,000</td>
<td>100</td>
</tr>
</tbody>
</table>

a Distance from the edge of the nearest traffic lane. The distance for intermediate traffic counts should be interpolated from the table values based on measured traffic counts. Values in this table taken from 40 CFR Part 58 Appendix E, Figure E-1 for neighborhood scale sites.

2.4.5 **Ongoing Siting Considerations.** Agencies must be mindful of conditions at the site that may impact siting criteria.

Infrequent, non-characteristic, or non-representative sources such as road and building construction may impact measured sample concentrations due to increased dust, emissions from materials utilized (paints, paint strippers, asphalt, etc.), and heavy machinery operation. Other such sources include demolition operations (e.g., buildings or roadways) generating dust which may impact PM$_{10}$ metals concentrations. Application of fresh pavement and painting of traffic lanes generates substantial concentrations of PAHs and VOCs. For sites in residential areas, storage of fuels, operation of charcoal grills, backyard fire pits, and fireplaces can contribute to elevated measured concentrations of PAHs and particulate matter (PM). Concentrations of HAPs measured at rural sites may be affected by forest fires, logging and farming operations, etc. Observation of such conditions must be noted on the sample collection records or site log and may require qualification of results (refer to Section 3.3.1.3.15.1 for use of AQS qualifiers). It is critical that site operators notate such observations, so these notes are available during data validation activities.

Fast growing trees, newly constructed buildings or traffic routes, and other interferences must be noted and recorded in the site log and data must be qualified, as appropriate. When these items negatively impact the siting criteria, the obstruction or interference must be addressed. Such necessary changes to instrument siting should be included in each site’s annual network monitoring plan. For unavoidable impacts to the site (such as a business acting as a significant source), these should be addressed in the network plan and may require siting adjustments. Such interferences and potential relocation should be discussed and addressed in concert with the EPA Regional office. EPA Regions may grant waivers for minor siting issues that cannot be corrected without drastic measures such as relocating a site.
2.5 References


10. Ambient Air Quality Surveillance, Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring, 40 CFR § 58 Appendix E, 2013
3.0: QUALITY ASSURANCE AND QUALITY CONTROL

3.1 NATTS Quality Management Plan

EPA OAQPS developed the NATTS Program QMP to provide a set of minimum requirements that must be followed by all monitoring organizations (SLT organization; or company) conducting NATTS Program work. Development of the QMP began in 2002 and the QMP was completed, approved, and implemented in 2005. Essential QA and QC elements are defined within the NATTS QMP\(^1\) and are excerpted and presented in this document. Monitoring organizations should have their own QMP that adheres to the minimum requirements for conducting NATTS Program work.

3.2 NATTS Main Data Quality Objective, Data Quality Indicators, and Measurement Quality Objectives

There is a single main DQO for the NATTS Program, which is stated as:

To be able to detect a 15\% difference (trend) between two successive 3-year annual mean concentrations (rolling averages) within acceptable levels of decision error.

To achieve this primary DQO, the DQIs of representativeness, completeness, precision, bias, and sensitivity must meet specific MQOs, or acceptance criteria. The MQOs for each of the DQIs are as follows:

- **Representativeness:** Sampling must occur at one-in-six day frequency, from midnight to midnight local time, over 24 ± 1 hours
- **Completeness:** At least 85\% of all data available in a given quarter must be reported
- **Precision:** The CV must be no more than 15\%
- **Bias:** Measurement error must be no more than 25\%
- **Sensitivity:** MDLs must meet the network requirements.

Each entity supporting NATTS Program data collection must ensure that these MQOs are met for each of the DQIs. Implementation of a robust quality system is part of the process to attain such.

3.3 Monitoring Organization QAPP Development and Approval

As noted in Section 2.3, the monitoring organization quality system is the framework that ensures that defensible data of appropriate quality – those that meet the network MQOs for the various DQIs – are generated and reported to EPA so that the NATTS DQO is attained. The NATTS QAPP is the roadmap for design of each organization’s quality system.

Given the importance of the QAPP, each monitoring organization operating a NATTS monitoring site and/or ASL performing analysis of NATTS Program samples must have an up-to-date and fully approved QAPP which covers all aspects of the sample collection, analysis, and QA/QC activities performed by the specific agency and at the associated ASL at which samples
are analyzed. All major stakeholders involved in the monitoring organization’s and/or ASL’s NATTS Program work should provide input to and review the QAPP to ensure that aspects of the QAPP for which they are responsible are accurately and adequately described. The QAPP must minimally be approved and signed by the monitoring organization’s NATTS Program Manager (however named) and the EPA Regional office (or EPA Regional office delegate as defined in the grant language) in which the monitoring site exists (note this applies to ASLs as well which can be in a different Region than the supported monitoring site(s)). The approved QAPP will be submitted to the cognizant EPA Region and the Region will enter the approval date into AQS (note that AQS does not yet permit input of files, such as a pdf of the approved QAPP). Monitoring agencies should work closely with their EPA Region to ensure the QAPP is approved and the approval date is recorded in AQS.

The NATTS QAPP must provide an overview of the work to be conducted, describe the need for and objectives of the measurements, and define the QA/QC activities to be applied to the project such that the monitoring objectives are attained. The QAPP should include information for staff responsible for project management, sample collection, laboratory analysis, QA, training, safety, data review, data validation, and data reporting.

The NATTS QAPP for each monitoring organization is the starting point or roadmap to ensure that the NATTS MQOs, and therefore NATTS monitoring objectives, are achieved. Review of the NATTS QAPP on an annual basis (or as required by the Region), conduct of audits and assessments, and implementation of effective corrective action ensure that NATTS sites and ASLs are in fact achieving NATTS program objectives, and, if not, are implementing corrective actions, as needed.

The NATTS QAPP for each monitoring organization must include the NATTS DQO, DQIs, and MQOs listed above in Section 3.2, and should include elements listed in Section 3.3.1.3 to ensure that data of sufficient quality are generated over time such that concentration trends may be successfully detected and that monitoring data of comparable quality are generated across the entire NATTS network. The NATTS Program DQO, DQIs, and MQOs take precedent over Regional and SLT monitoring objectives for the associated air toxics sampling that is performed unless the SLT requirements are more stringent than those indicated for NATTS. Monitoring agencies are free to prescribe more conservative acceptance criteria (e.g., lower blank acceptance concentrations, tighter recovery ranges, etc.).

### 3.3.1 Development of the NATTS QAPP

EPA has developed a model QAPP\(^2\) for the NATTS Program as described in *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans*\(^3\) and the accompanying document, *EPA QA/G-5, Guidance for Quality Assurance Project Plans*.\(^4\) This model QAPP may be a useful starting point in the development of the QAPP for each monitoring agency conducting NATTS Program work. Note that specific details regarding operational steps are more suitably included into supporting SOPs and that the QAPP should include the higher level requirements and summarize the activities, required frequencies, and acceptance criteria. Monitoring agency NATTS QAPPs are to be Category 2 as defined in the EPA QA Handbook Volume II (January 2017), Appendix C, Table 1.\(^5\) Further guidance on QAPP development can be found in EPA’s Air Monitoring QAPP Guide.\(^6\)
3.3.1.1 **NATTS QAPP – Program DQOs, DQIs, and MQOs.** The NATTS DQOs, DQIs, and MQOs, which are given in Section 3.2 of this TAD, must be included in the NATTS QAPP.

3.3.1.2 **NATTS QAPP – Performance-Based Method Criteria.** NATTS Program work must comply with the requirements listed in this TAD and with the collection and analysis methods specified in Section 4. Acceptance criteria specified in the methods must be met as prescribed; however, method deviations are permitted provided the acceptance criteria for precision, bias, and sensitivity are met and can be demonstrated to be scientifically sound and defensible. The NATTS Program is designed according to the EPA’s Flexible Approaches to Environmental Measurement (FAEM). The FAEM is a performance-based measurement systems approach which prescribes specific methods or approaches to be implemented, but permits deviations in the manner in which the specified methods are performed provided that the resulting data meet the data quality acceptance criteria for precision and bias.

Planned method deviations must be described in the monitoring organization’s QAPP and must be approved by the cognizant EPA Regional office (or delegate as detailed in the grant language). Adjustments to storage conditions and holding times are not permitted, nor are deviations which permit exceedances to the specified method acceptance criteria or to NATTS MQOs as such would allow data of a quality lower than, and not comparable to, that required to be generated in the NATTS network per the NATTS QMP and per this TAD. Agency QAPPs should incorporate much of the guidance listed in this TAD.

3.3.1.2.1 **Alternative Acceptance Criteria Studies.** Monitoring agencies and ASLs that seek to deviate from established/prescribed method conditions or acceptance criteria such as for holding times, storage conditions, sampling media specifications, etc., may do so with approval from EPA OAQPS. To seek OAQPS approval, the monitoring organization or ASL must provide an application to OAQPS that justifies the rationale for the intended deviation and a proposed study design with acceptance criteria for demonstrating equivalency to current status. The study design will include details for the number and nature of the measurements, including QC measurements, intended to demonstrate the equivalency. Additionally, the study design will include the acceptable outcomes of the study (i.e., bias, precision, etc.) for the study.

For example, a monitoring agency may seek a deviation to employ PAH sampling cartridges that include 10 grams (g) of resin sorbent instead of 15 g as the method prescribes. This reduction in resin sorbent mass would be expected to result in a lower collection efficiency for more volatile PAHs such as naphthalene. The application would need to describe the reason for the deviation and the method of comparison that would demonstrate the 10-g loading is equivalent to the 15-g loading. As collection efficiency cannot be demonstrated with laboratory spiked samples, a suitable study would include collection of collocated samples using the established and proposed method over a statistically meaningful number of sampling events to evaluate the equivalency. Monitoring agencies and ASLs may undertake pilot studies to assess the equivalency; however, they are strongly recommended to discuss intent to seek deviation approval with their Region and OAQPS prior to putting forth efforts for formal approval.

3.3.1.3 **NATTS QAPP – Incorporating Quality System Elements.** In addition to the example information contained in the model QAPP listed in Section 3.3.1, monitoring organizations...
should develop and prescribe within the QAPP the following quality system elements which are described in more detail in the following sections:

- Pertinent SOP documents
- Corrective action procedures
- QA surveillance and internal audit procedures
- Calibration and calibration verification of instruments
- Document control (if not covered by a superseding QMP or similar)
- Training requirements and documentation, and demonstration of capability
- Sample custody and storage
- Traceability of reagents and standard materials
- Labeling
- Early warning systems – control charts
- Control of data transformation regimes using spreadsheets and data reduction algorithms
- Software validation, updating, and upgrading
- Review of data and records
- Data verification and validation
- Reporting of results to AQS
- Records retention and archival
- Safety

3.3.1.3.1 Standard Operating Procedure Documents. The NATTS QAPP must list the pertinent SOPs, however named, to be followed to conduct all NATTS Program work. SOPs must prescribe the details of the activities applicable to sample collection at the monitoring site, preparation and analysis of the samples in the laboratory, and data review, reduction, validation, and reporting. Monitoring agencies and ASLs may use discretion for how to organize SOPs as activities (e.g., laboratory preparation of liquid calibration standards) which may be common across methods, therefore may be included by reference to established SOPs. SOPs must minimally cover the following aspects of the NATTS program:

- Sample collection for VOCs, carbonyls, PM\textsubscript{10} metals, and PAHs;
- Sample preparation and analysis for VOCs, carbonyls, PM\textsubscript{10} metals, and PAHs;
- Calibration, certification, and maintenance of each type of sample collection and analysis instrument;
- Calibration of critical support equipment;
- Data review, data validation, and data reporting, and,
- Conducting and reporting audits and assessments.

Additional SOPs should be prepared as necessary to cover routine procedures and repetitive tasks which, if performed incorrectly, could affect data quality such as COC and performing numerical calculations (describing rounding, significant figures, etc.).

Refer to Section 3.3.2 for further guidance on preparation of SOPs.
For portions of the sample collection and analysis which are contracted or otherwise performed elsewhere (not by the cognizant NATTS monitoring agency), the monitoring organization must reference the SOP of the third party in its NATTS QAPP and if the laboratory is other than the national contract laboratory (which are maintained by EPA), must maintain a current, approved copy of the third party’s SOP(s) on file. Monitoring agencies must ensure that third-party laboratory QAPPs and SOPs are available.

3.3.1.3.2 Corrective Action Process. Each monitoring organization must have a corrective action process in place that is executed upon discovery of nonconformances to the NATTS TAD, NATTS agency QAPP, and/or applicable agency SOPs. Each monitoring organization should ideally have a corrective action tracking procedure so that all corrective actions are available in a single location (e.g., binder, database, etc.) and may be readily referenced. Corrective actions are taken to remedy nonconformances found during audits or assessments; however, corrective action must also be performed and documented for systematic nonconformances or problems noted during routine, everyday operations. The corrective action process should be focused on remediating current problems or issues as well as preventing recurrence.

Note that simply exceeding the acceptance criteria for a continuing calibration verification (CCV) does not require a formal corrective action process with detailed documentation. Instead, the analyst will notate the failure and the actions taken to address the failure (e.g., instrument maintenance or recalibration) can be notated in the instrument logbook. The formal corrective action process should be employed when systematic issues occur, such as repeated criteria exceedances on a field blank filter for PM$_{10}$ metals determination, which may indicate a systematic procedural problem where the filter is contaminated. Common corrective actions include process changes documented in a revised SOP, additional staff training, and/or corrections to spreadsheets or software performing calculations.

The formal corrective action process is intended to address unique situations by correction to prevent recurrence. Routine QC failures should not be common, but are expected due to instrument drift or other anticipated condition, and therefore are not systematic in nature and do not require a formal corrective action report (CAR) unless the QC failure occurs routinely. QC charts (discussed in Section 3.3.1.3.10) may help provide some advanced warning that an out-of-tolerance condition may be approaching and may prompt action before an exceedance occurs.

Following closing out of corrective actions for nonconformances identified in an audit or assessment, the QA group should conduct a follow-up audit/assessment to ensure the out-of-tolerance condition is remediated for nonconformances identified. QA staff should also conduct a follow-up audit for other systematic items that rise to the level of requiring a CAR.

For documenting systematic issues, a CAR should be prepared which includes the following components:

- Unique CAR identifier
- Identification of the individual initiating the CAR (staff person’s name)
- Date of discovery of nonconformance
• Date of CAR initiation
• Area or procedure affected (e.g., PM\textsubscript{10} metals sample collection)
• Description of the nonconformance (what happened and how it does not conform)
• Investigation of the nonconformance (how discovered, what is affected by the nonconforming work)
• Root cause analysis (what caused the nonconformance)
• Investigation for similar areas of nonconformance
• Immediate and long-term (if needed) remedial corrective actions (and documentation of when completed) and reocurrence prevention
• Due date for remedial action completion
• Impact assessment of nonconformance
• Assessment of corrective action effectiveness
• Demonstration of return to conformance
• Follow up audit to ensure corrective actions were effective (with date completed)

Situations which would require a corrective action report include, but are not limited to:
• Repeated calibration failure
• Incorrect sample storage conditions
• Blank contamination
• Incorrect procedures followed
• Repeated QC acceptance criteria failures

Root cause analysis should be performed as soon as possible so remedial actions may be taken to correct the problem before it affects other procedural areas or additional samples and to minimize recurrence of the problem. For problems where the root cause is not immediately obvious, a stepwise approach should be taken to isolate the specific cause(s) of the nonconformance(s). Incorrect conclusions may result if too many variables are altered at one time, rendering the corrective action process ineffective.

An example CAR form is shown below in Figure 3.1-1.
3.3.1.3.2.1 Example Corrective Action Process

An example corrective action process follows:

**Nonconformance Discovery and CAR Initiation**: An internal QA auditor conducts a flow rate performance audit of a carbonyls sampler and finds that the flow rates are approximately 11% low on both the primary and duplicate sampling channels. The auditor notifies the site operator and their manager immediately about the out-of-tolerance condition. The auditor also initiates a formal CAR detailing the nonconformance and circumstances.

**Nonconformance Investigation and Root Cause Identification**: The site operator and their manager review the records for the most recent flow rate calibration verifications for indications that flow rates are trending low and toward the ±10% acceptance threshold. They
also review the calibration certificates for the flow rate transfer standards to ensure the certifications are not expired. The site operator performs a flow rate calibration verification on the sampling unit and finds it to be within tolerance (2% lower than the flow transfer standard reading). The site operator notifies the auditor and the auditor and site operator perform flow rate measurements with their respective flow rate transfer standards successively. The auditor and site operator results are confirmed at -11% and -2%, respectively. The auditor reviews the site operator flow transfer standard calibration certificate and notes that the calibration is referenced to standard conditions of 0°C and 760 mmHg and not EPA standard conditions of 25°C and 760 mmHg. The metrology laboratory that typically performs the flow rate calibration had subcontracted their flow rate calibrations to a laboratory in France that calibrates to European standard conditions of 0°C and 760 mmHg. Documentation of these activities (flow rate verification confirmations and their calibration, including email correspondence) is appended to the CAR (either as paper hard copy or as electronic pdfs).

**Immediate Corrective Action and Investigation for Similar Areas of Nonconformance:**
The flow transfer standard calibrated to incorrect standard conditions is taken out of service. The site operator and their manager review the calibration and calibration verification records for other instruments that were calibrated with the same flow transfer standard. Additionally, they compile a list of other flow transfer standards that underwent calibration with the metrology service that may have been certified by the metrology laboratory in France. These lists are communicated to the other monitoring staff and the QA group and this communication (e.g., email) is appended to the CAR. The site operator and their manager follow up on the lists of other instruments and flow transfer standards that may be affected. Instruments identified to have been calibrated with the incorrectly certified standards had their flow rate calibrations reset.

**Impact Assessment of Nonconformance:** The air monitoring group assesses the impact to collected data and whether qualification or invalidation is required. The correction from standard conditions of 0°C and 25°C results in a correction of 9%.

**Long Term Corrective Actions:** The monitoring agency institutes two practices when receiving flow rate transfer standards back from certification before they can be placed into service. The first is to examine the certification documentation to verify the certification was performed at the proper EPA standard conditions of 25°C and 760 mmHg. Second, the newly certified standard is to be compared to a known transfer standard to evaluate reasonableness of the measured flow rates to ensure they were within 5% of the known standard. These details were added to the monitoring agency quality management plan (QMP).

**Assessment of Corrective Action Effectiveness:** The monitoring agency management and QA group determine that affected instruments calibrated with transfer standards certified by the French laboratory will be subject to a flow rate correction of 9% for the carbonyls measurements. However, the French laboratory also certified transfer standards employed for flow rate calibrations of low volume PM₁₀ samplers. The flow rate deviation of 9% from the 25°C standard conditions was too large compared to the design flow rate tolerance of ±5%, therefore resulting in inaccurate particle size cutpoint. Therefore, measurement data from PM₁₀ samples collected with affected samplers were invalidated.
Return to Conformance and Follow-up Audit: Monitoring agency management submitted the flow transfer standards to the metrology service laboratory and informed them of the issue with the standard conditions. When returned from the metrology laboratory after certification, the monitoring staff verified the correct standard conditions on the calibration certificates and compared the transfer standards against known well-performing standards, finding them to perform within ±5%. QA staff conducted independent flow rate audits of the sampling units that had been recalibrated, and noted that all flow rates were within tolerances.

Corrective Action Closeout: The QA staff provided audit reports to management for the flow rate performance audits indicating acceptable performance. Following approval of the amended QMP, monitoring agency management and QA staff signed and closed out the CAR.

3.3.1.3.3 Quality Assurance Unit and Internal Audit Procedures. Each monitoring organization and ASL should have a QA group, or, minimally, an individual QA officer (however named) who is independent of the routine monitoring activities. This QA unit is typically responsible for performing assessments (audits) of sample collection procedures and equipment (i.e., performance audits), sample analysis procedures, data records, and the quality system as well as managing and overseeing the corrective action process, managing document control, performing QA training, and reviewing QC data as applicable. Monitoring organizations which contract laboratory analysis should ensure that the laboratory operates a QA program to oversee and conduct audits of these aspects for which the laboratory is responsible.

QA staff should be independent from project management and routine monitoring functions/activities to best ensure that nonconformances are addressed and remedied and to maximize the likelihood that data of sufficient quality are generated. Moreover, independent QA oversight is integral to ensuring that internal audits are objective. For agencies which may not have sufficient resources to dedicate an independent QA staff member, an individual not affiliated with a given activity may serve to perform QA functions; however, an independent QA unit/person is strongly preferred. The QA staff should conduct four types of audits:

- Technical systems audits (TSAs): An onsite review and inspection of the monitoring agency’s monitoring program to assess compliance with the established regulations governing the collection, analysis, validation, and reporting of ambient air quality data. The auditor observes staff conducting sample collection, sample handling, and analysis activities and compares the activities performed against procedures prescribed in the agency QAPP and applicable SOPs, ensures proper documentation practices, verifies staff training records, verifies proper data reporting, and ensures all operations are performed in accordance with appropriate safety practices.

- Audits of Data Quality (ADQs): The auditor reviews a representative amount (e.g., 10% of collected samples) of reported data to ensure traceability and veracity of measurements, calculations, and transformations from initial receipt of sample collection media through to the final reported results.
• Quality Systems Audits (QSAs): The auditor reviews quality systems documents such as the agency QMP, QAPP, and SOPs to ensure they are current and adequate and to assess compliance with program requirements, such as those stipulated in this TAD.

• Performance Audits: The auditor independently verifies the performance of a measurement system.
  
  o For monitoring sites, the auditor independently measures the flow rate of a sampling unit with a flow transfer standard independent from that employed to calibrate or verify calibration of the sampler. Flow rate audits are to be conducted minimally twice per year (recommended quarterly) and tolerances are those for calibration verification checks listed in Table 3.3-1.

  o Performance audits in the laboratory consist of preparing a standard sample in matrix at a concentration blind to the analyst and providing it to the analyst to evaluate the analyst proficiency. These performance evaluation (PE) samples will meet the laboratory control sample (LCS) acceptance criteria for the method or the CCV acceptance criteria (if no LCS is specified for the method). PEs of laboratory analysis methods should be conducted annually or more frequently, if possible. PEs in the laboratory may be difficult for QA staff to conduct if they do not have experience with the laboratory activities required to prepare the PE sample. The NATTS PT program can serve as a suitable substitute for this independent assessment.

The monitoring organization and/or ASL QAPP, SOP, or other suitable controlled document should define the schedule for audit frequency, the scope of each type of audit (i.e., which operational areas must be observed, which records must be reviewed, etc.), the timeline for following up on audit nonconformances, the timeline for conducting follow-up audits that ensure that nonconformances are being remedied in a satisfactory and timely manner, and the convention for reporting audit outcomes to agency management and staff.

3.3.1.3.4 Calibration and Calibration Verification of Instruments. Each critical instrument must be calibrated initially before being placed into use and the calibration thereafter verified periodically at a prescribed frequency. Recalibration - the adjustment of an instrument’s operation or response to match a standard - is required when calibration verifications fail the prescribed criteria (tolerance) or when maintenance or other conditions reasonably result in a change in the instrument operation or response and necessitate establishing or adjusting the calibration. Provided instruments continue to meet criteria for calibration verification (and the instrument has not been modified in a manner that impacts the sensitivity), recalibration (adjustment) is not necessary.

For clarity, calibration verification frequencies are to be interpreted such that an instrument currently in use has successfully passed calibration verification within the specified timeframe. For example, a flow transfer standard requires calibration verification annually; therefore, an in-service flow transfer standard must have undergone calibration verification in the previous 12 months. Each agency must define in the NATTS QAPP, SOP, or similar controlled document the frequency at which critical instruments must be calibrated and the acceptable tolerance for such calibrations. Critical instruments are defined as those whose measurements directly impact the accuracy of the final reported concentrations. The calibration of such instruments must be
traceable to a certified standard and standard calibration process such as those typically available as a service from an accredited provider (e.g., National Institute of Standards and Technology [NIST], American Association for Laboratory Accreditation [A2LA], American Society for Quality [ASQ], International Organization for Standardization/International Electrotechnical Commission [ISO/IEC]). Critical instruments include, but are not limited to:

- Flow rate transfer standards
- Mass flow controllers (MFCs), mechanical flow controllers, and meters generating flow readings for calculating total collected sample volumes and diluting standard gases
- Thermometers and barometers measuring temperature and barometric pressure for metering sampling flow rates
- Volumetric delivery devices such as fixed and adjustable pipettes, bottletop dispensers, etc.
- Balances
- Pressure gauges and transducers for measuring sample canister pressures and measurements for dilution or standard preparation

Such critical instruments must be calibrated initially before placed into service and the calibration verified (checked) periodically to ensure the calibration remains valid. Calibration verifications are detailed in the following section.

**3.3.1.3.4.1 Calibration Verification (Checks)**

Following instrument calibration, critical instruments must undergo periodic calibration verification (check) to ensure bias meets the assigned acceptance criterion. Calibration checks typically challenge the instrument at a single point typical of use or toward the middle of the calibration range and in the as-is or as-found condition (no adjustments are made to the instrument prior to the verification). Calibration checks may also include multiple points bracketing the range of use. Instruments must be recalibrated (or removed from service and replaced with a properly calibrated unit) when calibration verifications fail. Data generated with the failing equipment since the last acceptable calibration or calibration verification must be examined and the impact of the out of tolerance condition considered for qualification or invalidation. Monitoring agencies and ASLs are recommended/encouraged to perform calibration verification checks more frequently than the minimum requirement to limit the amount of data subject to qualification or invalidation when calibration verification checks fail acceptance criteria. Frequency of calibration verifications must conform to Table 3.3-1 and must be prescribed within the agency NATTS QAPP, SOPs, or similar controlled document.
<table>
<thead>
<tr>
<th>Instrument or Standard</th>
<th>Area of Use</th>
<th>Calibration Verification * Frequency and Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balances</td>
<td>Laboratory – Weighing standard materials, calibration of pipettes, determining mass loss for microwave metals digestion, weighing PAHs sorbent resin (e.g., XAD-2)</td>
<td>Each day of use with certified calibration check weights bracketing the balance load; tolerances within those specified by manufacturer</td>
</tr>
<tr>
<td>Certified Weights</td>
<td>Laboratory – Calibration verification of balances</td>
<td>Annual calibration certification by accredited metrology laboratory. A working set of weights need not be certified annually if a primary set of weights is certified annually, in which case the working set is verified quarterly against the primary set; tolerances within those specified by weight class or manufacturer. The working set is employed for routine balance calibration verification and the primary set is reserved for calibration verification of the working set.</td>
</tr>
<tr>
<td>Mechanical Pipettes</td>
<td>Laboratory – Dispensing liquid volumes</td>
<td>Minimally quarterly, recommended monthly, by weighing delivered volumes of deionized water bracketing those dispensed; tolerances within those specified by manufacturer. Presumes density of deionized water is 1 g/cm³; however, laboratories may correct density for temperature of water.</td>
</tr>
<tr>
<td>Bottletop Dispensers</td>
<td>Laboratory – Dispensing critical liquid volumes</td>
<td>Each day of use or when dispensed volume settings are adjusted by delivery into a ‘To Contain’ (TC) graduated cylinder; &lt; ±5.1%</td>
</tr>
<tr>
<td>Thermometers – Laboratory</td>
<td>Laboratory – Temperature monitoring of water baths, metals digestion, refrigerated storage units, canister cleaning ovens, and water for pipette calibration</td>
<td>Annual at temperature range of use or at not-to-exceed temperature – Correction factors applied to match certified standard thermometer. Correction factor is not needed if temperatures are &lt; ±0.5°C.</td>
</tr>
<tr>
<td>Flow Controllers and Meters – Laboratory</td>
<td>Laboratory – MFCs, flow rotameters, or similar devices for measuring/metering gas flow rates for critical measurements (standard gas mixing)</td>
<td>Minimally quarterly, monthly recommended Flow &lt; ±2.1% of certified standards</td>
</tr>
<tr>
<td>GC/MS for VOCs analysis</td>
<td>Laboratory – Analysis of VOCs from stainless steel canisters</td>
<td>Verified each day of analysis by analysis of a CCV. Tier I core VOCs must be &lt;±30.1% of theoretical nominal or relative response factor (RRF) &lt; ±30.1% of initial calibration (ICAL) average. Tier II analytes should meet this criterion. Refer to Section 4.2.8.6.2 for additional discussion and details.</td>
</tr>
</tbody>
</table>
Table 3.3-1. Calibration Verification Frequencies for Standards and Critical Instruments (Continued)

<table>
<thead>
<tr>
<th>Instrument or Standard</th>
<th>Area of Use</th>
<th>Calibration Verification a Frequency and Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>High performance liquid chromatograph (HPLC) for carbonyls analysis</td>
<td>Laboratory – Analysis of carbonyl-DNPH extracts</td>
<td>Verified each day of analysis by analysis of a CCV. Tier I core carbonyls must be &lt; ±15.1% of theoretical nominal. Tier II analytes should meet this criterion. Refer to Section 4.3.9.5.4 for additional discussion and details.</td>
</tr>
<tr>
<td>Inductively coupled plasma/mass spectrometer (ICP/MS) for metals analysis</td>
<td>Laboratory – Analysis of PM$_{10}$ digestates for metals</td>
<td>Verified after each day’s ICAL by analysis of a CCV and every 10 sample analyses thereafter and concluding analysis sequence. Tier I core metals must be &lt; ±20.1% of theoretical nominal. Tier II analytes should meet this criterion. Refer to Section 4.4.11.7.5 for additional discussion and details.</td>
</tr>
<tr>
<td>GC/MS for PAHs analysis</td>
<td>Laboratory – Analysis of PUF/resin/quartz fiber filter (QFF) extracts for PAHs</td>
<td>Verified each day of analysis by analysis of a CCV. Tier I core PAHs must be &lt; ±30.1% of theoretical nominal or RRF &lt; ±30.1% of ICAL average. Tier II analytes should meet this criterion. Refer to Section 4.5.5.5.5 for additional discussion and details.</td>
</tr>
<tr>
<td>Barometers</td>
<td>Field – Recording environmental conditions during sample collection Laboratory – Recording environmental conditions during instrument calibration</td>
<td>Minimally quarterly, monthly recommended Must be &lt; ±10.1 mm mercury (Hg) of certified standard at typical barometric pressure</td>
</tr>
<tr>
<td>Pressure Gauges or Transducers</td>
<td>Field and Laboratory – Measure canister pressure/vacuum before and after collection, measure final canister vacuum following cleaning</td>
<td>Annual calibration verification. Must be &lt; ±0.51 pounds per square inch (psi) or manufacturer-specified tolerance and cover the range of use</td>
</tr>
<tr>
<td>Thermometers, Thermistors, and/or Thermocouples – Meteorological</td>
<td>Field – Recording environmental conditions during sample collection for determining sampling flow rate Resolution 0.1°C</td>
<td>Annually, quarterly recommended &lt; ±0.51 of certified standard at working temperature</td>
</tr>
<tr>
<td>Flow Transfer Standards (including temperature and barometric pressure standards)</td>
<td>Field – Critical flow orifices and volumetric flow meters for calibrating and verifying sampling unit flows Built-in thermometers and barometers must be calibrated</td>
<td>Annual certification by an accredited metrology laboratory. Flow &lt; ±2%, temperature &lt; ±0.5°C, and barometric pressure &lt; ±5 mmHg.</td>
</tr>
</tbody>
</table>
Table 3.3-1. Calibration Verification Frequencies for Standards and Critical Instruments (Continued)

<table>
<thead>
<tr>
<th>Instrument or Standard</th>
<th>Area of Use</th>
<th>Calibration Verification a Frequency and Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC Sampling Units</td>
<td>Field – Collection of VOCs into canisters</td>
<td>Annually for pressure gauge/transducer, must be &lt; ±0.5 psi (required if used for critical measurements of beginning and ending canister pressure, otherwise optional)</td>
</tr>
<tr>
<td></td>
<td>Flow control (such as MFC)</td>
<td>Flow control quarterly &lt; ±10.1% of certified flow (required for subambient pressure collection to ensure flow rate does not exceed the constant flow rate pressure threshold of sampling, optional for pressurized sampling)</td>
</tr>
<tr>
<td></td>
<td>Pressure gauge/transducer</td>
<td></td>
</tr>
<tr>
<td>Carbonyl Sampling Units</td>
<td>Field – Collection of carbonyls on DNPH sorbent cartridges</td>
<td>Minimally quarterly, monthly recommended</td>
</tr>
<tr>
<td></td>
<td>Flow control (such as MFC)</td>
<td>Flow &lt; ±10.1% of certified flow and design flow</td>
</tr>
<tr>
<td>PM₁₀ Metals Sampling Units</td>
<td>Field – Collection of PM₁₀ on filter media for metals analysis</td>
<td>Minimally quarterly, monthly recommended</td>
</tr>
<tr>
<td></td>
<td>Flow control must be within tolerance</td>
<td>Low volume flows &lt; ±4.1% of transfer standard and &lt; ±5.1% of design flow</td>
</tr>
<tr>
<td></td>
<td>If equipped, thermometer and barometer must be within field tolerances specified above</td>
<td>High volume flows &lt; ±7.1% of transfer standard and &lt; ±10.1% of design flow</td>
</tr>
<tr>
<td>PAH Sampling Units</td>
<td>Field – Collection of PAHs on QFF, PUF, and resin sorbent media sampling modules</td>
<td>Minimally quarterly, monthly recommended</td>
</tr>
<tr>
<td></td>
<td>Flow control must be within tolerance</td>
<td>Flow &lt; ±10.1% of certified flow and design flow</td>
</tr>
<tr>
<td></td>
<td>If equipped, thermometer and barometer must be within field tolerance specified above</td>
<td></td>
</tr>
</tbody>
</table>

Calibration verification checks are a comparison to a certified standard, typically at a single point at which the instrument is used, to ensure the instrument or standard remains within a prescribed tolerance. Instruments or standards which exceed the tolerance upon performing calibration verifications must not be used until they can be adjusted to within prescribed tolerances. Alternatively, source a suitable calibrated substitute instrument.

3.3.1.3.5 Document Control System. Each monitoring organization and ASL must have a prescribed system defined in its NATTS QAPP or QMP for control of quality system documents such as QMPs, QAPPs, and SOPs. Monitoring agencies and ASLs may refer to Section 5 of the EPA QA Handbook Volume II (January 2017) for more information on document control systems. A properly operating document control system ensures that all documents integral in defining performance criteria and prescribing procedures are current, and that outdated or superseded documents are not available for inadvertent reference. All such controlled documents must minimally be approved by a cognizant manager (however named) who is ultimately responsible for the conduct of the work (e.g., monitoring agency director for an agency QMP, NATTS program manager for the NATTS QAPP, monitoring manager or laboratory manager for...
a field or analytical SOP, etc.), and by a QA staff member responsible for overseeing the work. Current versions of controlled documents must be readily available to each staff member conducting NATTS Program work and superseded documents must be removed from access.

The distribution of controlled documents should be managed and tracked such that only the current, approved versions are available in areas in which such documents are needed (for example, at field sites and in laboratories) and that outdated versions are removed once superseded. With the proliferation of networked computers at monitoring sites and within laboratories, it is convenient to have electronic versions of controlled documents available which are write-protected. Printing privileges of such read-only electronic documents should be disallowed, or, if printing is permitted, such documents should be identified via watermark with the date of printing and their expiration (e.g., 1 week from printing or date of superseding, whichever is sooner).

Procedures and frequency for changing and updating controlled documents should be clearly described in a quality systems document. Preparing amendments is an efficient way to address minor changes to controlled documents. An amendment describes the change and rationale for the change, and may be appended to the document without requiring a complete revision of the document. Such amendments should be approved minimally by the cognizant manager (field operations manager or laboratory manager) responsible for the conduct of the work, and by a member of QA staff responsible for the document and overseeing the work. For major changes to controlled documents, such as those required for a new sampling unit or updated laboratory information management system (LIMS), a new revision should be prepared and approved by all required signatories. A system for identifying revisions should be prescribed to allow tracking of versions. A typical example system uses whole numbers to designate major revisions and decimals to indicate minor revisions. For example, the first version of a QAPP would be version 1.0, a minor revision would update to version 1.1, and the next major revision would be version 2.0, and so on.

An effective date must be included on all controlled documents and the controlled should include an issue date if this is different from the effective date. A period between the issue date and effective date permits staff to become familiar with the SOP prior to its becoming effective. A header or footer should indicate the effective date, version number, page number, and total number of pages included in the document. A best practice is to include a revision history section for each controlled document so that readers can quickly and efficiently ascertain changes from the previous version of the document.

Monitoring agencies and ASLs should forbid uncontrolled excerpts to be printed from controlled documents such as operation instructions or calibration standard preparation tables. These excerpts are then uncontrolled and may inadvertently be referenced when the version of origin is no longer effective. For the same reason, unless permitted by the agency’s controlled document policy, uncontrolled shortcut procedural summary documents (summarizing SOP procedures) similarly should not be permitted. Such procedure summaries are useful and may be included in the NATTS QAPP or applicable SOP to ensure they are updated when the parent document is revised. Similarly, notes should not be recorded on controlled document hard copies unless permitted by the monitoring organization’s controlled document revision or amendment process.
The review frequency for controlled documents should be described within the QMP, QAPP, or similar controlled document. Periodic review of controlled documents must be performed to ensure that they adequately describe current policies and procedures. Each such review and outcome of the review (e.g., adequate, minor revision needed, major revision needed, etc.) must be documented and this documentation maintained. Monitoring agencies are strongly recommended to review their NATTS QAPP on an annual basis (i.e., a period not to exceed 13 months) and revise the QAPP when conditions change. At a minimum, the monitoring agency NATTS QAPP must be revised within five years of the most recent revision unless the respective Region indicates a different revision period. Associated SOPs are recommended to be reviewed annually, but must minimally be reviewed every three years. The NATTS QAPP is expected to undergo revision when there are programmatic changes to the NATTS program to which the monitoring agencies and/or ASLs must comply. SOPs must be reviewed following major changes to network guidance to ensure they are compliant with the updated guidance.

3.3.1.3.6 Training Requirements and Documentation, and Demonstration of Capability. The training required for each staff member who conducts NATTS Program work must be prescribed in the agency NATTS QAPP, SOP, or similar controlled document, and the completion of each required training element must be documented. Specifically, staff must read, and document that they have read and understood, the most recent versions of the NATTS quality system documents (QAPP, SOPs, etc.) pertaining to their responsibilities.

Each monitoring organization and ASL must have minimum requirements for staff position experience including a combination of education and previous employment experience. In addition to documented experience, each staff member must be approved by cognizant management to conduct the activities for which they are responsible. Such approval should be in place initially before beginning work and periodically thereafter, and should be minimally based on successful completion of a demonstration of capability (DOC) process. DOCs are described in the subsections below.

Each staff member must have training documented which indicates the staff member’s training is current for each procedure performed, as required by the agency QMP, NATTS QAPP, SOP, or similar controlled document. Training documentation can consist of hard copy or electronic documentation and may be organized in a convenient manner provided it can be retrieved for auditing purposes. In addition to relevant DOC documentation, the training records should include items related to experience such as a resume or curriculum vitae, certificates from training coursework, and a job description specific to the monitoring organization.

3.3.1.3.6.1 Initial Demonstration of Capability

Once the staff member has read the relevant current SOP(s), and documented such, the staff member must demonstrate proficiency with a given procedure prior to performing activities to generate or manipulate NATTS program data. One method by which such could be accomplished is as follows. First, the staff member observes an experienced staff member performing the procedure. Next, the trainee conducts the activity under the immediate supervision of and with direction from an experienced staff member. Finally, the trainee
performs the activity independently while being observed by an experienced staff member. To ensure all aspects of a procedure are captured in the initial demonstration of capability (DOC), it is recommended that a checklist be developed which includes all required steps consistent with the applicable quality system document(s) to perform the activity. Regardless of the actual initial DOC process selected for implementation, the process to be implemented and its acceptance criteria must be defined in the QAPP, SOP, or similar controlled document.

### 3.3.1.3.6.2 Ongoing Demonstration of Capability

Each staff member performing NATTS Program field work must demonstrate continued proficiency with tasks for which they are responsible, minimally every three years, but recommended to be annually. The staff member should be observed by a QA staff member (as part of an audit), experienced staff member, or responsible manager.

Laboratory staff must annually demonstrate continued proficiency by completing one of the following:

- Repeat of the initial DOC procedure.
- Acceptable performance on one or more blind samples (single blind to the analyst) following the approved method for each target analyte. Acceptable performance is indicated by demonstrating recovery within limits of the method LCS for each target analyte.
- Analysis of at least four consecutive LCSs with acceptable levels of bias. Acceptable performance is indicated by demonstrating recovery within limits of the method LCS for each target analyte for all four samples.
- Acceptable performance on a PT sample. Acceptable performance is defined by the provider of the PT sample, as indicated by no results marked as “Unacceptable” or equivalent, for target analytes.

As with the initial DOC, the continuing DOC process and its applicable process acceptance criteria must be prescribed in the agency NATTS QAPP, SOP, or similar controlled document.

### 3.3.1.3.7 Sample Custody and Storage

Procedures and details related to sample custody and sample storage must be included in each monitoring organization and ASL NATTS QAPP or similar document such as a sample handling SOP. Additional information related to sample custody can be found in Section 1.2.1.3.2 of and throughout EPA’s Best Practices for Review and Validation of Ambient Air Monitoring Data.

The COC is a documented trail of who had possession of a sample or group of samples at any specific point from collection through receipt at the laboratory. Custody records must include details of transfers of possession between individuals, between individuals and shippers (when applicable), and to storage at the laboratory and any pertinent details such as storage location and conditions. It is strongly recommended to maintain sample integrity that samples be protected and access to the samples be limited to those responsible for the samples.
Sample custody begins when media are readied for dispatch to the field monitoring site. At this point, a COC form, sample collection form with portions dedicated to documenting custody transfers, or other form as defined by the monitoring agency, must accompany the sampling media until they are received at the laboratory for analysis. Each time the sampling media are transferred, the individual relinquishing the sample and receiving the sample, the date and time, and the storage conditions (for carbonyl and PAH samples) should be documented so the history of the sample is traceable and can be reconstructed. Storage conditions for carbonyl and PAH samples must be monitored with a calibrated thermometer and storage records should include unique identifiers for the thermometers monitoring the storage units. Note that sample shipments do not require temperature monitoring during shipment; however, the shipment temperature conditions will need to be documented (e.g., shipped on ice or freezer packs, etc.) since the sample temperature will be measured when received at the laboratory.

Sample collection forms or other forms as defined by the monitoring agency may double as a COC form provided they include sufficient space for documenting sample transfers and storage conditions.

If not already assigned prior to dispatching to the field, upon receipt at the laboratory each specific field-collected sample medium (cartridge, filter, canister, etc. including all field QC) must be uniquely identified for tracking within the laboratory. This unique identifier allows each sample to be tracked to ensure proper storage within the laboratory and to avoid mix-up of samples which can invalidate sample data.

3.3.1.3.8 Traceability of Reagents and Standard Materials. Each monitoring organization must prescribe in its NATTS QAPP, or similar controlled document, the information to be recorded and maintained for traceability of reagents and standard materials and must codify the requirements for their labeling.

All reagents and standard materials utilized in the preparation and analysis of NATTS Program samples must be of known concentration or purity as documented by a certificate of analysis (COA) or similar certification and such certification documents must be retained. The following aspects of reagents and standard materials must be documented:

- Deionized water sourced from a water polisher
  - Records of the water polisher maintenance (e.g., filter or scrubber replacement)
  - Records for resistivity measurements to demonstrate that the water is of appropriate quality each day of use
- Reagents prepared from separate components
  - Source of all reagents must be traceable to the COAs - lot or batch numbers for each reagent (acid, solvent, etc.) and expiration date(s)
  - Critical volume measurements (e.g. delivered volumes of stock standards, final volumes of diluted standards) including unique identifiers (where applicable) for measurement devices:
- volumetric syringes
- mechanical pipettes
- volumetric flasks

- Conditions at which the reagents and standards are stored, particularly for those reagents and standards which require special conditions such as refrigeration or protection from light.
  - If maintenance of a specific temperature range or not-to-exceed temperature is required
    - Temperature(s) of storage unit(s) must be measured and documented at a prescribed frequency (recommend minimally daily during normal working hours)
    - Calibration of thermometers for monitoring storage unit temperature must be certified and traceable at a temperature range that includes the critical temperature or at the critical temperature (e.g., for a carbonyls sample storage refrigerator, the thermometer must be calibrated at 4°C or over a range including 4°C). A calibrated min-max type thermometer or continuous monitoring (e.g., with a datalogger) is recommended to ensure that the not-to-exceed temperature is maintained.

Expiration dates must be assigned to reagents and standards and must be set as the earliest expiration date among any component comprising the reagent or standard. If the expiration date is given as a month and year, the date after which the reagent or standard may not be used is understood to be the last day of the indicated month. For reagents or standards which were not assigned an expiration by the supplier, the monitoring agency may assign an expiration (recommended not to exceed five years) commensurate with the understood storage integrity of the materials. The policy for assigning the expiration date (when not provided by the manufacturer) must be prescribed in the monitoring agency QAPP, SOP, or similar controlled document.

3.3.1.3.9 Labeling. Each NATTS monitoring organization and ASL must have a prescribed procedure for labeling of samples, standards, and reagents. Each must be uniquely identified and the identifier clearly labeled on the applicable container (e.g., VOCs canister tag, DNPH cartridge foil pouch, metals filter holder, PAHs cartridge transport jar, gas chromatograph [GC] vial containing solvent, etc.).

Standards and reagents must be minimally labeled with the following:
- Identity of the contents (e.g., 69-component VOC blend in nitrogen, 2 µg/mL benzo(a)pyrene in hexane, 2% v/v nitric acid, etc.)
- preparation date
- expiration date
- required storage conditions.
Standards and reagents prepared or mixed in the laboratory must be traceable to a preparation log and the details described in Section 3.3.1.3.8 documented.

3.3.1.3.10 *Early Warning Systems – Control Charts.* Monitoring agencies and ASLs are recommended to employ control charting where practical to track QC parameters. If used, the process of control charting should be described in the NATTS QAPP, SOP, or similar controlled document. Parameters suitable for control charting include concentrations measured in QC samples such as blanks, laboratory control spikes, matrix spikes (MSs), second source calibration standards, internal standards, PT results, precision field collected samples, and field QC blanks (field blanks and trip blanks). Control charts may be prepared with spreadsheets and many LIMS incorporate control charting capabilities. Once implemented, control charts do not typically require substantial effort to maintain (particularly if a LIMS or data handling software program can populate the data) and are a valuable tool for evaluating trends and may provide an alert before nonconformances occur. Control charts should be periodically updated and reviewed to ensure data inputs are current and that associated control limits (CLs) meet method-specified criteria. The update frequency should be prescribed in the applicable controlled document. Additional information regarding implementation and use of control charts can be found in Section 10.5 of the EPA QA Handbook Volume II.5

3.3.1.3.11 *Spreadsheets and Other Data Reduction Algorithms.* While spreadsheets and other automated or semi-automated data reduction algorithms, for instance, those contained in LIMS software, are valuable tools for transforming and reducing data generated by sampling and analysis instruments, they have limitations and may be sources of error if not validated prior to use and upon revision or update. If a NATTS agency or ASL employs such processes it should prescribe within the NATTS QAPP, SOP, or similar controlled document the details for preparation, review, and control of data reduction spreadsheets or of other non-commercial automated and/or semi-automated data transformation and reduction algorithms and processes. Implementation of such processes will require an initial time investment to properly validate, but should minimize errors and subsequently increase the efficiency and speed of data reporting. If an agency was to implement such processes, it should prescribe the relevant procedures into its QAPP or other quality system document and may consider adoption of the following best practices.

Where possible, manual entry/transcription of instrument data into spreadsheets and/or non-commercial automated data transformation/reduction algorithms should be minimized. Rather, the direct importation of data outputs from instruments into such systems is preferable so as to avoid transcription errors. Furthermore, data reduction spreadsheets or other non-commercial algorithms must be validated and locked/non-editable to ensure that critical formulas are not inadvertently altered. The process of validation of the spreadsheet or non-commercial algorithm must be prescribed in a quality system document such that it is known and verifiable that all critical aspects of the data reduction procedure have been confirmed to be technically defensible, valid, and error-free. This validation should be performed when the spreadsheet or non-commercial algorithm is revised.
3.3.1.3.12 Software Validation, Testing, Updating, and Upgrading. Each monitoring agency and ASL performing NATTS Program work should have prescribed within the agency NATTS QAPP, SOP, or similar controlled document policies and procedures for testing, updating, and upgrading computer software systems employed for data generation and manipulation such as chromatography data systems (CDSs), LIMS, and other instrument software where applicable. The policies and procedures should detail the responsible individuals, testing required, and documentation to be maintained.

3.3.1.3.12.1 Software Validation

Off-the-shelf software packages such as spreadsheet programs (e.g., Microsoft® Excel) are presumed to be validated. It is strongly recommended that individual spreadsheets (i.e., those with calculation formulas and/or macros) employed as templates should be validated as described in Section 3.3.1.3.11. Other software packages such as CDS should undergo validation by manually calculating values to ensure that software outputs match the expected result. Due to the differences in algorithms or limitations to how software packages handle calculations, there may be slight differences between commercial software package outputs and spreadsheets or other software systems. Such differences should be noted and addressed where possible if they impact digits which are significant in the calculations. Records of software validation must be maintained.

3.3.1.3.12.2 Software Testing

Once validated, software packages should be tested minimally annually and when updated or upgraded to ensure that calculations are being performed as expected. This may be performed by processing a previously processed dataset through the software and comparing the outputs for parity. The rationale behind such testing is to ensure that software systems and calculation regimes have not become corrupted. Discrepancies in outputs must result in corrective action to rectify the discrepancies.

3.3.1.3.12.3 Software Updating and Upgrading

Software manufacturers periodically release software updates to correct bugs or coding errors, improve the user interface, or include new functionality, etc. Updates or upgrades installed should be documented in a log and be verified for proper operation by the testing regimen prescribed in Section 3.3.1.3.12.2. Monitoring agencies and ASLs should verify that upgrades were performed and the date they were performed.

3.3.1.3.13 Peer Review of Records. To ensure that sample collection and analysis activities were performed as prescribed, are documented completely and accurately, and to identify potential nonconformances that may invalidate data, all logbooks, forms, notes, and data must be reviewed by a second individual (peer) who has familiarity with the procedure but who did not generate the record. Field site notebooks, site equipment maintenance logs, sample collection forms, COC forms, laboratory preparation logs, analysis instrument logs, storage temperature logs, and all other critical information must be reviewed on a periodic basis by an individual who did not record the documentation. Each record should minimally be reviewed for legibility,
completeness, traceability, and accuracy (including hand calculations not performed by a validated spreadsheet). These reviews must be documented, either within the records themselves, or in a separate review notebook or form indicating the individual performing the review, the materials reviewed, the scope of the review (e.g., completeness and calculations), and the date(s) the review was performed. Details of the review scope, schedule, responsible individuals, and required documentation must be described in the NATTS QAPP, SOP, or similar controlled document. These reviews should occur minimally quarterly and a best practice would be to conduct reviews monthly (this more frequent review allows identifying documentation gaps and/or problems to reduce the number of affected samples than if the reviews were conducted quarterly).

If documentation errors are noted during review, they should be corrected as soon as practical. Correction of handwritten entries must be performed with a single line, the correct entry must be made nearby or be traceable to an annotated footnote, the individual making the correction must be identified by signature or initials, the notation must include the date the correction was made, and the notation should include the rationale for the correction. Corrections to electronic logs must likewise not overwrite the original record, must identify the individual making the correction, must include the date of the correction, and should include the rationale for the correction. Further guidance on maintaining electronic logs is available in the EPA Technical Note - Use of Electronic Logbooks for Ambient Air Monitoring. 8

Note that reviewing records as described in this section is a component of the data verification and data validation process described in the next section, but should not be substituted for the data verification and data validation process.

3.3.1.3.14 Data Verification and Validation. Data verification is the systematic process for evaluating objective evidence (data) for compliance with requirements for completeness and for correctness as stipulated by a specific method. Objective evidence consists of the records such as sample collection forms, sample storage records, laboratory preparation records, calibration records, analysis results, etc. Validation is the confirmation that verified data have met specific intended use requirements, i.e., meeting DQO requirements prescribed in the NATTS QAPP. 9

Spurious data have an outsized influence on statistical analysis and modeling; thus, data must be closely examined to ensure that concentration values accurately reflect air quality conditions at the monitoring site through verification and validation. Monitoring organizations must not censor (invalidate) data they consider to be anomalous or spurious. Data should only be invalidated if they do not meet the critical specifications in the validation tables in Section 7 or when there is a known problem with the data which would invalidate them. For data suspected to be spurious or anomalous but do not indicate a reasonable rationale for their invalidation, they should be qualified appropriately when entered into AQS so the end data user can decide the most suitable manner for handling the data.

Each monitoring organization and ASL must prescribe processes and policies within its NATTS QAPP or other quality systems document for data verification, data validation, and the associated documentation that is generated and retained during the processes of verification and validation of data. NATTS agencies are expected to perform data verification and validation in accordance
with the tables in Section 7 of this TAD where method-specific criteria are summarized. Additional information on implementing and structuring data validation and verification policies and procedures can be found in the following EPA reference documents:

- *Guidance on Environmental Data Verification and Data Validation* (EPA QA/G-8)\textsuperscript{9}
- Section 17 of the *EPA QA Handbook Volume II (January 2017)*\textsuperscript{5}
- *Best Practices for Review and Validation of Ambient Air Monitoring Data*\textsuperscript{7}

### 3.3.1.3.14.1 Data Verification

The data verification process begins when sample media are dispatched to the field for collection and ends following final review of a completed data package. Verification includes many of the aspects of data review described in Section 3.3.1.3.13 as well as additional QC checks such as verification of proper sample handling and verification of calculations. Once data verification is completed, data validation can be conducted. Given in this section is a generic data verification process that a NATTS agency may adopt. Aspects of data verification must be completed before data are reported to AQS. Minimum parameters for data verification are those listed in the tables in Section 7.

Upon retrieval of samples in the field, the field operator verifies that sample collection parameters comply with SOPs and documents the collection details on the field sample collection form. At the ASL, custody documentation is reviewed to ensure that sample collection documentation meets specification and does not exhibit anomalies which would compromise or invalidate the collected sample’s data. Laboratory analysts ensure that media have been stored properly and that QC samples are prepared according to method specifications. Following acquisition of the analytical data, the analyst reviews QC results as well as the acquired data to ensure proper analyte identification and to verify that method-specified acceptance criteria are met. A peer then reviews the entire data package beginning with sample collection and custody documentation through preparation, analysis, and calculation of analytical concentrations so as to ensure that method procedures were properly followed, calculations are correct (e.g., dilution factors correctly applied), and method-specific acceptance criteria are met. At any point during the initial and/or peer review, identified errors must be corrected and additional notes added to describe problems or anomalies in the sample collection and analysis processes. QC failures or method deviations must be documented and appropriate qualifiers applied to the results so staff performing data validation may be alerted regarding data which may be compromised or require invalidation.

### 3.3.1.3.14.2 Data Validation

Data validation is performed following the data verification process and is a separate process from the network-wide assessments made by data users to evaluate trends and assess whether data meet MQOs. It is EPA’s expectation that monitoring agencies will ensure their reported data have undergone validation prior to reporting to AQS. Additional information on data validation is available in EPA’s *Guidance on Environmental Data Verification and Data Validation*.\textsuperscript{9}
During validation, data are evaluated by the monitoring agency for compliance with specific use requirements which may include comparison of collocated sample results, examination of meteorology data, sample collection notes, and custody forms, and review of historical data for trends analysis and identification of outlier data. Such may involve preparation of time-series plots and stacked bar charts to review the temporal quality of a parameter or group of parameters, or may involve generating scatterplots to evaluate the relationship between directly or inversely proportional parameters. Additional comparisons and evaluations may be prepared by using data visualization tools to compare data from different networks at the same or nearby sites (e.g., PM$_{10}$ Pb concentration compared to TSP Pb).

Attainment of the NATTS MQOs should also be assessed by monitoring agencies to determine if the data will support attainment of the NATTS DQO. Failure to attain the NATTS MQOs must prompt corrective action. Given in the remainder of this section is a generic data validation process that a NATTS agency may adopt. Monitoring agencies are responsible for ensuring that data verification and validation are completed before the data are reported to AQS. While EPA may assess the data quality and completeness during periodic data assessment activities, EPA does not perform further validation on data reported to AQS.

An appropriate starting point for validating data involves preparing summary statistics by calculating the central tendency of the dataset along with the standard deviation and relative standard deviation of the concentrations of each HAP. The central tendency may be calculated as the arithmetic mean, geometric mean, median, or mode:

- **Arithmetic mean**: The sum of the measured concentration values divided by the total number of samples in the dataset.
- **Geometric mean**: The $n$th root of the product of $n$ concentration values.
- **Median**: The concentration value represented by the midpoint of the dataset when the concentration values are placed in numerical order. Fifty percent of the resulting concentration values will be above this value and 50% will be below.
- **Mode**: The concentration value with the highest frequency.

Once the summary statistics have been prepared, the datasets may be examined for maximum and minimum values and for those data points that are outside the mean ± three standard deviations or other appropriate metric such as the 5th and 95th concentration percentile.

Each HAP and combination of HAPs may be evaluated using graphical techniques to identify anomalous data and outliers. Graphical techniques permit comparison of concentrations of each HAP to the expected concentrations and relative concentrations of other HAPs to inspect for values which stand out. Time series plots, scatter plots, and fingerprint plots, described below, are valuable tools for validating data.

- **Time series plots**: Concentrations are plotted on the y-axis against collection date (time) on the x-axis (Figure 3.3-1). Extreme or anomalous values are immediately identifiable in individual HAP plots, and may be more powerful when multiple HAPs are plotted together. HAPs which are typically emitted from the same type of source (i.e., benzene and toluene from mobile sources) and from different sources (i.e., formaldehyde and PM$_{10}$ nickel) can provide insight on whether concentration...
anomalies are realistic to the collected sample or may be an artifact of the collection or analysis of the sample. Time series plots can quickly be examined for missing data and multiple parameters can be plotted on the same graph to evaluate relative concentrations over a given time frame.

**Figure 3.3-1. Example Time-Series Plot**

- **Scatterplots:** Concentrations of pairs of HAPs are plotted such that each HAP (e.g., benzene and toluene) is dedicated to the y-axis or x-axis such that the coordinates of each plotted point are set by the individual parameter concentrations measured during a given sampling event (Figure 3.3-2). The resulting plots generally show points which are clumped together such that they have a well-defined relationship. Points which lie outside of the well-defined area are then generally identifiable and can be further investigated.

**Figure 3.3-2. Example Scatterplot**
- **Fingerprint plots**: Concentrations of all HAPs within a given class (e.g., VOCs, carbonyls, etc.) are plotted on the y-axis against the molecular weight, alphabetical order, or some other consistent order on the x-axis which enable discerning patterns or identifying anomalies (Figure 3.3-3). Fingerprint plots prepared for each sampling event are compared and will typically be very similar among events. Plots which show markedly different patterns may indicate anomalous results. For instance, during a specific sampling event a HAP may be observed at a concentration much higher or much lower than expected given the typically observed pattern between concentration and molecular weight (alphabetical order, etc.), and such is evidence of a spurious result for this HAP for this sampling event.

![Figure 3.3-3. Example Composite Fingerprint Plot](image-url)
Confidence is increased for concentration data which follow expected patterns and relationships. For data which appear to be anomalous, they should be investigated more closely to determine whether additional actions are needed.

The free Data Analysis and Reporting Tool (DART) software was developed with EPA funding and incorporates preparation of the graphical displays mentioned above. DART is available at airmowtech.org at the following URL: http://airnowtech.org/dart/dartwelcome.cfm (all users must have an account with username and password).

3.3.1.3.15 Reporting of Results to AQS. Each monitoring organization must prescribe procedures and policies for the reporting of NATTS sampling measurement data and applicable QC measurement data to the EPA AQS database. AQS is a repository of data from SLT monitoring agencies as well as federal organizations. The stored data consist of descriptions of monitoring sites and associated monitoring equipment, reported concentrations of air pollutants, meteorological measurements, data qualifiers, and calculated summary and statistical information.

This section discusses reporting of data to AQS and provides details on the following monitoring agency requirements. Monitoring agencies must:

- Create the sampling unit or ‘monitor’ in AQS for the monitoring site. This requires assigning the monitor to the site’s Aerometric Information Retrieval System (AIRS) identifier, assigning a parameter occurrence code (POC) to the monitor, indicating a network affiliation (i.e., NATTS) and several other pieces of information such as the sampling period (date the monitor began/is to begin sampling)
- Report NATTS data to AQS within 180 days from the end of the calendar quarter in which samples were collected
- Report concentration data for all Tier I NATTS required HAPs
- Verify and validate data according to the monitoring agency policies
- Report QA data (field blanks, trip blanks, collocated, duplicate, replicate analysis, and lot blanks)
- Qualify data appropriately in relation to the MDL
- Add other qualifiers as necessary when data do not meet acceptance criteria (refer to Section 7)
- Report MDLs with the sample data
- Report data in appropriate units in standard conditions (except PM$_{10}$ metals)
- Verify data were input to AQS properly

Data preparation and entry are the responsibility of each participating monitoring organization. Portions of these activities may be delegated to the ASL, as appropriate per arrangement with between the organizations.
## 3.3.1.3.15.1 Use of AQS Qualifiers

Additional information on use of AQS qualifiers is available in EPA’s *Best Practices for Review and Validation of Ambient Air Monitoring Data*. AQS permits entry of qualifier codes consisting of the following four different types:

- Informational Only
- Null Data Qualifier
- QA Qualifier
- Request Exclusion

Request Exclusion qualifiers are solely for criteria pollutant data and do not apply to NATTS data. Qualifiers do not automatically indicate there is a problem with the reported data, but rather are codes communicating additional information about the data to the data user. More than one (up to 10) QA Qualifier may be reported with a raw data measurement value to provide additional information regarding the applicable concentration result. However, only one Null Data Qualifier can be appended to a reported data string, as the Null Data Qualifiers eliminate the concentration measurement and any other appended qualifiers.

Invalidation of concentration results and the subsequent assignment of a Null Data Qualifier code in AQS require careful consideration and should be consistent with data review and reporting procedures in the monitoring agency QAPP. Data which do not meet method QC requirements may still be useful to data users and should be entered with the appropriate QA qualifier codes to explain conditions (as possible) for what may be compromised with the data. AQS QA Qualifier Informational Only codes appropriate for qualification of NATTS data are listed in Table 3.3-2 (excludes Null Data Qualifier codes). The current AQS codes and descriptions, including qualifier codes and definitions, are available at the following URL:

[https://www.epa.gov/aqs/aqs-code-list](https://www.epa.gov/aqs/aqs-code-list)

Concentrations of HAPs uploaded to AQS must be qualified according to whether they are above or below the SQL or MDL thresholds. Concentration data less than the laboratory MDL for the target analyte must be qualified with the QA qualifier code MD, data greater than or equal to the MDL but less than the SQL (3.18-fold the MDL) must be qualified using the QA qualifier code SQ. **All measured concentration values for qualitatively identified analytes, even those less than MDL, must be reported to AQS and must not be censored by substitution of one half the MDL, by replacement with 0, or by any other substitution method.** Negative concentrations must not be replaced with zero for reporting purposes and must be reported as measured. If the negative concentration is less than the negative concentration value threshold in AQS for the analyte, AQS will reject the value. In such cases, the concentration data must be invalidated. Overly negative concentration data are indicative of a potential negative bias in the measurement as discussed in Section 6. Where qualitative identification acceptance criteria are not met for a given HAP, the analyte is not positively identified and its concentration must be reported as zero and qualified as ND. The convention for reporting concentration data and the associated QA qualifiers related to the concentration MDL or non-detects are shown in Table 3.3-3.
Table 3.3-2. AQS QA and INFORM Qualifier Codes Appropriate for NATTS Data

<table>
<thead>
<tr>
<th>Qualifier Code</th>
<th>Qualifier Description</th>
<th>Qualifier Type Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deviation from a CFR/Critical Criteria Requirement</td>
<td>QA</td>
</tr>
<tr>
<td>2</td>
<td>Operational Deviation</td>
<td>QA</td>
</tr>
<tr>
<td>3</td>
<td>Field Issue</td>
<td>QA</td>
</tr>
<tr>
<td>4</td>
<td>Lab Issue</td>
<td>QA</td>
</tr>
<tr>
<td>5</td>
<td>Outlier</td>
<td>QA</td>
</tr>
<tr>
<td>6</td>
<td>QAPP Issue</td>
<td>QA</td>
</tr>
<tr>
<td>7</td>
<td>Below Lowest Calibration Level</td>
<td>QA</td>
</tr>
<tr>
<td>IV</td>
<td>Data reviewed and validated</td>
<td>QA</td>
</tr>
<tr>
<td>CC</td>
<td>Clean Canister Residue</td>
<td>QA</td>
</tr>
<tr>
<td>CF</td>
<td>Canister Bias: NATTS/UATMP Data for compounds that have failed certification for the canister.</td>
<td>QA</td>
</tr>
<tr>
<td>CL</td>
<td>Surrogate Recoveries Outside Control Limits</td>
<td>QA</td>
</tr>
<tr>
<td>DI</td>
<td>Sample was diluted for analysis</td>
<td>QA</td>
</tr>
<tr>
<td>DN</td>
<td>DNPH peak &lt; NATTS TAD requirement, reported value should be considered an estimate.</td>
<td>QA</td>
</tr>
<tr>
<td>EH</td>
<td>Estimated; Exceeds Upper Range</td>
<td>QA</td>
</tr>
<tr>
<td>FB</td>
<td>Field Blank Value Above Acceptable Limit</td>
<td>QA</td>
</tr>
<tr>
<td>FX</td>
<td>Filter Integrity Issue</td>
<td>QA</td>
</tr>
<tr>
<td>HT</td>
<td>Sample pick-up hold time exceeded</td>
<td>QA</td>
</tr>
<tr>
<td>IC</td>
<td>Chem. Spills &amp; Indust Accidents</td>
<td>QA</td>
</tr>
<tr>
<td>ID</td>
<td>Cleanup After a Major Disaster</td>
<td>QA</td>
</tr>
<tr>
<td>IE</td>
<td>Demolition</td>
<td>QA</td>
</tr>
<tr>
<td>IF</td>
<td>Fire – Canadian</td>
<td>QA</td>
</tr>
<tr>
<td>IG</td>
<td>Fire – Mexico/Central America</td>
<td>QA</td>
</tr>
<tr>
<td>IH</td>
<td>Fireworks</td>
<td>QA</td>
</tr>
<tr>
<td>II</td>
<td>High Pollen Count</td>
<td>QA</td>
</tr>
<tr>
<td>IJ</td>
<td>High Winds</td>
<td>QA</td>
</tr>
<tr>
<td>IK</td>
<td>Infrequent Large Gatherings</td>
<td>QA</td>
</tr>
<tr>
<td>IM</td>
<td>Prescribed Fire</td>
<td>QA</td>
</tr>
<tr>
<td>IP</td>
<td>Structural Fire</td>
<td>QA</td>
</tr>
<tr>
<td>IQ</td>
<td>Terrorist Act</td>
<td>QA</td>
</tr>
<tr>
<td>IR</td>
<td>Unique Traffic Disruption</td>
<td>QA</td>
</tr>
<tr>
<td>IS</td>
<td>Volcanic Eruptions</td>
<td>QA</td>
</tr>
<tr>
<td>IT</td>
<td>Wildfire-U. S.</td>
<td>QA</td>
</tr>
<tr>
<td>J</td>
<td>Construction</td>
<td>QA</td>
</tr>
<tr>
<td>K</td>
<td>Agricultural tilling</td>
<td>QA</td>
</tr>
<tr>
<td>LB</td>
<td>Lab blank value above acceptable limit</td>
<td>QA</td>
</tr>
<tr>
<td>LJ</td>
<td>Identification Of Analyte Is Acceptable; Reported Value Is An Estimate</td>
<td>QA</td>
</tr>
<tr>
<td>LK</td>
<td>Analyte Identified; Reported Value May Be Biased High</td>
<td>QA</td>
</tr>
<tr>
<td>LL</td>
<td>Analyte Identified; Reported Value May Be Biased Low</td>
<td>QA</td>
</tr>
<tr>
<td>MD</td>
<td>Value less than MDL</td>
<td>QA</td>
</tr>
<tr>
<td>MX</td>
<td>Matrix Effect</td>
<td>QA</td>
</tr>
<tr>
<td>ND</td>
<td>No Value Detected</td>
<td>QA</td>
</tr>
<tr>
<td>NS</td>
<td>Influenced by nearby source</td>
<td>QA</td>
</tr>
<tr>
<td>P</td>
<td>Roofing operations</td>
<td>QA</td>
</tr>
<tr>
<td>Q</td>
<td>Prescribed burning</td>
<td>QA</td>
</tr>
<tr>
<td>QX</td>
<td>Does not meet QC criteria</td>
<td>QA</td>
</tr>
<tr>
<td>SB</td>
<td>Sampler Bias: NATTS/UATMP Data for compounds that have failed certification for the sampler.</td>
<td>QA</td>
</tr>
<tr>
<td>SP</td>
<td>NATTS/UATMP data with Spike Recovery outside acceptance limits.</td>
<td>QA</td>
</tr>
<tr>
<td>SQ</td>
<td>Values Between SQL and MDL</td>
<td>QA</td>
</tr>
<tr>
<td>SS</td>
<td>Value substituted from secondary monitor</td>
<td>QA</td>
</tr>
<tr>
<td>SX</td>
<td>Does Not Meet Siting Criteria</td>
<td>QA</td>
</tr>
<tr>
<td>TB</td>
<td>Trip Blank Value Above Acceptable Limit</td>
<td>QA</td>
</tr>
<tr>
<td>TT</td>
<td>Transport Temperature is Out of Specs</td>
<td>QA</td>
</tr>
<tr>
<td>V</td>
<td>Validated Value</td>
<td>QA</td>
</tr>
</tbody>
</table>
### Table 3.3-2. AQS QA and INFORM Qualifier Codes Appropriate for NATTS Data (Continued)

<table>
<thead>
<tr>
<th>Qualifier Code</th>
<th>Qualifier Description</th>
<th>Qualifier Type Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>VB</td>
<td>Value below normal; no reason to invalidate</td>
<td>QA</td>
</tr>
<tr>
<td>W</td>
<td>Flow Rate Average out of Spec.</td>
<td>QA</td>
</tr>
<tr>
<td>Y</td>
<td>Elapsed Sample Time out of Spec</td>
<td>QA</td>
</tr>
</tbody>
</table>

* Qualifier codes in **bold** are newly added in this TAD Revision.

### Table 3.3-3. Required AQS QA Qualifiers for Various Concentrations When Non-Detect and in Relation to the MDL and SQL

<table>
<thead>
<tr>
<th>Measured Concentration Level</th>
<th>Reported Value</th>
<th>Associated QA Qualifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥ SQL</td>
<td>measured concentration</td>
<td>no qualifier</td>
</tr>
<tr>
<td>≥ MDL but &lt; SQL</td>
<td>measured concentration</td>
<td>SQ</td>
</tr>
<tr>
<td>&lt; MDL</td>
<td>measured concentration</td>
<td>MD</td>
</tr>
<tr>
<td>HAP not qualitatively identified</td>
<td>0</td>
<td>ND</td>
</tr>
</tbody>
</table>

### 3.3.1.3.15.2 Reporting of MDLs to AQS

Monitoring agencies will report the MDL to AQS for each HAP with the sample concentration data. The reported MDL should ideally be normalized to the actual collected air volume for the respective air sample for PAHs, carbonyls, and PM$_{10}$ metals; however, the reported MDL will typically be determined as the ASL MDL and normalized to the typical or target collected air volume. Normalization of the MDL to the collected air volume is required when the collected air volume for the sample is greater than 10% different from the target collected air volume for PAHs, carbonyls, and PM$_{10}$ metals. If the total collected air volume is not within 10% of the target collected air volume, the monitoring organization should take corrective action which may involve troubleshooting the sampling unit and verifying calculations. VOC samples are collected as whole air so there is no normalization to the collected air volume for the MDL. Additional adjustments to MDLs are needed for samples that are diluted for analysis, where the determined MDL is multiplied by the sample’s dilution factor to correct for the analyzed portion of the sample relative to the typical analyzed portion. This process is described in the individual methods sections.

The following is an example of normalizing the MDL to the collected air volume that exceeds 10% difference from the target collected air volume:

**Example:** The target collected air volume for carbonyls sampling at 0.75 L/min is 1.08 m$^3$ and the formaldehyde MDL is 0.052 µg/m$^3$ for this target volume. For a total collected sample volume of 0.95 m$^3$, the collected volume is ~12% lower than the target, and requires normalization of the formaldehyde MDL as follows (MDL increases by the ~12% to account of the reduced sample volume):

\[
\frac{0.052 \, \text{µg/m}^3 \cdot 1.08 \, \text{m}^3}{0.95 \, \text{m}^3} = 0.059 \, \text{µg/m}^3
\]
3.3.1.3.15.3 Reporting AQS Measurement Units

Reporting units accompanying concentration data to AQS are to be consistent across the NATTS network to ensure that data may be statistically combined with minimal manipulation. While AQS includes reporting functions to allow users to export data in available units of their choice, data reported in local conditions (LC) cannot be exported in standard temperature and pressure (STP) conditions. HAPs must be reported in the following unit conventions:

- VOCs – parts per billion by volume (ppbv)
- Carbonyls – mass per unit volume (e.g., µg/m³ or ng/m³)
- PAHs – mass per unit volume (e.g., µg/m³ or ng/m³)
- Metals – mass per unit volume (e.g., µg/m³ or ng/m³)

All concentrations, with the exception of those for PM₁₀ metals, must be reported to AQS in EPA STP conditions of 760 mm Hg and 25°C. PM₁₀ metals data must minimally be reported in LC but may also be reported in standard conditions at the discretion of the monitoring organization, which requires reporting data using a different parameter code for each metal. Except for PM₁₀ metals, this requires that monitoring agencies calibrate sampling unit instruments in flows at STP or that conversion to standard conditions is performed with average temperature and barometric pressure measurements taken during sample collection.

3.3.1.3.15.4 Assignment of Parameter Occurrence Codes to Monitors within AQS

Each individual sampling unit, or ‘monitor,’ of a given type (VOCs, carbonyls, PM₁₀ metals, and PAHs) and each duplicate channel on a single sampler are to be assigned a two-digit POC by the SLT agency when setting up the monitor in AQS. There is no guidance on how POCs are assigned by SLTs and a survey of NATTS sites indicates that there is little to no consistency among monitoring sites on assigning POCs. Monitoring agencies will assign the primary and precision monitor and/or channels in AQS with their assigned POC and will include the POC assignments for the monitors in their annual network plan (ANP) and/or NATTS QAPP. A recommended convention is to assign a lower POC to the primary monitor and a higher POC to the duplicate and/or collocated monitor.

3.3.1.3.15.5 Reporting of QA Data to AQS

QA data including, but not limited to, field QA samples such as field blanks (FBs) and trip blanks (TBs) and collocated and duplicate test samples, laboratory QA results from replicate analyses (as required by the QAPP), and lot blanks must be reported to AQS. AQS also accepts laboratory blanks, therefore ASLs may report method blank (MB) data to AQS (this is not required).

Lot blank data are reported to AQS as the average value and ASLs will report this value for the monitoring sites supported. The measurement date is the date on which the first of the lot blanks (if lot blanks were measured on more than one date) was measured. For MBs, ASLs will report the value for each monitoring site for which sample data are included in the respective digestion or extraction batch.
Those responsible for reporting QA data to AQS should be aware that the QA transactions for AQS do not permit the addition of qualifiers to the data strings. Therefore, when QA data are to be invalidated, substitute the measurement value with -999 to indicate that the measurement was made but that the QA measurement does not meet acceptance criteria.

Guidance for reporting QA samples (blanks and precision samples – collocated, duplicate, and replicate samples) is included in Appendix B.

3.3.1.3.15.6 Error Checking Data for Reporting to AQS

Prior to submission of data to AQS, all data must be reviewed to ensure the parameter code, POC, unit code, method code, and any associated qualifier or null codes are properly assigned, as intended. AQS instructions for coding data for upload are updated periodically and are described in the AQS User Guide and additional AQS manuals and guides available at the following URL:

https://www.epa.gov/aqs/aqs-manuals-and-guides

Additional assistance is available by contacting your EPA Regional Office AQS Representative or calling the AQS help line at (866) 411-4372. The list of EPA Regional Office AQS Representatives is available at the following URL:

https://www.epa.gov/aqs/aqs-user-support

3.3.1.3.15.7 Corrections to Data Uploaded to AQS

If it is discovered that data reported to AQS require amendment, the monitoring agency will correct the data within AQS with AQS update transactions. Monitoring agencies must notify EPA Region staff when changes are needed to large swaths of data (e.g., a calendar quarter) or data from previous calendar years are to be altered and should notify the EPA Region if the data updates result in changes to MQO satisfaction such as when invalidating a significant amount of data would result in changing status from achieving to not achieving the completeness MQO. In such instances where a large quantity of data is updated or changed in AQS, monitoring agencies should work with Regions and OAQPS to notify data users who may have used data (e.g., AQS data queries for conducting the NATTS assessments and data analysis for preparing the NATA) to ensure that the data user is aware (to the extent possible) of the updated data.

3.3.1.3.16 Records Retention and Archival, and Data Backup. Records required to reconstruct activities to generate the concentration data for NATTS Program samples must be retained for a minimum of six years. The basis for the six-year retention period is that this covers the two successive three-year periods over which trends in HAP concentrations are determined per the NATTS DQO. If problematic or anomalous data are observed during trends analysis, the archived records will be available for review to investigate the data in question. Quality system documents (e.g., QMPs, QAPPs, and SOPs, sample collection and analysis records, maintenance logs, reagent logs, etc.) are supporting data records and must be retained for at least six years. Requirements for records retention, including electronic records, must be prescribed in the QMP, agency NATTS QAPP, or similar controlled policy document.
This six-year retention period also applies to electronic data generated for NATTS measurements and held within electronic databases. Such includes:

- data logged by sampling and analysis instruments
- QA/QC data
- data stored in databases (e.g., in a LIMS)

These electronic data must be backed up on a periodic basis and stored in a manner to protect them from inadvertent alteration as defined in an applicable quality system document such as the QAPP. Additionally, monitoring agencies must maintain accessibility to the archived data which may include maintaining legacy software systems or computers or may involve conversion of the data to a format which is compatible with current computers and software systems. Monitoring agencies should consider the compatibility of the archived data when upgrading or replacing computer systems and software to ensure the archived data remain accessible.

3.3.1.3.17 Safety. While not traditionally a quality system element, safety is integral to ensuring the continued collection of quality data. Each monitoring organization will prescribe appropriate safety requirements and procedures within the NATTS QAPP or similar controlled policy document. For monitoring organizations with existing safety plans or programs, these may be referenced within the QAPP. Safety plans should include information regarding safety equipment, inspection frequency of safety equipment, and safety training frequency.

3.3.2 Standard Operating Procedures. Each monitoring organization and ASL conducting NATTS Program work must develop and maintain SOPs, however named, which describe in sufficient detail the procedures for performing various activities needed to execute air sampling, sample analysis, data reduction, and data reporting, among others, for the NATTS Program. It is not acceptable to simply cite a method document (e.g., EPA Compendium Method TO-11A) or instrument manual as the SOP, although these documents may serve as the basis for an SOP and should be referenced in the SOP. Instrument manuals and the compendium methods do not include sufficient detail on the specific procedures and/or equipment information necessary to perform the procedures and generally offer several different procedures or conventions for performing activities or operating equipment.

SOPs are written with sufficient detail to allow an individual familiar with the process to perform the procedure unsupervised. SOPs will reflect current practices and should include the elements detailed in EPA’s Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, where each element applies. Production, review, revision, distribution, and retirement of SOPs must conform to the requirements prescribed by the monitoring organization or ASL document control system as described in Section 3.3.1.3.5.

SOPs can be developed in many formats but should minimally contain information regarding the following, where applicable:

- Title (e.g., Collection of Ambient Air VOCs Samples in Stainless Steel Canisters)
- Scope and Objectives (e.g., covers sample collection but not analysis, pressure transducer calibration is covered in a separate SOP)
• References (e.g., EPA Compendium Method TO-11A and/or instrument manual)
• Definitions and Abbreviations
• Procedures – instructions (usually step-by-step) for performing activities within the scope of the SOP including information and tolerances on required materials, reagents, standards, and instruments; sample preparation; instrument calibration and analysis, and data analysis and reporting procedures, among other information, as required
• Interferences
• Calculations
• Quality control acceptance criteria with associated corrective actions
• Safety information
• Revision history

The author of each SOP should be an individual knowledgeable with the procedure and with the organization’s internal structure who has the responsibility for the veracity and defensibility of the document’s technical content. A team approach may be followed to develop the SOP, especially for multi-tasked processes where experience of a number of individuals is critical to the procedure. SOPs must be approved in accordance with Section 3.3.1.3.5 of this TAD and must be revised when they no longer reflect current practices. At a minimum, SOPs are to be reviewed by the author and a member of QA to determine if revisions are needed and these reviews and revisions must be documented. The frequency for review is recommended to be annually, but must not exceed three years, and the period must be prescribed in the monitoring agency’s NATTS QAPP, QMP, or similar controlled document. Once a new SOP version is effective, the previous (superseded) version must be retired and removed from points of use to avoid inadvertent reference when conducting procedures.

3.4 References


4.0: COLLECTION AND ANALYSIS METHODS

4.1 Method Detection Limits

The EPA revised the longstanding MDL procedure in 40 CFR Part 136 Appendix B in December 2016 (following the Method Update Rule [MUR] procedure) and the final rule of Revision 2 was published in April 2017. The Revision 2 process included three major differences from the previous process:

1. The process includes the preparation and analysis of MBs to characterize the contribution of method background. This updated the definition of the MDL as:

   “The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from MB results.”

   Two separate MDLs are calculated for the method, one employing the previous MDL procedure of analyzing spiked samples in a blank matrix and the other employing analysis of multiple MBs. The higher of these two MDLs is reported as the laboratory MDL for the analyte and method. This provides a more meaningful MDL that signifies the detection limit of the procedure, inclusive of background contribution from the procedure and collection media, and not simply the detection limit of the instrument based on precision of the prepared standard samples.

2. The Revision 2 MDL process now requires that samples prepared for and included in the MDL determination are representative of the entire year (samples are prepared and analyzed approximately quarterly).

3. Laboratories may now pool MDL data from multiple instruments to calculate an MDL for the laboratory that represents the multiple instruments.

The MDL procedure in the 2016 Revision 3 of the NATTS TAD anticipated the intended changes to the MDL procedure and incorporated many of the aspects of the revised MDL process that had been proposed at that time. However, the NATTS MDL procedure has been further revised in this TAD revision to comprehensively incorporate the MDL Revision 2. While the initial MDL procedure promulgated in 1981 was developed and applied to wastewater analyses,² the Revision 2 MDL procedure applies to many more analytical techniques and can be applied to HAPs analysis in air.

The Revision 2 MDL procedure maintains the conservative detectability estimate and aims to ensure that there is a 1% false positive rate – incorrectly reporting the presence of an analyte above background when it is in fact attributable to background – at the determined MDL concentration. The MDL as determined by the Revision 2 procedure is no longer simply the estimated concentration at which the analyte is positively detected above zero, as the analyte may be present in the MB measurements at sufficiently high signal-to-noise ratios that identification and quantitation are certain. However, with low enough background as measured in the MB samples, the MDL Revision 2 procedure defaults to the previous MDL procedure based solely on the spiked sample measurement precision.
In order to streamline the MDL process for the NATTS Program, the theory and background of the MDL procedure have been removed from this TAD revision to focus on providing instruction on the procedure specifically for the NATTS air monitoring measurement methods. Much of the procedure in the 2016 NATTS TAD remains in this revision; however, the flexibility and additional guidance in the final MDL Revision 2 procedure are incorporated. The MDL remains a statistically estimated concentration, and detected measurements below the MDL may be valid and appropriate measurements, particularly if the MDL is a high estimate (such as might occur if contamination within a new instrument slowly decreased over time). Concentrations measured at less than the MDL, so long as the qualitative identification criteria have been met, are valid and necessary for trends analysis and substituting or censoring concentrations measured at less than MDL is not permitted. EPA recognizes that many laboratories are not comfortable reporting concentrations measured at less than the MDL as these concentrations may be outside of the calibrated range of the instrument and are associated with an unknown and potentially large uncertainty. However, actual values reported at less than the MDL are more valuable from a data analyst’s standpoint and superior to censored or substituted values. Addition of qualifiers as prescribed in Section 3.3.1.3.15 and in Table 3.3-1 indicates when values are near, at, and below detection limits and are therefore associated with larger uncertainties. While ASLs have indicated their reluctance and hesitancy to report measurement data measured below the MDL, all detected measurements of an analyte are to be reported to AQS accompanied by the MDL so the data user can understand the uncertainty to apply to the measurement data and whether it is true signal above background.

NATTS ASLs may still determine the instrument detection limit (IDL) to ascertain the sensitivity of the instrument, as it does not incorporate the potential effect of the matrix for samples taken through the preparation process (such as extraction or digestion). The IDL establishes the lowest concentration that may be measured with a defined confidence by the instrument, and knowing the IDL is particularly helpful when troubleshooting the MDL process; however, the IDL does not, and must not, replace the MDL.

The MDL Revision 2 procedure still incorporates some drawbacks with respect to inclusion of all aspects of the method from collection through analysis. Inclusion of the aspects of field sampling is impractical at best, or impossible in many cases; therefore, these are omitted. In particular, conducting an MDL study through the probe is impractical for gases and not currently possible for PM10 metals and PAHs. To the extent feasible the impact of the sampling process on detectability is minimized by strongly recommending that bias checks (zero and known standard checks) are performed for carbonyl and VOC field samplers.

The MDL concentration, as defined in the Revision 2 MDL procedure, is determined statistically initially by preparing and analyzing minimally seven separate aliquots of a standard spike prepared with the method sample collection media and seven separate MBs. All portions of the method and matrix (i.e., sampling media – such as for PAHs the sampling media includes resin, PUF, and a QFF) are to be included in the preparation and analysis such that any matrix effects and preparation variability are considered.

The revised MDL procedure recognized that the 1981 MDL procedure assumed that blank values were centered around a concentration of zero and did not consider the potential for background
contamination to be present in the sample collection media. The Revision 2 MDL procedure corrects this oversight as it applies to the NATTS air measurement methods. If there is a consistent background level of contamination on the sample collection media, as is typical for carbonyls on DNPH cartridge media and metals elements on QFF media, measured blank values will not be centered around zero; rather, they will be centered on the mean blank value. The Revision 2 MDL procedure considers the media background and adjusts for matrix blank levels that are not centered around zero.

The revised MDL procedure for the NATTS Program is prescribed in Section 4.1.3.1 and adds a few recommendations to those specified in the CFR. The Detection and Quantitation Federal Advisory Committee (DQ FAC) Single Laboratory Procedure v 2.4 described in Section 4.1.3.2 is a similar procedure to determine the MDL which also considers the media background and other potential background contributions. This procedure is more involved and is better suited to laboratories with high sample throughput; however, laboratories may opt to determine MDLs via this procedure. Note that if certain criteria are not met in the DQ FAC MDL procedure, the ASL must determine the initial MDL as described in Section 4.1.3.1.

4.1.1 Frequency of Method Detection Limit Determination. An initial MDL must be determined for each target analyte to establish the MDL until sufficient MDL data are generated to calculate the ongoing annual verification of the MDL. Additionally, when changes to the instrument or preparation procedure result in significant changes to the sensitivity of the instrument and/or procedure, the initial MDL must be redetermined. Examples of situations where the initial MDL must be redetermined include, but are not limited to:

- Detector replacement
- Replacement of the entire analytical instrument
- Replacement of a large (e.g., > 50%) portion of an agency’s canister fleet
- Changing the cleaning procedure for sample collection media or labware which results in a marked reduction in contamination levels

Once the initial MDL is determined (as described in Section 4.1.3.1.1), each calendar quarter in which method samples are analyzed, the ASL will prepare and analyze at least two MDL spiked samples and two MBs. The goal is that there are at least eight MDL spikes and eight MBs available at the end of the calendar year to calculate the ongoing annual verification of the MDL (as detailed in Section 4.1.3.1.1.4).

4.1.2 MDL Measurement Quality Objectives. In order to ensure that measurements of air toxics in ambient air are sufficiently sensitive to assess trends in concentrations which may result in health effects due to chronic exposures, a minimum required method sensitivity, or MDL MQO, has been established for each of the core NATTS analytes. Though few changes have been made to MDL MQOs since the beginning of the NATTS Program, as new toxicology data become available, MDL MQOs may be adjusted. The annual NATTS network workplan template includes the current MDL MQO for each core analyte. Laboratories must meet (be equal to or less than) the MDL MQO listed in the most recent NATTS workplan template. EPA recognizes, however, that there are limitations in the ability to meet MDL MQOs due to
background levels of contaminants on sample collection media that cannot be mitigated. Commonly these are formaldehyde, and to a lesser extent, acetaldehyde, on DNPH cartridges employed for collecting carbonyls by Method TO-11A, as well as nickel and manganese on QFF media for high-volume PM$_{10}$ metals sample measurements by Method 103.5. As part of adoption of the MDL MUR procedures in the 2016 NATTS TAD revision, the magnitude of media background relative to the MDL MQOs was assessed and determined that a minimum additional amount of concentration data would be marked as less than the MDL when reported to AQS than when employing the 1981 MDL procedure.$^3$

NATTS Tier I core analytes and the concentrations as of April 2022 (the most recent workplan template available at the time this document was prepared) that correspond to $10^{-6}$ cancer risk levels, to noncancer risk HQs of 0.1, and to MDL MQOs are listed in Table 4.1-1. Refer to the latest NATTS workplan template for the most up-to-date values.

Table 4.1-1. Concentrations of the NATTS Tier I Core Analytes Corresponding to a $10^{-6}$ Cancer Risk, a Noncancer Risk at a HQ of 0.1, and to the MDL MQO

<table>
<thead>
<tr>
<th>Tier I Core Analyte</th>
<th>Cancer Risk $10^{-6}$ (µg/m$^3$)</th>
<th>Noncancer Risk at HQ = 0.1 (µg/m$^3$)</th>
<th>MDL MQO (µg/m$^3$)</th>
<th>MDL MQO (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>NA</td>
<td>0.020</td>
<td>0.090</td>
<td>0.039</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.13</td>
<td>3.0</td>
<td>0.13</td>
<td>0.041</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.030</td>
<td>0.20</td>
<td>0.10</td>
<td>0.050</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.17</td>
<td>10</td>
<td>0.17</td>
<td>0.027</td>
</tr>
<tr>
<td>Chloroform</td>
<td>NA</td>
<td>9.8</td>
<td>0.50</td>
<td>0.10</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>0.0002</td>
<td>NA</td>
<td>0.054</td>
<td>0.030</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>3.8</td>
<td>4.0</td>
<td>0.17</td>
<td>0.025</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.21</td>
<td>0.20</td>
<td>0.20</td>
<td>0.037</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>0.11</td>
<td>10</td>
<td>0.11</td>
<td>0.043</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.45</td>
<td>0.90</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.080</td>
<td>0.98</td>
<td>0.080</td>
<td>0.065</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.00057</td>
<td>NA</td>
<td>0.00091</td>
<td>NA</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.029</td>
<td>0.4</td>
<td>0.029</td>
<td>NA</td>
</tr>
<tr>
<td>Arsenic (PM$_{10}$)</td>
<td>0.00023</td>
<td>0.0015</td>
<td>0.00023</td>
<td>NA</td>
</tr>
<tr>
<td>Beryllium (PM$_{10}$)</td>
<td>0.00042</td>
<td>0.0020</td>
<td>0.00042</td>
<td>NA</td>
</tr>
<tr>
<td>Cadmium (PM$_{10}$)</td>
<td>0.00056</td>
<td>0.001</td>
<td>0.00056</td>
<td>NA</td>
</tr>
<tr>
<td>Lead (PM$_{10}$)</td>
<td>NA</td>
<td>0.015</td>
<td>0.015</td>
<td>NA</td>
</tr>
<tr>
<td>Manganese (PM$_{10}$)</td>
<td>NA</td>
<td>0.03</td>
<td>0.0050</td>
<td>NA</td>
</tr>
<tr>
<td>Nickel (PM$_{10}$)</td>
<td>0.0021</td>
<td>0.009</td>
<td>0.0021</td>
<td>NA</td>
</tr>
</tbody>
</table>

4.1.3 Determining MDLs. MDLs may be determined via one of two procedures; however, unless the ASL experiences high throughput with many sample preparation and analysis batches annually, the procedure in 4.1.3.2 will likely not apply. The first procedure in Section 4.1.3.1 is the revised CFR MDL adapted to analysis of NATTS air samples. The second procedure in Section 4.1.3.2 is to determine MDLs via the procedure described in the December 2007 Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs.$^4$ Both methods incorporate media blank background levels in the determination of analyte-specific MDLs.
MDL studies must include data from each instrument to be employed for routine sample measurement, so their contribution to the determined MDL is included. If only one instrument is employed, the MDL data must be generated with that instrument.

**4.1.3.1 MDLs via 40 CFR Part 136 Appendix B, Revision 2.** The MDL procedure described in this section is adopted from Revision 2 of the MDL procedure.¹

**4.1.3.1.1 Initial MDL.** The initial MDL requires selecting a spiking level and then preparing and analyzing the MDL spiked samples and MBs.

**4.1.3.1.1.1 Selecting an MDL Spiking Level**

The first step in determining the initial MDL is to select a spiking level for preparing the MDL spiked samples. If too low of a spiking level is chosen, the analyte may not be reliably detected. If too high of a spiking level is chosen, the variability of the method near the actual limits of detection may not be properly characterized. The chosen spiking level will be consistent for all spiked MDL samples for the initial MDL and the ongoing MDL spikes. An appropriate spiking level may be selected by considering the following (in order of importance):

1. Analysis of a suite of MB samples – equivalent of the average plus three standard deviations.
2. The concentration at which the instrument signal-to-noise ratio is three- to five-fold for the analyte.
3. Analysis of a suite of low concentration (e.g., concentration equivalent of signal to noise ratio of 5:1 to 10:1) spiked samples – concentration equivalent of three standard deviations of the suite.
4. The concentration at which qualitative identification criteria for the analyte are lost (note that this will be approximately the concentration determined from the MDL spiked samples when determining the MUR).
5. Previously acceptable MDL studies and related experience.

Note that the MDL spiking level will typically not be a concentration within the calibration curve; rather, the MDL spiking level will routinely be less than the lowest calibration standard in order to best approximate the MDL absent blank background (MDLsp). Concentrations within the calibration curve are required to meet precision and bias acceptance criteria and are of a high enough concentration that qualitative identification (i.e., signal to noise ratio is > 5:1) is certain.

**4.1.3.1.1.2 Determining the Initial MDL**

A minimum of seven spiked samples and seven MBs must be prepared in matrix (i.e., employing the sampling medium) over the course of a minimum of three different preparation batches. A preparation batch is defined as a group of samples prepared on one day, therefore three different preparation batches would require preparation on three separate (preferably non-consecutive) days. An analysis batch is defined as a group of samples analyzed on one day. Analysis of these blanks and spikes must similarly be conducted over the course of three different analysis batches.
where each sample is only analyzed once (the preparation and analysis can occur on the same date for a given batch) on a discrete instrument. Spreading the preparation and analysis over multiple preparation and analysis batches is intended to incorporate the variability of both sample preparation and analytical instrumentation that occurs over time.

It is preferable to determine an MDL that is representative of the laboratory’s capability and to characterize the state of the media background in the typical state than to have an unrealistically low MDL determined by selecting the best sampling media (i.e., canisters) and attempting to generate the lowest MDL value possible. Selection of media should include as much variety as possible (e.g., different canister manufacturers or individual DNPH cartridges selected from different boxes or lots) to best characterize the variability of the method attributable to the use of media representative of field-collected samples. Two MDL values are calculated, one MDL for the spiked samples (MDL_{sp}) and one for the MBs (MDL_{b}).

Existing data may be used for the initial MDL determination provided they meet the following criteria:

1. Include all portions of the method in the preparation and analysis. All components of the matrix (sampling media) must be included in the MDL spikes and MBs (DNPH cartridge, canister, PAH cartridge with QFF, or metals Teflon® filter or QFF strip).
2. The MDL spiking concentration must be identical in all MDL spiked samples. It is not permitted to include data for spiked samples prepared with different spiking concentrations.
3. Data must be from the previous 24 months and data may not have been generated using different method parameters (e.g., a different chromatography column, different acid digestion concentrations, different injected sample volume, etc.). If changes to the method were made since the existing data were generated, the associated data may not be included in the initial MDL (or ongoing MDL).

In order to best mimic field-collected samples, each spiked and MB sample must include, to the extent feasible, all portions of the sample matrix (sampling media) and be subjected to the same procedures performed to process field samples in preparation for analysis.

Analyze the MDL spikes and MBs against a valid calibration curve. QC criteria for the analytical sequences must be met (blanks, LCS, calibration checks, etc.). Analyze the samples over the course of minimally three different analytical batches.

If multiple instruments are to be used for routine sample analysis, there are three ways to handle the MDL determination:

1. The laboratory determines a single pooled MDL incorporating data from all method instruments and reports this single MDL for the method. The MDL spikes and MBs should be evenly distributed among the instruments. A minimum of two spiked samples and two MBs prepared in separate preparation batches and analyzed in different analysis batches (i.e., prepared on different dates and analyzed on different dates) are required. A spike sample and MB can be prepared and analyzed in common preparation and analysis batches.
2. The laboratory determines an MDL for each individual instrument and reports a single MDL for the method as the highest of these individual MDLs. Determine an MDL individually for each instrument by preparing and analyzing 7 discrete spiked samples and 7 discrete MBs for each instrument following the three separate batches rule. This requires analyzing the prepared MBs and MDL spiked samples discretely on each instrument (the same samples can be analyzed on all instruments) and selecting the highest overall MDL of the instruments for reporting.

3. The laboratory determines an MDL for each individual instrument and reports multiple MDLs for the method whereby the measurement data are associated with the MDL from the instrument on which they were analyzed. Determine an MDL individually for each instrument by preparing and analyzing 7 discrete spiked samples and 7 discrete MBs for each instrument following the three separate batches rule. This requires analyzing the prepared MBs and MDL spiked samples discretely on each instrument (the same samples can be analyzed on all instruments) and reporting the MDL with the measurement data reported for that instrument.

Prepared MBs and MDL spiked samples may be analyzed on multiple instruments provided the overall requirement that seven different spiked samples and seven different MBs are prepared and analyzed in minimally three different preparation and analysis batches.

Review the analysis data to ensure that the analyte is detected in each of the spiked samples, i.e., that qualitative identification criteria are met. If the measurements do not meet minimum qualitative identification criteria, increase the spiking concentration and repeat the MDL spike preparation and analysis (again with three separate preparation and analysis batches). A good rule of thumb is to increase the concentration by a factor of two- to three-fold. Note that when spiking multiple analytes into a matrix, the differences in analyte recoveries through the preparation procedure (e.g., extraction or digestion) and instrument sensitivity may require tailoring the concentrations of specific analytes. When all target analytes are in the stock standard at the same concentration, the MDL spiked samples may require several batches to be prepared at several concentrations to acquire data with sufficient signal for qualitative identification. When multiple spiking concentrations are utilized, the lowest spiking concentration that meets the qualitative identification criteria in all seven MDL spiked samples should be employed in the subsequent calculations.

4.1.3.1.1.3 Calculating the Initial MDL

Once the data are collected and the analyst has verified there is sufficient MB data (i.e., seven or more MBs) and the MDL spiked samples have generated data for which the target analytes are qualitatively identified in all seven (or more) spiked samples, the initial MDL is calculated:

1. Calculate the MDL of the spiked samples, MDL_{sp}:
   a. Following acquisition of the concentration data for each of the seven or more spiked samples, calculate the standard deviation of the calculated concentrations for the spiked samples (s_{sp}). Include all replicates unless a technically justified reason can be cited (faulty injection, unacceptably low
internal standard response, etc.), or if a result can be statistically excluded as an outlier.

b. Calculate the MDL for the spiked samples (MDL_{sp}) by multiplying \( s_{sp} \) by the one-sided 99\% percentile Student’s \( t \)-statistic corresponding to the number of spikes analyzed according to Table 4.1-2. Other values of \( t \) for additional samples (\( n > 13 \)) may be found in standard statistical tables.

\[
\text{MDL}_{sp} = s_{sp} \cdot t
\]

### Table 4.1-2. One-sided 99th Percentile Student’s \( t \) Values

<table>
<thead>
<tr>
<th>Number of MDL Samples (( n ))</th>
<th>Degrees of Freedom (( n-1 ))</th>
<th>Student’s ( t ) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6</td>
<td>3.143</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>2.998</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>2.896</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>2.821</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>2.764</td>
</tr>
<tr>
<td>12</td>
<td>11</td>
<td>2.718</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
<td>2.681</td>
</tr>
</tbody>
</table>

2. Calculate the MDL of the MBs, MDL_{b}:

a. If none of the MBs provide a numerical result for the analyte, the MDL_{b} does not apply. A numerical result includes both positive and negative results for analytes which are positively identified (i.e., qualitative identification criteria were met). Non-numeric values such as “ND” would result when the analyte is not positively identified. Only MBs that meet the specified qualitative criteria for identification (signal to noise, qualifier ion presence, etc.) are to be given a numerical result.

b. If the MB pool includes a combination of non-numeric (ND) and numeric values, set the MDL_{b} to equal the highest of the MB results. Note:

*Analysts should be aware that MBs with very high measurements (e.g., many-fold the average) due to non-routine contamination or other anomalous event may uncharacteristically inflate the MDL_{b}. While the goal of the MDL_{b} is to characterize the average MB measurement with a protection factor of approximately three-fold the standard deviation, it is not meant to prescribe the inclusion of MBs with known anomalous contamination.*

If more than 100 MB results are available for the analyte, set the MDL_{b} to the level that is no less than the 99\textsuperscript{th} percentile of the MBs. In other words, for \( n \) MBs where \( n \geq 100 \), rank order the concentrations. The value of the 99\textsuperscript{th} percentile concentration (\( n \cdot 0.99 \)) is the MDL_{b}. For example, to determine MDL_{b} from a set of 129 MBs where the highest ranked MB concentrations are \( \ldots 1.10, 1.15, 1.62, 1.63, \) and 2.16, the 99\textsuperscript{th} percentile concentration is the 128\textsuperscript{th} value (129 \cdot 0.99 = 127.7, which rounds to 128), or 1.63. Alternatively,
spreadsheet programs may be employed to interpolate the MDLb more precisely.

c. If all concentration values for the MB pool are numeric values, calculate the MDLb as follows:
   i. Calculate the average concentration of the MBs ($\bar{x}_b$). If $\bar{x}_b < 0$, let $\bar{x}_b = 0$.
   ii. Calculate the standard deviation of the MB concentrations, $s_b$.
   iii. Multiply $s_b$ by the one-sided Student’s T value at 99% confidence corresponding to the number of blanks analyzed according to Table 4.1-2. Other values of T for additional samples ($n > 13$) may be found in standard statistical tables.
   iv. Calculate MDLb as the sum of $\bar{x}_b$ and the product of $s_b$ and the associated student’s T value:

   $$\text{MDL}_b = \bar{x}_b + s_b \cdot t$$

3. Compare MDL_sp and MDL_b. The higher of the two values is reported as the laboratory MDL for the given analyte.

4. If the MDL is determined as the MDL_sp, the analyst is recommended to verify the MDL by:
   a. Preparing one or more spiked samples at one- to five-fold the determined MDL and analyzing the sample per the method to ensure the determined MDL is reasonable. At the MDL_sp concentration there is a 50% chance that the analyte will not be detected; however, the analyte should be detected at two- to five-fold the determined MDL concentration.
   b. Comparing the measured values to reasonable bias acceptance criteria for the measured concentration of the MDL verification samples. For example, an MDL verification that recovers 2% of the nominal amount is not realistic, nor is one that recovers 300%. Appropriate potential acceptance limits are to double the acceptance window prescribed by the method for the given analyte. For example, TO-11A normally permits formaldehyde LCS recoveries to be 80 to 120% (± 20% error), therefore the MDL verification acceptance limits would be established at 60 to 140% recovery. Note that agencies may develop alternate acceptance criteria through control charts or other similar tools. For methods with significant background or matrix contamination, blank subtraction may be necessary to evaluate the recovery of the MDL verification sample (note this is unlikely if the MDL_b is not higher than the MDL_sp).
   c. Examining the MDL procedure for reasonableness if the verification sample is outside of the laboratory-defined acceptance criteria. Such an examination might include investigating the signal-to-noise ratio of the analyte response in the spiked samples, comparing the MDL to existing instrument detection limits (if known), and relying on analyst experience and expertise to evaluate the MDL procedure.
and select a different spiking level. The MDL study should then be repeated with a different spiking level.

4.1.3.1.2 Generating Ongoing MDL Data. The MUR includes an efficient method to collect MDL data routinely throughout the year and verify the initial MDL with the ongoing MDL data at the end of the year. This process incorporates a modest additional effort into routine analyses and alleviates the need to dedicate a significant contiguous block of time to preparing and analyzing MDL samples and MBs. Additionally, the temporal variability of the method and different states of instrument calibration are incorporated to better characterize the overall method variability in determining the MDL.

Minimally twice per calendar quarter, in two separate preparation and analysis batches, prepare and analyze two MDL spiked samples in matrix and two MB samples on each instrument with which routine analyses are performed.

The following should be taken into consideration when preparing and analyzing ongoing MDL spikes and MBs:

1. The MDL spike concentration for the given target analyte must be that employed when determining the initial MDL.

2. All portions of the method matrix (sampling media) must be incorporated/included into the prepared MDL spikes and MBs. Omission of components is not permitted.

3. MBs from routine analyses can be incorporated (it is presumed MBs will be generated and analyzed routinely).

4. If quarterly MDL spiked sample results indicate the target analyte is not identified (is ND), the spiking level is not sufficient and the MDL\textsubscript{sp} portion of the initial MDL will need to be redetermined with a higher spiking level. It is not necessary to prepare additional MBs in this instance as the existing MB data population should be sufficient to calculate an MDL\textsubscript{b}.

5. At least annually, re-evaluate the spiking level for the MDL spiked samples. If more than 5% of the MDL spiked samples do not return positive numerical results that meet the qualitative identification criteria, the spiking level is not sufficient and the MDL\textsubscript{sp} portion of the initial MDL will need to be redetermined with a higher spiking level (existing data for MDL\textsubscript{b} may be used).

6. If a new instrument is added to the ASL to be used for routine analyses, analyze a minimum of two MDL spiked samples and two MBs. If both MB results are less than the existing MDL, then this validates the existing MDL\textsubscript{b}. Incorporate the two MDL spiked sample results in the existing spiked sample results from the other instruments and recalculate the MDL. If the recalculated MDL does not vary by more than a factor of 2 (50 to 200% of the established MDL), then the existing MDL\textsubscript{sp} is validated. If either MDL\textsubscript{b} or MDL\textsubscript{sp} is not validated with the new instrument’s data, the initial MDL must be redetermined (and new MB data must be incorporated).
4.1.3.1.3 Ongoing Annual Verification of the MDL. At least once every 13 months, recalculate the MDL\textsubscript{b} and MDL\textsubscript{sp} as above in Section 4.1.3.1.1.2 from the ongoing collected data.

1. Include the initial MDL spikes and MB samples if they were generated in the previous 24 months. Laboratories may reduce the MB pool to the previous six months or 50 most recent MBs, whichever is the greater number, at their discretion.

2. Include data from the last 24 months, but only for MDL spikes prepared at the same concentration. Only exclude data if there are known instances of technical problems with the data (e.g., failed injection) with a documented rationale for exclusion. If the method sensitivity is believed to have changed in recent months, only recent data need to be included in the calculation. Such may be the case if the method was altered, therefore only include data after the changes were implemented. In such cases, there must be minimally seven MBs and seven MDL spiked sample results (these MDL spike results cannot be non-detect) meeting the three separate preparation and analysis batch criteria described in Section 4.1.3.1.1.2. If insufficient acceptable data exist, the initial MDL must be redetermined.

3. Include only data from batches with acceptable QC (calibration, extraction batch QC samples, etc.) and do not include data from rejected batches.

4. The verified MDL is the greater of the MDL\textsubscript{sp} or MDL\textsubscript{b}.

5. If the verified MDL is within two-fold of the established MDL (i.e., 50 to 200\% of the established MDL, approximately correlating to the 95\% confidence interval for the initial MDL with \( \nu = 6 \)), and fewer than 3\% of the MB results for the target analyte measure results above the established MDL, then the ASL may continue to report the established MDL. Otherwise, the ASL will update the MDL to the newly calculated MDL above in Step 4.

4.1.3.1.4 Example Initial MDL Calculation. A laboratory is determining the initial MDL for formaldehyde by TO-11A by spiking commercially-prepared DNPH cartridges and analyzing MBs. The analyst spiked and extracted eight cartridges with formaldehyde-DNPH at 0.030 \( \mu \text{g/cartridge} \) (in terms of the amount of the free formaldehyde) and eight MB cartridges over three separate preparation batches (i.e., three separate dates). Results were analyzed over three different analysis batches (i.e., three separate dates) per the ASL’s Method TO-11A yielding the following results:

<table>
<thead>
<tr>
<th>Cartridge Number</th>
<th>Preparation Batch and Date</th>
<th>Analysis Batch and Date</th>
<th>Spikes (( \mu \text{g/cartridge} ))</th>
<th>Method Blanks (( \mu \text{g/cartridge} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A - September 12, 2021</td>
<td>QR9 - September 13</td>
<td>0.1685</td>
<td>0.1412</td>
</tr>
<tr>
<td>2</td>
<td>A - September 12, 2021</td>
<td>QR9 - September 13</td>
<td>0.1651</td>
<td>0.1399</td>
</tr>
<tr>
<td>3</td>
<td>A - September 12, 2021</td>
<td>QR9 - September 13</td>
<td>0.1701</td>
<td>0.1402</td>
</tr>
<tr>
<td>4</td>
<td>B - September 19, 2021</td>
<td>QR12 - September 21</td>
<td>0.1673</td>
<td>0.1405</td>
</tr>
<tr>
<td>5</td>
<td>B - September 19, 2021</td>
<td>QR12 - September 21</td>
<td>0.1692</td>
<td>0.1408</td>
</tr>
<tr>
<td>6</td>
<td>C - September 28, 2021</td>
<td>QR16 - September 29</td>
<td>0.1686</td>
<td>0.1403</td>
</tr>
<tr>
<td>7</td>
<td>C - September 28, 2021</td>
<td>QR16 - September 29</td>
<td>0.1705</td>
<td>0.1402</td>
</tr>
<tr>
<td>8</td>
<td>C - September 28, 2021</td>
<td>QR16 - September 29</td>
<td>0.1696</td>
<td>0.1410</td>
</tr>
</tbody>
</table>
The average ($\bar{x}$) and standard deviation ($s$) of measured formaldehyde mass were determined for both the spikes and the MBs (all in units of µg/cartridge):

$$\bar{x}_{sp} = 0.1686$$
$$\bar{x}_b = 0.1405$$
$$s_{sp} = 0.0017$$
$$s_b = 0.0004$$

To calculate the MDL$_{sp}$, the standard deviation of the spiked aliquots is multiplied by the associated Student’s $t$-statistic. The Student’s $t$ value for eight aliquots is 2.998, corresponding to seven degrees of freedom ($8 - 1 = 7$):

$$\text{MDL}_{sp} = 0.0017 \, \text{µg/cartridge} \cdot 2.998$$
$$= 0.0051 \, \text{µg/cartridge}$$

To calculate the MDL$_b$, the standard deviation of the MB cartridge measurements is multiplied by the associated Student’s $t$-statistic and this product is added to the average blank value, $\bar{x}_b$:

$$\text{MDL}_b = 0.0004 \, \text{µg/cartridge} \cdot 2.998 + 0.1405 \, \text{µg/cartridge}$$
$$= 0.1417 \, \text{µg/cartridge}$$

The MDL$_{sp}$ and MDL$_b$ are compared to determine which is greater, and the greater of the two values is reported as the initial MDL for formaldehyde.

$$0.1417 \, \text{µg/cartridge} > 0.0051 \, \text{µg/cartridge}$$

In this case, the formaldehyde MDL$_b$ of 0.1417 µg/cartridge is greater than the MDL$_{sp}$ of 0.0051 µg/cartridge, and is reported as the ASL MDL for formaldehyde as measured by Method TO-11A. This mass/cartridge value is normalized to the sampled air volume to determine the initial MDL for air equivalent measurements. The associated monitoring site collects carbonyls samples for 1440 minutes at a flow rate of 1 L/minute at standard conditions for a total collected volume of 1.44 m$^3$, therefore the in-air MDL is:

$$0.1417 \, \text{µg}/1.44 \, \text{m}^3 = 0.0984 \, \text{µg/m}^3$$

### 4.1.3.2 MDLs via DQ FAC Single Laboratory Procedure v 2.4

The MDL procedure described in this section involves examination and statistical analysis of historical MB data to derive the MDL. If the method is new, has been updated (e.g., digestion acid concentrations changed, analytical column type changed, etc.), or the instruments are new, the MDL must be initially determined as described in Section 4.1.3.1. Once sufficient MB data have been generated with the method, the MDL can be calculated as detailed in this section.

This procedure must be performed only with MBs that include all media contributions and processing procedure elements and the method employed to generate the MB data must be consistent among the MB samples (i.e., different instruments may be employed; however, the
method conditions are to be common). Also, MB analyses which were the result of laboratory preparation or analysis errors must not be included.

The DQ FAC procedure requires that historical MB data be examined to verify that at least 50% of the results are a numerical value (zero, positive concentration, or negative concentration). If fewer than 50% of the MB values are numerical, or stated another way, if 50% or more of the values are reported as non-detects, use the procedure described above in Section 4.1.3.1. Once it is determined that the DQ FAC method is applicable, assign MBs without a numerical value (i.e., non-detect) as zero. Calculate the standard deviation of the included MBs. A minimum of seven MBs meeting these criteria is required within the calendar year. If results of more than seven MBs within the year meet these criteria, all such MB data should be included in the evaluation.

Calculate the MDL as follows:

\[
MDL = \bar{x}_{mb} + s \cdot K
\]

where:

\[
\bar{x}_{mb} = \text{mean result of the MBs}
\]

\[
s = \text{standard deviation of the MBs}
\]

\[
K = \text{multiplier for a tolerance limit based on the 99th percentile for n-1 degrees of freedom according to Table 4.1-3.}
\]

Note that if \(\bar{x}_{mb}\) is a negative value, substitute zero for this value.

If 5% or more of the blank results are greater than the established MDL, raise the MDL as follows:

1. To the highest MB result if less than 30 MB results are available.
2. To the next to highest MB result if 30 to 100 MB results are available.
3. To the 99th percentile, or the level exceeded by 1% of all MB results, if there are more than 100 MB results available.

Only MBs that meet the specified qualitative criteria for identification (signal to noise, qualifier ion presence, etc.) are to be given a numerical result.

**Table 4.1-3. K-values for n Replicates**

<table>
<thead>
<tr>
<th>n</th>
<th>K</th>
<th>n</th>
<th>K</th>
<th>n</th>
<th>K</th>
<th>n</th>
<th>K</th>
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<tbody>
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<td>7</td>
<td>6.101</td>
<td>30</td>
<td>3.317</td>
<td>53</td>
<td>2.993</td>
<td>76</td>
<td>2.855</td>
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<td>9</td>
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<td>32</td>
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<td>55</td>
<td>2.970</td>
<td>78</td>
<td>2.847</td>
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<tr>
<td>10</td>
<td>4.829</td>
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<td>3.253</td>
<td>56</td>
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<td>79</td>
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<td>4.599</td>
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<td>3.234</td>
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<td>80</td>
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<tr>
<td>12</td>
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<td>81</td>
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<tr>
<td>13</td>
<td>4.264</td>
<td>36</td>
<td>3.199</td>
<td>59</td>
<td>2.943</td>
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<td>2.832</td>
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### Table 4.1-3. K-values for n Replicates (Continued)

<table>
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<th>K</th>
<th>n</th>
<th>K</th>
<th>n</th>
<th>K</th>
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</thead>
<tbody>
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<tr>
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<td>3.494</td>
<td>47</td>
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<td>70</td>
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<td>25</td>
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<td>48</td>
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<td>2.860</td>
<td>98</td>
<td>2.782</td>
</tr>
</tbody>
</table>

### 4.1.4 References


4.2 VOCs – Overview of EPA Compendium Method TO-15A

Each monitoring agency and ASL is to prescribe in an appropriate quality systems document, such as an SOP, its procedures for collecting and analyzing VOC samples. These procedures include, but are not limited to, performing instrument and media qualification, VOC sampling, canister cleaning, analysis, and data reporting. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, the method performance specifications as given in Section 4.2.13 are to be met. QC performance metrics are to be summarized in the monitoring agency QAPP.

Of the 188 HAPs listed in Title III of the CAA Amendments of 1990, 97 of these are VOCs. VOCs are defined as organic compounds having a vapor pressure greater than $10^{-1}$ Torr at 25°C. Air toxic VOC ambient air (non-source impacted) concentrations are typically measured at the single part per trillion by volume (pptv) to single part per billion by volume (ppbv) level. Measurement of these VOCs is based on the techniques described in EPA Method TO-15A, which describes collection of whole air samples into evacuated stainless steel canisters followed by preconcentration of the volatiles for analysis via GC/MS. EPA published Method TO-15A in September 2019 as an update to Compendium Method TO-15 and many of the aspects in the updated method are included within this section. Method TO-15A includes techniques and instrumentation that permit measurements of VOCs in ambient air in this concentration range.

EPA added EtO to the list of Tier I HAPs and required its measurement at all NATTS monitoring sites in 2019. Monitoring agencies and their ASLs have communicated difficulty in developing appropriate procedures for measurement of EtO with TO-15A, and while some aspects of EtO analysis remain challenging, this section includes guidance and best practices to measure EtO.

4.2.1 General Description of Sampling and Analytical Methods. An MFC, mechanical flow control device (MFCD), and/or critical orifice regulates the flow of ambient atmosphere into an evacuated passivated stainless steel canister at a known, constant flow rate over the 24-hour collection period. Following completion of collection, the canister is transported to a laboratory for analysis within 30 days of collection. Previous studies suggest that most compounds analyzed via TO-15A are stable for up to 30 days in passivated stainless steel canisters however, the condition of the wetted surfaces of each individual canister is likely to influence the stability of the VOCs. Analysis of the sample as soon as possible after collection is strongly recommended to minimize changes in concentrations of VOCs in the collected sample, especially for HAPs that exhibit degradation or enhancement such as acrolein, 1,3-butadiene, and EtO, among others.

Sampling of VOCs is integrated over time such that sampling occurs over a 24-hour period and results in a final canister pressure that is subambient (less than the typical ambient atmospheric pressure at the field location) or pressurized (above the typical ambient atmospheric pressure at the field location). There have not been definitive studies demonstrating one collection convention (subambient or pressurized) to be superior; however, a previous study conducted by McClenny et al. indicated that ambient air samples collected above atmospheric pressure may exhibit condensation on the interior canister surfaces. This condensed water inside the canister...
resulted in degraded (poorer) precision for replicate canister analysis. As atmosphere was removed from the canister during analysis, the amount of condensed water decreased which resulted in changes to the equilibrium of VOCs in the gas phase and dissolved in the liquid phase. Therefore, monitoring agencies are cautioned that collecting pressurized samples may result in a low measurement bias (when VOCs are dissolved in the condensed water they are not available for measurement) and poor replicate precision when canister pressures are very high. When conducting pressurized sampling, it is strongly recommended to collect samples such that final canister pressures remain ≤ 3 pounds per square inch gauge (psig) (~17.7 pounds per square inch absolute [psia]) to minimize the potential for water condensation inside the canister. Regardless of the chosen final canister pressure, each agency is responsible for ensuring that method performance specifications are met, and specifically that method precision and bias are acceptable for their selected combination of sampling instrument; final canister pressure; canister type; and preconcentration, water management, and analysis techniques.

Monitoring agencies are strongly encouraged to maintain a high-quality calibrated vacuum/pressure gauge (or fleet/combination of gauges) to measure canister pressures at various points before and after sampling. Pressure measurements with a high-quality calibrated gauge assure the canister has sufficient vacuum before sampling, that ending sample pressures are as expected, and that leaks have not occurred after sampling completion and during handling and transport to the ASL.

VOCs are identified and quantified via (typically cryogenic) preconcentration GC/MS and a typical analysis scheme is as follows. A known volume of the whole air (an air parcel from which gases have not been removed and are completely captured for sample collection) is passed through a preconcentrator in which the VOCs are trapped onto a sorbent bed trap or similar substrate trap while nitrogen (N₂), oxygen (O₂), argon (Ar), carbon dioxide (CO₂), and to the extent possible, H₂O are selectively removed. The sample introduction pathway and sorbent bed are then swept with dry carrier gas (such as hydrogen or helium) to remove residual water, while the VOCs are retained on the trap. After the preconcentration and dehydration, the trap is backflushed (typically while undergoing rapid heating) with carrier gas to desorb the VOCs and the VOCs are entrained in the carrier gas stream where they are refocused and subsequently introduced onto the GC column for separation. After separation on the column, VOCs are ionized in a quadrupole, ion trap, or time of flight (TOF) MS which detects the resultant ions according to their mass to charge (m/z) ratio. The responses of the resultant ion masses are plotted against the chromatogram run time and compared to the standard chromatogram to identify the target compounds in the sample based on retention times (RTs) and abundance ratios of ions of target analyte standard materials analyzed under the same chromatographic and MS conditions. Analyte concentration is determined by comparison to a calibration response curve established on the GC/MS instrument by introduction of standard concentrations of target analytes covering the desired concentration range for measurement. QC samples are prepared and analyzed to verify continued calibration acceptance and hygiene of the instrument and procedures.

VOCs commonly analyzed by Method TO-15A include, but are not limited to, those in Table 4.2-1.
Table 4.2-1. VOC Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-15A

<table>
<thead>
<tr>
<th>Target Compound</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>67-64-1</td>
</tr>
<tr>
<td>acrolein a b</td>
<td>107-02-8</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>107-13-1</td>
</tr>
<tr>
<td>benzene a b</td>
<td>71-43-2</td>
</tr>
<tr>
<td>benzyl chloride</td>
<td>100-44-7</td>
</tr>
<tr>
<td>bromodichloromethane</td>
<td>75-27-4</td>
</tr>
<tr>
<td>bromoform (tribromomethane)</td>
<td>75-25-2</td>
</tr>
<tr>
<td>1,3-butadiene a b</td>
<td>106-99-0</td>
</tr>
<tr>
<td>2-butanone (methyl ethyl ketone)</td>
<td>78-93-3</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>75-15-0</td>
</tr>
<tr>
<td>carbon tetrachloride (tetrachloromethane) a b</td>
<td>56-23-5</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>108-90-7</td>
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<tr>
<td>chloroform (trichloromethane) a b</td>
<td>67-66-3</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>110-82-7</td>
</tr>
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<td>dibromochloromethane</td>
<td>124-48-1</td>
</tr>
<tr>
<td>1,2-dibromoethane b</td>
<td>106-93-4</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>95-50-1</td>
</tr>
<tr>
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</tr>
<tr>
<td>1,4-dichlorobenzene</td>
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### Table 4.2-1. VOC Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-15A (Continued)

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<td>127-18-4</td>
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<td>109-99-9</td>
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<td>toluene</td>
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<td>1,2,4-trichlorobenzene</td>
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<td>trichlorofluoromethane (Freon 11)</td>
<td>75-69-4</td>
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<tr>
<td>1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113)</td>
<td>76-13-1</td>
</tr>
<tr>
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<td>95-63-6</td>
</tr>
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<td>1,3,5-trimethylbenzene</td>
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<tr>
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* NATTS Tier I analyte (required)
* NATTS PT target analyte

### 4.2.1.1 Ethylene Oxide Measurements

EPA added EtO to the list of Tier I required VOCs HAPs in 2019 and ASLs worked to adapt their TO-15 measurement procedures. As of the publication of this TAD, challenges remain to providing settled guidance on a standard EtO measurement method by TO-15A, primarily due to:

1. Currently available stock gas standards from vendors have shown concentration instability where concentrations decrease dramatically (e.g., > 30%) over several months.
2. Canister media, regardless of age, condition, and interior surface treatment, may exhibit EtO contamination and concentration increases (growth) within the typical holding time (up to 30 days) in some cleaned canisters.
3. The analytical method of separation and quantitation by GC-MS and the selected analytical columns could suffer from coelutions that interfere with resolution, identification, and chromatographic peak integration.

Any one of these challenges by itself can complicate accurately measuring and reporting EtO; however, the three challenges combined have proven difficult for NATTS VOC ASLs to optimize their EtO measurement method. EPA continues to study these challenges and intends to notify the NATTS stakeholder community and provide training when definitive studies and
resulting guidance are available. In the meantime, ASLs should consider the following when developing or refining their TO-15A procedures to include EtO measurements.

4.2.1.1.1 EtO Stock Standards. EPA has procured EtO stock gas standards from a number of gas vendors and is currently studying their concentration stability. EPA released a memo in August 2019 recommending that ASLs acquire EtO gas standards at a minimum concentration of 1 part per million by volume (ppmv) from among a list of potential vendors. Discussions with gas vendors that have demonstrated success in preparing concentration stable EtO gas stock standards indicate that the interior cylinder surface treatment is critical in ensuring the EtO concentration stability. ASLs should purchase stock EtO gas standards from a reputable provider and seek specific information (e.g., data supporting) on EtO stability in the specific cylinder type employed to prepare the standard. Additionally, ASLs must employ a second source calibration verification (SSCV) standard to verify the concentration of the primary calibration standard gas. While it is possible that both the primary and second source cylinders could exhibit concentration degradation at the same rate, this is not likely. Particularly, if the ASL acquires a gas standard containing EtO that exhibits concentration stability (e.g., < 5% change over approximately 12 months) as demonstrated by recertification, that cylinder should be recertified routinely (e.g., just prior to the expiration period of the certification or recertification). EtO standard concentration degradation will be evident when the second source standard recovery trends toward and eventually exceeds the ±30.1% threshold. When the SSCV recovers high, it indicates the EtO concentration in the primary standard cylinder (or the canister diluted from the primary standard) concentration is degrading. Conversely, if the SSCV recovery is trending increasingly lower, the second source standard is implicated. It is critical to employ QC charts of the SSCV recovery over time and examine them for recovery trends. There is little recourse when a standard’s EtO concentration begins to degrade other than to replace it with a new standard (recertification is not acceptable on standards exhibiting degradation). Gas vendors may accept such cylinders on return and provide replacements or discounts on replacements. Further discussion on data handling in this situation can be found in Section 4.2.8.6.1.

4.2.1.1.2 EtO in Canister Media. ASLs have widely reported EtO concentration growth in cleaned canisters. The underlying mechanism of the growth is not completely understood, but a working theory is that carbon compound residue in the canister is reacting in the presence of oxygen (i.e., ambient air and hydrocarbon-free [HCF] zero air) and is catalyzed to form oxygenated VOC's, among which is EtO. This problem has frustrated ASLs that have attempted to solve this problem by purchasing new canisters only to find that some newly manufactured canisters exhibit EtO growth when attempting canister qualification as described in Section 4.2.4.1. Additionally, this EtO formation and growth phenomenon has been observed in a variety and certain percentage of legacy and new silicon-ceramic lined and electropolished canisters from several manufacturers. ASLs have reported that numerous cycles of canister cleaning have reduced, but not completely eliminated the problem in some canisters. For this reason, canister qualification as described in Section 4.2.4.1 is critical to ensuring measured concentrations of EtO are, in fact, those in the sampled atmosphere and not due to EtO formation and growth within and due to the canister. To date, a definitive and thorough study to confirm the formation mechanism, root cause, and mitigation of the EtO canister formation and growth has not been published.
As practical, ASLs should identify canisters that perform poorly for EtO and exclude them from use on the NATTS Program when sampling or preparing QC samples and standards for EtO measurements. ASLs must qualify the canisters (new and legacy) in their fleet to demonstrate acceptably low EtO levels of interferences (e.g., growth) in the canisters before use as described in Section 4.2.4.1. EtO measurements from canisters which do not exhibit acceptable performance will need to be qualified (QA Qualifiers LK indicating high bias and CF indicating canister qualification bias check failure) when reported to AQS. Further, when canister qualification results show contamination exceeds 5-fold the MDL, the data are to be invalidated (Null data qualifier EC indicating exceeds a critical criterion) when reported to AQS.

4.2.1.1.3 EtO GC/MS Separation and Quantitation. EtO elutes in the early part (first half) of the GC/MS chromatogram and is subject to coelution interferences from several compounds. Notably, the most severe interferences occur from water in the chromatogram due to excess water remaining in the focused injection from the preconcentrator, which result in a broad unfocused EtO peak. ASLs should adjust the preconcentrator settings and ensure the system is acceptably leak-tight to minimize the amount of water introduced to the column. Additionally, when employing the 100% polydimethylsiloxane (PDMS) separation column typically employed in TO-15A analyses, a list of potential coeluting interferences have been identified and ASLs may experience others depending on their airshed. These coelutions share several ions in common with EtO. The most abundant ions for EtO in the 70 electron volt (eV) electron impact (EI) ionization mass spectrum are m/z 15, 29, and 44, and less abundant (minor abundance) are m/z 26, 42, and 43 as shown below in Figure 4.2-1. Documented potential coeluting species sharing m/z with EtO (common m/z in parentheses) include acetaldehyde (15, 29, 42, 43, and 44), methanol (m/z 15 and 29), trans-2-butene (m/z 15, 29, 42, and 43) and 2,2-dimethyl propane (m/z 15, 29, 42 and 43).\textsuperscript{10} Note this list is not comprehensive and other coeluting substances may appear based on the pollutant burden in the sampled airshed.

CO\textsubscript{2} retained in the focused injection can also interfere with EtO identification and quantitation due to leaks in the instrument system. CO\textsubscript{2} shares m/z 44 with EtO and typically results in a large broad elevation in the baseline of the total ion chromatogram (TIC) (in SCAN mode) and for m/z 44 (in selected ion monitoring [SIM] mode). Operating the MS solely in SCAN mode is unlikely to yield acceptable results as there will not be necessary sensitivity and numerous substances can elute in the elution area of EtO in the TIC and very low concentrations (< 0.1 ppbv) are unlikely to be sufficiently resolved. MS systems should be operated in SIM or SIM/SCAN mode and the MS should be configured to monitor as many of the EtO m/z as possible to provide the potential for interference free ions for quantitation and confirmation.
To address these coelutions, several tactics may reduce or eliminate the interferences, most of which have drawbacks or tradeoffs for the analysis of TO-15A for the remaining suite of target VOCs. These tactics include:

- Adjusting preconcentrators to maximize water removal and investigating and mitigating leaks to minimize water and CO2 ingress. These steps will likely improve chromatographic performance for the entire suite of target VOCs with potentially some loss of performance for very volatile VOCs (e.g., acetylene).

- Changing the separation column. Installing a column with a more polar stationary phase (e.g., 95% PDMS with 5% cyanopropylmethyl) or a longer column (e.g., change from 60 m to 100 m) may improve the separation of EtO from coelutions. The column phase change may alter the elution order, may result in coelution interferences with other target analytes, and may degrade chromatographic performance (e.g., poor peak shape) for other target VOCs. A longer PDMS column will extend the run time and reduce sample throughput.

- Modifying the GC oven temperature program. Starting the run with oven temperatures at 20°C or lower using cryogenic cooling of the oven (for instruments so enabled) may provide the necessary resolution for EtO. This will require additional consumption of cryogens, particularly if very low starting temperatures are employed.

In almost all cases, the analyst should closely review the area of the chromatogram for potential EtO peaks that were overlooked by the CDS and should closely examine identified peaks for coelutions and proper relative abundances of selected qualifier ions.
4.2.2 Precision – Sample Collection and Laboratory Processing. Each agency and ASL is to prescribe procedures that it will follow to assess VOC precision in the NATTS QAPP, SOP, or similar controlled document. Given in the sections below are the various types of precision and associated frequency requirements for VOCs.

Precision is assessed by calculating the RPD for duplicate, collocated, and replicate analysis samples. The RPD is evaluated when at least one of the measurements in the precision pair is ≥ 5x MDL and must be < 25.1%. When both measurements in the precision pair are 5x MDL, the calculation is straightforward. However, for precision pairs for which one measurement is ≥ 5x MDL and the other is ≤ 5x MDL, calculate the RPD by substituting the 5x MDL concentration for the measurement ≤ 5x MDL per the convention in Section 2.1.3.1. This determination of RPD is solely for assessing precision; the concentrations measured of the precision pair are to be reported to AQS as measured.

Failure to satisfy the precision criterion will prompt root cause analysis to investigate and correct the failure. If the issue cannot be corrected satisfactorily, the associated sample data are to be qualified when entered into AQS. For example, concentration results for both measurements within a collocated or duplicate sample pair exceeding this criterion are to be estimated (e.g., with the LJ QA qualifier code for the AQS RD transactions, where applicable). Replicate analysis pairs for which the precision criterion is exceeded requires that sample results within that analytical sequence be estimated. Refer to the list of qualifiers in Table 3.1-2.

4.2.2.1 Sample Collection and Analysis Precision. Collocated and duplicate samples are compared to the primary sample to determine the precision inclusive of all sample collection and analysis procedures.

For samples to be collocated, each sampling unit must have its own pathway to the ambient atmosphere. If collected from a manifold, each sampling unit must have a dedicated manifold for it to be collocated; otherwise this configuration is defined as duplicate. The rationale behind this distinction is that there is potential non-homogeneity of the sampled atmosphere in the manifold when compared to the ambient atmosphere. Any effect of the manifold impacts both sampling units and they are not sampling truly independently from the ambient atmosphere. If both sampling unit inlets connect to the same inlet manifold, the samples are duplicate, not collocated, as shown in Figure 4.2-2. To summarize,

- Collocated samplers must have two separate flow control devices and two separate discrete inlet probes to the ambient atmosphere. If applicable, each sampling unit must connect to a separate manifold. Collocated sampling inlet probes must be within 4 m of the primary sampling inlet probe and there is no minimum distance (i.e., may be right next to one another).
- Duplicate sampling is performed in situations where two canisters are collected through a single inlet probe, which includes a common inlet manifold.
Collocated or duplicate VOC sampling, if performed (as detailed in the QAPP), must be conducted at a minimum frequency of 10% of primary sampling events. This is equivalent to a minimum of six collocated samples per year, or roughly one every other month, for sites conducting one-in-six days sampling for a total of 61 primary samples annually. More frequent collocated sample collection provides additional sample collection precision and is encouraged where feasible.
4.2.2.2 Laboratory Analytical Precision. Several analysis aliquots can be removed from a collected canister which affords replicate analysis to evaluate analytical precision. The same canister sample is analyzed twice and the results are evaluated for precision as RPD. The required frequency for replicate analyses reported to AQS is prescribed in the workplan template, but is recommended to be performed on a one-per-batch frequency or one-in-20 sample injections, whichever is more frequent. Monitoring organizations are encouraged to report all replicate analysis results to AQS.

For replicate analysis, the ASL will typically assign a convention that the first replicate for a replicate analysis is that which is reported to AQS for the sample result. However, if the first replicate is invalidated for any reason (e.g., as may occur when a coeluting peak significantly interferes with the target peak) and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as the sample result as described in Section 2.1.3.2.

4.2.3 Sample Collection

4.2.3.1 Sampling Equipment Specification. VOC sampling instruments are commercially available that are simple and dedicated to collecting a single sample or may be more complex and incorporate computerized control of sampling events, permit simultaneous collection of VOC canisters and carbonyl cartridges, or include secondary channels for collection of duplicate VOC canister samples. Regardless of the additional features, each sampling unit must minimally include the following components:

- Elapsed time indicator
- Multi-day event control device (timer)
- Electronic latching solenoid valve with a low temperature rise coil
- Pressure gauge or pressure transducer to perform leak checking of canister connection
  – a high-quality analog vacuum/pressure gauge is strongly recommended
- Component to control sampling flow: MFC (preferred), MFCD, or critical orifice

In general, for NATTS Program sampling, sampling units will be installed within a monitoring shelter and will employ an MFC (or a MFCD) to meter sampling flow, a vacuum/pressure gauge or pressure transducer to measure canister vacuum/pressure, and a clock timer or computer to control sampling events (sampling start and stop time) and indicate elapsed sampling time.

4.2.3.1.1 Sampling Pathway Composition. All wetted sampling surfaces that contact the sampled atmosphere, including the inlet probe, must be constructed of inert materials such as chromatographic grade stainless steel (minimum type 316 or silicon-ceramic coated), quartz glass, or borosilicate glass. Use of Viton and fluoropolymers such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP) materials should be minimized due to their absorption/desorption and permeability properties, and when used, monitoring agencies are cautioned that sampling instruments with these materials need to demonstrate the sampling instruments do not unacceptably bias the collected sample (refer to Section 4.2.3.3). Use of other incompatible materials in the flow path such as copper or brass (these behave as catalysts to oxidize VOCs) and FEP Teflon®, plastics, and rubber (these offgas target VOCs and/or exhibit
absorptive/desorptive behavior) is not permitted. Use of glass-lined stainless steel is not recommended due to the fragility of the glass substrate that can crack and break, resulting in exposed active sites within the tubing.

If the VOCs sampling manifold inlet is shared with criteria gas monitors, the inlet manifold must be constructed only of borosilicate glass (stainless steel is incompatible with reactive gases such as sulfur dioxide and ozone).

Several manufacturers offer different grades of silicon-ceramic lined stainless steel tubing and fittings suitable for use in VOC sample collection (e.g., Sulfinert®, Silonite™, SilcoSteel®). Care should be taken to clean these materials only with deionized water. The manufacturers recommend solvent use for removal of residues; however, solvents will contaminate the materials with target analytes. Use of manual methods for cleaning, such as with brushes or abrasive materials, is prohibited, as it can scratch the coated surface and reveal bare untreated metal. Materials should not be cleaned with basic cleaners (e.g., pH ≥ 8) and should not be subjected to steam as these will damage the coating.  

4.2.3.1.1.1 Particulate Filtration

A stainless steel particulate filter (recommended 2-µm to 7-µm pore size) must be installed in the sampling flow path upstream of the sampling unit for VOC sample collection to prevent the ingress of PM. The particulate filter should be installed in the sampling pathway as far upstream as practical to limit the ingress of PM and prevent its deposition within the sampling flow path. Additionally, the PM filter will prevent insect nests and other debris in the sampling flow path that may act as sorbents to adsorb VOCs and scrub them from the sampled air stream resulting in a low bias in the collected air sample, and desorbing at a later time, contaminating the sampled air stream. Omission of a particulate filter allows particulate residue such as dust and pollen to adhere to the interior of the sampling unit (e.g., solenoid valves and MFCs) and to be pulled into the sampling canister during sample collection. Once inside the canister, PM is difficult to remove with traditional pressurization and evacuation cleaning procedures and can form sites within the canister that adsorb and desorb analytes and/or provide reactants which may oxidize to form target analytes or interferants, potentially rendering the canister irreversibly contaminated.

Such stainless steel particulate filters are to be replaced or cleaned minimally annually or more frequently if in areas with high airborne PM levels which may clog the filter pores and result in decreased flows or decreased collected pressures. Replacement of the filter element is preferred due to the ease and low cost of replacement and associated difficulty with cleaning and decontaminating the filter element. If cleaned, sintered metal filters should be removed from the sampling inlet and sonicated in water and/or methanol for 15 minutes, after which they should be rinsed with fresh methanol, dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 hours, and flushed for several hours with humidified HCF zero air or nitrogen. Even with such cleaning practices, the filter may not be fully returned to proper function and may additionally exhibit residual contamination from the cleaning solvent. A best practice is to replace the filter.
4.2.3.1.2 Cleaning of Sampling Components

The manufacturer’s instructions should be followed for cleaning components such as flow controllers and sampling unit parts. Note that disassembly of such instruments may void warranties or calibrations.

Metallic and glass components of sampling units, canister cleaning apparatuses, and wetted pathways such as stainless steel tubing, sintered particulate filters, critical orifices, and connecting components should be flushed with humidified HCF zero air or ultrapure nitrogen to remove contamination. They may be further cleaned by disassembling and sonicating in water and/or methanol for 15 minutes, after which they should be rinsed with fresh methanol and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 hours. Ovens may be set to higher temperatures if the components can withstand the temperatures. To avoid damage to deactivated stainless steel components due to oxidation in the presence of oxygen-containing atmospheres (e.g., HCF zero air), components treated with silicon-ceramic coatings should not be heated above 80 °C unless evacuated or under an inert atmosphere (e.g., nitrogen).

Nonmetallic components such as Viton seals and O-rings should be disassembled and inspected for cracks, abrasions, and residue (such as from PM) and sonicated in ASTM Type I water for 15 minutes. After sonication, components should be rinsed with fresh ASTM Type I water and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 hours.

Following drying, components should be inspected for integrity (e.g., to be sure critical orifices are not cracked or compromised), reassembled, and flushed with humidified HCF air or ultrapure nitrogen for at least 12 hours.

4.2.3.1.2 Subambient Sample Collection. Collecting canister samples to final pressures less than ambient barometric pressure requires a sampling unit with the minimal components listed above in Section 4.2.3.1. Subambient pressure sample collection concludes in a final canister pressure that is in an approximate range of 9 to 13 psia (4 to 11 inches Hg vacuum); however, each monitoring agency will determine the proper ending pressure for subambient sampling based on the flow rate characteristics of the flow controller. The final canister pressure cannot exceed the pressure at which the flow rate ceases to be constant over the 24-hour collection period. Flow rates are typically 2.5 to 3.5 milliliter (mL)/minute for 6-liter (L) canisters; however, they must be experimentally determined to ensure that the constant flow condition for the flow controller is maintained over the 24-hour sampling period. The process to determine this pressure limit is described below in Section 4.2.3.1.2.1. A more in-depth discussion of this process is described in Method TO-15A Section 9.1.

As noted earlier in Section 4.2.1, humidity in the sampled atmosphere may condense within canisters if the canister pressure is higher than the partial pressure of the water vapor at the given temperature, and this condensation causes several problems with the analysis. At subambient pressures, the partial pressure of water vapor does not typically exceed the equilibrium vapor pressure at the typical temperature in the analysis laboratory, thus water generally will not condense on the interior surfaces of the canister. Subambient pressure sample collection typically
uses the canister vacuum (pressure differential) to drive flow into the canister and therefore does not require a pump in the sampling pathway. With fewer overall components, moving parts, seals, and surfaces, there is generally less risk of the sampling unit contaminating a collected sample. A less complex sampling system has fewer parts to wear out and potentially fail, also simplifying maintenance.

Two disadvantages with subambient sample collection relate to contamination from ingress of unintended atmospheres into the canister due to leaking and a smaller overall volume of collected gas for analysis when compared to pressurized sampling. A canister leak on a subambient pressure sample canister will cause unintended ambient air to enter the canister and contaminate the sample. Moreover, a canister at subambient pressure contains less volume of air than an equivalent pressurized sample, which limits the number of aliquots that may be effectively removed from the canister for analysis before there is insufficient gas remaining for analysis.

4.2.3.1.2.1 Subambient Pressure Sampling Flow Rate Determination

Sampling units for collecting subambient pressure samples must have the flow rate control characterized to determine the canister and barometric pressure differential at which the flow rate ceases to be constant. For 24-hour sampling, the sampling flow rate must be constant over the sampling period to ensure the sample integration is consistent and not weighted toward the beginning of the sample collection period. The sampling unit manufacturer may provide information on this pressure differential limit; however, it must be determined and verified experimentally. To determine this pressure differential, the canister pressure, barometric pressure, and sampling flow rate are to be continually measured during sampling at the intended sampling flow rate until the sampling flow rate shows a decrease that exceeds 15% from the initial flow rate (this will show a downward trend in the flow rate data curve). Once this critical pressure differential is determined, the flow rate that accomplishes sample collection to that pressure differential is to be calculated per the following:

\[
Q_{setting} = \frac{V_{canister}}{D_{sampling}} \cdot \frac{P_{flow\ limit}}{P_{barometric}} \cdot 0.9
\]

where:
- \(Q_{setting}\) = flow rate setting (mL/minute)
- \(D_{sampling}\) = sampling duration (minutes)
- \(V_{canister}\) = canister volume (mL)
- \(P_{barometric}\) = barometric pressure (mmHg)
- \(P_{flow\ limit}\) = canister pressure at which the flow rate decreases from constant
- \(0.9\) = correction to reduce the flow rate by 10%

For example, a monitoring agency tested a sampling unit that regulates flow rate with a MFCD and determines the canister pressure at which the flow rate ceases to be constant is 552 mmHg at a barometric pressure of 758 mmHg. For collecting a 6-L canister for 24 hours (1440 minutes), the programmed flow rate was calculated to be:
4.2.3.1.3 Pressurized Sample Collection. Pressurized sampling involves collection of samples to a final collection pressure above atmospheric pressure utilizing a pump to push sampled air into the canister. As noted earlier in Section 4.2.1, sample collection at pressures above ambient pressure may result in water condensation on the interior walls of the canister.\(^6\) It is theorized that this condensation may lead to poor representation (low bias) of hydrophilic polar compounds in the aliquot of gas removed from the canister for analysis. For this reason, it is strongly recommended to not exceed 3 psig (~18 psia) for final canister pressure. An advantage of pressurized sample collection is that if the canister leaks slightly, the sample will not become contaminated so long as the canister pressure remains greater than atmospheric pressure. This 3 psi buffer above barometric pressure allows for a very small canister leak while balancing a low enough pressure that should minimize the likelihood of condensation in the canister.

A disadvantage of pressurized sample collection is that it requires incorporation of a pump and additional valves and components in the sampling pathway, which provide additional opportunities for contamination over time when compared to subambient sampling methods which do not require the additional components. Prior to field deployment, canister sampling units must be qualified as non-biasing as described in Section 4.2.3.3.

Some sampling systems are susceptible to condensation in the flow pathway during high-dewpoint conditions. This condensation manifests in the high pressure area between the pump and the bypass valve and is evidenced by transient pressure responses (surging) when the bypass valve is operating. To alleviate this condensation, the bypass valve should be kept as open as possible to maximize the air flow through the sampler to encourage proper venting and to minimize condensation.

4.2.3.1.3.1 Pressurized Sampling Flow Rate Determination

The flow rate of sample collection for pressurized sampling conventions is not critical for ensuring a constant flow rate over the 24-hour sampling duration. However, it is important to ensure the flow rate is sufficient to attain the desired canister pressure at the conclusion of the sampling event. Use the following formula to determine the necessary flow rate:

\[
Q_{setting} = \frac{V_{canister}}{D_{sampling}} \times \frac{P_{final}}{P_{barometric}}
\]

where:
- \(Q_{setting}\) = flow rate setting (mL/minute)
- \(D_{sampling}\) = sampling duration (minutes)
- \(V_{canister}\) = canister volume (mL)
- \(P_{barometric}\) = barometric pressure (mmHg)
- \(P_{final}\) = final canister pressure - should not exceed 3 psig (~915 mmHg)
For example, a monitoring agency wants to collect pressurized samples to 3 psig (~915 mmHg) for a 24-hour (1440 minutes) sample into a 6-L canister. Typical barometric pressure is 758 mmHg. The programmed flow rate was calculated to be:

\[
\frac{6000 \text{ mL}}{1440 \text{ mins}} \cdot \frac{915 \text{ mmHg}}{758 \text{ mmHg}} = 5.03 \text{ mL/min}
\]

4.2.3.2 Sampling Train Configuration and Residence Time. Sampling unit inlets are to be configured to minimize the residence time from the ambient atmosphere to the sampling unit while complying with the siting criteria in Section 2.4. The VOC sampling unit inlet may be connected to the ambient atmosphere with a dedicated sampling inlet line and inlet probe or may be connected to a sampling inlet that incorporates connections for other sampling instruments, such as a manifold, which is common at monitoring sites with multiple measured parameters such as criteria pollutant gases. While 40 CFR Part 58 Appendix E specifies that sampling residence time for VOCs for PAMS network measurements must be 20 seconds or less, no specification is given on VOCs for air toxics measurements. However, since the measurement principles are essentially equivalent, the VOC residence for the PAMS program is adopted here for the NATTS Program. Sample data for sampling systems with residence time exceeding 20 seconds are to be qualified (QA Qualifier SX indicating does not meeting siting criteria) when reported to AQS.

**Residence Time:** The linear velocity of the VOC sampling stream should be maximized where possible to reduce potential interactions (reactions and/or adsorption) with the flow path materials. In general, this means maintaining a sampling residence time of not more than 20 seconds, and preferably not more than 10 seconds, to the sampling unit inlet. This residence time requirement applies to both sampling inlets dedicated to only the NATTS VOC sampling unit and to sampling inlets configured with multiple sampling instruments (e.g., manifold inlets). Given the potentially low flow rate range of VOC sampling of ~2.5 to 5 mL/minute (unless the sampling unit employs a pump to achieve a higher flow rate), in most cases a pump will be needed to increase the flow rate to minimize the residence time at the VOC sampling unit. Such a configuration is shown below in Figure 4.2-3, which details the region of higher flow rate employed to transport the ambient air quickly and access point for the VOC sampler, shown in the region of lower flow rate. In addition, the dead volume (tubing length and internal diameter) of the sampler inlet line connection to the region of higher flow should be minimized to the extent possible while not inappropriately restricting the flow to the VOC sampler. Unless recommended by the manufacturer, inlet tubing for the VOC sampler should not have an internal diameter smaller than 0.03 inches (7.6 mm) so as to not overly restrict flow at flow rates of approximately 30 mL/minute.
Inlet manifolds incorporate a high flow pump or blower to pull ambient air through the manifold; the manifold flow rate should be minimally two times greater than the total demand of the systems connected to the manifold and should ideally cover a range of approximately three- to five-fold above the total airflow draw of the instruments connected to the manifold, or at a rate equal to the total sampling requirement plus 140 L/minute. 12

**4.2.3.3 Sampling Unit Non-Biasing Qualification.** Prior to field deployment and annually thereafter, each VOC sampling unit must be qualified as non-biasing by collection of both a sample of HCF zero air (or equivalent VOC- and oxidant-free air) and of a known concentration of VOC standard in humidified HCF air. Note that use of humidified ultra-high purity (UHP) nitrogen for the qualification gas or for diluting standard gases for the qualification is not appropriate as the inert nitrogen environment does not permit reactions that may occur when the sampling unit flow path surfaces are exposed to oxygen as they are when sampling ambient air.

This qualification may be performed as part of an internal audit, however, it is best performed following annual maintenance which includes calibration (or calibration checks) of flow controllers and pressure gauges as well as other preventive maintenance, as needed, to ensure the sampling unit is non-biasing prior to field deployment. Prior to use for conducting the non-biasing qualifications, equipment for delivering humidified HCF zero air and known concentration standards such as dynamic dilution systems, connecting tubing, and MFCs should be purged with humidified zero air for sufficient time (typically one hour) to ensure the challenge delivery system is sufficiently clean and purged of contaminants.

A best practice is to perform this procedure through the probe (TTP) where the entire sampling train is assessed for bias. However, conducting the TTP procedure requires equipment such as portable zero air generators and portable gas-phase dynamic dilution systems and staff trained and familiar with their operation; therefore, TTP procedures may not be practical. While the TTP procedure is the best practice, each sampling unit must minimally be bench tested. Suitable test procedures are described below. For monitoring agencies that cannot perform the annual
maintenance and qualification challenge in house, manufacturers, the national service contract laboratory, or third-party vendors may offer qualification services as a commodity. Regardless of the exact procedure adopted, the performance specifications listed below must be met.

4.2.3.3.1 Sampler Zero Check. The zero check is performed by providing humidified (~40 to 70% RH – it is critical that the gas not be dry) HCF zero air (note that nitrogen is not appropriate here) to the sampling unit for collection into a canister as is done for a typical ambient sample. The source humidified HCF zero air is also collected upstream of the sampling unit and this sample serves as a reference. Compounds which show increased concentrations in the challenge sample compared to the reference sample indicate contamination attributable to the sampling unit. Humidified HCF zero air used for this procedure should be as free of contaminants as possible, recommended to comply with the criteria cited for dilution gas in Section 4.2.7.2; however, the comparison to the reference sample corrects for background in the humidified HCF zero air.

The best practice is to collect the reference and challenge samples simultaneously and for 24 hours to best simulate the interactions in the sampling unit that would occur over a typical ambient sampling event. The following section describes a procedure for conducting this zero check challenge. In instances where sampling for 24 hours is not possible, sampling for shorter durations (e.g., for 4 hours, as may be accomplished by increasing the sampling flow rate) may similarly approximate the interaction and is suitable to demonstrate qualification. Additionally, if the reference and challenge sample cannot be collected together, the reference sample can be collected as a grab sample into a canister. Of primary importance is that the canisters used for the zero and challenge samples are properly qualified to ensure that observed analyte enhancement or suppression is properly attributed to the sampling unit and not confounded by interactions within the canister(s) chosen for the sampling unit challenge.

To conduct sampling simultaneously, the humidified HCF zero air flow is provided to a challenge manifold constructed of chromatographic stainless steel comprising four ports (refer to Figure 4.2-4). Of these four ports, one is dedicated to the supply of the source gas and the other three provide connections to the sampling unit inlet, reference sample, and a vent that is configured with a rotameter to ensure the manifold has a constant supply of fresh challenge gas. The reference port can be configured to permit time integrated sampling with a flow controller (which may itself introduce bias if its quality is not known) or consist of a single port for collecting a grab reference sample. If the reference sample is to be time-integrated, it is attached to a flow controller to meter the gas into the reference sample canister and the flow rate is set to fill the canister to the desired pressure (recommend just under ambient pressure) over the 24-hour sampling duration. Humidified HCF zero air is to be supplied to the manifold such that there is excess flow to the manifold as indicated by the rotameter on the vent port. The VOC sampling unit then ingests gas from the manifold to collect the challenge sample. Following collection of the reference and challenge samples, they are analyzed. Technicians should follow the conventional VOC sample collection procedures, e.g., performing canister pressure measurements, performing leak checks, etc.
Analysis by GC/MS for target compounds should ideally show the concentrations of target VOCs do not exceed their concentration in the reference sample by more than 0.02 ppbv; however, some analytes may not meet this threshold. Therefore, formal qualification must show the concentrations of all Tier I core analytes in the zero challenge canister do not exceed those in the reference by > 0.03 ppbv or 3x MDL, whichever is lower. The remaining Tier II compounds should also meet these criteria. Where exceedances are noted for Tier I core compounds, corrective action must be taken to remove the contamination attributable to the sampling unit and the sampling unit zero challenge repeated to ensure criteria are met before the sampling unit is deployed for sampling. If the sampler must be deployed with failing Tier I and/or non-Tier I analytes, subsequent collected field sample results are to be qualified (QA Qualifier SB indicating sampler bias checks do not meet criteria and LK indicating value is estimated with a high bias) when data are input to AQS. Tier I and/or non-Tier I analytes that exceed 5-fold MDL for the sampling unit zero challenge bias check indicates an unacceptably high background attributable to the sampler and the associated routine sample data for affected compounds are to be invalidated (Null data qualifier EC indicating exceeds a critical criterion) when reported to AQS.

**4.2.3.3.2 Sampler Known Standard Challenge.** The known standard challenge is performed by providing a humidified (~40 to 70% RH – it is critical the gas not be dry) known concentration standard of target VOCs (at approximately 0.1 to 0.5 ppbv each, or other suitable concentration representative of those in measured at the site in ambient air) in HCF zero air to the sampling unit for collection into a canister as is done for a typical ambient sample. The diluted humidified standard in HCF zero air is also collected into a canister upstream of the sampling unit and this reference sample serves as a basis for comparison to evaluate sampling unit negative or positive bias. Compounds which show enhanced or suppressed concentrations (i.e., recovery) in the
challenge sample compared to the reference sample indicate contamination or suppression attributable to the sampling unit.

As mentioned above for the zero challenge, it is best practice to collect the reference and challenge sample simultaneously and for 24 hours. The configuration and procedures followed in Section 4.2.3.5.1 above apply to the known standard challenge except that a humidified known standard diluted in humidified HCF zero air is substituted for the humidified HCF zero air.

It is strongly recommended that the known standard challenge gas include all target VOCs; however, a smaller subset of compounds is sufficient provided all Tier I target compounds are included and that each target compound type is represented in the gas mixture (e.g., low molecular weight, fluorinated, chlorinated, brominated, high molecular weight, etc.).

The standard challenge gas is supplied to the challenge manifold by dilution of a gas mixture of VOCs via dynamic dilution with humidified HCF zero air. In general, the gas dilution system should be powered on and flowing diluent and standard gases through the challenge manifold for minimally one hour prior to commencing reference or challenge sample collections.

Analysis by GC/MS for target compounds must demonstrate that each Tier I VOC in the challenge sample is < ±15.1% of the concentration measured in the reference sample. Tier II compounds should meet this criterion as well; however, exceedances of non-Tier I compounds will not disqualify the sampling unit from deployment. For Tier I core compounds exceeding these criteria, corrective action must be taken to address the bias in recovery attributable to the sampling unit. If the sampler must be deployed with failing Tier I and/or non-Tier I analytes, subsequent collected field sample results are to be qualified (QA Qualifier SB indicating sampler bias checks do not meet criteria) and indicating the direction of the bias (QA qualifier LL indicating an estimate with low bias and QA Qualifier LK indicating the an estimate with high bias) when data are input to AQS.

Following completion of the known standard challenge, the sampling unit should be flushed with humidified HCF zero air or humidified UHP nitrogen for a minimum of 24 hours and longer (e.g., over a weekend) is preferred.

Once sampling units are demonstrated to be acceptably non-biasing, a best practice to assess ongoing bias is to compare fingerprint plots (discussed in Section 3.3.1.3.14.2) of each sample from the site to evaluate relative compound concentration changes for compounds known to be reactive (e.g., ethylene oxide) or labile (e.g., 1,3-butadiene).

4.2.3.4 Sampler Setup, Sample Collection, and Sample Retrieval

4.2.3.4.1 Sampling Schedule and Duration. VOC sample collection must be performed according to the national sampling schedule (https://www.epa.gov/amtic/sampling-schedule-calendar) at one-in-six days for 24 ± 1 hours (1380 to 1500 minutes) beginning at midnight and concluding at midnight of the following day, standard local time, unadjusted for daylight savings time. Data for samples collected for less than 23 hours or more than 25 hours are to be invalidated (Null Qualifier AG indicating sample time out of limits) when reported to AQS. For
missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that computers and digital timers are within ±5 minutes of the reference time (cellular phone, global positioning system [GPS], or similar accurate clock) and mechanical timers are within ±15 minutes and this check and any adjustment documented in the sampling unit maintenance log.

Regardless of the inlet configuration (dedicated or manifold) described in Section 4.2.3.2, the inlet line to the VOC sampling unit should be purged with ambient air such that the equivalent of a minimum of 10 air changes is completed just prior to commencing sample collection. This purge eliminates stagnant air and flushes the inlet line for collection of fresh ambient air.

If utilizing a standalone combination timer and solenoid valve unit for VOC sampling (note: these are not commonly employed for routine monitoring; however, they may be employed for special studies where installation of a shelter is not practical. These combination units have exhibited problems with leaks in the seals within the solenoid valve that permit air ingress into the canister that contaminates the sample. When employing such standalone combination timers/solenoid valves, it is strongly recommended that monitoring agencies be aware of limitations with this equipment and follow guidance described in EPA’s Use of Stand-Alone Timers for Volatile Organic Compound (VOC) Sample Collection in Canisters. 13

4.2.3.4.2 Sample Setup. Sample setup involves ensuring the sampling canister has sufficient vacuum, that the connection of the canister to the sampling unit is leak-free, and that the sampling unit program (sample start date and time, sample stop date and time, and sampling flow rate) is correct. A COC form accompanies the canister from the ASL and through all field activities until received at the ASL after sample collection.

Presampling Canister Pressure Check: Canisters for sampling should be cleaned per Section 4.2.4.2 and evacuated to high vacuum prior to field deployment. Vacuum should be ≤ 0.0067 kPa absolute or ≤ 50 mTorr and should not permit more than an overall 5% dilution of the sample collected into the canister and must not permit more than an overall 10% dilution of the collected sample. Refer to Table 4.2-2 for equivalent 5% and 10% thresholds in psia and inHg vacuum (these are commonly used units on pressure gauges and pressure transducers). Note that for subambient pressure sampling, the monitoring agency will determine the acceptable ending canister pressure for each employed flow controller.

Such a 5% dilution is equivalent to a starting canister pressure of approximately 4 kPa absolute (0.6 psia) for samples collected to a subatmospheric pressure of 81 kPa absolute (11.7 psia) or approximately 7 kPa absolute (1 psia) for samples collected to positive pressure of 122 kPa absolute (17.7 psia). Starting canister pressure should not exceed 7 kPa absolute, which is equivalent to ~28 inHg vacuum at standard barometric pressure. The starting canister pressure measurement is a critical criterion and the initial canister pressure at sample setup must be measured in the field with a calibrated pressure gauge or pressure transducer and the pressure documented in the sample collection records. If a built-in gauge on the sampling unit cannot be appropriately calibrated, an accurate standalone gauge should be employed for this measurement.
<table>
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<th>ending canister pressure</th>
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<td></td>
<td></td>
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<td>0.93</td>
<td>28.0</td>
<td>1.85</td>
<td>26.2</td>
</tr>
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</table>

Values shown exhibit a range of ending canister pressures expected for subambient and pressurized sampling and not an acceptable range of ending canister pressures. Monitoring agencies conducting subambient sampling will determine the ending canister pressure for each flow controller based on the instructions in Section 4.2.3.1.2.1.

Assumes ambient pressure is at standard atmospheric pressure of 14.7 psia or 0 inHg vacuum. Site operators are encouraged to use absolute pressure measurements to avoid confusion with pressure measurements relative to atmospheric pressure (e.g., psig, inHg vacuum, etc.).

Samples for which the starting canister pressure was not measured or for which the starting pressure exceeds 10% of the target final ending collection canister pressure are to be invalidated (Null Qualifier AA indicating sample pressure out of limits) when input to AQS.
**Leak Check:** Once sufficient vacuum of the sampling canister is verified, the canister is connected to the sampling unit (if not already connected) and a leak check is performed to ensure the connection to the canister is acceptably leak-tight. Sampling unit manufacturers may recommend a leak check procedure for their sampling unit, which should adequately verify the canister connection exhibits a leak rate of less than 0.2 psi over 5 minutes. Note that in general a leaking connection will typically be immediately evident; acceptably leak-free connections typically indicate no perceptible pressure change over five or more minutes.

A leak check may be performed by quickly opening and closing the valve of the canister to generate a vacuum in the connection to the sampling unit or, if the sampling unit is so configured, the sampling unit pump may be powered on to evacuate the connection line to the canister. The vacuum/pressure gauge in the sampling unit should indicate that vacuum has been applied and should be observed for a minimum of 5 minutes to ensure that the vacuum/pressure does not change by more than 0.2 psi. If this criterion is exceeded and a leak is suspected/detected, connection fittings should be gently snugged to eliminate the source of the leak. Sample collection must not commence until a successful leak check is attained. Once the connection is shown to be acceptably leak-free, open the canister valve. The result of the leak check and sample setup date and time are documented in the sample collection records. When canister connections are not leak checked and a leak is present, the canister will typically be at ambient pressure when the pressure is measured at sample retrieval.

**Program Verification:** Following successful leak check, verify the sampling unit sample collection program is correct and is activated/enabled and that the canister valve is opened (best practice is to document these verifications in the sample collection records).

4.2.3.4.3 Sample Retrieval. Following completion of sample collection, the best practice is to retrieve the canister sample as soon as possible to maximize the holding time for analysis, to minimize the opportunity for leaks into the canister, and to minimize changes in the sample contents that may occur as the sample ages. Measuring the canister pressure upon retrieval with a calibrated gauge and recording the measurement in the sample collection records is:

- **Required** for subambient pressure sampling
- **Strongly recommended** for pressurized sampling

For subambient samples, the final canister pressure must be ≤ the final desired canister pressure where the flow rate is no longer constant (refer to Section 4.2.3.1.2.1). If this pressure is exceeded, invalidate the sample data (Null Qualifier AA indicating sample pressure is out of limits) when reporting data to AQS. Pressurized samples should be > ambient barometric pressure.

For example, a sampling unit flow rate linearity check demonstrated that the flow rate ceased to be constant at a canister pressure of 10.7 psia. The ending canister pressure was then assigned as 90% of this value (refer to Section 4.2.3.1.2.1), 9.6 psia. When measuring the final pressure of a collected canister sample at retrieval, the canister pressure measurement must be ≤ 9.6 psia or the sample must be invalidated.
Sample canisters with final pressures ≥ 10% different than the intended pressure should prompt the technician to investigate whether the difference is due to a leak(s) or if the flow controller setting has drifted and requires adjustment.

If an on-board gauge on the sampling unit cannot be calibrated for this purpose, a standalone calibrated gauge is to be used. The sample start and stop times and the elapsed collection time are to be recorded in the sample collection records. The sample COC form (that complies with Section 3.3.1.3.7) is also to be completed and must accompany the collected sample at all times until relinquished to the laboratory.

Sampling units which incorporate computer control of the sampling events with associated data logging may provide the above information (e.g., sample start and stop date and times, beginning and ending pressures, and flow rate) which should be printed and accompany the sample collection records or which can be transcribed into the sample collection record and the transcription verified by another individual. For such sampling units, the data logged by the sampler computer should be downloaded, transferred to the ASL, and reviewed to ensure the sample collected appropriately and that there are no qualifiers (flags) or other collection problems that may compromise or invalidate the collected sample.

4.2.4 Canister Media. At the time of this TAD revision, measuring VOCs in ambient air using passivated stainless steel canisters is approximately a 40-year old technology. While measurement systems have become more sensitive with the advent of SIM and TOF detection, laboratories may be unable to realize the instrument sensitivity gains due to bias effects of their fleet’s canisters. The following sections present requirements and best practices for qualifying canisters as acceptably non-biasing and maintaining sufficiently low background levels of target VOCs to ensure that VOC concentrations measured in samples are attributable to the ambient air and not to the bias of the canisters in which they were collected.

Canisters employed for ambient air sampling should be dedicated to such use and not employed for conducting sampling of source level (e.g., stack testing), vapor intrusion, or soil gas types of sampling where VOC concentrations are expected to be many-fold higher than in ambient air. Once exposed to high concentration atmospheres, canisters are difficult to sufficiently clean, which will typically result in a high bias for ambient concentration measurements. It is strongly recommended that canisters be labeled for their intended use if the monitoring organization or ASL supports programs where high concentration samples are to be collected.

4.2.4.1 Canister Qualification. Canisters must be qualified before placed into service and minimally every three years thereafter. This applies to canisters employed for ambient air sample collection and for QC purposes (preparing standards, blanks, etc.). The previous version of this TAD strongly recommended, but did not require, canister qualification; however, significant canister effects on EtO measurement (among other VOCs) have highlighted the importance of this procedure, which was evident for acrolein measurements since the inception of the NATTS Program.

New canisters may contain residues such as lubricants for milling or cutting metal valve components or for pumps, coating byproducts from the manufacturing process, and/or residual
VOCs or carbon compound contamination from compounds added by manufacturers to perform QC checks on the canisters prior to release to customers. Additionally, new canisters may have defects making them unsuitable for use even after the canisters have been cleaned and treated for the residual contaminants. Such defects may relate to poor valve sealing, active sites from incomplete coating or surface deactivation, or poor canister integrity due to inadequate welds.

Monitoring agencies have requested EPA perform studies on whether certain canister types (e.g., silicon-ceramic lined or electropolished) perform better for certain analytes, e.g., EtO; however, definitive studies have not been undertaken. While there may be performance differences between canister types for specific analytes, generally canisters perform uniquely regardless of canister type and each must be qualified for use with the target analytes to demonstrate suitability for use.

To qualify canisters, they are to be properly cleaned, tested for leaks, and evaluated for bias such that the requisite canister performance specifications are met. All canisters in a given fleet need not be qualified at the same time but rather a subset of the canister inventory can be qualified on a rolling basis such that all canisters employed for ambient air sampling and analysis are qualified within a 3-year period. Canisters in an existing inventory that have not been qualified in the past 3 years should be qualified as soon as possible to verify they are non-biasing and canisters that are suspect of poor performance should be removed from active use until qualification or remediation can be completed. For monitoring agencies or ASLs with large canister fleets, the organization should prepare a schedule to assess canisters in a reasonable timeframe (e.g., to complete canister qualifications within 18 months).

Suitable procedures for performing canister qualification are described in the following sections. Canisters which exhibit a positive or negative bias exceeding the criteria below should be segregated and reconditioned before reuse or discarded. Some commercial canister manufacturers offer reconditioning services for their canisters. Consult the manufacturer for methods to clean or recondition cans which fail these bias criteria. Measurement data for canisters which have not undergone qualification or have failed bias qualification will be qualified (QA Qualifier CF indicating canister bias) when reported to AQS.

**4.2.4.1.1 Canister Leak Tightness Check.** Prior to initial use, new canisters should be verified to be leak-free by performing a pressure decay test as prescribed in TO-15A. This check should be performed prior to canister qualification zero check or known standard check (Sections 4.2.4.1.2 and 4.2.4.1.3, respectively). Vacuum/pressure should be measured with a high-quality, calibrated vacuum/pressure gauge or transducer. Vacuum/pressure should not change by more than 0.69 kPa/day (0.1 psi/day), otherwise the canister leak rate is excessive, and the canister should be removed from service and repaired. This leak rate permits ~5% of the sample volume to leak over 7 days and a ~20% sample volume leak over 30 days. As an aid in identifying the location of leaks for possible repair, the canister can be pressurized with helium, which permits quick pinpointing of any leaks with a helium leak detector.

The canister leak check is accomplished by either evacuating or pressurizing the canister. If the evacuation method is used, the canister is evacuated, preferably to high vacuum ≤ 0.0067 kPa absolute (0.05 mm Hg or 50 mTorr), the valve is closed, the vacuum/pressure gauge is attached,
the valve is opened, and the initial vacuum is measured and recorded. The valve is then closed, the vacuum/pressure gauge is removed, and the canister valve is left loosely capped until the next pressure reading several days later. In the pressurization method, the procedure is identical except that instead of evacuated, the canister is pressurized to approximately 203 kPa absolute (29.4 psia) with clean fill gas. The evacuation method is the preferred method for assessing leak tightness of canisters as it best represents the contamination potential from collected field samples (also reduces the potential for contaminating the canister) and should be performed so that the final canister pressure closely matches that of the typical pressure of field sample canisters. In either case, canisters should be minimally 10 psi above or below ambient pressure to provide a sufficient gradient with which to permit assessment of canister leaks. It is critical that canister valves are loosely capped with a brass cap to ensure that leakage through the valve is accurately assessed while avoiding potential entry of debris into the valve.

4.2.4.1.2 Zero Check. Preferably the same day of, and not more than two days following, cleaning completion (i.e., final evacuation), canisters should be pressurized with humidified (approximately 40 to 60% RH) HCF zero grade air to begin the zero check.

Note: Performing this qualification with UHP nitrogen does not adequately test the canister bias as the inert nitrogen atmosphere does not permit reactions within the canister that may occur when ambient air is sampled.

This short duration following cleaning is intended to characterize the canister condition and minimize the chance for analytes to grow in the canister. Measure and record the canister pressure upon completion of filling. The measured VOCs concentrations will be corrected to 101.3 kPa (760 mmHg).

The canister should be analyzed within two days of initial pressurization and all Tier I core analytes must be < 3x MDL or < 0.03 ppbv whichever is lower, when corrected to 101.3 kPa. Non-Tier I compounds should also meet this criterion. Ideally, all target compounds will be less than 0.02 ppbv when corrected to 101.3 kPa. This correction to barometric pressure is needed to normalize the amount of background in the canister, as the concentration measured in the canister is directly affected by the volume of zero air in the canister.

For example, a canister is filled to approximately 1.7 atmospheres absolute (170 kPa or 24.7 psia) for the zero qualification check. The canister is analyzed the next day and shows non-detect for most analytes except for benzene (0.012 ppbv), acrolein (0.021 ppbv) and vinyl chloride (0.032 ppbv). To determine whether these concentrations meet the threshold criteria, they need to be corrected to standard atmospheric pressure of 101.3 kPa (14.7 psia).

\[
C_{zcorr} = \frac{C_{zmeas} \cdot P_{can}}{P_{stp}}
\]

where:
- \(C_{zcorr}\) = concentration corrected to standard atmospheric pressure (ppbv)
- \(C_{zmeas}\) = concentration measured in the canisters (ppbv)
- \(P_{can}\) = canister absolute pressure measured at canister fill (kPa)
- \(P_{stp}\) = absolute standard atmospheric pressure (kPa)
For the example above, the measured concentrations are multiplied by the ratio of canister pressure to standard atmospheric pressure (170 kPa/101.3 kPa), 1.68, resulting in corrected concentrations of 0.020, 0.035, and 0.054 ppbv, respectively, for benzene, acrolein, and vinyl chloride.

Subsequent analysis will be performed at minimally one later timepoint, recommended to be 30 days, or the longest expected duration an ambient sample, standard, or blank will be held prior to analysis (e.g., 21 days if all samples are analyzed within this time frame). Additional (i.e., earlier) timepoints may be added, and may reveal canisters that show unacceptable performance before the later timepoint(s). Analyses at later timepoints must show all Tier I core analytes remain < 3x MDL or < 0.03 ppbv, whichever is lower, and non-Tier I compounds should meet this criterion. Canisters can be measured at intermediate timepoints; however, this intermediate analysis is only advantageous to identify canisters which exceed criteria and should be remediated, as canisters will need to meet the criteria at the ending timepoint to verify they are acceptably free from bias and suitable for use. If analysis can be performed at only one later timepoint after initial pressurization, it is recommended to be at ~30 days.

Note: Substituting a MB for a canister zero check is not appropriate due to the continual removal of aliquots of gas from the canister during routine analyses. These routine aliquot removals will remove contaminants from the canister and will underestimate the potential contaminant buildup that would occur in the canister for analysis at the last timepoint (e.g., at 30 days).

Laboratories have reported growth of oxygenated compounds (e.g., ketones, alcohols, aldehydes) in canisters. Of particular concern in the canister humidified HCF zero air checks are Tier I VOCs acrolein and EtO, which evidence suggests may grow or accumulate in canisters that are stored for extended periods. The mechanism for such concentration increases is not well understood; however, such is widely regarded as problematic in performing analysis at concentrations typical in ambient air. Suspected underlying causes of concentration increases for these oxygenated VOCs are decomposition of particulate (soot containing semi-volatile organic compounds [SVOC]) residue, slow time-release from interstitial spaces or PM within the canister, breakdown of cutting oil residues in valves, ingress of carbon from Vespel® ferrules employed in canister valve installation, or decomposition of other volatile/SVOC/organic constituents within the canister (typically in the presence of oxygen and water). Concentrations of target compounds measured above two-fold the laboratory MDL in the zero qualification should be closely scrutinized as they indicate the presence of canister background concentrations which may cause complications with future sample collection measurements. Canisters failing the zero challenge for Tier I compounds will preferably not be placed into service; however, if placed into service, measurement data will be qualified (QA Qualifier LK indicating an estimated value with a high bias and QA qualifier CF indicating canister bias certification failure) when reported to AQS. Routine sample measurement data for Tier I compounds from canisters which exceed 5-fold the MDL for zero qualification for are to be invalidated (Null Qualifier EC indicating an exceedance of critical criteria). As practical, more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers may be attempted before recleaning with traditional methods and retesting. Concentration measurement data for Tier II analytes failing the zero challenge criteria are (in specific canisters) to be likewise qualified (QA Qualifier LK indicating an estimated value with a high bias and QA qualifier CF indicating canister bias certification failure) when reported to AQS.
4.2.4.1.3 Known Standard Gas Check. Following successful completion of the canister qualification zero check in Section 4.2.4.1.2, the canister must undergo known standard qualification to assess overall bias of the canister on target VOC concentrations over the typical canister holding time period. The clean canister is filled with a known standard gas containing minimally the Tier I analytes and representative Tier II analytes diluted with humidified (approximately 40 to 60% RH) HCF zero air to known concentrations of approximately 0.1 to 0.5 ppbv each (or other suitable concentration representative of those measured at the site in ambient air). As with the zero check, it is critical that the standard gas matrix (diluent gas) be humidified HCF zero air and not an inert matrix such as UHP nitrogen.

Note: Performing this qualification with UHP nitrogen does not adequately test the canister bias as the inert nitrogen atmosphere does not permit reactions within the canister that may occur when ambient air is sampled.

The procedure is essentially equivalent to the zero qualification challenge described above in Section 4.2.4.1.2 except that a diluted standard gas replaces the clean HCF zero air.

The canister should be analyzed within two days of initial pressurization for the first timepoint and all Tier I core analytes must be within ±30.1% of the theoretical nominal concentration. Non-Tier I compounds should also meet this criterion. There is no correction for the canister pressure as is required for the zero challenge.

Subsequent analysis will be performed at minimally one later timepoint, recommended to be 30 days, or the longest expected duration an ambient sample, standard, or blank will be held prior to analysis (e.g., 21 days if all samples are analyzed within this time frame). Additional (i.e., earlier) timepoints may be added, and may reveal canisters that show unacceptable performance before the later timepoint(s). Analyses at later timepoints must show all Tier I core analytes remain within ±30.1% of the theoretical nominal concentration, and non-Tier I compounds should meet this criterion. Measurement data for target compounds failing this criterion in specific canisters will be qualified (QA Qualifier CF indicating canister certification checks do not meet criteria) and indicating the direction of the bias (QA qualifier LL indicating an estimate with low bias and QA Qualifier LK indicating the value is estimated with high bias) when data are input to AQS.

4.2.4.2 Canister Cleaning. Cleaning of canisters for ambient sample collection may be performed in a variety of ways which may reliably result in acceptably low background levels of target VOCs and interferences in the canister. Cleaning systems are commercially available from a variety of manufacturers or may be custom-built. Many incorporate the following elements:

1. Manifold constructed of chromatographic grade stainless steel for connection of several canisters (typically 4 to 8)
2. Rough vacuum pump to achieve vacuum of approximately 1 inch Hg
3. High vacuum pump (such as a molecular drag pump) to achieve a final canister pressure of approximately 50 mTorr or less
4. Heating oven or heating jackets that completely encompass the canister and valve (Note that heating bands do not uniformly heat the canister, do not heat the valve, and
may result in applying unacceptably high temperatures to the surfaces of the canister to which the heating band contacts – heating bands are not recommended)

5. Humidification system for the purge gas

6. Automated switching between evacuation and pressurization stages

7. A pressure release valve to reduce the likelihood of system overpressurization

8. Trap (cryogenic or molecular sieve) to eliminate backstreaming of contaminants into canisters (only necessary for systems with a non-oil free vacuum pump – note use of such pumps is strongly recommended against)

9. Chromatographic grade stainless steel tubing and connections – recommend utilizing tubing and fittings with smaller inside diameter and limiting tubing length to minimize system dead volume to minimize pressurization/evacuation time and to provide less surface area for contaminants

10. Source of clean purge gas such as HCF zero air or UHP nitrogen

11. Absence of butyl rubber, polymers, and fluoropolymer materials, or other materials that may adsorb and/or offgas compounds of interest or other potential interferences

Canister cleaning procedures are described below, and more detail can be found in EPA Method TO-15A. Regardless of how canisters are cleaned (i.e., equipment employed, temperature, number of evacuation cycles, use of hydrocarbon traps, composition of purge gas, humidification system, etc.), canister cleanliness criteria must be met. Monitoring agencies should prescribe a policy establishing holding time for cleaned canisters, which may not exceed 30 days unless objective evidence indicates that the additional time does not negatively impact measured sample concentrations. Such may be the case when cleaned canisters are stored containing clean purge gas and evacuated to high vacuum just prior to field deployment.

Prior to connecting canisters to the cleaning system, it is strongly recommended that they undergo venting (into a fume hood or other exhaust port) and evacuation with a rough pump. This reduces the amount of overall contaminants introduced to the cleaning system that are available for reintroduction to the canisters during pressurization cycles or diffusion into canisters during high vacuum evacuation cycles.

Additionally, the source of clean purge gas employed should be as free of target VOCs and interferences as possible such as the diluent gas described in Section 4.2.7.2. Such ensures that cleaning steps do not introduce contaminants that the process is intended to remove.

4.2.4.2.1 Canister Cleaning Heating. Heating of canisters during cleaning is strongly recommended. Various methods of heating canisters during cleaning may be employed; however, only those that heat the entire canister and valve evenly are recommended (e.g., heating oven or heating jacket). Heating bands do not evenly heat canister surfaces and may not provide adequate heating further from the bands (e.g., may leave the valve insufficiently heated). The canister type, silica-lined or electropolished, and temperature rating of the valve and vacuum/pressure gauge (if so equipped) should dictate the temperature at which canisters are cleaned. Heating jackets and ovens heat the canister evenly; however, they may not permit
isolating the valve from the heat source, which may cause damage to the valve if cleaning is performed at high temperatures (> 80°C). Some heating jackets or ovens allow the valve to protrude from the jacket or oven and allow the valve to only be exposed to radiant heat.

If employing humidified HCF zero grade air during canister cleaning (specifically the canister pressurization steps), silica-lined canisters should not be heated above 80°C as oxidation of the surface may occur which leads to active sites within the canister.¹⁴ One canister manufacturer recommends against the use of zero air for cleaning due to concerns with damaging the interior lining of the canisters. Manufacturers may have more stringent recommendations than those listed here, which should be followed to avoid damaging canisters and/or voiding warranties.

Heating is recommended for cleaning of ambient concentration canisters; however, heating to temperatures above 80°C has not been shown to provide additional benefit (and as mentioned above may damage canisters). For canisters of known history employed for ambient sample collection (and for which particulate filters are routinely employed), heating to approximately 75°C during cleaning is generally sufficient.

Canisters employed for collection of VOCs at source level (part per million) or atmospheres with matrices including organic compounds with high boiling points (e.g., SVOCs) are not recommended for ambient air measurement use. If used, such canisters should be cleaned in separate batches (to prevent contaminating ambient sampling canisters) and heated to a higher temperature (100°C or higher), if permitted by the canister and valve. Note, however, that removal of such organic material and/or high concentrations is difficult to perform effectively with pressurization and evacuation methods. Following cleaning, such canisters should be analyzed to demonstrate sufficient cleaning and sequestered from use for collecting ambient samples if analysis shows insufficient cleaning.

4.2.4.2.2 Cycles of Evacuation and Pressurization. Pressurization and evacuation canister cleaning methods involves several variables:

- number of cycles of pressurization and evacuation
- level of vacuum
- duration at vacuum
- level of pressurization
- duration at pressure
- temperature (covered above in Section 4.2.4.2.1)

The following are recommendations; however, modifications that demonstrate adequate performance are acceptable. In general, automated canister cleaning systems permit unattended operation and simplify the inclusion of additional cleaning cycles and controlling pressurization and evacuation pressures and durations.

**Number of Cycles:** In general, the greater the number of evacuation and pressurization cycles, the more effective the cleaning will be. Minimally five cycles of evacuation and pressurization are recommended and ten or more have been shown to be effective in removing stubborn oxygenated compounds (e.g. acetone, methyl ethyl ketone, and isopropanol).¹⁵ Following the
principle of extraction efficiency where each cycle recovers a specific percentage of each compound (i.e., 85%), additional (i.e., more than 5) evacuation and pressurization cycles are highly recommended to achieve sufficiently clean canisters.

**Canister Evacuation:** Longer durations of vacuum generally result in more effective cleaning, provided contaminants are not permitted to back-diffuse into the canisters. Canisters should be evacuated to minimally 7 kPa absolute (28 inch Hg vacuum) during each evacuation cycle, and higher vacuum is recommended if time permits (note that high vacuum levels may lengthen cycle time significantly). This vacuum should be maintained for a minimum of 1 minute before the pressurization step, and longer durations may be advantageous.

**Canister Pressurization:** If canisters are heated during cleaning, pressurization of canisters to approximately not more than 5 psig for each pressurization cycle is recommended to avoid rupture of the canister when heat is applied. For canisters which are not heated during cleaning, pressurization to approximately ≤ 30 psia is recommended. The pressure should be maintained for a minimum of 1 minute before the next evacuation step. Higher pressures (do not exceed 40 psig, particularly with heat) have not been demonstrated to be advantageous and will require additional time and increase purge gas consumption.

**Final Evacuation:** Final evacuation should be to ≤ 50 mTorr and maintaining this vacuum for minimally 5 minutes is recommended. Canisters may be held at this high vacuum for a short period prior to closing the canister valves; however, extended periods (> approximately 5 min) at high vacuum with canisters openly connected to the cleaning manifold may result in diffusion of contaminants into the canisters from elsewhere in the manifold or cleaning system. Canisters maintained on the cleaning system at high vacuum for extended periods should be subjected to a subsequent cycle of pressurization prior to final evacuation. An alternative to performing the final evacuation at the end of the cleaning cycles is to store canisters pressurized with clean purge gas and evacuated to high vacuum (≤ 50 mTorr) at a later date (e.g., just prior to deployment).

4.2.4.2.3 **Pressurization Purge Gas Source.** Purge gas for canister cleaning should be as free of VOCs and organic contaminants as possible, and is recommended to be HCF zero air or UHP nitrogen. While not strictly required, it is recommended to analyze purge gas to ensure target analyte contaminants are as low as possible, preferably < 0.02 ppbv. To achieve sufficiently clean purge gas, additional treatment such as scrubbing with hydrocarbon traps and/or catalytic oxidation may be necessary. HCF zero air purchased from commercial vendors in pressurized cylinders typically contains measurable hydrocarbons and may necessitate additional treatment to be suitable for use. Zero air generators (ZAG) typically provide cleaner zero air than gas available in pressurized cylinders; however, users of this document should be aware that poorly maintained or functioning ZAG systems may permit elevated levels of contaminants. ZAG systems may not sufficiently remove VOCs for purge gas use, as oxidation of VOCs may be incomplete, forming low molecular weight (one to three carbon molecules) oxygenated VOCs (formaldehyde, methanol, ethanol, acetone, etc.) as byproducts. UHP nitrogen may be sourced from cylinders or may be the headspace gas from a liquid nitrogen dewar.

The purge gas is to be humidified to approximately 30 to 70% RH as practical; higher humidity levels are generally considered more effective. The water assists in removal of polar compounds and lower volatility organic compounds which may otherwise remain adsorbed to interior
canister surfaces. Most commercial canister cleaning systems incorporate a type of humidifier; however, the level of humidity may not be sufficient depending on the type of humidification system. Humidification systems may be constructed which incorporate a diptube in water which humidifies by bubbling the purge gas through the water or via an impinger placed above the surface of the water in the humidifying chamber. Humidification systems should be constructed of glass, stainless steel, or fluoropolymer. Plastics (polyethylene, polypropylene, polycarbonates, etc.) degrade over time and impart hydrocarbons to the humidified gas. If a bubbler type humidifier is employed, care should be taken to ensure the downstream pressure is lower than the humidifier upstream pressure to avoid backflow of the water into the purge gas source. It is recommended that the RH of the purge gas be measured with a hygrometer to ensure the desired RH is attained. Water for the humidification device should be deionized, distilled, or HPLC-grade as specified by the cleaning system manufacturer. Additional treatment of humidification water by boiling and/or sparging with nitrogen or helium will eliminate dissolved VOCs.

4.2.4.2.4 Verifying Canister Cleanliness. Following completion of canister cleaning activities, the effectiveness of the cleaning will be demonstrated. A best practice is to assess each cleaned canister; however, minimally one canister, a batch blank, per cleaned batch of 8 samples will be pressurized with humidified HCF zero air (preference) or UHP nitrogen for cleanliness verification. A batch is defined as the number of canisters attached to the same cleaning manifold and vacuum source and cleaned simultaneously. For batch sizes with 9 to 16 canisters, minimally 2 batch blanks are needed; for batches with 17 to 24 canisters, minimally 3 batch blanks are required, and so on. Increasing this frequency is strongly recommended. Canisters for cleanliness assessment are pressurized (typically to approximately the pressure of field collected samples) with humidified purge gas, held minimally overnight, and analyzed for target analyte concentrations.

Selection of the canister(s) for batch blanks may be targeted or random. For targeted selection of a cleaning batch blank canister the selected canister(s) should be from those which indicated the highest total VOC concentration or the highest single target compound concentration in the most recent collected sample. Other targeted selection conventions for the batch blank canister include evaluating concentrations of low volatility organic compounds or oxygenated target compounds which are typically more difficult to effectively remove from canisters.

To better characterize the effectiveness of the cleaning process on the batch of cleaned canisters, a composite batch blank sample may be prepared at the conclusion of a canister cleaning session. Prepare such a composite just prior to the last pressurization step by closing the valve of a chosen canister (which is still under vacuum) and pressurizing the manifold with clean purge gas such that the other connected canisters are pressurized. The chosen (still evacuated) batch blank canister is then opened to fill the canister with the composite gas from all of the canisters connected to the manifold. Close the canister valve and reserve the filled batch blank canister composite for analysis.

Following analysis, canisters employed for batch blank analysis and that meet cleanliness criteria are re-evacuated to ≤ 50 mTorr. Analysts will further investigate failure of batch blanks to meet the cleanliness criteria and will not release canisters for use if the associated canister cleaning batch blank does not meet the acceptance criteria. If each cleaned canister from the batch is
surveyed, only those canisters which fail the criteria must be recleaned. If one canister
representing the batch fails, either the entire batch can be recleaned (recommended) or two
canisters from the batch can be selected and analyzed to confirm the batch does not pass criteria.
If both of these canisters meet the acceptance criteria, only the failing canister must be recleaned,
otherwise, the batch of canisters must be recleaned. Continued failure of batch blanks may
indicate that the purge gas, cleaning manifold, and/or other parts of the system has become
contaminated. If failure to meet criteria is isolated to specific canisters, those canisters should be
removed from circulation until their contamination can be acceptably remediated. For canisters
which cannot be remediated successfully, the canister may require retirement. Alternatively,
canister manufacturers offer canister reconditioning services which can restore canisters to brand
new condition for less than the cost of a new canister.

**Cleanliness criteria:** Canister cleanliness criteria are established and related to ambient
pressure, normalizing measured concentrations of target analytes in the cleaned canisters to EPA
standard barometric pressure conditions of 101.3 kPa (14.7 psia or 760 mm Hg). Additional
acceptance criteria corrections are employed for laboratories or programs that dilute ambient
samples as a routine practice. Target analytes will preferably be not detected at concentrations >
0.020 ppbv and may not exceed the MDL MQO for Tier I target VOCs and either 0.030 ppbv or
3-fold the MDL, whichever is lower, after correction to standard barometric pressure. Results for
samples collected in canisters in the cleaning batch (per the guidance in the fourth paragraph in
Section 4.2.4.2.4) for target analytes failing the acceptance criteria will be qualified (QA
Qualifier CC indicating clean canister residue and QA Qualifier LK indicating the value is
estimated with high bias) when reported to AQS.

The rationale for this correction to ambient pressure, calculations for correction, and an example
calculation are included with canister qualification in Section 4.2.4.1. These aspects are briefly
summarized:

When preparing a canister cleaning batch blank, the final pressure of the batch blank canister
is measured with a calibrated gauge/pressure transducer. The amount of clean gas in the
canister is critical, as the higher the pressure, the more dilute any contaminants in the canister
will be. Therefore, the cleanliness acceptance criteria are corrected based on the ratio of the
batch blank canister pressure to EPA standard conditions barometric pressure. Further, if the
laboratory routinely dilutes ambient sample canisters for analysis, this dilution factor is also
taken into account. To correct the acceptance criteria for the batch blank dilution pressure,
the criterion is multiplied by the ratio of the standard conditions absolute pressure to the
measured absolute pressure of the batch blank canister (both absolute pressure values must
be in the same units):

\[
C_{bcorr} = C_{bstd} \cdot \frac{P_{std}}{P_b}
\]

where:
- \( C_{bcorr} \) = cleanliness criterion corrected to batch blank canister pressure (ppbv)
- \( C_{bstd} \) = cleanliness criterion at EPA standard pressure conditions (ppbv)
- \( P_{std} \) = EPA standard absolute pressure (psia) = 14.7 psia
- \( P_b \) = measured batch blank canister pressure (psia)
Cleanliness criteria must be lowered for agencies which dilute field samples such that the cleanliness criteria are met for undiluted samples. For instance, if a laboratory dilutes all samples by two-fold by addition of gas to the collected sample canister, the cleanliness criteria are not doubled, but are cut in half. For this correction, the batch blank pressure corrected criteria are adjusted by dividing by the typical dilution factor for diluting samples. The dilution factor is calculated as the quotient of the final canister pressure after dilution to the canister pressure upon sample receipt at the laboratory:

\[
C_{\text{bdilcorr}} = C_{\text{bcorr}} \cdot \frac{P_{\text{rec}}}{P_{\text{dil}}}
\]

where:
- \(C_{\text{bdilcorr}}\) = cleanliness criterion corrected to batch blank canister pressure and routine dilution factor (ppbv)
- \(C_{\text{bcorr}}\) = cleanliness criterion corrected to batch blank canister pressure (ppbv)
- \(P_{\text{rec}}\) = measured canister absolute pressure as received (undiluted) (psia)
- \(P_{\text{dil}}\) = measured canister absolute pressure following dilution (psia)

**Example:** A laboratory determined MDL for benzene is 0.0092 ppbv and has assigned the canister cleanliness criterion of 3-fold MDL at EPA standard pressure conditions of typically pressurized canister cleaning batch blank samples of 0.0276 ppbv. The laboratory typically pressurizes canister cleaning batch blanks to ~25 psia. Additionally, the laboratory dilutes ambient samples by a factor of 2 prior to analysis (to ensure sufficient pressure in the canister for withdrawing a sample) with HCF zero air. The typical received sample pressure and final diluted pressure are 10.0 and 20.0 psia, respectively.

where:
- \(C_{\text{bstd}}\) = 0.0276 ppbv
- \(P_{\text{std}}\) = 14.7 psia
- \(P_{b}\) = 25.0 psia
- \(P_{\text{rec}}\) = 10.0 psia
- \(P_{\text{dil}}\) = 20.0 psia

Combining the equations above to correct for canister batch blank pressure and typical sample dilution factor results in the following equation:

\[
C_{\text{bdilcorr}} = C_{\text{bstd}} \cdot \frac{P_{\text{std}}}{P_{b}} \cdot \frac{P_{\text{rec}}}{P_{\text{dil}}}
\]

Substituting values for each variable:

\[
C_{\text{bdilcorr}} = 0.0276 \text{ ppbv} \cdot \frac{14.7 \text{ psia}}{25.0 \text{ psia}} \cdot \frac{10.0 \text{ psia}}{20.0 \text{ psia}} = 0.00811 \text{ ppbv}
\]

**4.2.4.3 Canister Maintenance and Preventive Maintenance.** Maintenance of canisters involves a combination of preventive actions and best practices related to initial canister qualification, sample collection, cleaning, and general handling.
4.2.4.3.1 **Prevention of Particulate Ingress.** Sampling into canisters will be performed with a particulate filter as described in Section 4.2.3.1.1. Installation of a particulate filter is a necessary preventive maintenance step that eliminates the introduction of PM into the canister as it is difficult or impossible to remove from canisters using traditional pressurization and evacuation cleaning and can cause performance reduction indistinguishable from degradation of canister interior surfaces. Particulate residue inside of a canister creates active sites and adsorption sites which may have a detrimental effect on the concentration of VOCs in sampled atmospheres. Such effects may not be predictable, but may be evidenced by increases of oxygenated VOC concentrations or decreases of concentrations of brominated VOCs or labile VOCs. Particulates may deposit into canister valves, potentially leading to the damage of the threads, mating surfaces, and seals, resulting in leaks.

When not connected to a system for cleaning, sample collection or analysis, the canister opening should always be capped with a (brass) cap to ensure particulates do not deposit into the valve opening. To avoid galling the threads of the connection, the cap should be brass construction (softer metal than stainless steel), installed finger tight, and tightened gently, not more than 1/8 turn with a wrench.

4.2.4.3.2 **Valve Connection and Valve Operation.** Cross threading of connections or connection of incorrect fittings to the canister valve should be avoided as they may deform the threaded portion of the valve or the compression fitting seat. Connections should be tightened by hand and troubleshooting or adjustments should be performed if the connection cannot be easily made by hand. Wrenches should only be used for the final tightening of the connections to the valve. The amount of torque required to close a valve depends on the particular type of valve; however, overtightening will likely damage the valve, particularly older-style bellows-type valves. Canister valves should never be closed with excessive force or by using a wrench or pliers.

Damaged valves may not seal appropriately and may exhibit leaking. Canister valves requiring excessive force to successfully close and/or with damaged threads or valve seats should be repaired or replaced, as appropriate. Valves with damaged valve seat components should either be replaced entirely or rebuilt using kits available from the manufacturer. Valves with damaged external threads require replacement of the entire valve. Using a thread chaser or thread file to restore damaged threads is rarely effective in reversing the thread damage and is not recommended.

4.2.4.3.3 **General Canister Handling.** Canisters should be handled with care to ensure that weld integrity is maintained, that the interior canister surface is not compromised, and that the valve-to-canister connection remains intact. Shocks to the surface of the canister may damage welds or create small cracks in the interior canister surface which may expose active sites. Excessive torque applied to unbraced canister valves and valve stems may cause leaks in the valve stem weld or at the ferrule sealing the canister valve and canister stem. Canister valves may be installed with Vespel® ferrules, which can be damaged (cracked) with rough handling, resulting in leaks or ferrule material depositing into the canister.
Shipment of canisters in protective hard-shell boxes and/or sturdy cardboard boxes is recommended to ensure canister longevity. Replace boxes which have lost integrity or rigidity.

4.2.5 Canister Receipt. When received at the laboratory, canister samples are to be accompanied by a COC form that documents the unique canister identifier (e.g., serial number) and sample handling details according to Section 3.3.1.3.7. The sample collector will sign the COC form to relinquish custody, either when packaged for shipment with a courier or when delivered to the laboratory. The sample custodian will sign and date the COC form indicating acceptance of transfer of custody and will examine the sample collection documentation.

Canister pressure for canisters collected to subambient pressure is to be measured with a calibrated gauge or pressure transducer when received at the laboratory to ensure that the sample has not leaked during shipment. For subambient pressure samples, leaks allow contamination of the collected sample with ambient air. Measurement of the canister pressure is also recommended for canisters collected to pressures above ambient pressure (i.e., positive pressure samples); however, leaks will not permit contamination of the sample and are not critical. For subambient pressure samples, an acceptable pressure change between the measured pressure at sample retrieval in the field and the pressure upon receipt in the laboratory will be defined in an SOP or similar quality systems document and should not exceed 0.5 psi. Under no circumstances should a sample (other than a grab sample collected to ambient pressure) be received at the laboratory at ambient pressure without the associated concentration measurement data qualified (QA Qualifier LJ indicating the value is an estimate) when reported to AQS. Additional requirements for subambient pressure samples follow:

Canister pressure differences exceeding 0.5 psi may be due to temperature differences between the field site and laboratory. Acceptance of samples exceeding this criterion will be documented with appropriate rationale. A difference of 10°C from the temperature in the laboratory at receipt and the temperature of the sample canister at retrieval pressure measurement will result in an approximately 0.5 psi difference for a canister that has not leaked. A lower temperature at the monitoring site (in the monitoring shelter) than the receipt laboratory will result in a perceived pressure increase and a perceived decrease when the monitoring site temperature (shelter temperature) is higher. Use the following formula to calculate a theoretical expected canister pressure at laboratory receipt due to such temperature discrepancy (this assumes the canister has not leaked):

$$P_{exp} = \frac{P_{retrieval} \cdot T_{lab}}{T_{retrieval}}$$

where:

- $P_{exp}$ = canister pressure expected at sample receipt at laboratory (psia)
- $P_{retrieval}$ = canister pressure measured at sample retrieval at monitoring site (psia)
- $T_{lab}$ = laboratory temperature (degrees K)
- $T_{retrieval}$ = temperature at monitoring site (in shelter) when sample is retrieved (degrees K)

For example, the temperature at the monitoring site (in the monitoring shelter) at the time of sample retrieval is 13°C (286.15K) and the measured canister pressure is 12.1 psia. The laboratory temperature is 24°C (297.15K).
Therefore, the measured pressure upon receipt must be within ±0.5 psia of 12.6 psia (range of 12.1 to 13.1 psia).

Use of calibrated gauges for the field retrieval and laboratory measurements is critical, and staff measuring canister pressures should ensure the gauges read in absolute pressure measurements (e.g., psia), and not gauge pressure (e.g., psig or inHg vacuum). Gauge pressure is relative to the local ambient barometric pressure and is not comparable when the barometric pressure changes (i.e., different altitudes or locations). When the receipt pressure exceeds 0.5 psi from the canister pressure measured at sample retrieval for subambient pressure samples, the sample data are to be qualified or invalidated as follows:

- Pressure differential of > 0.5 psi but ≤ 1.5 psi: qualify data as estimated with low bias, QA Qualifier LJ
- Pressure differential > 1.5 psi, invalidated, invalidate with Null qualifier AA

Exceptions to this data treatment requirement include when temperature differences can be shown to be responsible for the difference in pressure and allowance to permit subambient samples to have more vacuum (i.e., lower absolute pressure) and pressurized samples to have higher pressure without need for qualification or invalidation. To assess whether temperature differences are responsible, the temperature at the monitoring site (inside the shelter) must be lower than the laboratory temperature to account for the higher received pressure.

4.2.6 VOCs Standard Materials and Reagents

4.2.6.1 Stock Standards Gases

4.2.6.1.1 Primary Calibration Stock Standards. Stock calibration standard gases may be procured at concentrations ranging from approximately 50 to 1000 ppbv of each target VOC in UHP nitrogen with analytical concentration tolerances of ±10%. Target VOCs in this concentration range are generally stable in high pressure passivated cylinders for at least one year and some gas vendors certify their mixtures for longer time periods. Calibration gases must be used within their certification period and can be recertified by the supplier or third party annually unless a longer expiration period is assigned by the supplier. Alternatively, a new stock standard or set of stock standard gases may be procured; however, this is typically several-fold more expensive than recertification. Dilution of typical stock calibration gas by approximately several hundred-fold permits preparation of working range calibration standards in canisters at single-digit ppbv concentrations.

Off-the-shelf stock calibration gas mixes are available containing approximately 65 target VOCs at 1 part per million (ppm); however, they do not typically contain EtO. Gas mixtures with tailored compound lists and concentrations are available through custom orders from certain suppliers. It may be necessary to procure multiple stock gases to acquire all desired VOCs.

Calibration stock gases must be purchased from a supplier that provides a COA stating each target VOC’s concentration with associated uncertainty. An expiration (certification period) must
be assigned to each standard gas mixture. When available, standard mixtures of target VOCs in high-pressure cylinders should be traceably certified to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) or to a NIST/EPA-approved Certified Reference Material. Gas standard COAs should be retained.

EPA Method TO-15A includes recommendations for preparing stock standard gases from neat materials, however; this is not recommended for the NATTS Program due to the required skills with associated techniques and the difficulty in performing them properly.

4.2.6.1.2 Second Source Calibration Verification Stock Standards. Second source stock calibration gases must be procured from a separate supplier and meet the criteria prescribed for primary calibration stock standard gases listed above in Section 4.2.6.1.1. A standard prepared with a different lot of source material from the same supplier as the primary calibration stock is only acceptable if it is unavailable from another supplier. As with the calibration stock gases, the second source stock must be used within its certification period and may be recertified. The SSCV stock standard must minimally contain all Tier I core VOCs and it is recommended that the SSCV also contain at least one compound representative of each type of compound in the calibration (e.g., low molecular weight, chlorinated, fluorinated, brominated, high molecular weight, etc.). It is strongly recommended that the SSCV contain all compounds for which the instrument is calibrated (i.e., those in the primary calibration stock standard).

4.2.6.1.3 Stock Standard Gas Expiration and Recertification. As mentioned above, stock standard gases may be recertified to ensure their continued suitability for use. This will typically involve the certification laboratory to provide an analytical concentration and an extended expiration period. In certain situations, it may be necessary to continue use of a standard past the expiration period (as may be the case when an ordered standard is delayed for an extended period). When this is the case, the concentration data associated with the expired standard must be reserved until recertification results are available, and if not available (as would occur when a new cylinder replaces the in-use cylinder), results are to be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS. Provided the recertification results show the target VOCs are within ±10% of the original certified value, the associated sample data may be reported without qualification. If the recertified cylinder’s VOC concentrations show a concentration difference from the original concentrations exceeding ±10%, but not more than 20%, the resulting ambient sample data generated with the expired standard must be qualified when reported to AQS. If the recertification result shows the concentration is < 90% of the original certified concentration, the sample data are to be qualified to indicate a high bias (QA Qualifier LK indicating an estimate with high bias), and conversely, if the recertification result concentration is > 110% of the original concentration, the sample data are to be qualified as to indicate a low bias (QA Qualifier LL indicating an estimate with low bias), indicating a low bias. Standard cylinders that show concentration differences of > ±20% from the original concentration exhibit poor concentration stability and must be retired. Data generated with standard materials that show a recertification concentration change of ≥ ±20% are to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.
4.2.6.1.3.1 Stability of Stock Standard Gases

With the addition of EtO to the suite of Tier I NATTS target analytes, laboratories reported concentration degradation problems with their stock standards for EtO concentration. While EtO may be the most problematic VOC to exhibit such concentration instability in stock standard gases, other compounds (e.g., acrolein or styrene) may exhibit similar concentration instability. Such degradation can be observed by comparison of the primary and second source working standards where the SSCV concentration is measured unacceptably high or low (outside ±30% of the theoretical nominal). Use of control charts (refer to Section 3.3.1.3.10) is helpful in observing a trend in concentration instability, which is thought to occur gradually over time (e.g., months) once the cylinder is prepared. Standard cylinder EtO concentrations have exhibited degradation and not enhancement, therefore if the SSCV recovery is high, it implies the primary standard gas concentration is unstable and degrading. Conversely, if the SSCV recovery is low, the second source standard is implicated to have an unstable concentration.

Analysts should use caution in immediately implicating a stock standard gas and should ensure that the canisters employed for preparing calibration standards are not the root cause of the discrepancy, as EtO is known to increase in canisters that have not been appropriately qualified as in Section 4.2.4.1. The suspect standard should be diluted into several canisters at several concentrations to verify the discrepancy. If confirmed, the ASL should contact the gas vendor to arrange recertification and confirmation of the suspected concentration.

If the concentration of the second source standard is identified as the degraded standard and the SSCV exceeds ±30.1% of the theoretical nominal, the data associated are still valid but should be qualified (QA Qualifier QX indicating a QC failure) when input to AQS. If the primary calibration stock standard is identified as the degraded standard (as determined by SSCV exceeding ±30.1% of the theoretical nominal), the associated data are to be invalidated (Null Qualifier EC indicating critical failure).

4.2.6.1.4 Internal Standard Stock Gases. Internal standard (IS) gases should be procured including a minimum of three VOCs covering the early, middle, and late elution range of the target VOC elution order. At minimum a single IS compound must be used. ISs must either be deuterated isotopes of target VOCs or VOCs which behave chromatographically similarly to, but are not, target VOCs. Three typical VOCs internal standards are 1,4-difluorobenzene, chlorobenzene-d5, and bromochloromethane.

IS stock gases are commercially available at 100 ppbv in UHP nitrogen, or can be purchased with a custom suite of compounds at desired concentrations. IS stock gases should be evaluated upon receipt for the presence of contaminants. Typical contaminants in IS mixtures include methylene chloride and carbon disulfide. Increasing volumes of IS should be analyzed and investigated for VOCs that increase proportionally in response to the introduced IS gas volume. Those exhibiting a proportional response indicate they are contaminants in the IS gas. IS gas standards which contribute unacceptable levels of target VOCs, such that, for instance, system blanks fail acceptance criteria, must not be employed for analysis and must be replaced. This contamination issue is widely reported from VOCs laboratories. A suitable mitigation to this problem is to order the IS gas at a high concentration (5 ppm or higher) such that the IS gas...
requires dilution to the point that contaminants are below the threshold where they interfere with analysis.

The IS is to be added to and analyzed with each injection at the same concentration in order to monitor instrument sensitivity and assess potential matrix effects. ISs are not added directly to the sample canister, rather they are introduced through a different dedicated non-sample port in the preconcentrator and trapped along with the sample aliquot on the first trapping module in the preconcentrator. The concentration of IS added to each injection should be chosen such that the IS compounds provide a chromatographic peak (for the primary ion) which is on scale and approximates the area response of the highest calibration standard.

4.2.6.1.5 **MS Tuning Standard – BFB.** 4-bromofluorobenzene (BFB) can be purchased as a standalone gas at approximately 30 to 100 ppbv in UHP nitrogen or purchased as a component in the IS mixture.

4.2.6.2 **Support Gases.** Various support gases are required for VOC analysis. Previous versions of this TAD and TO-15 (1999) permitted use of UHP nitrogen (N₂) for many purposes in VOC standards and QC sample preparation; however, in recent years the growth of oxygenated VOCs in canisters has highlighted that use of N₂ in many instances does not adequately represent the interactions that occur when the equipment (sampling pathways and canister media, etc.) is exposed to ambient air. HCF zero air and ambient air contain oxygen that will permit reactions to occur that are inhibited by the inert N₂ environment. Therefore, there will be situations where the use of N₂ is not appropriate and instead requires the use of HCF zero air. HCF zero air is recommended for all diluent and clean gas purposes; however, N₂ can still be used for diluent gas when preparing calibration standards since the purpose is solely to introduce the standard material to the instrument. N₂ cannot be employed to perform canister qualification checks, instrument bias checks, or sampler bias checks as the N₂ will inhibit reactions that may occur when the system is exposed to ambient air (e.g., growth of oxygenated VOCs).

**Carrier gas:** Helium is used as a carrier gas in the GC. Ultrapure (99.999% pure or better) helium is available in high-pressure cylinders. Hydrogen and nitrogen may also be used as carrier gases if all performance criteria are met. Consult with the instrument manufacturer for required support equipment (flow controllers, etc.) if employing alternative carrier gases.

**Cryogenic Gases:** Cryogenically cooled preconcentration systems typically require liquid nitrogen as a cryogen. Refer to the instrument manufacturer for requirements for cryogenic gases.

**Air:** HCF zero air can be purchased in high-pressure cylinders from reputable gas vendors or prepared by passing ambient air through molecular sieves, catalytic oxidizers, and subsequent charcoal filters or similar substrate to effectively remove impurities to a concentration of < 20 parts per trillion by volume (pptv) per compound of interest.

**Nitrogen:** Ultrapure (99.999% pure or better) nitrogen may be sourced from cylinders procured from commercial gas vendors or from the headspace gas from a liquid nitrogen dewar. (Note: Dewar headspace is theoretically VOC-free as VOCs in the source nitrogen gas should stay frozen in the liquid phase of the dewar contents. Users are encouraged to analyze headspace gas from each dewar or dewar refill prior to use to ensure the gas is fit for use in this method.)
Diluent gases are described in Section 4.2.7.2.

4.2.6.3 Reagent Water for Humidifying Gases. Reagent water for humidification of gases must be ASTM Type I (≥ 17.9 MΩ·cm). Additional purifying steps, such as sparging with nitrogen or helium or boiling, may be necessary to reduce or eliminate dissolved interfering gases in the water.

4.2.7 Preparation of Calibration Standards and Quality Control Samples. Calibration standards will typically be prepared from stock standard gases by dilution using humidified HCF zero air or ultrapure nitrogen. Standards may be prepared by dynamic or static dilution methods employing the equipment described in Section 4.7.3.2. Dynamic dilution techniques involve blending the standard gas mixture with the diluent gas in a manifold prior to transfer to the canister. Static dilution techniques involve dilution of the standard gas mixture with the diluent gas directly in the canister. Diluted standard gases should be humidified to approximately 40% to 50% RH. Following preparation, it is recommended that each canister be allowed to equilibrate for a minimum of 24 h prior to an initial analysis.

4.2.7.1 Humidification of Standards and QC Samples. The humidity of the gas within a canister is important in the preparation of calibration standards and QC samples and impacts analysis in several ways. First, water vapor within a canister displaces gases from the interior surfaces of the canister, retaining the displaced gases in the gas phase. This is especially important for VOCs with higher boiling points (BPs) and for electropolished canisters. Insufficient humidification of calibration standards may result in incomplete quantitative transfer of VOCs to the preconcentrator. Insufficient humidification may also impact transfer to or from subsequent canisters when canister gas standards serve as intermediates for preparing lower level standards. Second, depending on the meteorological conditions at the time of collection, ambient air samples will include some humidity, typically above 10% RH and may be saturated to 100% RH. Since matrix matching between collected samples and the associated standards and blanks is desirable, standard and blank canisters should be humidified to approximately 40% to 50% RH at ambient laboratory temperature. The range of 40% to 50% RH represents a practical compromise to ensure sufficient humidification given the impracticality of matching humidity for the variety of humidity levels possible in collected samples. This helps ensure that hydrophilic and high-BP VOCs meet relevant method performance specifications.

Humidification can be accomplished in several ways: employing a bubbler or impinger within the dilution gas stream, addition of deionized water to the canister, or a combination of these two methods. Adding water directly to canisters with a syringe via rubber septum is strongly not recommended as the syringe needle can core the septum and result in deposits of rubber into the canister and valve. This may lead to potentially irreproducible and biased VOC recoveries from the canister. For direct injection of water into a canister with a syringe, a high-pressure PTFE-sealed septum (such as a Merlin Microseal [Merlin Instrument Company, Newark, DE]) should be installed on the canister valve. For canisters to be connected to a gas source for pressurization via a dynamic or static dilution system, the water can be added to the valve opening of the evacuated canister prior to connecting to the dilution system. Once connected, the valve is opened, and the water is pulled into the canister along with the diluted standard gas.
The following formula is used to determine the volume of water to add to a canister to achieve the desired % RH: 17

\[ V_w = D_{\text{sat}} \cdot \frac{\text{RH}_d \cdot V_c \cdot P_c}{P_s \cdot D_w} \]

where:
- \( V_w \) = water volume to add to canister (μL)
- \( D_{\text{sat}} \) = saturation vapor density of water (mg/μL) at ambient laboratory temperature (refer to Table 4.2-3 below noting that units in the table are mg/L)
- \( \text{RH}_d \) = desired RH level expressed as a decimal
- \( V_c \) = nominal internal volume of canister (L)
- \( P_c \) = final pressure of canister (kPa absolute)
- \( P_s \) = standard ambient pressure (101.3 kPa absolute)
- \( D_w \) = density of water (1 mg/μL)

Notes: The formula above does not correct the density of water for the ambient temperature and assumes the density of water to be 1 g/mL. It also assumes that 100% of the added water is in the gas phase. Water may condense inside the canister if the temperature is reduced to the point at which the amount of water in the canister exceeds the saturation density. For more information regarding canister humidity, refer to “Variation of the Relative Humidity of Air Released from Canisters after Ambient Sampling.” 6

Table 4.2-3. Water Saturation Vapor Density at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Water Saturation Vapor Density (mg/L)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>12.8</td>
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<tr>
<td>16</td>
<td>13.6</td>
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<tr>
<td>17</td>
<td>14.4</td>
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<td>18</td>
<td>15.3</td>
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<td>19</td>
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<td>20</td>
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<td>21.8</td>
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<td>32</td>
<td>34.0</td>
</tr>
<tr>
<td>33</td>
<td>35.8</td>
</tr>
</tbody>
</table>

* Water Saturation Vapor Density values are generated according to the following formula18:

\[ \text{vapor density (mg/L)} = 5.018 + 0.32321 \cdot T + 8.1847 \times 10^{-3}T^2 + 3.1243 \times 10^{-4}T^3 \]

where: \( T \) = temperature in °C
Example: An analyst prepares a VOC standard in a 6-L canister, diluting to a final pressure of 202.6 kPa (2 atmospheres absolute [ata]) with dry HCF zero air. The laboratory temperature is 25 °C and the analyst wants the standard to be 50% RH. The volume of water needed is calculated as follows:

\[
V_w = 23.1 \frac{mg}{L} \cdot 0.50 \cdot 6L \cdot \frac{202.6 \text{ kPa absolute}}{101.3 \text{ kPa absolute}} \cdot \frac{1 \mu L}{mg} = 139 \mu L
\]

4.2.7.2 Diluent Gas. Diluent gases may consist of HCF zero air or UHP nitrogen. Zero air is typically sourced from a ZAG and may be further scrubbed by treatment with activated carbon scrubbers or catalytic oxidizers. HCF zero air is also commercially available in high pressure cylinders; however, may be cost prohibitive to procure meeting cleanliness specifications or may require further cleanup to remove impurities which affect analysis. Nitrogen gas must be from a UHP source (purity \( \geq 99.999\% \)) or from the headspace of a liquid nitrogen dewar. Regardless of which gas is chosen as a diluent, it must be analyzed to demonstrate to verify that levels of target VOCs are acceptably low; \(<\text{ MDL MQO for Tier I VOCs and } \leq 3\times \text{ MDL or 0.03 ppbv, whichever is lower, and preferably } < 0.02 \text{ ppbv. For diluent gas contained within a cylinder or from discrete liquid nitrogen tanks, the gas must be analyzed prior to preparing dilutions with the gas. For ZAGs or replenished onsite fixed liquid nitrogen Dewars, the diluent gas must be analyzed monthly.}

4.2.7.3 Preparation of Working Level Calibration Standards. Working calibration standards are prepared by diluting the stock standard gases with diluent gas and capturing the prepared diluted standard in a canister (or may be introduced directly to the preconcentrator). This dilution can be accomplished by dynamic dilution or static dilution methods.

Working calibration standards are typically prepared with concentrations of target VOCs at approximately 0.025 to 5 ppbv; however, this concentration range is dependent on the method of standards introduction which will drive the number of calibration levels to be diluted and their concentrations. Details of standard introduction for establishing the calibration curve are provided in Section 4.2.8.5.

4.2.7.3.1 Dynamic Dilution. Preparing working level VOC gas standards with dynamic dilution requires a dedicated flow control device for the diluent gas and for each stock standard gas to be diluted as well as a mixing chamber/manifold where the gases can be well-mixed before introduction to the canister. This is typically accomplished by controlling gas flows with calibrated MFCs capable of controlling the flow rates within ranges appropriate to achieve the desired dilution factor.

4.2.7.3.1.1 Calibration of Dynamic Dilution Systems

MFCs in dynamic dilution systems must be calibrated, with the calibration verified at least annually by comparison to a certified or primary reference flow standard. MFCs that fail a calibration check criterion of \( \pm 2\% \) must undergo recalibration to have the calibration (slope and intercept) adjusted. For commercially available dilution instruments, the manufacturer’s
instructions should be followed for recalibration. For custom-built systems that employ MFCs, the MFCs may be removed and shipped to a manufacturer or third party for recertification.

Note: Since MFCs operate on principal of gas density and thermal conductivity and this is highly specific to the metered gas, it is critical that the gas to be metered by the MFC is the same employed for calibration, e.g., nitrogen, and that the MFC gas setting reflect this gas. For stock VOCs standard gases, these are typically in a balance of nitrogen, therefore MFCs should be calibrated with nitrogen for such standard gas metering.

Alternatively, a linear least squares regression calibration curve can be generated by challenging the MFC with the appropriate gas, recording the MFC setting, and measuring the flow with a flow transfer standard for a minimum of five flow rate points covering the 10% to 100% portion of the flow range of the MFC. The resulting regression slope and intercept is then used to provide the MFC setting for a given desired flow rate. As a best practice, flows of the dynamic dilution system should be measured each day of use with a primary reference flow standard if possible, depending on the system configuration and accessibility to the MFCs.

4.2.7.3.1.2 Dynamic Dilution of Standard Gases

Dynamic dilution systems should be powered on and the diluent and stock gases allowed to flow through the respective MFCs for a minimum of 1 hour prior to use. A best practice is to experimentally determine the actual equilibration times necessary for each concentration level and document this in the SOP as appropriate. This equilibration period allows passivation and equilibration of the system to ensure the concentrations of the VOCs in the blended gas are stable prior to transferring to the canister (or directly to the preconcentrator).

Before proceeding with the preparation of canister standards by dynamic dilution, determine the method of humidification to be used as described in Section 4.2.7.1. Standards should be prepared from low concentration to high concentration to prevent high bias in lower concentration standards due to carryover. When changing stock gas flow rate(s) to prepare a different concentration, calibration gas(es) should flow through the system for a minimum of 30 minutes prior to preparation of the working calibration canister (or delivering the working standard directly to the preconcentrator). These equilibration times are particularly important for laboratories analyzing compounds with higher BPs such as hexachlorobutadiene and 1,2,4-trichlorobenzene. Extended equilibration times may be necessary to fully passivate the flow path and mixing chamber of the dynamic dilution system when higher BP compounds are included in the standard.

Note: Final pressures of calibration standard canisters must not exceed the maximum pressure permitted by the preconcentrator unit. Closely matching the pressure of the calibration standard canisters to the expected pressure of the collected field samples is recommended when analysis is performed with preconcentrators that measure volumes with MFCs. Consult the preconcentrator instrument manual for further guidance on matching canister pressures.

The final concentration of the diluted standard is calculated as follows:

\[
C_f = \frac{C_s \cdot F_s}{F_s + F_d}
\]
where:

\[ C_f = \text{final diluted standard concentration (pptv)} \]
\[ C_s = \text{certified concentration of stock standard (pptv)} \]
\[ F_s = \text{flow of stock standard (mL/min)} \]
\[ F_d = \text{flow of diluent gas (mL/min)} \]

*Note: If multiple gas standards are combined for dilution, the denominator is the sum of all gas flows combined for preparing the dilution.*

### 4.2.7.3.2 Static Dilution

Static dilution methods involve the precise measurement of the pressure changes in, or delivery of known volumes of gas into, a container of known constant volume. Static dilution is performed into a fixed-volume vessel such as a canister or into a manifold where the known volumes or partial pressures of each gas are measured. Before proceeding with the preparation of canister standards by static dilution, determine the method of humidification to be used as discussed in Section 4.2.7.1. Method TO-15A also discusses preparing standards by static dilution into canisters by addition of known volumes and by employing neat standard materials; however, these conventions require excellent technique and hygiene and are not recommended for routine use and therefore will not be discussed in this TAD.

#### 4.2.7.3.2.1 Static Dilution by Addition of Partial Pressures into Canisters

Starting with an evacuated canister, a calibrated pressure transducer or gauge is connected to the canister to monitor the canister pressure as gases are added. Stock and diluent gases are added separately by direct connection of the gas to the canister. The canister pressure is measured before and after standard and diluent gases are added to the canister, and these pressures are input into the calculation of the dilution factor and final concentrations. The final concentration of each VOC in the diluted standard is calculated as follows:

\[
C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{P_f}
\]

where:

\[ C_f = \text{final diluted standard concentration (pptv)} \]
\[ C_s = \text{certified concentration of stock standard (pptv)} \]
\[ P_{sa} = \text{absolute pressure of canister after adding standard gas (kPa)} \]
\[ P_{sb} = \text{absolute pressure of canister before adding standard gas (kPa)} \]
\[ P_f = \text{final canister absolute pressure after adding standard and diluent gases (kPa)} \]

#### 4.2.7.3.2.2 Static Dilution by Addition of Partial Pressures into Manifolds

Humidified (refer to Section 4.2.7.1) diluent gas and standard gas(es) are introduced stepwise into a manifold constructed of chromatographic-grade stainless steel or silicon-ceramic-coated stainless steel connected to a canister. The pressure of the manifold and canister is measured with a calibrated pressure transducer or combination of pressure transducers prior to and after the addition of each gas to the manifold. The final concentration of the diluted standard is calculated as follows:
\[ C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{(P_{sa} - P_{sb}) + (P_{da} - P_{db})} \]

where:
- \( C_f \) = final diluted standard concentration (pptv)
- \( C_s \) = certified concentration of stock standard (pptv)
- \( P_{sa} \) = absolute pressure of manifold and canister after adding standard gas (kPa)
- \( P_{sb} \) = absolute pressure of manifold and canister before adding standard gas (kPa)
- \( P_{da} \) = final manifold and canister absolute pressure after adding diluent (kPa)
- \( P_{db} \) = manifold and canister absolute pressure before adding diluent (kPa)

4.2.7.4 Preparation of Second Source Calibration Verification Working Standard. A SSCV standard is prepared in a canister at approximately the mid-range of the calibration curve by dilution of the second source stock standard as an independent verification of the calibration curve. The SSCV working standard can be prepared with the dynamic or static dilution procedures described in Sections 4.2.7.2.1 or 4.2.7.2.2, respectively.

4.2.7.5 Method Blank. The MB canister is prepared by filling a cleaned canister with humidified diluent gas. The MB verifies the diluent gas is sufficiently clean. To best represent canisters which are sent to the field for sample collection, the MB should be prepared in a clean canister which was verified by batch blank analysis. Analysis of a canister cleaning batch blank as the MB complicates the corrective action process to locate the source if the MB canister analysis indicates contamination.

4.2.7.6 Laboratory Control Sample. The LCS is prepared at approximately the lower third of the calibration range by dilution of the calibration stock gas. While not required, preparation and analysis of the LCS is recommended. The LCS may serve as the CCV and the volume of LCS analyzed should be the same volume as that taken from sample canisters for routine analysis. The LCS serves to both verify that calibration standards were prepared correctly and that the instrument remains in calibration. The LCS can be prepared with the dynamic or static dilution procedures described in Sections 4.2.7.2.1 or 4.2.7.2.2, respectively. The LCS should recover within 69.9 to 130.1% or associated measurement data is to be qualified (QA Qualifier LJ indicating estimated, LL indicating estimated with a low bias, or LK estimated with a high bias) as appropriate, when reported to AQS.

4.2.8 GC/MS Tuning, Calibration, and Quality Control. The GC/MS instrument system consists of primarily three discrete components: the preconcentrator (which includes the autosampler), the GC, and the MS detector. The preconcentrator introduces the sample from the canister, selectively removes and traps the VOCs for concentration, and injects them to the GC for separation. The GC separates the target VOCs which create a response in the MS detector when eluting from the GC column. The entire system is configured to optimize the trapping, separation, and detection of the target VOCs while eliminating interferences and minimizing contamination as practical.

4.2.8.1 Analysis Interferences. Interferences in the analytical system can be caused by contamination within the analytical instrument, active sites within the sample introduction or
Contamination within the analytical system may come from several sources including, but not limited to, offgassing of materials within the sample introduction or preconcentrator flow path, carryover from high-concentration samples or standards, and solvent vapors within the laboratory.

Active sites within the sample introduction or preconcentration flow path are often caused by use of improper materials or degradation of deactivated surfaces. To minimize the potential for contamination and active sites, analytical system wetted parts should consist of the materials described in Section 4.2.3.1.1.

Carrier, diluent, and internal standard (IS) gases may be sources of contaminants. Carrier gases should be dry (dew point < -40 °C) and should be ultrapure (purities > 99.999%). Additional in-line carbon scrubbers and desiccant traps may be necessary to remove residual VOCs and water from the carrier and diluent gases. Impurities in source materials or diluent gases for IS gas mixtures may result in contamination of target VOCs. Qualification of ISs is further discussed in Section 4.2.6.1.4.

Water and the delivery systems used to humidify canisters or diluent gas streams may contaminate the canister contents or humidified gases. Specifications for reagent water are described in Section 4.2.6.3.

Moisture in the sample gas may interfere with VOC analysis by GC-MS, whereas a properly configured moisture management system (as discussed in Section 4.2.8.2) can reduce or eliminate the interference of water. Poor or inconsistent water management during preconcentration can cause peak broadening and RT shifts and result in peak misidentification, particularly for hydrophilic polar compounds. Water management systems that use semipermeable fluoropolymer membranes are not recommended for use in this method as they remove oxygenated and polar VOCs from the sample matrix and exhibit memory effects for a number of VOCs. VOCs entrained in the fluoropolymer membrane can convert to ketones and alcohols, which are transported across the membrane bidirectionally such that these ketones and alcohols can contaminate the sample stream and VOCs in the sample stream can be adsorbed into the fluoropolymer and removed from the sample stream.

Carbon dioxide in the collected sample can coelute with more volatile VOCs eluting early in the GC-MS run and interfere with their quantitation.

Artifacts in chromatograms, such as silanol compounds formed from the breakdown of silicon-ceramic linings of canisters and siloxane compounds from the breakdown of the stationary phase in an analytical column, can interfere with identification and quantitation of less volatile VOCs.

Target analytes and interfering substances can offgas from new components in the analysis system, e.g., preconcentrator trap. Manufacturer recommendations should be followed to reduce and eliminate these artifacts. Further information on preconcentrator trap conditioning is discussed in Section 4.2.8.2.1.
4.2.8.2  **Preconcentrator.** A measured aliquot of the whole air sample (typically 100 to 1000 mL) is drawn from the sample canister by vacuum through a preconcentrator. Moisture and bulk atmospheric gases such as oxygen, nitrogen, argon, and carbon dioxide must be largely removed from the sample aliquot prior to introduction of the target VOCs to the GC. Instrument manufacturers have developed different methods for removal of moisture and bulk gases, most of which typically involve freezing water from the sample aliquot by cryogenic or electronic cooling.

One general convention passes the sample aliquot through an empty metal or quartz trap cooled to approximately -30 to -50 °C to freeze the water but permit the target VOCs and bulk gases to pass through to a sorbent bed trap. The empty trap containing the ice is then isolated from the sorbent bed trap, warmed to melt the ice, swept with a dry purge gas to vent, and readied for the next sample.\(^{19}\)

In another convention, the sample aliquot is routed through an empty trap or a trap packed with glass beads that is cooled to approximately -110 to -160 °C to retain all of the target VOCs and water and to permit the bulk gases to pass through. The trap is then warmed slightly above the freezing point of water and flushed with dry carrier gas to sweep the target VOCs onto a subsequent sorbent bed trap and retain most of the water on the first trap.\(^{20}\)

In either convention described above, the second trap may contain sorbent beds with one or more sorbents arranged to selectively trap the target VOCs and permit remaining bulk gases, such as water and carbon dioxide, to pass through. Following trapping of the target VOCs on this second trap, it is isolated, heated quickly to desorb the target VOCs, and backflushed to the GC column or to a subsequent focusing trap (typically a cooled empty trap). The focusing step provides the VOCs to the GC column in a small volume of carrier gas, which facilitates sharp chromatographic peaks and improved baseline separation of peaks. If multiple sorbents are employed in the trap, the sorbents are arranged such that the sample aliquot first enters the weakest sorbent and then successively stronger sorbents. This configuration permits trapping of the higher-BP VOCs in the weaker sorbent. Lower-BP VOCs are not retained as completely on the weaker sorbents and partially pass through to the stronger sorbents where they are retained. Once trapping is complete, the trap may be purged with dry carrier gas to remove excess moisture, or the preconcentration may progress directly to heated desorption. During heated desorption, the trap is rapidly heated and backflushed to release the target VOCs from the sorbents. Such multisorbent bed arrangements allow efficient trapping and desorption of target VOCs. Sorbent configurations, trap cooling temperatures, flush volumes, and desorption temperatures are recommended by the preconcentrator instrument manufacturers and are tailored to the suite of target VOCs desired for quantification.

A third type of preconcentration uses a series of capillary columns to trap and maintain target VOCs while allowing water and bulk gases to pass through. Upon backflushing, the target VOCs are trapped onto a second series of capillary columns for focusing and then backflushed for injection onto the GC column.

Preconcentrator instrument manufacturers will typically indicate the optimum factory default settings for the sample aliquot volume, trapping time, trapping temperature(s), gas flows, and
additional preconcentration parameters. Each of these variables may be adjusted based on the needs of the individual user and the suite of desired VOCs for measurement. Sample and standard introduction to the preconcentrator is preferably performed via autosampler which allows connection of many canisters that permits unattended analysis of anywhere from four to 16 or more canisters and permits unattended operation. Ports are also typically available on the preconcentrator for internal standard and/or standard introduction.

4.2.8.1.1 Preconcentrator Trap Conditioning. New preconcentrator traps may contribute contaminants and/or interferences that are evident in chromatograms. Preconcentrator traps should be conditioned when first installed to eliminate these interferences. Instrument manufacturer instructions should be followed and a general process follows. Conditioning may be performed with prolonged baking of the trap at an elevated temperature (e.g., 200 to 300 °C) while flowing dry, inert carrier gas (hydrogen or helium as recommended by the manufacturer) through the trap. The conditioning temperature depends on the sorbents in the trap and is typically recommended by the sorbent or trap manufacturer. Note that preconcentrator traps with multiple sorbent beds should be conditioned at the lowest temperature of the sorbents contained in the trap. For example, if a sorbent trap contains both Tenax-TA (MilliporeSigma, St. Louis, MO, recommended conditioning temperature 320 °C) and Carbopack (available from MilliporeSigma, St. Louis, MO, recommended conditioning temperature 350 °C), the trap conditioning temperature should not exceed 320 °C. The temperature during conditioning should be raised slowly in a stepwise manner (e.g., 20 °C/hour) until the conditioning temperature is achieved. Bakeout periods of approximately 48 hours at the conditioning temperature have shown to be effective; however, manufacturer recommendations should be followed. After this ~48-h period, most of the trap contamination will have been removed. Lower concentration (sub-ppbv) levels of target compounds may still evolve from the trap for an extended period following conditioning. Analysis of instrument blanks (IBs) and MBs will demonstrate sufficient trap conditioning when IB and MB acceptance criteria are met.

Differing configurations of preconcentrator systems and the associated sorbent traps and conventions for moisture management require the operating conditions and settings of the preconcentrator to be optimized based on the desired suite of target VOCs. The manufacturer’s guidelines should be used as a starting point. For NATTS VOCs analysis for EtO, laboratories have indicated that comprehensive removal of water improves chromatographic separation of EtO, as a relatively large water response in the chromatogram negatively impacts the EtO chromatography (e.g., wide, unresolved peaks).

4.2.8.3 Analysis via GC/MS. The analyst should optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methylpolysiloxane stationary phase is an indication of acceptable chromatographic performance. GC carrier gas flows, oven temperature program, and instrument run time should be based on the manufacturer’s recommendations and customized for separating the list of desired target VOCs. In general, heated transfer lines from the preconcentrator to the GC should be set to manufacturer recommendations, typically approximately 80 to 100 °C.

As noted in Section 4.2.1, canisters are to be analyzed within 30 days of the end of collection (field-collected samples) or preparation (laboratory QC samples and standards). Results input to
AQS must be appropriately qualified (QA Qualifier LJ indicating the value is estimated) if this holding time is exceeded.

### 4.2.8.3.1 Example GC Conditions.

The GC should be temperature programmable and ideally will have cryogenic cooling capabilities. VOCs should be separated with a 60 m by 0.32 mm capillary column with 1-µm lining of 100% dimethylpolysiloxane (e.g., DB-1), or with a column capable of separating the target analytes and ISs so that method performance specifications are attained. Alternative separation columns comprising a more polar stationary phase may improve separation performance for polar VOCs. Example GC analytical conditions are given in Table 4.2-4 for carrier gas, carrier gas flow rate, and oven temperature program. These conditions assume the use of a 60-m length fused-silica column with an inner diameter (I.D.) of 0.25 or 0.32 mm and a PDMS film thickness of 1 µm.

#### Table 4.2-4. Example GC Analytical Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas:</td>
<td>Helium</td>
</tr>
<tr>
<td>Carrier gas flow rate:</td>
<td>1–3 mL/min as recommended</td>
</tr>
<tr>
<td></td>
<td>by manufacturer</td>
</tr>
<tr>
<td>Oven temperature program:</td>
<td>Initial temperature: * 35 °C</td>
</tr>
<tr>
<td></td>
<td>Initial hold time: 2 min</td>
</tr>
<tr>
<td></td>
<td>Ramp rate: 8 °C/min</td>
</tr>
<tr>
<td></td>
<td>Final temperature: 220 °C</td>
</tr>
<tr>
<td></td>
<td>Final hold time: Until all target compounds elute</td>
</tr>
</tbody>
</table>

* This is a default initial temperature and users may need to employ a subambient initial oven temperature to effectively separate VOCs and interferences eluting in the early portion of the chromatogram.

### 4.2.8.3.2 Example MS Conditions.

The analysis instrument must employ detection via mass spectrometer (MS). The MS may be a quadrupole, ion trap, or TOF detector. Detection via flame ionization detector (FID) does not permit sufficient sensitivity for positive compound identification and quantitation of the suite of target VOCs, particularly halogenated VOCs. Flame ionization detection is useful for measurement of hydrocarbons, such as those measured as ozone precursor VOCs in the PAMS Program and may be performed by way of splitting the column effluent with the MS such that the separated sample can be quantitated on both MS detector and FID. Due to the non-specific nature of FID detectors, analytes must be qualitatively identified via the MS detector.

The MS instrument manufacturer’s recommendations should be followed for detection of the desired suite of target VOCs. For laboratories performing analysis of lower molecular weight analytes such as acetonitrile (ACN), methanol, acetylene, etc., the MS scan range may need to be adjusted to a range of 25 to 250 atomic mass unit (amu). Note that the lower scan range often increases the presence of low mass interferences in the chromatogram.

The following are examples of MS settings for linear quadrupole, ion trap, and TOF MS detectors:

- Linear quadrupole MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. The scan range should be commensurate with the target analytes; the recommended range is 35 to 270 amu unless the desired target VOCs
require a different scan range. Scan ranges that include m/z 28 and 32 may experience interference problems with nitrogen and oxygen, respectively. Creation of custom scan ranges that are tailored to specific analyte RTs may be appropriate and may avoid these interferences when an expanded scan range (e.g., m/z 25 to 270) is needed. The MS should be configured to perform at least one scan per second. Ideally, the scan rate should be fast enough that at least ten \(^{22}\) and preferably 12 or more scans are available for each peak.

- Ion trap MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. As with linear quadrupole instruments, the scan range should cover the desired target VOC suite, and the recommended range is 35 to 270 amu unless an expanded range is needed. The same interferences with nitrogen and oxygen apply when including lower masses in the scan range. The scan time should be set to approximately 0.4 to 1 s/scan; faster scan rates will provide improved resolution. Axial modulation, manifold temperature, and emission current should be adjusted per the manufacturer’s recommendations.

- TOF MS instruments should be configured per the manufacturer recommendations. Typical example settings include: EI setting of 70 eV, ion source temperature of 260 °C, and transfer line temperature of 260 °C. Spectral acquisition rates of approximately 2 to 4 Hz (2 to 4 scan sets/s) or higher will provide appropriate resolution for eluting peaks.

### 4.2.8.3.3 Tuning/Optimizing the Mass Spectrometer and Verifying the Tune

#### 4.2.8.3.3.1 Tuning/Optimizing the Mass Spectrometer

The MS (quadrupole, ion trap, or TOF MS) is tuned/optimized according to the manufacturer’s specifications upon initial installation of the instrument and following significant preventive maintenance or repair activities that impact the performance of the GC-MS system. This includes, but is not limited to, cleaning the ion source or analyzer, trimming or replacing the capillary column, and adjusting MS tune or optimization parameters. Once optimized, the MS tune must be verified according to manufacturer specifications each day of use. The purpose of MS tuning is to demonstrate acceptable performance across the selected ion m/z range, where acceptable performance demonstrates sufficient responses of desired masses, correct mass ratios, and adequately low vacuum leak rates. Analysis cannot continue if proper MS tuning has not been demonstrated.

*Note: The analytical instrument (quadrupole, ion trap, or TOF MS) should be tuned/optimized according to the manufacturer’s specifications. Method TO-15 previously required a BFB tune verification. This BFB tune verification is no longer required in Method TO-15A or in this TAD, although analysts may choose to continue using this protocol as outlined below.*

#### 4.2.8.3.3.2 Verifying the MS Tune Using BFB

To confirm that the MS meets tuning and standard mass spectral abundance criteria prior to initiating data collection, the GC-MS system is set up according to the manufacturer’s
specifications, and the mass calibration and resolution of the system may then be verified by analysis of the tuning check compound, BFB. Most modern MS systems include an automatic tuning optimization routine that is operated through the instrument software. The use of BFB as the tuning compound is specific to ensure acceptable MS response ratios up to approximately 200 amu.

4.2.8.3.3.2.1 Introducing the BFB

If the BFB is included in the IS stock gas mixture, it is introduced to the preconcentrator with the IS mixture through the dedicated port. If not a component of the IS mixture, BFB can be purchased as a stand-alone compound in a high-pressure cylinder and introduced to the preconcentrator through a step-down regulator or may be diluted appropriately into a canister and introduced through a sample or IS port. The tuning check is performed by introducing 1 to 2 ng into the preconcentrator and analyzing the standard using the preconcentrator, GC, and MS parameters established and used for the analysis of calibration standards, QC samples, and field samples. The method integration and analysis parameters employed should also be those for routine analysis of standards, QC samples, and field samples.

4.2.8.3.3.2.2 BFB Tuning Verification Frequency

Before analyzing samples, blanks, or calibration standards on each day of analysis, the analyst should confirm that the GC-MS system meets the mass spectral ion abundance criteria, as listed in Table 4.2-5, for the BFB tuning check for linear quadrupole or ion trap MS instruments. The tuning check should be analyzed and pass criteria before ICAL and every 24 hours of analysis thereafter. The 24-hour time period for the tuning check begins at the injection (acquisition time) of the BFB.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Ion Abundance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>8.0% to 40.0% of m/z 95</td>
</tr>
<tr>
<td>75</td>
<td>30.0% to 66.0% of m/z 95</td>
</tr>
<tr>
<td>95</td>
<td>Base peak, 100% relative abundance</td>
</tr>
<tr>
<td>96</td>
<td>5.0% to 9.0% percent of m/z 95</td>
</tr>
<tr>
<td>173</td>
<td>Less than 2.0% of m/z 174</td>
</tr>
<tr>
<td>174</td>
<td>50.0% to 120.0% of m/z 95</td>
</tr>
<tr>
<td>175</td>
<td>4.0% to 9.0% of m/z 174</td>
</tr>
<tr>
<td>176</td>
<td>93.0% to 101.0% of m/z 174</td>
</tr>
<tr>
<td>177</td>
<td>5.0% to 9.0% of m/z 176</td>
</tr>
</tbody>
</table>

*aAll ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

4.2.8.3.3.2.3 BFB Tuning Corrective Action

If the BFB tuning criteria in Table 4.2-5 are not met, the analyst should adjust the tune of the MS, which may require adjusting the ion focus or lens settings, for example. Repeated failure to meet tuning abundance acceptance criteria requires corrective action, which may include cleaning the ion source, checking for leaks, and/or servicing the MS vacuum pump. If the analyst
cannot attain an acceptable MS tune after performing instrument maintenance, a service technician visit may be required. The manufacturer’s manual should be consulted for assistance with instrument troubleshooting. Automated tuning routines may be helpful in adjusting MS tuning parameters to achieve an acceptable state of tune.

4.2.8.4 Internal Standards, Calibration, and Quality Control. The calibration and QC criteria described in the following subsections must be met for Tier I VOCs and should be met for non-Tier I VOCs. Data reporting practices for non-Tier I VOCs that do not meet acceptance criteria are described below.

4.2.8.4.1 Internal Standards. The IS is added at the same concentration to each injection (standard, sample, blank, etc.) to monitor instrument sensitivity and assess potential matrix effects. Significant changes in the IS RT and response may be warning signs of chromatographic issues such as leaks, column degradation, or insufficient water management techniques in the preconcentrator. ISs are not added directly to the sample canister but instead are introduced through a different dedicated nonsample port in the preconcentrator and trapped along with the sample aliquot on the trapping module in the preconcentrator. The concentration of IS added to each injection should be chosen such that the IS compound peak area response approximates the target compound quantitation ion area responses in the lower half of the calibration curve range, but that minimally provides a peak that is on scale and does not exceed the quantitation ion area response of target analyte with highest response in the high calibration standard.

4.2.8.4.1.1 Internal Standard Retention Time

Each IS compound in each injection should be within ±2 seconds of the average RT for each IS compound in the ICAL. An occasional outlier may not be problematic but may indicate a poor injection, in which case the analysis should be repeated. If RTs are consistently outside of ±2 s of the average RT, then the operator should further investigate possible reasons for the shift. The average RT for each IS in the ICAL is calculated using the following equation:

$$\bar{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

where:
- $\bar{RT}$ = average RT for the IS compound (minutes)
- $RT_i$ = RT for the IS compound for each calibration level (minutes)
- $n$ = number of concentration values used to generate the calibration (minimum of 5)

4.2.8.4.1.2 Internal Standard Response

The area response for each IS compound in each injection (calibration standard, field sample, blank, CCV, etc.) must be within ±40% of the mean area response of the IS compound determined from the ICAL per the following equation:

$$\bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n}$$

where:
\[ Y = \text{average area response for the given IS compound} \]
\[ Y_i = \text{area response for the IS for each calibration level} \]
\[ N = \text{number of concentration values used to generate the calibration (minimum of 5)} \]

The quantitation ion for each IS compound is chosen as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, an abundant secondary ion may be selected for quantitation.

Changes in the IS response may be due to leaks in the system, issues associated with the IS delivery, matrix effects, or a decline in detector sensitivity. It is advised that a control chart of all IS area responses (chronological sample analyses along the horizontal axis and IS response on the vertical axis) be prepared (refer to Method TO-15A Figure 15-1), be maintained, and monitored on a daily basis to aid in the detection and diagnosis of problems. Erratic increases and decreases of approximately 15% in response for all IS compounds simultaneously can indicate system leaks, issues with delivery of the IS, and/or other problems with the analytical system. A trending decline of IS responses typically indicates a decline in system sensitivity. If there is a trending decline, sequences involving multiple samples should not be started if there is a likelihood that the IS responses (based on the indicated trend) will fall outside the ±40% range. Otherwise samples falling outside this range will need to be reanalyzed once the instrument sensitivity is restored and a new ICAL is established. Samples for which the IS area response differs by more than 40% from the mean IS area response as determined from the ICAL are to be reanalyzed when possible. If reanalysis is not possible, the target analytes are to be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS.

Note that while changes in the instrument sensitivity are tracked by IS responses and calculation of RRFs (refer to Section 4.2.8.5.2), decreased IS response indicates a decrease in method sensitivity with concomitant increased measurement imprecision and increased likelihood of false negatives. Implementing corrective actions when IS responses decrease beyond predetermined thresholds minimizes the impact of the sensitivity changes. In light of this, laboratories may choose to implement a ±30% acceptance criterion for IS response tracking.

### 4.2.8.5 Establishing Calibration

The GC-MS is calibrated initially and when the system is out of control as indicated by IS responses or CCV standards exceeding acceptance criteria. Once the decision has been made to calibrate or after the instrument has been tuned/optimized, it is recommended that a sufficient number of humidified HCF zero air blanks or humidified check standards be analyzed to verify that instrument sensitivity is stable, as indicated by IS response. This will minimize potential instrument drift during the ICAL. When this has been completed, the ICAL can proceed as discussed below.

#### 4.2.8.5.1 Calibration Standards

The calibration curve is prepared by analysis of different concentration levels covering the concentration range desired by the laboratory as determined by the expected concentration of the samples, the sensitivity of the instrumentation, and the mass of analytes delivered to the column. A typical calibration range for ambient air analysis is approximately 20 to not more than 5000 pptv (ranging from tens of picograms to tens of nanograms on column). A best practice is to include a calibration point to approximate concentrations of target VOCs typically measured in ambient air, approximately 20 pptv.
Minimally five concentration levels are to be included in the ICAL, and more levels are recommended, especially at the lower end of the calibration curve if the lowest standard concentration is in the tens of pptv. If a quadratic regression is used to model the curve, a minimum of eight levels is recommended.

Calibration curves may be established on the instrument by two conventions:

- **Individual Standards Method:** A separate standard canister is prepared for each concentration level of the calibration curve and the same volume from each canister is analyzed. For example, to establish an eight-level calibration curve, the analyst prepares canisters at concentrations of: 20, 50, 100, 250, 1000, 2000, and 5000 pptv and analyzes the same volume (e.g., 250 mL) of each standard as is performed for field samples.

- **Effective Dilution Method:** Standard canisters are prepared at different concentrations from which proportional volumes are analyzed to establish the calibration curve. For example, the analyst prepares two standard canisters at 250 and 5000 pptv. The typical injection volume for samples is 250 mL; therefore, to establish a calibration curve of: 20, 50, 100, 250, 1000, 2000, and 5000 pptv, the analyst injects 20, 50, 100, and 250 mL from the 250 pptv canister and 50, 100, and 250 mL from the 5000 pptv canister. Users are strongly recommended to employ a minimum of two separate standard canisters for generating calibration curves. When using a single canister for introducing standards, an error in preparation of the canister will not be apparent as the calibration will meet the technical linearity and accuracy criteria. When employing a single standard canister to generate the calibration curve, it is necessary to verify the calibration with a canister prepared independently from the primary calibration canister. The SSCV described in Section 4.2.8.6.1 can serve this purpose.

Note that when the individual standards method is employed to establish calibration, the same gas volume from each canister is delivered to the preconcentrator resulting in the same amount of moisture and the same degree of penetration of compounds onto the preconcentrator sorbent trap. When the effective dilution standards method is employed to establish calibration, various gas volumes are delivered to the preconcentrator resulting in differing amounts of moisture and degrees of penetration of the compounds on the preconcentrator trap. As a result, it is important to demonstrate that the sample introduction volume measurements are reproducible, linear, and proportional and that the moisture and penetration variability do not impact the analysis. To accomplish this, analysts should follow prescribed manufacturer procedures for demonstrating linear and proportional volume metering of gases for preconcentration. Acceptance should also be demonstrated by establishing a calibration based on the individual standards method followed by establishing a second calibration based on the effective dilution method by injecting various volumes of the individual standard method’s high calibration standard. A comparison of the two calibration curves should demonstrate linearity of compounds covering the volatility range of the target analyte suite. This demonstration then validates the effective dilution is appropriate.

For measuring low (tens of pptv) levels of VOCs as is needed for ambient air analysis, it is important to properly characterize instrument response at these lower concentrations by loading a greater number of calibration points toward the bottom of the calibration curve (as shown in the examples above). Including more calibration level points in the lower end of the curve better
defines the low end of the curve and minimizes calibration bias of higher concentration standards
in the least squares regression curves.

*Note: To establish the calibration curve, the theoretical nominal concentrations of the
working calibration standards should be calculated using the certified concentration from
the gas vendor COA. COAs for stock standard gas mixtures typically include both a nominal
(or "requested") concentration (e.g., 100 ppbv) for each analyte and a certified
concentration (e.g., 108 ppbv), which should be within a specified tolerance (e.g., ±10%).
These tolerances may permit the certified concentration to differ from the nominal
calibration by 10 to 20%, resulting in final theoretical concentration errors for the
working level standards when the nominal concentration is input into standard concentration
calculations instead of the certified concentration.*

4.2.8.5.2 Introduction of Working Calibration Standards. Once the calibration convention has
been decided and working standards have been prepared as per Section 4.2.7.3, the working
calibration standards are analyzed to establish the ICAL.

An air/water check of the MS also should be performed prior to beginning analyses to ensure that
the system is leak-free. Prior to starting the ICAL analytical sequence, the analyst should conduct
a thorough system bakeout per the manufacturer’s instructions for the preconcentrator and also
ramp the GC column temperature. This readies the system by effectively removing any
accumulated impurities in the analytical system. Analysis of an IB (Section 4.2.6.3.8.1) or
performing a BFB tune check (Section 4.2.8.3.3.2) accomplishes this as well. An MB (Section
4.2.8.6.3.2) should be analyzed before beginning the analysis of the calibration standards.
Analysis of the MB should demonstrate that the system is acceptably clean and meets the
canister blank acceptance criteria in Section 4.2.4.2.4. Once the criteria have been met, analysis
of the calibration standards from lowest to highest concentration is performed. It is
recommended that an additional MB be analyzed following the highest calibration standard to
ensure there is no carryover in the system in preparation for analysis of the SSCV (refer to
Section 4.2.8.6.1).

4.2.8.5.3 Calibration Curve Modeling. Following analysis of the calibration standards, a
calibration curve is prepared for each target analyte by determining the RRF of each
concentration level. Following data acquisition for the calibration standards, the RRF of each
target compound in each calibration level is determined as follows:

\[
RRF = \frac{A_s \cdot C_{IS}}{A_{IS} \cdot C_s}
\]

where:

- \( A_s \) = peak area for quantitation ion of the target compound
- \( C_{IS} \) = concentration of the assigned IS compound (pptv)
- \( A_{IS} \) = peak area for quantitation ion of the assigned IS compound
- \( C_s \) = concentration of the target compound (pptv)

The quantitation ion for the target VOC is chosen as the most abundant ion (base peak) unless
there is a spectral interference from a coeluting or nearby compound or interference that impacts
the quantitation of the base peak. In such cases, an abundant secondary ion may be selected for
quantitation.
Analysts should use their professional judgment to select an appropriate calibration model, which may include using average RRFs or linear or quadratic regressions.

If using an average RRF calibration model, the RSD of the RRF for each target VOC must be < 30.1%. Chromatographic software programs typically include these calculations and can be configured to generate the RRF at each level, the average RRF for all calibration standards, and the RSD of the RRF for each target compound and to qualify (flag) calibrations that exceed the RSD criterion.

Note that the calibration model using average RRF assumes a linear calibration with the origin as the curve intercept. For analytes with calibration behavior known to demonstrate background or other behavior where the curve is not expected to pass through the origin, the analyst is recommended to consider an alternative calibration model. For example, a calibration curve may be prepared by linear or quadratic least squares regression of the ratios $A_S/A_{IS}$ as the dependent variables and the ratios $C_S/C_{IS}$ as the independent variables. The user should be aware that use of quadratic regression may mask nonlinear behavior that is due to errors in standards preparation or introduction and is not a function of the compound behavior or instrument limitations. The correlation coefficient ($r$) for linear or quadratic curves must be $\geq 0.995$ for each target VOC. Such linear or quadratic curves may be weighted (e.g., $1/\text{concentration}$ or $1/\text{concentration}^2$) to provide better representation at the low end (bottom 10 to 15% concentration range) of the curve.

Linear or quadratic curves should pass through the origin unless the system exhibits consistent elevated background levels of target VOCs. Consistent low-concentration background levels in the calibration may be introduced from contamination in canisters, diluent gas, humidification processes, or the analytical system. Presence of background may be confirmed by analysis of a dilution blank canister prepared identically to calibration standards without introduction of standard gas. In such cases, the calibration behavior may be better characterized with a calibration regression curve fit using a calculated y-intercept, which will typically be positive in magnitude. However, analysts should use caution when employing calculated intercepts and calibration models including a zero point, especially in situations where the compound background is an artifact of the calibration process (such as in dilution gases, canisters selected for preparing calibration standards, or the gas dilution system) and not a consistent behavior of the measurement system that affects all measurements (such as low-level contamination in the preconcentrator, ISs, or transfer line). In instances where the positive calibration y-intercept is due to the calibration process, negative concentration measurements may result in samples and QC samples omitting the materials employed to prepare the calibration working standards.

Irrespective of the curve fit method selected, the calculated concentration for each VOC at each calibration level should be $< \pm 30.1\%$ of the theoretical concentration when quantitated against the resulting calibration curve. Exclusion of calibration standard levels is not permitted unless it is the lowest one or two calibration standard levels (due to not meeting qualitative identification criteria, primarily due to low signal to noise ratio or absence of qualifier ions) or unless a
justifiable technical reason is cited (for example, a known error in standard preparation or a known poor injection of the standard). Corrective action should be taken for target compounds that fail this criterion. This evaluation of each concentration level is important to properly demonstrate calibration curve accuracy across the chosen concentration levels as both the correlation coefficient and RSD assessment of linear regression are poor overall estimations of the goodness of fit of the curve.

Note: Since this method may be employed to analyze numerous target VOCs with a wide range of chemical properties (volatility, polarity, etc.), some non-Tier I target VOCs may not meet the calibration criteria. In such instances of failed calibration criteria, the affected target analyte concentrations measured in samples are to be qualified when entered into AQS based on the laboratory policy.

Sample data for Tier I VOCs for which the ICAL criteria are not met (and cannot be reanalyzed against a valid ICAL) are to be invalidated (Null Qualifier EC indicating critical criteria failure) when reported to AQS. Sample data for non-Tier I VOCs for which the ICAL criteria are not met are to be qualified (QA Qualifier LJ indicating values are estimated) when reported to AQS.

4.2.8.6 Quality Control. Sample data for Tier I VOCs for which SSCVs and/or CCVs do not meet criteria (i.e., cannot be reanalyzed with passing QC) are to be invalidated (Null Qualifier EC indicating failure of critical criteria) when reported to AQS. Sample data for non-Tier I VOCs for which SSCVs and/or CCVs do not meet criteria are to be qualified (QA Qualifiers LJ, LL, or LK indicating the value is estimated, value is estimated with low bias, or value is estimated with high bias, respectively) when reported to AQS.

4.2.8.6.1 Second Source Calibration Verification. Following each successful ICAL, a SSCV standard is analyzed to verify the ICAL for minimally each Tier I VOC and for a representative of other non-Tier I VOCs (as described in Section 4.2.6.1.2). The SSCV standard is prepared as described in Section 4.2.7.4. The Tier I VOCs in the SSCV standard must recover < ±30.1% of the theoretical concentration and non-Tier I VOCs should meet this criterion.

4.2.8.6.2 Continuing Calibration Verification Standard. Each day of analysis, the operator will verify that the system continues to meet sensitivity and quantitation criteria for each target VOC prior to analyzing samples. This is accomplished by establishing a new ICAL as described in Section 4.2.8.5 or may be satisfied by analysis of a CCV standard if an ICAL is already established. Sensitivity is based on monitoring the IS responses, and quantitation is based on comparing the measured amount of target compounds to the theoretical nominal amount. A humidified CCV standard is prepared as a dilution of a certified stock standard in a canister at a concentration in the lower third of the calibration curve.

At a minimum, a CCV standard is analyzed at the beginning (unless an ICAL is performed at the beginning of the day) and end of the daily analytical sequence. Additionally, and as a best practice, it is recommended that a CCV standard be analyzed after every 10 sample analysis injections. The IS area responses for each CCV standard must meet the criteria outlined in Section 4.2.8.4.1.2 (within ±40% of ICAL average), and the quantitated concentrations of the Tier I VOCs for each CCV standard must be < ±30.1% of the theoretical concentration and this criterion should be met for non-Tier I VOCs. CCV acceptance criteria failures indicate a drift in calibration response or degradation of concentrations of target VOCs within the CCV standard.
canister, therefore corrective action should be taken to investigate and address the root cause of the CCV acceptance criteria failures, including, for example, reanalyzing the CCV (for confirmation), preparing and analyzing a new CCV standard canister, and establishing a new ICAL. If the criteria failure is due to drift in system performance requiring maintenance, analysts may need to perform system maintenance including, for example, trimming or replacing the column, cleaning MS components followed by retuning the MS, or replacing preconcentrator traps, all of which require establishing a new ICAL.

The following equation is used to calculate the percent difference of the measured concentration of each target VOC in the CCV standard (%D_{CCV}) from the theoretical nominal concentration:

\[
\% D_{CCV} = \frac{C_{CCV} - C_{\text{theoretical}}}{C_{\text{theoretical}}} \times 100
\]

where:
- \( C_{CCV} \) = measured concentration of the CCV for the target VOC (pptv)
- \( C_{\text{theoretical}} \) = theoretical nominal concentration of the CCV for the target VOC (pptv)

Alternatively, percent recoveries may be calculated and must be between 69.9% and 130.1%. To calculate percent recovery:

\[
\% \text{Recovery}_{CCV} = \frac{C_{CCV}}{C_{\text{theoretical}}} \times 100
\]

where:
- \( C_{CCV} \) = measured concentration of the CCV for the target VOC (pptv)
- \( C_{\text{theoretical}} \) = theoretical nominal concentration of the CCV for the target VOC (pptv)

### 4.2.8.6.3 Blank Analyses

Blank analyses are negative QC samples that confirm that the analytical system and reagent gases are suitably clean and free of interferences. Analysis of blanks should demonstrate each target compound is \( \leq 20 \) pptv and must demonstrate that Tier I VOCs are \( \leq \) MDL MQO and \( \leq 3 \times \) MDL or 0.030 ppbv, whichever is lower.

#### 4.2.8.6.3.1 Instrument Blank

IBs are strongly recommended and should be analyzed following the daily tune check procedure and prior to analysis of the ICAL and/or daily CCV standard as a preliminary demonstration that the carrier gas and instrument system (preconcentrator, GC, and MS detector) shows acceptably low levels of target VOCs and potential interferences. Target VOCs should be ideally \( \leq 0.02 \) ppbv and should not exceed 0.030 ppbv. Sample data associated with an IB exceeding 0.030 ppbv for a given target VOC are to be qualified (QA Qualifier LB indicating lab blank above limits) when reported to AQS. The IB is a preconcentration analysis cycle performed where the preconcentration steps are taken without introduction of diluent (e.g., HCF zero air or ultrapure nitrogen) or sample gas into the preconcentrator. Preconcentration traps are desorbed and swept with carrier gas to the GC to evaluate contaminants within the preconcentrator sample introduction and concentration pathways. ISs should be included in this injection to ensure proper quantitation of contaminants and to aid in conditioning the IS lines and introduction loop.
4.2.8.6.3.2 Method Blank

A laboratory MB is to be analyzed at least once in each daily analytical sequence. The MB not only indicates possible laboratory contamination but also fully verifies that target VOCs and potential interferences are acceptably low in the system as a whole. The MB consists of a canister filled with humidified (~40% to 50% RH) clean diluent gas and is analyzed via the same instrument method as the standards and field samples in the analytical sequence (i.e., if 250 mL of field sample are typically analyzed, the MB analysis volume will also be 250 mL). Negative QC samples created with dilution gas and shown to be acceptably clean (e.g., dilution blank) can serve as the MB.

The MB is analyzed following the ICAL (and prior to the SSCV) or beginning daily CCV standard to demonstrate acceptably low carryover in the analytical system prior to analysis of field collected samples. The MB will show that Tier I VOCs are ≤ MDL MQO and ≤ 3xMDL or 0.030 ppbv, whichever is lower, and all target VOCs should be ideally ≤ 0.020 ppbv. Sample data in the analysis batch associated with a MB exceeding 0.030 ppbv for a given target VOC are to be qualified (QA Qualifier LB indicating lab blank above limits) when reported to AQS. Field collected samples with expected high concentrations of target VOCs may be followed by one or more MB injections to flush the analytical system (though this is expected to be rare for ambient air samples). In such instances where a blank is used to clean the instrument, additional MB aliquots should be run until the instrument is demonstrated to be acceptably clean to ensure carryover does not impact subsequent analyses.

4.2.8.6.3.3 Dilution Blank

A dilution blank (DB) is prepared with each set of standard canisters prepared for an ICAL. The DB is a canister filled with the humidified (~40% to 50% RH) clean diluent gas. Note that it is not recommended that the DB be prepared from the dilution system as it is difficult to properly flush dilution systems sufficiently to eliminate potential low-level carryover, and that the purpose of the DB is to demonstrate that the diluent gas is sufficiently clean such that all target VOCs do not impart positive bias to the calibration. The DB is analyzed via the same instrument method as standards and field samples when the ICAL is established. The typical analysis volume is to be analyzed (i.e., if 250 mL of field sample are typically analyzed, the DB analysis volume will also be 250 mL). The DB may also serve as the MB if shown to be acceptably clean. The DB will show that Tier I VOCs are ≤ MDL MQO and ≤ 3xMDL or 0.030 ppbv, whichever is lower, and all target VOCs should be ideally ≤ 0.020 ppbv.

If measured concentrations above 0.020 ppbv are attributable to the dilution gas, and not the canister or other components within the instrument, enhancement of the lower concentration standards is anticipated which will result in measurement errors in the low concentration range that will typically result in underestimation of the concentration in samples not containing dilution gas (i.e., field collected samples). Analysts are encouraged to take steps to perform additional scrubbing or cleanup on dilution gas to eliminate such background.
4.2.8.6.4 Method Precision. Precision of the method can be assessed by analysis of collocated or duplicate samples as well as with replicate sample analyses. Calculate the precision of pairwise precision measurements according to Section 2.1.3.1.

Acceptable precision analyses will demonstrate RPD < 25.1% for each target analyte when at least one of the measurements in the precision pair is ≥ 5-fold the MDL. Failure to meet this criterion must prompt the analyst to investigate the reason for the discrepancy which may involve review of sample collection records. Associated ambient sample measurements are to be qualified (QA Qualifier QX indicating QC failure and LJ indicating the value is estimated) when reported to AQS (note that AQS does not permit addition of QA qualifiers for AQS QA transactions, therefore qualifiers are to be added to AQS RD transactions, as appropriate).

4.2.8.6.4.1 Field Sample Precision

Precision of the method inclusive of the field collection activities is evaluated through measurements of collocated or duplicate samples, as defined in Section 4.2.2.1.

4.2.8.6.4.2 Replicate Analysis

Replicate analyses are used to demonstrate precision of the instrumental analysis and do not provide information on field-sampling precision. Each analysis sequence will minimally include replicate analysis of a field-collected sample. Replicate analysis pairs for which the precision criterion is exceeded require that sample results within that analytical sequence be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS. The analyst should troubleshoot the instrument and reanalyze the sequence to confirm the precision criterion exceedance. If reanalysis demonstrates appropriate replicate analysis precision, qualification is not needed.

4.2.8.6.5 Ambient Air Check. Several of the target chlorofluorocarbon VOCs are ubiquitous in ambient air due to their long half-life in the atmosphere. These compounds include trichlorofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), carbon tetrachloride, and 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114). The National Oceanic and Atmospheric Administration (NOAA) periodically updates the global background concentrations of these compounds, which can be queried at the NOAA halocarbon website, [https://www.esrl.noaa.gov/gmd/hats/](https://www.esrl.noaa.gov/gmd/hats/). Analysts can compare their measured concentrations of these analytes in ambient air samples to the values reported by NOAA to increase confidence in the representativeness of the field-collected sample and in the precision, accuracy, and sensitivity of the collection and analysis methods. However, this evaluation must not serve as the sole basis for invalidation of sample data.

4.2.9 Method Detection Limits. MDLs for VOCs must be determined per the guidance in Section 4.1, which details the MDL determination process generally for the NATTS program. This section will briefly provide details for determining the MDL for VOCs measurements by GC-MS.

The MDL procedure in Section 4.1 prescribes preparing and analyzing MDL spikes and MBs for determining an initial MDL and for collecting ongoing data for MDL verification. MDLs must
be determined following the procedure in 4.1.3.1 unless there is a sufficient number \((n \geq 7)\) of MBs in which the specific target analyte has been detected (positively identified and meet qualitative identification criteria listed in Section 4.2.11), in which case the procedure in Section 4.1.3.2 may be employed. ASLs should closely review the requirements in Section 4.1.3.1.1.4 to evaluate whether previously collected MDL spike data and MB data meet the requirements for calculating an initial and ongoing MDL. If the previously collected data do not meet the specified criteria, the initial MDL must be determined as detailed in Section 4.1.3.1.1.

As practical, ASLs should employ a variety of canisters (silicon-ceramic lined and electropolished) in their fleet to prepare the MDL spikes and MBs to best characterize variability of measurements attributable to the variation in the canister fleet. For each of the individual MDL spike and MB measurements, these are to be discrete canisters and data from the same canister can only be included in the calculations when analyzed on a separate instrument (when more than one instrument is employed).

While the MDL capabilities of each laboratory may vary due to a number of factors (canister hygiene, condition of equipment, cleanliness of diluent gases, etc.), spiking concentrations of individual target VOCs of a range of approximately 0.01 to 0.05 ppbv should facilitate evaluation of the MDLs in concentrations approximating the MDL MQOs.

Determining VOC MDLs will typically involve preparing MDL spiked samples at several concentrations to ensure that VOCs of different sensitivities (i.e., the concentration corresponding to a signal to noise ratio of 5:1) are adequately captured. For example, the ASL may be successful in determining the MDL for carbon tetrachloride with an MDL spike level of 0.012 ppbv; however, may need to prepare MDL spikes at 0.025 ppbv for vinyl chloride.

All steps performed in the preparation and analysis of field sample canisters (such as dilution) are to be included in the MDL procedure. Canisters must be prepared at the selected spiking concentration with humidified HCF zero air diluent gas. It is not appropriate to prepare a higher concentration spike and analyze a smaller aliquot than analyzed for field collected samples. For example, for laboratories which analyze 500 mL of field collected sample, a spike concentration of 0.06 ppbv is chosen. The spiked canisters must then be prepared at 0.06 ppbv with humidified HCF zero air and 500 mL analyzed. It would not be acceptable for the laboratory to prepare spikes at 0.30 ppbv and analyze only 100 mL of the sample (for an effective five-fold dilution) as this would not be representative of the analysis procedure for field collected samples.

Determined MDLs for Tier I core analytes must meet (be equal to or lower than) the MDL MQO values listed in the most current workplan template, available at the air toxics monitoring section on EPA’s AMTIC: https://www.epa.gov/amtic/air-toxics-ambient-monitoring#natts

4.2.10 Sample Analysis. Field-collected samples are analyzed using the same instrument and acquisition methods as for blanks and standards; the preconcentrator operation parameters, GC oven program, MS parameters, calibration, and integration methods will be identical. Field-collected samples, laboratory blanks, and QC standards are equilibrated to ambient laboratory temperature prior to analysis. A typical sample aliquot volume is used for all samples.
Adjustment of this sample aliquot volume requires adjustment of a dilution factor to account for the difference in relative analyzed volume, as discussed in Section 4.2.10.2.

4.2.10.1 Analytical Sequence. Prior to starting an analytical sequence, the operator should conduct a thorough system bakeout per the manufacturer’s instructions for the preconcentrator and also ramp the GC column temperature. This readies the instrument system by effectively removing any accumulated impurities in the analytical system. An IB (as discussed in Section 4.2.8.6.3.1) or a BFB tune check (as discussed in Section 4.2.8.3.3.2) accomplishes this as well. An air/water check of the MS also should be performed according to the manufacturer’s specification prior to any analyses to ensure that the system is acceptably leak-free. An MB (discussed in Section 4.2.8.6.3.2) should be analyzed before beginning the analysis of the calibration standards and will meet the acceptance criteria described in Section 4.2.8.6.3.2. Once these checks meet criteria (summarized in Table 4.2-6), the instrument may be calibrated by establishing the ICAL (as discussed in Section 4.2.8.5) or the calibration verified by analysis of a CCV.

The recommended GC-MS analytical sequence is as follows:

1. Ready the system for subsequent analysis by verifying/optimizing the MS tune as per Section 4.2.8.3.3 (perform and air/water check, bake out the system, verify the MS tune).
2. Analyze an IB.
3. Analyze the calibration standards to establish the ICAL or analyze a CCV standard to verify the calibration.
4. Analyze a SSCV (required after ICAL, recommended after CCV).
5. Analyze a MB.
6. Analyze field samples and additional CCV standards and MBs to complete the sequence, ending with a CCV, as discussed in Section 4.2.8.6.2. CCVs and MBs are recommended after every 10 sample analyses.

4.2.10.2 Sample Introduction. Instrument manufacturers offer various configurations for sample introduction ports on the preconcentrator. These configurations may consist of a series of ports on a manifold, with each port connected through a rotary valve, solenoid valve, or other means that permits connection and isolation of sample canisters.

It is critical that the sample aliquot volume be accurately measured for analysis. This can be accomplished by metering the sample with an MFC or with the combination of a fixed-volume vessel and a pressure transducer. Sample introduction volume measurements must be consistently reproducible to ensure that analyzed volumes of samples and standards are precise. While absolute accuracy is not critical, that the metering system operates reproducibly, linearly, and proportionally is critical, particularly for instruments employing analysis of differing volumes of standards to establish calibration or analysis of differing volumes of sample to prepare effective dilutions. Users should follow manufacturer procedures for demonstrating linear and proportional volume metering of gases for preconcentration. For users of the method performing effective dilutions, once the measurement system is demonstrated to perform linearly and proportionally, the system should be demonstrated to similarly perform linearly for
concentration response for the target VOCs. This demonstration is important to validate the linearity of the instrument response as the target compounds penetrate to different degrees into the trap sorbent beds as a function of the sampled volume and amount of moisture in the sample and accordingly demonstrate different adsorption/desorption properties. This linear target compound response can be accomplished by establishing a calibration as discussed in the first bullet under Section 4.2.8.5.1 by performing an effective dilution of the high calibration standard covering the volume range used (e.g., 20 to 250 mL) and examining the linearity of compounds covering the volatility range of target analyte suite. This demonstration then validates the effective dilution is appropriate.

4.2.10.2.1 Leak Check of Preconcentrator Connections. Prior to beginning an analytical sequence, including an ICAL sequence, each canister connection must be verified as leak-free through the preconcentrator. During the leak check, canisters are connected to ports on the autosampler or other sample introduction port and the canister valves are kept closed. Each port is evacuated and isolated and the pressure monitored over 30 seconds to 1 minute for a change in pressure. Pressure changes of < 3.4 kPa/min (0.5 psi/min) are generally acceptable; however, no change in pressure is preferable. Should a canister/port fail exceed this criterion, a typical corrective action includes tightening the fittings then retesting. If leaks persist, then other troubleshooting measures should be undertaken as per the manufacturer’s recommendations. Leak check criteria in automated leak check routines should be equivalent to or better than those listed above. Analysis must not be performed using any canister connection that does not pass the leak check. Canisters that do not pass the leak check may leak to atmospheric pressure, allowing laboratory air into the analyzed sample stream. Many preconcentration control software systems include a leak check function that provides standard QC reports. Following the leak check, all autosampler ports or sample introduction lines are evacuated and the canister valves are opened. Leak check results are to be documented in the analysis records. If canisters failing leak check are analyzed, results are to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

4.2.10.2.2 Sample Dilution. Field-collected samples may require dilution to ensure sufficient gas volume in the canister to remove an aliquot for analysis (for subambient pressure samples) or may require dilution when measured concentrations of target analytes exceed the calibration curve.

Sample Dilution to Achieve Sufficient Pressure: Canister samples collected at subambient pressures may require pressurization with HCF zero air or UHP nitrogen to provide sufficient pressure for removing an aliquot from the canister for analysis. When such dilution is performed, the diluent gas will be collected in a separate certified clean canister as a dilution blank (DB) or by directly plumbing to the instrument preconcentrator and analyzed to ensure that the dilution process does not contaminate collected samples.

The canister pressure will be measured with a calibrated pressure gauge or pressure transducer just prior to dilution and immediately following dilution. A canister dilution correction factor (CDCF) is calculated from the two absolute pressure readings as follows:
\[
\text{CDCF} = \frac{P_d}{P_i}
\]

where:

- \( P_d \) = The pressure of the canister following dilution (psia)
- \( P_i \) = The pressure of the canister immediately preceding dilution (psia)

Diluted canisters should be allowed to equilibrate minimally overnight, and preferably 24 hours before analysis.

**Sample Dilution for Measurements Exceeding the Calibration Range:** If the on-column concentration of a target VOC in a sample exceeds the calibration range, the sample should be diluted for reanalysis. A dilution can be performed either by reducing the sample aliquot volume for an effective dilution or by adding diluent gas to the sample canister to physically dilute the sample. To select an appropriate dilution factor, the analyst should estimate the concentration of the sample requiring dilution and aim to have diluted concentrations fall into the upper third of the calibration range (e.g., 3500 pptv for a calibration with a 5000 pptv high standard). The dilution factor is then equal to the estimated concentration divided by this desired diluted concentration.

It is recommended that an effective dilution be used first, if an appropriate dilution factor can be achieved. This eliminates the need to add diluent gas to the canister. Note that this dilution method is limited by the ability of the preconcentrator to accurately extract smaller volumes from the canister. For some preconcentrators this lower limit is approximately 20 mL. For example, if an analyst needs to perform a 10-fold dilution on a sample and the typical injection volume is 250 mL, the analyst would reduce the analyzed volume to 25 mL. If more dilution than 10-fold was necessary, physical dilution of the canister sample with diluent gas may be necessary in combination with effective dilution, as described above in this section. If a 30-fold dilution was needed, for example, a two-fold physical dilution (doubling the sample pressure) would be suggested, followed by a 15-fold effective dilution. These dilution factors are multiplied to calculate the total dilution factor. Refer to Section 4.2.12 for resulting sample concentration calculations.

**4.2.11 VOCs Identification.** Target VOCs are identified based on their RT and the relative abundance of their characteristic ions from the MS.

Four criteria must be met to positively identify a target compound qualitatively:

1. The RT of the compound must be within the RT window of ±2 s as determined from the ICAL average.
2. The relative abundance ratio of qualifier ion response to target ion response for at least one qualifier ion must be < ±30.1% of the average relative abundance ratio from the ICAL.
3. The signal to noise ratio of the target and qualifier ions must be > 3:1, preferably > 5:1.
4. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other).23
Figure 4.2-5 shows an example of the qualitative identification criteria listed above. The RT is within the RT window defined by the method (red box A), and the relative abundance ratios of the qualifier ions are $< \pm 30.1\%$ of the ICAL average relative abundance ratio (red box B). The signal to noise ratio of the peak is shown to be greater than 5:1 (red oval C), and the target and qualifier ion peaks are co-maximized (dotted purple line D).

Note that it is critical that ion abundance ratios are relative to the average relative abundances established with the ICAL. Incorrectly assigning abundance ratios as absolute abundance percentages will lead to improperly wide or narrow acceptance ranges. Improperly wide acceptance ranges may include an abundance ratio of 0%, which the CDS may show as an acceptable identification though the qualifier ion may not in fact be present. For the example in Figure 4.2-5, the average relative abundance of m/z 49 and 86 are 139.8% and 64.4%, respectively. Calculating lower and upper relative abundance ranges based on these averages and tolerances of 30% relative abundance results in acceptance ranges of 97.9% to 181.7% and 45.1% to 83.7%, respectively.

Refer to Figure 4.2-6 for the following example for determining the signal to noise ratio. To determine the signal to noise ratio, the characteristic height of the noise of the baseline (A) just before the peak and the height of the analyte peak (B) are measured. The ratio of the analyte peak height (B) is divided by the noise height (A) to calculate the signal to noise ratio. In the example, the peak at 17 min is discernable from the noise, but is not well resolved and is very close to a signal to noise ratio of 3. In the example, the peak heights of the noise and the analyte peaks (at approximately 17 min) are approximately 700 units and 1700 units, respectively, for a signal to noise ratio of 2.4. Analysts may choose instead to determine the signal to noise ratio by
determination of the average area of a selected portion of the chromatogram characteristic of the noise (e.g., 0.2 minutes before the target peak) and the area of the target peak.

Figure 4.2-6. Determination of Chromatographic Peak Signal-to-Noise Ratio

Determining the signal to noise ratio is somewhat subjective based on an individual analyst’s characterization of the noise and analyte peak. Some chromatography data systems/software programs include signal to noise ratio functions that require the analyst to assign the noise range in the chromatogram and target peak. For well-resolved peaks, the signal to noise ratio will greatly exceed 5:1 and does not need to be measured. For peaks with low signal to noise ratio that are questionable as to whether they meet criterion 3 above, the 3:1 signal to noise ratio is only a guideline; it is unnecessary to measure each peak, and the experienced analyst’s opinion should weigh heavily on whether the peak meets the signal to noise ratio criterion.

As with the signal to noise ratio determination, evaluation of whether target and qualifier ion peaks are co-maximized does not need to be rigorously evaluated with each peak. Rather interpretation by an experienced analyst is sufficient for deciding whether the qualifier ion peaks are co-maximized with the target ion.

Evaluation of criteria 1 (retention time) and 2 (relative ion abundances) above may be automated by the analytical data system such that they are automatically qualified (flagged) when exceeded. Such automation reduces the time required for analyst data review; however, it is important that the RT windows and ion abundances be updated with each new ICAL.

If any of the four criteria are not met, the compound cannot be positively identified. The only exception to this is when the compound is positively identified in the opinion of an experienced analyst. The rationale for such exceptions must be documented and should be subject to review and concurrence by a technical peer reviewer. Such an instance may occur for asymmetrical peaks when the peak apex RT shifts with concentration or due to matrix changes (humidity) from those of the ICAL. In such cases, the RT is assigned as the peak apex, and provided a portion of the peak elutes within the defined RT window and the relative abundance criteria for the
qualifier ion(s) are within the defined range, the analyst may justify the peak’s identification (with documented rationale). Note that in some instances of large peaks where the detector response is saturated or close to saturation, the relative ion abundances may not fall within the < ±30.1% range. Such peaks typically require dilution of the sample and reanalysis. If the abundance criterion is not met and the sample cannot be reanalyzed, the experienced analyst’s opinion should be considered for compound identification.

4.2.12 VOCs Quantitation. Quantitation of the target VOC concentration is performed by comparing the peak area response of the selected characteristic target ion (typically the base peak, or most abundant, ion) to the established calibration curve for the target VOC. Characteristic ions are shown in Table 1-1 of Method TO-15A and can be found in NIST mass spectral libraries (https://chemdata.nist.gov/).

Each chromatogram should first be closely examined to ensure chromatographic peaks are appropriately resolved and integration does not include peak shoulders or inflections indicative of a coelution. Additionally, analysts should review chromatograms to investigate chromatographic peaks that were improperly integrated by the CDS software or target analytes whose peaks may have been overlooked and not properly identified. Additional guidance on chromatographic peak integration can be found in Appendix D.

Concentrations of target compounds detected in the analyzed aliquot are quantitated by relating the area response ratio of each target compound and assigned IS in the unknown sample to the area response ratio from the established calibration curve.

**Average RRF (RRF):**

\[
C_D = \frac{A_T \cdot C_{IS}}{A_{IS} \cdot RRF}
\]

where:
- \(C_D\) = instrument-detected analyte concentration (pptv)
- \(A_T\) = area response of target compound quantitation ion
- \(C_{IS}\) = concentration of assigned IS (pptv)
- \(A_{IS}\) = area response of assigned IS quantitation ion
- \(RRF\) = average RRF from the ICAL

**Linear Regression Calibration Model:**

\[
C_D = \left(\frac{A_T - b}{A_{IS}}\right) \cdot C_{IS}
\]

where:
- \(C_D\) = instrument-detected analyte concentration (pptv)
- \(A_T\) = area response of target compound quantitation ion
- \(C_{IS}\) = concentration of assigned IS (pptv)
- \(A_{IS}\) = area response of assigned IS quantitation ion
- \(m\) = slope of linear least-squares regression curve
- \(b\) = y-intercept of the linear least-squares regression curve
 Quadratic Regression Calibration Model:

\[ C_D = \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot \left( c - \frac{A_t}{A_{IS}} \right)}}{2a} \cdot C_{IS} \]

where:
- \( C_D \) = instrument-detected analyte concentration (pptv)
- \( A_t \) = area response of target compound quantitation ion
- \( C_{IS} \) = concentration of assigned IS (pptv)
- \( A_{IS} \) = area response of assigned IS quantitation ion
- \( a \) = quadratic coefficient of the quadratic least-squares regression curve
- \( b \) = linear coefficient of the quadratic least-squares regression curve
- \( c \) = constant of the quadratic least-squares regression curve

If an aliquot is analyzed from the sample canister that is different than the typical analysis volume (as described in Section 4.2.10.2.2 for performing effective dilution), an instrument dilution correction factor (IDCF) is calculated:

\[ \text{IDCF} = \frac{V_{\text{nom}}}{V_{\text{inj}}} \]

where:
- \( V_{\text{nom}} \) = nominal volume of sample injected (typical volume analyzed)
- \( V_{\text{inj}} \) = volume of sample injected

The final concentration of each target compound in air is determined by multiplying the instrument-detected concentration by the CDCF and the IDCF:

\[ C_F = C_D \cdot \text{CDCF} \cdot \text{IDCF} \]

where:
- \( C_F \) = concentration of the target compound in air (pptv)
- \( C_D \) = concentration measured at the instrument (pptv)
- CDCF = canister dilution correction factor (refer to Section 4.2.10.2.2)
- IDCF = instrument dilution correction factor

*Note: The MDL reported with the final concentration data will be corrected by multiplying the MDL by the CDCF and IDCF applied to the sample concentrations. For example, if the benzene MDL is 9.1 pptv for an undiluted sample and the sample was diluted by 2.5, the reported MDL is 23 pptv.*

**4.2.13 Summary of Quality Control Parameters.** A summary of QC parameters is shown in Table 4.2-6.
### Table 4.2-6. Summary of Quality Control Parameters for NATTS VOCs Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument Blank (IB)</td>
<td>Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean to begin analysis</td>
<td>Prior to ICAL and daily beginning CCV</td>
<td>Each target VOC’s concentration preferably &lt; 0.020 ppbv but may not exceed &lt; 3x MDL or 0.030 ppbv, whichever is lower</td>
</tr>
<tr>
<td>MS Tuning</td>
<td>Establishment and verification of the MS tune according to the MS manufacturer instructions. May be accomplished for linear quadrupole MS instruments by analysis of 50 ng BFB</td>
<td>Prior to initial calibration and strongly recommended every 24 hours of analysis thereafter</td>
<td>Tuning criteria established by manufacturer must be met</td>
</tr>
<tr>
<td>Initial Calibration (ICAL)</td>
<td>Analysis of a minimum of five calibration levels covering approximately 0.03 to 5 ppbv, if quadratic curve modeling is desired, minimum of eight levels is recommended</td>
<td>Initially, following failed tuning verification, failed CCV, or when changes/maintenance to the instrument affect calibration response</td>
<td>Average RRF &lt; 30.1% RSD and each calibration level must be &lt;= ±30.1% of theoretical nominal. For quadratic or linear curves, r ≥ 0.995, each calibration level must be &lt;= ±30.1% of theoretical nominal</td>
</tr>
<tr>
<td>Second Source Calibration Verification (SSCV)</td>
<td>Analysis of a second source standard at a concentration approximately the mid-range of the calibration curve for minimally each Tier I VOC and a representative compound of each calibrated target VOC (recommended all target VOCs) to verify ICAL accuracy</td>
<td>Immediately after each ICAL and recommended after each CCV</td>
<td>Recovery &lt;= ±30.1% of theoretical nominal or RRF &lt;= ±30.1% of the mean ICAL RRF</td>
</tr>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>Analysis of a known standard at a concentration in the lower third of the calibration range for each calibrated target VOC to verify ongoing instrument calibration</td>
<td>Every 24 hours of analysis; recommended after each ten sample injections and to conclude each sequence</td>
<td>Recovery &lt;= ±30.1% of theoretical nominal or RRF &lt;= ±30.1% of the mean ICAL RRF</td>
</tr>
<tr>
<td>Canister Cleaning Batch Blank</td>
<td>Canister selected for analysis from a given batch of not more than 8 clean canisters to ensure acceptable background levels in the batch of cleaned canisters. Recommend more than 1/8 canisters per batch and best practice is to analyze all clean canisters for verification.</td>
<td>One canister from each batch of cleaned canisters – Canister chosen must represent no more than 8 total canisters</td>
<td>Each target VOC’s concentration &lt; 3x MDL or 0.030 ppbv, whichever is lower at equivalent to ambient standard pressure (760 mmHg) All Tier I Core analytes must meet this criterion</td>
</tr>
<tr>
<td>Internal Standards (IS)</td>
<td>Deuterated isotopes or not naturally occurring compounds co-analyzed with samples to monitor instrument response and assess matrix effects</td>
<td>Added to all analyzed canisters (i.e., calibration standards, QC samples, and field-collected samples)</td>
<td>Area response for each IS compound &lt;= ±40.1% of the average response of the ICAL</td>
</tr>
<tr>
<td>Preconcentrator Leak Check</td>
<td>Pressurizing or evacuating the canister connection to the preconcentrator to verify as leak-free</td>
<td>Each standard and sample canister connected to the instrument</td>
<td>&lt; 0.2 psi change/minute or equivalent manufacturer recommendations</td>
</tr>
</tbody>
</table>
### Table 4.2-3. Summary of Quality Control Parameters for NATTS VOCs Analysis (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method Blank (MB)</td>
<td>Canister filled with clean diluent gas</td>
<td>One with every analysis batch of 20 or fewer field-collected samples</td>
<td>Each target VOC’s concentration preferably &lt; 0.020 ppbv but may not exceed 3x MDL or 0.030 ppb, whichever is lower</td>
</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>Canister spiked with known amount of target analyte at approximately the lower third of the calibration curve</td>
<td>(Recommended) One with every analysis batch of 20 or fewer field-collected samples</td>
<td>Each target VOC’s recovery must be 69.9 to 130.1% of its theoretical nominal spiked amount</td>
</tr>
<tr>
<td>Duplicate Sample</td>
<td>Field sample collected through the same inlet probe as the co-collected primary sample</td>
<td>10% of primary samples for sites performing duplicate sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 25.1% RPD of primary sample when the concentration in at least one of the precision pair is ≥ 5x MDL</td>
</tr>
<tr>
<td>Collocated Sample</td>
<td>Field sample collected through a separate inlet probe from the co-collected primary sample</td>
<td>10% of primary samples for sites performing collocated sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 25.1% RPD of primary sample when the concentration in at least one of the precision pair is ≥ 5x MDL</td>
</tr>
<tr>
<td>Replicate Analysis</td>
<td>Replicate analysis of a field-collected sample (chosen by analyst)</td>
<td>Once with every analysis sequence (as prescribed in QAPP)</td>
<td>Precision &lt; 25.1% RPD of initial sample analysis when the concentration in at least one of the precision pair is ≥ 5x MDL</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>RT of each target compound and internal standard</td>
<td>All qualitatively identified compounds and internal standards</td>
<td>Target VOCs and ISs must be within ±2s of the average ICAL RT</td>
</tr>
</tbody>
</table>

### 4.2.14 References


7. NATTS Implementation Plan for Ethylene Oxide Measurement. EPA Office of Air Quality Planning and Standards. June 27, 2019


15. EPA NATTS Proficiency Testing Results Calendar Year 2016 Quarter 1 – Referee Results from EPA Region V


18. Carl R. (Rod) Nave, Department of Physics and Astronomy, Georgia State University. Atlanta, Georgia 30302-5060, available at: (accessed June 2022): [http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/rellhum.html#c3](http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/rellhum.html#c3)


4.3 Carbonyl Compounds via EPA Compendium Method TO-11A

Each NATTS monitoring agency and supporting ASL will prescribe in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for collection of airborne carbonyls onto cartridges, extraction of the cartridges, and analysis of the extracts. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.3.10 must be met.

4.3.1 General Description of Sampling Method and Analytical Method. Carbonyl compounds such as aldehydes and ketones are collected and analyzed via EPA Compendium Method TO-11A. The atmosphere to be characterized is drawn at a known flow rate for a known duration of time through a heated ozone denuder and through a silica gel sorbent cartridge coated with DNPH, where the carbonyl compounds react with the DNPH and are derivatized to form carbonyl-hydrazones. These carbonyl-hydrazones are solids at typical ambient temperatures and are retained on the cartridge sorbent bed until eluted with ACN. Eluted extracts are analyzed by HPLC with an ultraviolet (UV) detector at a wavelength 360 nm.¹

The carbonyls including, but not limited to, those in Table 4.3-1 may be determined by this method.

Table 4.3-1. Carbonyl Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-11A

<table>
<thead>
<tr>
<th>Target Carbonyl</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetaldehyde</td>
<td>75-07-0</td>
</tr>
<tr>
<td>acetone</td>
<td>67-64-1</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>100-52-7</td>
</tr>
<tr>
<td>butyraldehyde</td>
<td>123-72-8</td>
</tr>
<tr>
<td>crotonaldehyde</td>
<td>4170-30-3</td>
</tr>
<tr>
<td>2,5-dimethylbenzaldehyde</td>
<td>5779-94-2</td>
</tr>
<tr>
<td>formaldheyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>heptaldehyde</td>
<td>111-71-7</td>
</tr>
<tr>
<td>hexaldehyde</td>
<td>66-25-1</td>
</tr>
<tr>
<td>isovaleraldehyde</td>
<td>590-86-3</td>
</tr>
<tr>
<td>m&lt;p-tolualdehyde</td>
<td>(m) 620-23-5/(p) 104-87-0</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>78-93-3</td>
</tr>
<tr>
<td>methyl isobutyl ketone</td>
<td>108-10-1</td>
</tr>
<tr>
<td>o-tolualdehyde</td>
<td>529-20-4</td>
</tr>
<tr>
<td>propionaldehyde</td>
<td>123-38-6</td>
</tr>
<tr>
<td>valeraldehyde</td>
<td>110-62-3</td>
</tr>
</tbody>
</table>

¹ NATTS required Tier I analytes  
² NATTS PT analytes

In 2014 EPA commissioned a study to evaluate and, to the extent possible, optimize the performance of Method TO-11A.² This study was completed in 2019 and a draft final report was delivered to EPA in June 2021. The primary goal of the study was the determination of the collection efficiency of formaldehyde, acetaldehyde, propionaldehyde, and benzaldehyde at various flow rates and RH conditions onto the two commercially-available DNPH cartridges.
commonly employed in the NATTS network. Study outcomes demonstrated collection efficiencies are strongly dependent on the target carbonyl, the RH of the sampled atmosphere, and the type of DNPH cartridge employed. Three important outcomes were that collection efficiencies were independent of sampling flow rates between 0.25 to 1.25 L/min; formaldehyde and acetaldehyde MDL MQOs are attainable when sampling at 1 L/min, despite observed cartridge blank levels; and collecting a second cartridge in series was of negligible benefit (breakthrough was modest). The study solely investigated aldehyde compounds and did not investigate the performance of other carbonyls such as acrolein or ketones. The forward reaction of ketones such as acetone and 2-butanone with DNPH are not as favored as those for formaldehyde and acetaldehyde \(^1\), therefore collection efficiency of ketones is not anticipated to be as high.

4.3.2 Minimizing Bias in Measuring Carbonyls. Many of the limitations of the method are known; therefore, practices and procedures are recommended here to maximize collection efficiency and minimize interferences that degrade sample collection performance, degrade collected samples, and impact analysis separation and detection. Nitrogen oxides react with DNPH to form compounds which are extracted from the cartridge and may coelute with target carbonyl-hydrazones during HPLC analysis. Moreover, ozone reacts with DNPH to form possible coeluting interferences and also reacts with and causes negative bias in the measurement of various carbonyl-hydrazones that have been collected onto a sampled cartridge. (More information on ozone management is given in Section 4.3.4.) To minimize introduction of contamination and to keep bias to a minimum, manage ozone per Section 4.3.4 and handle cartridge media as in Section 4.3.5.2. Decontaminate labware and select high-purity reagents as in Section 4.3.9. Qualifications of sampling units to be acceptably non-biasing is discussed in Section 4.3.7.1.1.

The cartridge inlet and outlet caps must be installed when the cartridge is not in use for sampling or extraction so as to isolate it from the ambient atmosphere where carbonyl compounds and interfering compounds may be passively sampled. Further, cartridges must be stored sealed in the foil pouch or similar opaque container, as light may degrade the DNPH derivatives. Finally, DNPH cartridges must be stored at \(\leq 4^\circ\text{C}\) after sampling as such slows the reaction of contaminants or loss of collected derivatized carbonyls. Handling of cartridges after using personal care products such as lotions and hand sanitizers as well as use of solvent-containing markers (such as permanent markers) can contaminate DNPH cartridge media before, during, and after sample collection. Cartridges should only be handled while wearing powder-free nitrile or vinyl gloves and only non-solvent writing implements (e.g., ballpoint pens) or stickers should be used for labeling samples.

4.3.3 Carbonyls Measurement Precision

4.3.3.1 Carbonyls Sampling Precision. Depending on the configuration of the sampling unit or units at the monitoring site, sampling precision may be assessed by way of the collection and analysis of collocated or duplicate sample cartridges. Sampling precision is a measure of the reproducibility in the sampling, handling, extraction, and analysis procedures. Monitoring agencies are encouraged to collect collocated and duplicate samples; however, this is not required (the NATTS network goal is that 10% of monitoring sites collect precision samples –
collocated or duplicate samples). For monitoring sites collecting collocated and/or duplicate samples (as detailed in each site’s QAPP), they are to be collected at a minimum frequency of ≥ 10% of primary samples (routine 1-in-6 days sampling). For a site collecting 60 or 61 primary samples annually, this is equivalent to minimally six or seven precision samples annually.

Precision is assessed by calculating the RPD for duplicate, collocated, and replicate analysis samples. The RPD is evaluated when at least one of the measurements in the precision pair is ≥ 0.5 µg/cartridge and must be < 20.1%. When both measurements in the precision pair are ≥ 0.5 µg/cartridge, the calculation is straightforward. However, for precision pairs for which one measurement is ≥ 0.5 µg/cartridge and the other is < 0.5 µg/cartridge, calculate the RPD by substituting 0.5 µg/cartridge (the threshold value) for the measurement that is < 0.5 µg/cartridge, per the convention in Section 2.1.3.1. This determination of RPD is solely for assessing precision; the concentrations measured of the precision pair are to be reported to AQS as measured.

Failure to satisfy the precision criterion will prompt root cause analysis to investigate and correct the failure. If the issue cannot be corrected satisfactorily, the associated sample data are to be qualified when entered into AQS. For example, concentration results for both measurements within a collocated or duplicate sample pair exceeding this criterion are to be qualified (QA Qualifier LJ indicating the value is estimated QA Qualifier QX indicating a QC failure) when reported to AQS (note that qualifiers can only be added to AQS RD transactions in this case and not to AQS QA transactions). Replicate analysis pairs for which the precision criterion is exceeded requires that sample results within that analytical sequence also be qualified (QA Qualifier LJ indicating the value is estimated and QA Qualifier QX indicating a QC failure) when reported to AQS (unless those samples are reanalyzed in a sequence with a passing replicate analysis pair). Please refer to the list of qualifiers in Table 3.1-1.

For replicate analysis, the ASL will typically assign a convention that the first replicate for a replicate analysis is that which is reported to AQS for the sample result. However, if the first replicate is invalidated for any reason (e.g., as may occur when a coeluting peak significantly interferes with the target peak) and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as the sample result as described in Section 2.1.3.2.

### 4.3.3.1 Collocated Carbonyls Sample Collection

A collocated sample is a precision sample for which the sampled air is drawn through an inlet probe independent from the primary sampling inlet probe and by a separate discrete sampling unit with which a sample cartridge is co-collected with the primary sample. If two cartridges are collected together with a single sampling instrument, to be collocated the air passing onto each cartridge must flow through wholly separate flow path channels, where each channel has a discrete inlet probe, flow path plumbing, and flow controller such as an MFC or rotameter. For sites which employ a manifold inlet to which one or more carbonyls sampling unit inlets is connected, this comprises a single inlet probe to the ambient atmosphere and therefore the samples co-collected with the primary sample will be designated as duplicate, as shown in Figure 4.3-1.
Figure 4.3-1. Collocated and Duplicate Carbonyls Sample Collection

More information on collocated samples is given in Section 4.3.8.2.3.

4.3.3.1.2 Duplicate Carbonyls Sample Collection. Duplicate sampling assumes that both the primary and duplicate sampling is accomplished through the same single inlet probe to the atmosphere; regardless to whether sampling units are connected to a manifold or a standalone (dedicated) inlet probe.
A duplicate sample may be collected, for example, by splitting (with a tee, or similar) the primary sample flow path onto two separate cartridges, where each cartridge has its own discrete and separate flow channel and/or flow control device (MFC, orifice, or rotameter) located within a single sampling unit. Duplicate sampling may also be accomplished by collecting a primary sample on one sampling unit and a duplicate sample on another sampling unit, where the inlets of both sampling units are connected through the same inlet probe to the atmosphere.

More information on duplicate samples is given in Section 4.3.8.2.4.

4.3.3.2 **Laboratory Precision.** Laboratory precision for field-collected carbonyls cartridges is limited to replicate analysis of a single carbonyls sample extract. Each DNPH cartridge is extracted as a discrete sample which does not permit assessing precision through the extraction process. Replicate analysis of a given extract is required with each analysis sequence and must show < 10.1% RPD when the concentration of one or both extracts is ≥ 0.5 µg/cartridge as detailed in Section 2.1.3.1.

Precision incorporating both the extraction and analysis procedures may be assessed by preparation, extraction, and analysis of duplicate LCSs. An LCS and LCS duplicate (LCSD) are to be prepared minimally quarterly, and are recommended with each extraction batch at a concentration in the lower third of the HPLC calibration range for each target analyte. The LCS/LCSD pair is to show precision of < 20.1% RPD.

4.3.4 **Managing Ozone.** Ozone is present in the atmosphere at various concentrations ranging from approximately 20 ppb at rural sites to as much as 150 ppb at peak times in urban environments. Ozone is a strong oxidant and may impact and interfere with the sampling and analysis of carbonyls in various ways. Ozone which is not removed from the sampled air stream reacts directly with the DNPH reagent thereby consuming the DNPH and making it unavailable for derivatizing carbonyl compounds, effectively reducing collection efficiency. Ozone may also react with captured carbonyl-hydrazones on the sampled cartridge to degrade these compounds, leading to underestimation of carbonyl concentrations. The byproducts of ozone reactions with carbonyl-hydrazones may also be difficult or impossible to separate chromatographically from target compounds, resulting in overestimation or false positive detection of target compounds.

In order to mitigate the impact of ozone on carbonyl measurements, an ozone denuder/scrubber must be installed in the sampling unit flow path upstream of the DNPH cartridge(s). The removal of ozone by potassium iodide (KI) is affected by the oxidation of the iodide ion to iodine in the presence of water, as follows:

\[
\begin{align*}
\text{Reaction 1} & : & O_3 & \rightarrow O_2 + O \\
\text{Reaction 2} & : & 2\text{KI} + H_2O + O & \rightarrow 2\text{KOH} + I_2 \\
\text{Net Reaction} & : & O_3 + 2\text{KI} + H_2O & \rightarrow I_2 + O_2 + 2\text{KOH}
\end{align*}
\]

Several different KI ozone scrubbers are described in the following sections; however, the heated denuder described in Section 4.3.4.1 is the only acceptable configuration for the NATTS program.
4.3.4.1 Copper Tubing Denuder/Scrubber. Method TO-11A describes an ozone denuder/scrubber and this is the only permitted ozone removal method for the NATTS Program due to its proven efficacy at ozone removal and robust performance. The scrubber is fashioned from coiled copper tubing whose interior has been coated with KI and which is heated to approximately 50°C or above to discourage water condensation. Heating discourages condensation and prevents the deposition of liquid water onto the denuder interior surfaces which may both dissolve the KI coating and may also clog the silica gel pores in the DNPH cartridge with KI as it recrystallizes. As this type of scrubber/denuder operates via titration, its efficacy over time is related to the amount of KI deposited on the tubing interior surfaces, the total volume of sampled air, and the average ozone concentration of the sampled air. In general, it is presumed that this type of denuder/scrubber should be effective for up to 100,000 ppb-hours at flow rates of less than 1 L/minute.1 A study conducted to evaluate the denuder’s capacity has found that such ozone scrubbers are effective for the 100,000 ppb-hours cited in TO-11A; they were able to efficiently remove 150 ppb O₃ over 30 consecutive days when operated at a flow rate of 1 L/min at RHs ranging from 10 to 85% at a nominal temperature of 25°C.2 Given an average ozone concentration of approximately 70 ppb, this type of denuder/scrubber should effectively scrub ozone from the sampled air stream for the 61 annual 24-hour samples required by the NATTS Program without depleting the KI reagent. If the average concentration of ozone is greater than 70 ppb over the course of the year, the sampling flow rate is higher than 1 liter/minute, the sampling frequency is increased from one-in-six days, or if duplicate sampling is performed more frequently than every other month such that the flow rate through the denuder is doubled during most sampling events (thereby exposing the scrubber to twice the burden of ozone), the life span of the KI denuder/scrubber will be proportionately reduced.

The denuder/scrubber must be replaced or recharged with KI minimally annually to ensure there is sufficient KI substrate to eliminate co-sampled ozone; the denuder should also be recharged if ozone breakthrough is observed by evidence of decomposition products of O₃ reacting with DNPH and the formaldehyde hydrazone derivative in the HPLC chromatogram.1 Denuders are commercially-available or they may be constructed and charged/recharged by recoating the interior of the copper tubing with a saturated solution of KI in deionized water (144 g KI in 100 mL deionized water). The solution is maintained inside the copper tubing for minimally 15 minutes (some agencies suggest 24 hours or more), then the solution drained. Additional cycles of adding and maintaining KI solution in the tubing may ensure more comprehensive coating. The coated tubing is then dried by a gentle stream of dry UHP nitrogen or dry zero air for minimally one hour.

When a sampling instrument is removed from service for replacing/recharging the KI denuder/scrubber and/or for calibration/maintenance, a best practice is to challenge the denuder being decommissioned with ozone at ~120% of the site’s maximum measured ozone concentration for several hours and to measure the resultant downstream concentration. Such will demonstrate the ozone scrubber’s efficacy when removed from the field. For denuders shown to be less than fully effective upon removal from the field, defined as downstream ozone concentration > 10 ppb or a breakthrough > 5% of the challenged ozone concentration (whichever is lower), HPLC chromatograms from recent sampling events should be examined for indications of ozone interference. Following recharge/replacement of the KI denuder/scrubber, the 120% ozone concentration challenge should be conducted to demonstrate
effective ozone removal prior to its deployment for field use. Some manufacturers conduct
efficacy testing of new and decommissioned denuders as part of their QC process and may
provide a certificate attesting to meeting the above listed acceptance criteria. For ozone
denuders/scrubbers failing these criteria, examine the HPLC chromatograms for artifacts
indicative of ozone breakthrough and qualify associated sample data (QA Qualifier LJ indicating
the value is estimated) when reporting data to AQS.

When replacing/recoating denuders, monitoring agencies should closely examine the copper
tubing for cracks or holes that may develop after multiple years of use as these will result in
leaks in the sampling flow path that may not be evident when conducting pre-sampling leak
checks. After installation of flow path components, including the denuder, a best practice is to
evacuate or pressurize the entire flow path of the sampling unit (as tolerated by the sampling
unit) to a static pressure of approximately 4 psi above or below atmospheric pressure and
observe that the pressure does not change by more than 0.5 psi over 5 minutes. In addition to
causing leaks in the sampling flow path that will contaminate collected samples with monitoring
shelter air, poorly coated sections of the denuder will expose copper tubing, which does not
comply with the requirements for the composition of the sampling flow path described in Section
4.3.7.2.

Following recharging or replacing of the denuder, the carbonyls sampling unit must undergo bias
qualification to demonstrate the sampling unit is not unacceptably biasing the collected sample.
This qualification involves collecting reference and challenge samples of humidified zero air and
a known standard as described in Section 4.3.7.3.

4.3.4.2 Other Ozone Scrubbers. Non-NATTS monitoring agencies may opt to develop
custom-made KI ozone scrubbers/denuders. The efficiency of ozone removal is to be
demonstrated for such custom systems. To demonstrate efficiency of ozone removal, the
homemade scrubber/denuder is to be challenged over a continuous 24-hour period with a
minimum of 100 ppb ozone at the intended flow rate for normal carbonyls sampler operation
(typically approximately 1 L/min) and demonstrate breakthrough of < 5%. Agencies should also
quantify the capacity of such scrubbers (for example, in ppb-hours) and prescribe the
replacement/recharge frequency in their monitoring program quality system. Additional ozone
scrubbers are described below that may be employed by non-NATTS monitoring agencies;
however, these have a number of drawbacks when compared to the heated coiled copper tubing
denuder described above.

4.3.4.2.1 Sorbent Cartridge Ozone Scrubbers. Sorbent cartridges, such as silica gel, coated
with KI are commercially available, but their use is not permitted for the NATTS Program (and
monitoring agencies are discouraged from using them) due to their sorption of water vapor.
Sampling in humid environments results in the sorbent bed becoming saturated with water,
resulting in clogging of the cartridge substrate which substantially reduces or eliminates sample
flow or causes channeling in the cartridge where ozone passes through without mitigation. While
inexpensive and convenient for use, sorbent bed KI cartridges must not be employed for the
NATTS Program sampling.
4.3.4.2.2 **Cellulose Filter Ozone Scrubbers.** The California Air Resources Board (CARB) in the past has employed cellulose filters coated with KI to remove ozone on the RM Environmental Systems Incorporated 924 and Xontec 924 sampling units. These samplers are standalone outdoor samplers configured with the DNPH cartridge port essentially right at the inlet, so do not accommodate a heated copper tubing ozone scrubber. The KI-coated filter is installed at the inlet probe, just upstream of the DNPH cartridge. Due to the need to replace these coated filters frequently, the carbonyls sampling units cannot effectively be challenged for bias qualification.

4.3.4.2.3 **Modified Dasibi™ Ozone Scrubber.** In the Dasibi™ scrubber fifteen 2-inch diameter copper mesh screens are arranged in a stacked formation. The magnesium oxide coated screens provided with the unit are exchanged for copper screens which are coated with KI. To coat the screens, they are immersed in a saturated KI solution in deionized water and air dried. The coated screens are assembled in the Dasibi enclosure with a fiberglass particulate filter at each end, the O-rings installed, and the enclosure secured with the supplied screws. This procedure imparts approximately 4 mmoles or 700 mg of KI over the fifteen 2-inch diameter screens. With this mass of KI, the scrubber should effectively remove ozone for approximately 300 sampling dates assuming 24 hours of sampling at 1 L/minute with ozone concentrations of 100 ppb.

In order to ensure that condensation does not impact the scrubber’s performance, it should be maintained at a minimum temperature of 50°C.

4.3.5 **Carbonyls Sample Collection Media.** EPA Compendium Method TO-11A specifies DNPH-coated silica gel sorbent cartridges for the collection of carbonyl compounds from ambient air. These DNPH cartridges may be prepared in-house or purchased from commercial suppliers. NATTS sites utilize one of two commercial brands of media, specifically the Waters WAT037500 or Supelco LpDNPH S10 cartridges (DNPH on 350 mg of silica gel sorbent). These cartridges are specified to meet the background criteria of TO-11A and typically exhibit proper flow characteristics with respect to pressure drop. Examination of background concentrations and proficiency test data do not indicate an obvious difference in the performance between the two brands/models of cartridges. A study for optimizing Method TO-11A reported that there is slight difference in the collection efficiency for the two types of cartridges for aldehydes, respective to the RH of the sampled atmosphere.

Laboratories may prepare DNPH cartridges in house; however, preparation is a time- and labor-intensive process which requires meticulous detail to cleanliness to ensure the resulting media are contaminant-free. The expense and resources involved in preparation of DNPH media in-house is generally greater than the cost of purchasing commercially-available DNPH cartridge media. Regardless of the type of cartridge selected, the method performance specifications in Section 4.3.10 must be met.

4.3.5.1 **Lot Evaluation and Acceptance Criteria.** For each lot or batch of purchased (as designated by the manufacturer-assigned lot or batch identifier) or prepared DNPH cartridge, a representative number of cartridges must be analyzed to demonstrate that the lot or batch is sufficiently free of contamination. Most commercially-available DNPH cartridges are accompanied by a COA indicating background of various carbonyls in the lot or batch. While a
COA provides a level of confidence that the lot or batch is sufficiently clean, laboratories will verify the background levels of carbonyls in each batch or lot of cartridges.

For commercially-purchased cartridges, a minimum of three cartridges, or 1% of the total lot, whichever is greater from each lot or batch, are to be extracted and analyzed. For cartridges prepared in-house, a minimum of three cartridges per each preparation batch are to be extracted and analyzed. Each cartridge tested in the lot or batch must meet the criteria listed in Table 4.3-2. Ongoing analysis of MBs permits continual assessment of the lot’s contamination levels. ASLs are encouraged to report the lot background value to AQS on the monitoring site’s behalf.

Additionally, agencies may elect to perform flow evaluations of the lot(s) to ensure cartridges do not overly restrict sampling flows.

Table 4.3-2. Not-to-Exceed Background per Lot of DNPH Cartridge

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>Not-to-Exceed Limit (µg/cartridge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>&lt; 0.15</td>
</tr>
<tr>
<td>Acetone</td>
<td>&lt; 0.30</td>
</tr>
<tr>
<td>Other Individual Target Carbonyl Compounds</td>
<td>&lt; 0.10</td>
</tr>
</tbody>
</table>

*A* Acetone is not a required target compound for the NATTS Program and should not be grounds for lot disqualification unless the monitoring agency requires its analysis or it interferes with other target analytes in the chromatogram.

If any cartridge tested exceeds these criteria, an additional three cartridges, or 1% of the total lot, whichever is greater, must be tested to evaluate the lot. If the additional cartridges meet the criteria, the lot or batch is acceptable for sampling. If any of the additional cartridges fail criteria, the lot or batch must not be used for NATTS sampling and acceptable cartridges should be acquired. If appropriate cartridges are not available and the lot(s) exceeding criteria are employed, the measurement data for affected target carbonyls are to be invalidated (Null Qualifier EC indicating critical criteria failure) when reported to AQS.

**4.3.5.2 Cartridge Handling and Storage.** DNPH sampling cartridge media may be shipped unrefrigerated by the supplier; however, are to be stored refrigerated at ≤ 4°C upon receipt. Light exposure may degrade the DNPH reagent on unsampled cartridges, therefore, they are to be maintained sealed in their original packaging and protected from light (foil pouch or similar opaque container) until installed for sample collection or prepared as QC samples. Cartridges which are not stored appropriately may suffer from degradation of the DNPH reagent and may show increased levels of contaminants from passive sampling of target compounds and/or interferants. Measurement data for samples stored ≥ 4°C after retrieval are to be qualified (QA Qualifier LJ indicating value is estimated) when reported to AQS.

DNPH cartridges should only be handled by staff wearing powder-free nitrile or vinyl gloves (or equivalent). Measures are to be taken to avoid exposure of DNPH cartridges (unsampled or collected samples) to exhaust fumes, sunlight, elevated temperatures, and laboratory environments where solvents and/or carbonyl compounds such as acetone may contaminate sampling media.
As soon as possible after sample collection, cartridges are to be capped (if caps are provided), sealed in a foil-lined zipseal pouch (to protect from light and the ambient atmosphere), and transported (shipped) and stored refrigerated at ≤ 4°C. Cartridges are to be transported in insulated coolers with ice, freezer packs (ice substitute), or equivalent method for providing refrigeration during transport to and from the laboratory. Monitoring the shipping temperature with a calibrated min-max type thermometer is a best practice.

4.3.5.3 Damaged Cartridges. DNPH cartridges are susceptible to water damage and to physical damage. Unused or sampled cartridges, including those collected as blanks, must not exhibit clumping of the silica gel sorbent which is indicative of water condensation inside the cartridge sorbent bed. Physical damage to cartridges such as cracks, broken inlet or outlet fittings, or openings of the cartridge body into the sorbent bed are pathways for the ingress of contamination. Cartridges which indicate such damage must not be used in the NATTS Program, or if already used for sample collection, are to be invalidated (Null Qualifier BI indicating lost or damaged in transit) when reported to AQS, and a make-up sample should be collected per Section 2.1.2.1, where possible.

4.3.5.4 Cartridge Shelf Life. DNPH cartridges that are purchased commercially are typically provided with an expiration from the manufacturer specifying storage conditions. Agencies will comply with the manufacturer expiration, if given. Degradation of the DNPH reagent or silica gel sorbent bed which may reduce collection efficiency to unacceptable levels may occur after the assigned expiration date. Additionally, as DNPH cartridge media age, their levels of background contamination are likely to have increased, perhaps to unacceptable levels, due to passive sampling and uptake from the ambient atmosphere. For cartridges which are not assigned an expiration date or are assigned an arbitrary expiration date (i.e., six months from time of receipt) by the manufacturer, agencies should work within this expiration period as practical. For such cartridges which have exceeded an arbitrarily-assigned expiration period, the lot of media may be shown to be acceptable if levels of contaminants meet the criteria in Table 4.3-2 and there remains sufficient DNPH to conduct sampling and ensure excess DNPH levels remain following sample collection. This level of DNPH on unsampled cartridges is recommended to be a reduction of DNPH area counts in the HPLC chromatogram of no more than ~15% from the original lot acceptance analysis. Data for cartridges exceeding the expiration period and showing DNPH area response < 85% of the initial lot analysis will be qualified (QA Qualifier LJ indicating value is an estimate) when reported to AQS.

4.3.6 Method Detection Limits. MDLs for carbonyls must be determined per the guidance in Section 4.1, which details the MDL determination process generally for the NATTS Program. This section will briefly provide details for determining the MDL for carbonyls measurements by solvent extraction and analysis by HPLC (or ultra-high performance liquid chromatography [UHPLC]).

The MDL procedure in Section 4.1 prescribes preparing and analyzing MDL spikes and MBs for determining an initial MDL and for collecting ongoing data for MDL verification. MDLs must be determined following the procedure in Section 4.1.3.1 unless there is a sufficient number (n ≥ 7) of MBs in which the specific target analyte has been detected (positively identified and meet qualitative identification criteria listed in Section 4.3.9.5.7), in which case the procedure in
Section 4.1.3.2 may be employed. ASLs should closely review the requirements in Section 4.1.3.1.1.4 to evaluate whether previously collected MDL spike data and MB data meet the requirements for calculating an initial and ongoing MDL. If the previously collected data do not meet the specified criteria, the ASL must determine the initial MDL as detailed in Section 4.1.3.1.1.

As practical, ASLs should use DNPH cartridge media from several available manufacturer lots and/or different boxes/cases to prepare the MDL spikes and MBs to best characterize variability of measurements attributable to the variation in the pool of available cartridges. For each of the individual MDL spike and MB measurements, these are to be discrete cartridges and data from the same cartridge extract can only be included in the calculations when analyzed on a separate instrument (when more than one instrument is employed).

All steps performed in the preparation, extraction, and analysis of field sample cartridges (e.g., extract volume, subsequent dilution, etc.) are to be included in the MDL procedure. Cartridges must be prepared at the selected spiking concentration by spiking with known masses of derivatized or underivatized carbonyls onto the cartridge silica gel bed (as is done for the LCS as described in Section 4.3.9.4.1) and cartridges should be allowed to rest briefly (e.g., ~5 minutes) for the solvent to permeate the cartridge and dry. It is not appropriate to simply analyze a cartridge extract spiked after extraction or a solvent standard at the desired concentration. MBs are to be prepared with the processes employed for routine analysis as in Section 4.3.9.4.

Determined MDLs for Tier I core analytes must meet (be equal to or lower than) the MDL MQO values listed in the most current workplan template, available at the following URL for the NATTS program on EPA’s AMTIC: https://www.epa.gov/amtic/air-toxics-ambient-monitoring#natts

4.3.7 Carbonyls Sample Collection Equipment, Certification, and Maintenance.
Carbonyls are collected by drawing the ambient atmosphere through a DNPH cartridge at a known standard conditions flow rate of approximately 0.25 to 1.25 L/minute (recommended flow rate is ~ 1 L/minute) over the 24-hour collection period. An EPA-funded study indicated that at 1.25 L/minute there was no perceptible breakthrough at aldehyde concentrations of 5 ppbv.\(^2\) Collection of samples with flow rates of approximately 1 L/minute represents an appropriate compromise between maximizing collection efficiency and method sensitivity.

4.3.7.1 Carbonyls Sampling Equipment. The sampling unit may control flow rate by an MFC or by a combination critical orifice and flow rotameter. Advantages of MFCs include that they provide real-time control of a specified flow rate, adjusting for changes in backpressure and sampling conditions and sampling units with MFCs may also record flow rate data to a datalogger to collect integrated flow rate data and total sampling volume. Such is in contrast with sampling units with rotameters for which only beginning and ending flow rate measurements are available for total collected sample volume calculations. Another limitation of rotameters is that their indicated flows must be manually corrected to standard conditions using the barometric pressure and temperature at the monitoring site on the day of sample collection. Rotameters are less complicated and expensive than MFCs but they require more staff time to calibrate and calculate sampling flow rates at standard conditions.
A variety of commercial and custom-built sampling instruments is available. These range from simple vacuum sampling pumps with flow rates controlled via critical orifice and flow rotameter to multi-channel/multi-pump systems connected through multiple MFCs and operated by touchscreen control. Some units also include capability to simultaneously collect VOC canister samples or allow remote computer login to monitor sampling events and download logged sample collection data. Note that such options are advantageous, but not required.

Regardless of the additional features, each sampling unit must minimally include the following functions:

- Elapsed time indicator
- Multi-day event control device (timer)
- MFC (preferred) or combination critical orifice and flow rotameter to control sampling flow
- Heated ozone denuder as described in Section 4.3.4.1

Regardless of design or configuration, each carbonyls sampling unit must have undergone flow rate calibration (establishment or verification) and bias qualification (refer to Section 4.3.7.1.1) in the previous 12 months prior to field deployment.

### 4.3.7.1.1 Carbonyls Sampling Unit Bias Qualification

Bias qualification for carbonyls samplers involves conducting the zero qualification check and known standard qualification check. The zero qualification check is required and the known standard check is *strongly recommended* before initial field deployment and annually thereafter following recharging/replacing the ozone denuder and replacing other components of the flow path upstream of the sample cartridge installation ports such as particulate filters, tubing, and valves. To minimize sampler downtime, it is strongly recommended that all typical sampler annual maintenance and component replacement be completed prior to conducting the sampling unit bias qualification checks. Additionally, it is strongly recommended that the DNPH cartridges employed for collecting qualification samples be from the same lot of media so that cartridge media background is common among the reference and challenge samples.

Each flow channel (i.e., separate flow-controlled flow path such as a duplicate channel) of the carbonyls sampling instrument should be qualified. A best practice is to perform this procedure TTP where the entire in-situ sampling flowpath is tested. Many monitoring agencies do not possess the resources to perform TTP procedures, therefore the bias qualification check should include as much of the flow path as possible (e.g., the run of connection tubing to a manifold, or similar), and must minimally include the portion of the flow path comprising the ozone denuder/scrubber and sampling unit flow path through to the DNPH cartridge installation port.

A recommended sampler qualification check procedure is described below. For agencies which cannot perform the annual maintenance (ozone scrubber/denuder recharge, flow control calibration) and bias qualification in-house, manufacturers, the national contract laboratory, or third party laboratories may perform this service for a fee. Regardless of the specific procedure adopted, when performed, the performance specification criteria listed below for the zero qualification must be met.
As is required for flow path composition for carbonyls sampling of ambient air, the bias qualification sampling apparatuses (upstream of the DNPH cartridge) must be constructed of only chromatographic stainless steel, borosilicate glass, and/or PTFE Teflon®.

4.3.7.1.1 Sampling Unit Zero Qualification Check (Positive Bias Check)

The zero qualification check demonstrates the carbonyls sampling unit is acceptably free of positive bias (i.e., contamination) by collection over 24 hours of a sample of humidified (to approximately 40 to 60% RH) HCF zero air. The humidified zero air source is also collected onto a reference cartridge that samples the humidified zero air to characterize the background of both the DNPH cartridge media and the gas provided to the sampling unit for the challenge. Both the challenge sample and reference sample are extracted and analyzed. The challenge sample result is corrected for the reference sample result and the corrected carbonyls measurements for the challenge sample are presumed to be contribution of carbonyls background from the sampling unit and any included portions of the sampling train.

Note: Installing a DNPH cartridge on the sampling apparatus inlet to provide carbonyl-free air for the challenge may theoretically be effective at removing carbonyls; however, monitoring agencies have reported breakthrough of target carbonyls such as acetone when employing this method, particularly over a 24-hour sampling period, thereby confounding the challenge sample results. For this reason, use of a DNPH cartridge to provide carbonyl-free air to the inlet is not recommended. Instead, humidified zero air should be provided as the test gas and the reference cartridge results should be employed to background correct the carbonyls contribution from the humidified zero air and cartridge media.

To minimize variables between the reference and challenge samples and to prevent confounding results, it is strongly recommended that the sampling flow rates and sampling durations are measured (so a total sampled volume is known) and that they be closely matched to one another. As much as practical, the sampling unit undergoing qualification should be operated in its normal sampling mode. Also, to ensure proper equilibration and passivation of the challenge gas source plumbing, it is strongly recommended that the gas generation systems be powered on and flowing gas for minimally one hour prior to connection to the reference sampling train or challenged sampling unit inlet.

Collecting the challenge and reference samples can be performed simultaneously (which requires constructing a manifold) or sequentially. In both conventions, the humidified zero air is collected directly onto a reference DNPH cartridge and is also plumbed through the sampling unit(s) for direct collection onto a challenge DNPH cartridge(s). The provided gas stream is pressurized (above barometric pressure) and a vent is installed upstream of the sampling apparatuses with a rotameter to ensure sufficient gas flow for the sampling demand (the rotameter will indicate a positive reading indicating gas flow out the vent). Collecting the samples simultaneously reduces the overall time required to conduct the qualification and also eliminates a temporal variable that the composition of the humidified zero air may be different between the two sampling events.

To collect the samples simultaneously, the humidified zero air source is routed to a manifold constructed of chromatographic grade stainless steel with the following four ports (as shown in Figure 4.3-2):
- Vent [A]
- Challenge sample to sampling unit [B]
- Challenge gas (humidified zero air or diluted humidified known standard) [C]
- Reference sample [D]

**Figure 4.3-2. Carbonyls Sampler Qualification Simultaneous Challenge Example Manifold Configuration**

To collect samples sequentially, the humidified zero air is provided to a chain of components for collecting either a reference cartridge or a challenge sample cartridge. Refer to Figure 4.3-3 for an example configuration. The reference sample should be collected first. Figures 4.3-2 and 4.3-2 show an MFC/flow controller and sampling pump for the reference sample train. These components should be closely matched to those employed on the carbonyls sampler undergoing qualification, i.e., the MFC/flow controller should control flow rate to match the typical sampling flow rate (e.g., 1 LPM) and the sampling pump should permit flows that exceed the desired flow rate to ensure the flow controller has sufficient pressure differential to properly control flow (e.g., 2 LPM). The sample should be collected following the normal sampling regimen for 24 hours at the typical sampling flow rate. Once the reference sample is collected, the gas stream is disconnected from the reference sampling apparatus and connected to the sampling unit. Collection of the challenge sample(s) is performed likewise at the typical sampling flow rate for 24 hours.
Zero Qualification Reference Sample: It is strongly recommended that the humidified zero air for the reference sample be plumbed directly to the reference sample apparatus, and not through a dilution system, such that the only component between the reference DNPH cartridge and the humidified zero air source be the connecting tubing and vent tee. The sampling pump should be at the extreme downstream end of the sampling train and should have sufficient flow range to sample at least 1 liter/minute through the selected flow controller. The flow controller (e.g., MFC) is installed between the sampling vacuum pump and the reference DNPH cartridge.

Zero Qualification Challenge Sample: It is strongly recommended that the humidified zero air for the challenge sample be plumbed directly to the sampling unit undergoing qualification, and not through a dilution system, such that the only component between the reference DNPH cartridge and the humidified zero air source be the connecting tubing and vent tee. The sampling unit is operated in its normal sampling mode for the challenge sample.

Acceptance Criteria: Analysis for target compounds in the zero qualification challenge cartridge must show that each target carbonyl is ≤ 0.2 ppbv (0.245 µg/m³, or 0.35 µg/cartridge assuming a 1 L/minute sampling flow rate and 1440 minutes of collection) greater than the reference cartridge. Comparison to the reference cartridge permits evaluating the contribution of the sampling unit irrespective of cartridge and zero air system background. Where exceedances are noted for the zero challenge cartridge, corrective action is to be taken to remediate the contamination attributable to the sampling unit and the sampling unit zero challenge repeated to ensure criteria are met before conducting the known standard bias qualification check (refer to Section 4.3.7.1.1.2).
Corrective action for exceedances may include additional flushing periods (e.g., 24 hours or more) of the sampling unit flow path with humidified zero air. Minimally, the Tier I carbonyls (formaldehyde and acetaldehyde) must meet the ≤ 0.2 ppbv acceptance criterion (after correction for the reference cartridge measurement). If the sampler must be deployed with failing Tier I and/or non-Tier I analytes, subsequent collected field sample results are to be qualified (QA Qualifier SB indicating failing sampler bias checks and QA Qualifier LK indicating the value is estimated with a high bias) when data are input to AQS. For Tier I and/or non-Tier I analytes that exceed 5-fold MDL for the sampling unit zero challenge bias check, this indicates an unacceptably high background attributable to the sampler and the associated routine sample data for affected compounds are to be invalidated (Null qualifier EC indicating exceeds critical criteria) when reported to AQS.

4.3.7.1.1.2 Sampling Unit Known Standard Qualification Check (Bias Check)

Once the sampling unit successfully passes the zero qualification check described above in Section 4.3.7.1.1.1, it strongly recommended that the sampling unit undergo a known standard qualification check to demonstrate acceptable overall bias (i.e., verifying that the sampling unit is not contributing to an unacceptable high bias and that it is not contributing to an unacceptable low bias).

The known standard qualification check is conducted essentially identically to the zero qualification check; however, a standard gas diluted with humidified HCF zero air is provided to the reference and sampling unit sample collection apparatuses. The same conditions and conventions for collecting field samples apply for collecting the known standard qualification check samples (e.g., leak checks, flow rates, and sampling durations) to best represent actual field sampling and to minimize variables between the reference and challenge samples.

To best assess the potential bias of the sampling unit on ambient air measurements, the diluted standard concentration provided to the sampling apparatuses should be in concentration ranges approximating those typically measured in ambient air. If typical measured concentrations of target carbonyls in ambient air are non-detect or approximating the MDL, a recommended concentration range is approximately 10- to 15-fold the MDL to ensure there is sufficient collected mass to measure and assess a potential discrepancy between the reference and challenge samples. Technicians are cautioned against selecting too high of a concentration, which can contaminate sampling units, result in poor collection efficiency, and be so high that discerning a 15% concentration difference is difficult or of limited utility.

Theoretically, there would be 100% transfer of the carbonyls in the standard gas from the dilution system to the sampling apparatuses; however, the collection efficiency of carbonyls onto DNPH cartridge media is less than 100% and formaldehyde additionally exhibits some fraction of loss during standard gas transfer. In order to adjust for these variable biases, the sampling unit bias assessment is based on the collected carbonyls measurements on the reference sample cartridge, and not the theoretical nominal concentration of the standard gas concentration corrected for the dilution factor.
The concentration of each target carbonyl in the challenge sample must be within ±15% of the concentration of the reference sample (RPD < ±15.1%). Concentrations of target analytes in the challenge sample less than 85% or greater than 115% of the measured concentration in the reference sample indicate an unacceptable low or high bias, respectively, attributable to the sampling unit flow path that requires corrective action. If the known standard challenge is conducted, Tier I analytes (formaldehyde and acetaldehyde) should meet this criterion before the sampling unit can be deployed for sampling, or if deployed, data are to be qualified (QA Qualifier LJ indicating estimated with a low bias QA Qualifier LK indicating estimated with a high bias) when reported to AQS.

When bias qualification results indicate failure to meet criteria, technicians should verify calculations supporting the assessment prior to undertaking corrective action. If calculations verify the exceedance, corrective action should be taken to mitigate the bias. A positive bias may require additional periods of flushing with humidified zero air to eliminate the contaminants. Apparent low bias suggests presence of active sites in the flow path that adsorb and/or destructively react target carbonyls. Such a condition is not likely to be remedied by additional flushing with humidified zero air; instead, components within the sampling flow path should be examined or replaced in a piecewise fashion. One such component to check is the ozone denuder, for which incompletely coated copper tubing could result in catalytic destruction of target carbonyls.

4.3.7.1.2 Carbonyls Sampling Unit Flow Calibration. Initially prior to field deployment and whenever independent flow calibration verification indicates the flow tolerance (< ±10.1%) has been exceeded, the flow control device (MFC or flow rotameter) must be calibrated against a calibrated flow transfer standard and the calibration of the flow control device (or regression for a flow rotameter) adjusted to match the transfer standard (or the regression characterizing its response must be reset to match the transfer standard). The flow rate calibration must be verified quarterly (recommended monthly) and must be within ±10.1% of the flow transfer standard. Flow rate calibration verifications exceeding this criterion prompts invalidation (Null qualifier AH indicating sample flow rate or CV out of limits) of sample data when reporting to AQS for the affected sampling unit since the previous passing flow rate calibration verification.

Note that manufacturer procedures for calibration may be followed if flow rates can be calibrated at standard conditions (760 mmHg and 25°C). A suitable calibration procedure for MFCs is as follows. The sampling unit pump(s) and MFC should be warmed up and run for approximately five minutes to ensure the MFC is stable. A DNPH cartridge should be installed into the air sampler to provide a pressure drop to the pump, and airflow through the cartridge commenced. The calibrated flow transfer standard should be connected at the upstream end of the sampling unit so air is drawn by vacuum into the flow transfer standard and to ensure as much of the flow path is included as possible in order to identify potential leaks in the flow path that may not otherwise be evident. MFC calibration (adjustment) should be performed at minimally three flow rates: the typical flow rate for sample collection, approximately 30% less than the typical flow of sample collection, and approximately 30% higher than the typical flow of sample collection. Particular attention should be paid to ensure that the temperature and pressure references for EPA standard conditions of (25°C and 760 mm Hg) are specified for both the reading on the
flow transfer standard and MFC (some manufacturers default calibration standard conditions to 0°C which results in an approximate 9% flow bias).

Calibration of flow rotameters is more complex than calibration of MFCs. The temperature and barometric pressure both at the time of calibration and during sample collection are needed to correct the indicated rotameter flow rate to the actual flow rate. A suitable rotameter calibration procedure is given below.

The flow rotameter should be challenged with a flow of air which is simultaneously measured by a calibrated flow transfer standard. At each flow rate set point, the flow reading from the flow transfer standard and the corresponding reading from the flow rotameter are recorded. The challenged flow range should include a minimum of five flow rates that span the useful scale of the flow rotameter and include the expected indicated flow rate during field operation. A linear least-square regression is then generated by plotting the flow transfer (known) readings on the x-axis and the flow rotameter readings (unknown) on the y-axis. The resulting linear regression equation allows the rotameter’s indicated flow (on the y-axis) to be related to the known calibrated flow of the rotameter on the x-axis at the specific conditions of ambient temperature and barometric pressure at which the flow calibration is performed.

To calculate the actual flow rate during operation of the rotameter in the field, the rotameter flow rate during calibration is found by way of cross reference with the indicated flow from the rotameter calibration plot. Stated another way, the rotameter is read, and this indicated flow is found on the y-axis of the calibration plot and the corresponding flow rate during calibration is read from the x-axis (or the regression equation is solved for x). This flow rate during calibration, $Q_c$, along with the ambient temperature and pressure during calibration and during sample collection are input into the following equation to calculate the flow during sample collection:

$$Q_a = Q_c \sqrt{\frac{P_a T_a}{P_c T_c}}$$

where:

- $Q_a$ = volumetric flow rate at ambient (or local) conditions where the rotameter is operated
- $Q_c$ = volumetric flow rate at ambient (or local) conditions during rotameter calibration
- $P_c$ = barometric pressure during rotameter calibration
- $P_a$ = barometric pressure at ambient (or local) conditions where the rotameter is operated
- $T_a$ = absolute temperature at ambient (or local) conditions where the rotameter is operated
- $T_c$ = absolute temperature during rotameter calibration

For flow rotameters which are calibrated by delivery of a known flow measured at standard conditions, the calculation of the ambient flow at standard conditions is performed according to the following equation:
where:

\[ Q_{a, std} = \text{flow rate where the rotameter is operated, in standard conditions (760 mm Hg, 25°C)} \]
\[ Q_{c, std} = \text{flow rate where the rotameter was calibrated, in standard conditions} \]
\[ T_c, P_c, T_a, \text{and } P_a \text{ are as above.} \]

As an example, assume that a rotameter is calibrated – its indicated flow is cross-referenced to a calibrated flow – by delivery of known flows measured at standard conditions. Assume as well that the calibration is performed near sea level at a typical laboratory temperature such that \( P_c = 750 \text{ mm Hg} \) and \( T_c = 20° \text{ C} = 293.15 \text{ K} \), and that a field sample is collected in the summer in Grand Junction, Colorado, such that \( P_a = 650 \text{ mm Hg} \), \( T_a = 35° \text{ C} = 308.15 \text{ K} \). Assume the indicated rotameter flow is 800 mL/min, which from the calibration plot corresponds to a known flow rate at standard conditions of 750 mL/min. The actual flow rate, in standard conditions, for this carbonyl sample in Grand Junction is equal to

\[ 750 \text{ mL/min} \cdot \sqrt{\frac{650}{750} \cdot \frac{293.15}{308.15}} = 681 \text{ mL/min}. \]

To perform a flow calibration verification on the sampling unit flow, the sampling unit pump(s) should be warmed up and run for approximately five minutes to ensure flows are stable. A blank DNPH cartridge should be installed into the air sampler to provide a pressure drop to the pump, and airflow through the cartridge commenced. The calibrated flow transfer standard should be connected at the upstream end of the sampling unit so as much of the flow path is included as possible in order to identify potential leaks in the flow path that may not otherwise be evident. The sample flow is then set to the flow setting of typical sample collection and the flow compared to the transfer standard. Ensure that both the sampling unit and flow transfer standard are set to report flows at standard conditions of 25°C and 760 mm Hg. Rotameter flows must be converted to standard conditions \( Q_{a, std} \) with the temperature and barometric pressure measured at the time of the calibration check via the equation above. The sampling unit flow in standard conditions must be < 10.1% of the flow indicated by the transfer standard. If outside of this range, the regression equation for the flow rotameter must be re-established.

### 4.3.7.1.2.1 Flow Rate Verification and Flow Rate Audit Reporting

Following flow rate calibration verifications and flow rate audits, the results are to be input into AQS. Guidance for establishing the monitor and flow channels in AQS is described in Appendix E. Monitoring agencies should input these data quarterly and ensure that flow rates are in EPA standard temperature and pressure (STP) conditions of 760 mmHg and 25°C.

### 4.3.7.1.3 Moisture Management

Humidity plays several roles with regard to carbonyls sample collection. Water vapor can condense on interior portions of the sample flow path potentially resulting in a low measurement bias due to carbonyls dissolving in the liquid water. To minimize the condensation of liquid water onto the interior surfaces of the flow path, the ozone scrubber is maintained at approximately 50°C. Additionally, portions of the inlet pathway within the
monitoring shelter connecting to the carbonyls sampling unit may be insulated and/or heated to
maintain an elevated temperature to discourage condensation. High RH in sampled atmospheres
may also lead to somewhat lower carbonyl collection efficiencies due to the possible back
reaction of the DNPH-carbonyl derivative with water which reverts to form the free carbonyl.
The reverse reaction is less likely for aldehydes due to their higher reactivity; however, can lead
to lower collection efficiencies for ketones. 3

4.3.7.2 **Sampling Train Composition.** Components comprising the wetted surfaces of the
flow path between the carbonyls sampling unit and the inlet probe to the atmosphere must be
constructed of borosilicate glass, PTFE Teflon, or chromatographic grade stainless steel. Due to
the reactivity of materials such as copper or brass and the adsorptive/desorptive properties of
materials such as FEP Teflon®, rubber, or plastic tubing, these materials must not be utilized
within the flow path. Data associated with sampling trains including incompatible materials are
to be qualified (QA Qualifier SX indicating does not meet siting criteria) when reported to AQS.

Carbonyls sampling units connected to an inlet probe comprising several sampling instrument
inlet connections may be constructed of chromatographic stainless steel if the only connections
to such a manifold are for carbonyls and VOCs measurements. Otherwise, manifold inlets to
which monitors for criteria gases (CO, NO/NO₂/NOₓ, SO₂, and O₃) are connected must be
constructed of borosilicate glass.

4.3.7.3 **Sampling Train Configuration and Residence Time.** The carbonyls sampling inlet
probe may be dedicated to the carbonyls sampling unit (standalone) or connected to one or more
sampling instruments (a manifold inlet). For either configuration of inlet, whether standalone or
manifold, the residence time of the sample from the ambient atmosphere to the back of the
sampling unit must be ≤ 20 seconds. For standalone inlet configurations, unless the inlet tubing
has a large internal diameter and/or a long distance to the ambient atmosphere, sampling rates of
~1 L/minute are likely sufficient to maintain a sampling residence time of ≤ 20 seconds;
however, the monitoring agency will calculate the residence time to ensure this criterion is met.
For manifold inlet systems, the inclusion of a bypass pump or blower is connected to the
manifold to continuously pull ambient air though the manifold to ensure a constant supply of
fresh ambient air to the sampling instrument inlets. The flow rate of the bypass pump must be
minimally twice the total maximum sampling load for all sampling units connected to the
manifold. Unless the manifold inlet has a large internal volume (large internal diameter or long
distance to the ambient atmosphere), the blower or support pump should help to ensure a
sampling residence time of ≤ 20 seconds; however, the monitoring agency must calculate the
residence time. The residence time calculations are to be performed whenever changes to the
inlet configuration are made and are to be documented and maintained in the monitoring site
records. Data collected on samplers with residence time > 20 seconds are to be qualified (QA
Qualifier SX indicating does not meet siting criteria) when reported to AQS.

Guidance on the required measurements and the calculations for residence time determination
are common to and required for criteria pollutant gas measurements and are described in Section
7.3.2 of the EPA QA Handbook Volume II 7 and clarified in a June 2019 EPA Technical Note. 8
An additional resource for determining sampling residence time includes a Microsoft® Excel worksheet EPA has made available at the following URL:

https://www.epa.gov/sites/production/files/2020-10/residence_time_determination_worksheet.xls

4.3.7.4 Carbonyls Sampling Inlet Maintenance. Over time, the carbonyl inlet probe and connecting tubing will become laden with particulate residue. This particulate residue may scrub target analytes from the gas stream and may act as sites for adsorption/desorption. Wetted surfaces of inlet probes and sampling flow path connecting tubing are to be cleaned or replaced minimally annually, and preferably every six months, particularly if operated in an urban environment where there is a higher concentration of PM.

Site operators should use only deionized water (no detergents or solvents) to clean inlet lines. If the tubing lines are short enough, a suitably small brush can be employed in concert with the deionized water to effectively clean the interior of the tubing (note that such manual methods are not appropriate for cleaning silicon-ceramic lined stainless steel (refer to Section 4.2.3.1.1). It may be more effective to simply replace the tubing on a prescribed basis. Many carbonyl sampling units utilize PTFE particulate filters upstream of the sampling cartridge ports to alleviate particulate loading of internal parts (valves and MFCs). It is strongly recommended that a PTFE particulate filter be installed downstream of the ozone denuder to capture particles of KI that may become dislodged and to prevent their infiltration into solenoid valves (resulting in failure to pass leak checks). Such particulate filters must be replaced periodically, recommended to be replaced after six months but must not exceed annually.

4.3.8 Sample Collection Procedures and Field Quality Control Samples

4.3.8.1 Sample Collection Procedures. Prior to beginning sampling for carbonyls, the following must have been completed:

- Characterization of the background for the lot of DNPH cartridge media as in Section 4.3.5.1;
- Sampling unit bias zero qualification check within the previous 12 months;
- Sampling inlet line cleaned or replaced within the previous 12 months;
- Flow control device calibration verified within the previous 3 months;
- Residence time determined to be ≤ 20 seconds and documented in the site records; and
- Particulate filter(s) (if so equipped) replaced within the previous 12 months.

It is critical that cartridge media are handled as prescribed in Section 4.3.5.2.

4.3.8.1.1 Sampling Schedule and Duration. Carbonyls sample collection must be performed on a one-in-six days schedule per the national sampling calendar for 24 ± 1 hours beginning at midnight and concluding on midnight of the following day, local time unadjusted for daylight
savings time. The national sampling calendar is available at the following URL (accessed June 2022):

https://www.epa.gov/amtic/sampling-schedule-calendar

For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes and mechanical timers within ±15 minutes of the reference time (cellular phone, GPS, or similar accurate clock). Document verification and adjustments to clocks within monitoring site records (e.g., the sampling unit logbook).

4.3.8.1.2 Presampling Inlet Line Purge. Regardless of the inlet configuration, it is strongly recommended that the inlet line to the sampling unit be purged with ambient air such that the equivalent of a minimum of 10 air changes is completed just prior to commencing sample collection. This purge eliminates stagnant air and flushes the inlet line to ensure the sampled air is freshly introduced ambient air.

4.3.8.1.3 Sample Setup. Blank DNPH cartridge media are transported to the site in an insulated cooler on ice/freezer packs where they are either stored onsite in a refrigerator or freezer (with calibrated temperature monitoring), or installed into the sampling unit for sample collection. Sample cartridges may be installed in the sampling unit up to 5 days before the sampling event (i.e., when the previous sample is retrieved); however, this period should be as short as practical (e.g., the day before sample collection) to minimize degradation of the cartridge DNPH reagent and the potential for passive sampling of carbonyls on the cartridge.

Appropriate blank, non-exposed DNPH cartridge(s) are installed into the sampling unit and the sample collection program verified to comply with Section 4.3.8.1.1. The flow rate of collection should be set to a known calibrated flow rate of approximately 0.7 to 1.5 L/minute (at standard conditions of 25°C and 760 mmHg) for a total collection volume of 1.0 to 2.2 m³ at standard conditions. Method sensitivity (detectability) is directly proportional to the total collected sample volume, and the sampling flow rate should be adjusted within the specified range so that MDL MQOs are attained. An EPA funded study on Method TO-11A² indicated that collection efficiency is essentially unaffected at flow rates between 0.7 and 1.5 L/minute; however, it is not known whether flow rates greater than 1.5 L/minute result in decreased collection efficiency.

For sampling units which permit a leak check function on the sample pathway, a leak check is to be initiated prior to sample collection. Leak check acceptance criteria and the included portions of the sampling flow path are specific to the manufacturer and model of sampling unit. Sampling must not commence until a completed leak check indicates acceptable performance, therefore leak checks should not be automated to occur when the site operator is not present to troubleshoot leak check failures. Leak checks should indicate no flow occurring during the leak check or meet the criteria specified in the instrument manual. Samples collected with a failing leak check will be invalidated (Null qualifier AQ indicating collection error) when reported to AQS.

Site operators will record the programmed flow rate, date and time of sample cartridge installation, date and time of intended start of sample collection, leak check result (if performed), and cartridge identification information on the sample collection form. Additional information
recorded may include the initial flow rate (if this measurement is needed for determining average flow rate), sampling unit identifier (e.g., serial number), and cartridge lot.

4.3.8.1.4 Sample Retrieval. The collected cartridges are to be retrieved as soon as possible after the conclusion of sampling in order to minimize degradation of the carbonyl-DNPH derivatives. Sample retrieval will preferably occur the next day, (e.g., within 24 hours after collection end) but should not exceed 72 hours from the end of sample collection. Measurement data for samples retrieved after 72 hours from the end of collection are to be qualified (QA Qualifier HT indicating sample pickup hold time exceeded) when reported to AQS. The average flow rate, total collected volume (if given), and sample duration are to be documented on the sample collection form. Additional information such as the final flow rate (if this measurement is needed for determining the average flow rate) may need to be recorded. The site operator dons powder-free gloves and removes cartridges from the sampling unit, installs the caps on the inlet and outlet of each cartridge, seals each cartridge in its dedicated zipseal foil-lined pouch, and immediately places the pouches in cold storage (onsite refrigerator or insulated cooler with ice/freezer packs) at ≤ 4°C. An added safeguard against cartridge contamination (and a best practice) is to place the sealed foil-lined pouches into a zipseal plastic bag containing activated carbon (this will adsorb VOCs). The sample cartridges are to be kept cold during transport to the laboratory such that the temperature remains ≤ 4°C upon receipt. Note that if the transport time to the laboratory is very short (less than 4 hours – typical when the laboratory is in close proximity to the monitoring site), the cartridge temperature measured upon receipt at the laboratory may not be ≤ 4°C; however, the measured temperature should indicate the shipment is refrigerated (e.g., < 10°C). Data associated with sample cartridges received at elevated temperatures are to be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS. Samples must be received at the laboratory with their appropriate custody documentation.

Sampling units which incorporate computer control of the sampling event (e.g., solenoid valve opening/closing, flow control, etc.) with associated data logging may provide the above information which should be printed (if possible) and attached or transcribed to the sample collection form. For such sampling units, the data logged should be reviewed to ensure the sample was collected appropriately and there were no sampler applied qualifiers (flags indicating out of tolerance conditions) or other collection problems that may compromise and/or invalidate the collected sample. Collected data should be downloaded from the sampling unit, stored by the monitoring agency (e.g., on a network drive), and provided to the ASL. The sample custody form must be completed and accompany the collected sample(s) at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7.

4.3.8.2 Field Quality Control Samples. Field QC samples that may be co-collected with ambient air samples include FBs, TBs, collocated and duplicate samples, field matrix spikes, and breakthrough samples. Blank cartridges (negative controls) provide information on the potential for field-collected samples to be subjected to positive bias, whereas spiked cartridges assess the potential for the presence of both positive and negative bias. Breakthrough samples assess a negative bias condition due to incomplete capture of target carbonyls. Collocated and duplicate samples assess sampling precision through extraction and analysis.
4.3.8.2.1 Field Blanks and Exposure Blanks. Field blanks must be collected minimally once per month; however, it is a best practice to increase this frequency, ideally to collect a FB with each collection event. FBs must be handled in the same manner as all other field-collected samples, transported in the same cooler, and stored in the same refrigerator/freezer storage units. FBs are exposed to the ambient atmosphere for approximately five to ten minutes by installation of the blank cartridge into the (active) sampling position on the primary sampling unit with no air drawn through the cartridge. The FB cartridge is then removed from the sampling unit and placed immediately into the zipseal foil-lined pouch and into cold storage. Collection of the FB in this manner characterizes the handling of the blank cartridge in the sampling position in the primary sampling unit and standardizes FB collection across the NATTS network for carbonyls and with metals and PAHs FB collection.

An exposure blank is similar to a FB, but is not required, and may be collected via several protocols. The exposure blank includes opening the cartridge pouch, removing the caps exposing the cartridge to the ambient atmosphere briefly (typically), and exposing it to the temperature conditions of the primary sampling cartridge for the same duration as the co-collected field samples. Like a FB, air is not drawn through the exposure blank cartridge. Some sampling units have a dedicated “field blank” channel for installation of the exposure blank through which air is not permitted to flow. For multi-channel sampling units, the exposure blank may be installed in channel which is not activated for sample flow. For sampling units which have neither a dedicated blank channel nor unused channel available on the sampling unit, the exposure blank cartridge may be removed from the foil pouch, installed in the sampling unit for five to ten minutes, the cartridge uninstalled and the end caps reinstalled, and the cartridge placed near the sampling unit for the duration the primary sample is installed in the sampling unit. The purpose of the exposure blank is to assess background contamination that may occur during cartridge installation, exposure to monitoring shelter conditions, and retrieval.

FBs and exposure blanks may passively sample ambient air throughout the time of exposure (i.e., when not sealed in the foil-lined pouch and in cold storage), and as a result may have somewhat higher background levels as compared to lot blanks, trip blanks, or laboratory MBs. Field blanks must meet and exposure blanks should meet the following criteria listed in Table 4.3-3.

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>Not-to-Exceed Limit (µg/cartridge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>&lt; 0.40</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>&lt; 0.30</td>
</tr>
<tr>
<td>Acetone *</td>
<td>&lt; 0.75</td>
</tr>
<tr>
<td>Sum of Other Target Carbonyls</td>
<td>&lt; 7.0</td>
</tr>
</tbody>
</table>

* Acetone is not a NATTS Program target compound and should not be grounds for field blank criteria failure unless the monitoring agency requires acetone measurements and/or it interferes with other target analytes in the HPLC chromatogram.

Failure to meet the FB criteria indicates a source of contamination in the sampling, handling, and/or transport and an investigation to determine the root cause and take subsequent corrective action must be performed as soon as possible. For agencies which collect associated TBs, comparison of the FB to TB values may provide meaningful insight regarding the contamination source. For FBs which fail criteria and are collected with each sampling event, the co-collected
field sample results must be qualified (QA Qualifier FB indicating field blank exceeds acceptable limit) when input to AQS. For failing FBs which are collected on a less frequent basis (i.e., monthly basis), field collected samples since the last acceptable FB must be likewise qualified when input to AQS.

Field samples must not be corrected for FB values. FB values must be reported to AQS so that data users may estimate field and/or background contamination.

4.3.8.2.2 **Trip Blanks.** TBs are a useful tool to diagnose potential contamination in the sample collection and transport of carbonyl samples. TBs are not required, but are a best practice. A TB consists of a blank unopened cartridge which accompanies field sample cartridges at all times during transport to the monitoring site, during sample collection, and during transport to the laboratory. The TB cartridge is stored in the same refrigerator/freezer, transported in the same cooler to and from the site, and kept at ambient conditions during sample collection. The cartridge must remain sealed in the foil pouch and not be removed from its zipseal foil-lined pouch until extracted in the laboratory.

Background levels on the TB should be comparable to the lot blank average determined as in Section 4.3.5.1 and must not exceed the values listed in Table 4.3-2. Exceedance of these thresholds must prompt corrective action and the results of the associated field-collected samples must be appropriately qualified (QA Qualifier TB indicating trip blank value above acceptable limit) when input to AQS.

4.3.8.2.3 **Collocated Samples.** Collocated sampling is described in detail in Section 4.3.3.1.1. When such is performed, it must be done at a frequency of no less than 10%, equivalent to approximately one collocated sample every other month.

Following extraction and analysis the collocated cartridge results are compared to evaluate precision. Precision must be < 20.1% RPD for results which one of the precision pair is ≥ 0.5 µg/cartridge (refer to Section 2.1.3.1). Root cause analysis must be performed for instances in which collocated samples fail this precision specification and the results for both the primary and collocated samples must be qualified (QA Qualifier LJ indicating value is estimated and QA Qualifier QX indicating QC failure) when entered into AQS.

4.3.8.2.4 **Duplicate Samples.** Duplicate sampling is described in detail in Section 4.3.3.1.2. Where such is performed, it must be done at a frequency of no less than 10%, equivalent to approximately one duplicate sample every other month.

Following extraction and analysis the duplicate cartridge results are compared to evaluate precision. Precision must be < 20.1% RPD for results which one of the precision pair is ≥ 0.5 µg/cartridge (refer to Section 2.1.3.1). Root cause analysis must be performed for instances in which duplicate samples fail this precision specification and the primary and duplicate results must be qualified (QA Qualifier LJ indicating value is estimated and QA Qualifier QX indicating QC failure) when entered into AQS.
4.3.8.2.5  **Field Matrix Spikes.** Performance of field matrix spike sample collection is a best practice, but is not required. Field matrix spikes are prepared by spiking a blank DNPH cartridge with a known amount of analyte (either derivatized or underivatized) prior to dispatching to the field for collection. The field matrix spike is handled identically to field samples; sample storage, transport, and extraction are identical. Field matrix spiked samples are collected concurrently with a non-spiked primary sample as a duplicate sample per Section 4.3.8.2.4 via duplicate channel or split sample flow.

The primary field sample and matrix spike sample analysis results are evaluated for spike recovery based on the amount spiked prior to shipment to the field as follows:

\[
\text{%Recovery} = \frac{(\text{Field Matrix Spike Result} - \text{Primary Sample Result})}{\text{Theoretical Nominal Spiked Amount}} \cdot 100
\]

Spike recovery should be within 79.9 to 120.1% recovery of the theoretical nominal spiked amount. In the event of an exceedance, root cause analysis should be performed to determine sources of negative or positive bias, as needed, for example, sources of contamination or reasons for the loss of analyte. High recoveries may indicate contamination in the matrix spike sample collection channel or poor collection efficiency (low bias) in the primary sample collection channel. Low recoveries may indicate a poorly functioning ozone denuder, which permits ozone to pass through the sample collection flow path and degrade the spiked analytes.

4.3.8.2.6  **Breakthrough Samples.** While not required, collection of breakthrough samples is a best practice. A breakthrough sample is a second DNPH cartridge connected in series immediately downstream of the primary sample cartridge. Periodic collection of breakthrough samples provides a level of assurance that the primary sample cartridge is efficiently trapping target carbonyls. For sites at which breakthrough sampling is conducted, the recommended frequency is once per month which should be described in the agency NATTS QAPP, SOP, or similar controlled document.

Note that this breakthrough cartridge will increase the pressure drop in the sampling system and may require an adjustment in the operation of the sampling unit to achieve the desired flow rate.

Breakthrough sample results are to meet the FB criteria listed in Table 4.3-3.

4.3.9  **Carbonyls Sample Extraction and Analysis.** Target carbonyls collected on DNPH cartridges are extracted and analyzed per EPA Compendium Method TO-11A\(^1\) according to the following guidance.

4.3.9.1  **Analytical Interferences and Contamination**

4.3.9.1.1  **Analytical Interferences.** The carbonyl-hydrazone derivatives are separated with a HPLC system and are typically detected at 360 nm with a photodiode array (PDA) or similar detector operating at UV wavelengths. Identification is based on RT matching with known standards. MS and PDA detectors are also an option if more definitive identification and quantification are desired or required. Minimally, analysis by HPLC-UV must be performed.
Laboratories may also employ UHPLC separation methods; however, the performance specifications for sensitivity, bias, and precision remain unchanged. UHPLC permits use of higher pumping pressures, faster run times, and separation columns offering better chromatographic resolution; however, are not required for analysis of extracts of collected cartridge samples.

Interferences from coeluting peaks may result from hydrazones formed by co-collected compounds or reactions with co-collected compounds which form artifacts. Such coeluting peaks may form as dimers or trimers of acrolein or be the result of chemical reactions with nitrogen oxides. Target analyte peaks in chromatograms which indicate shoulders, tailing, or inflection points should be investigated to ensure these chromatographic problems are not related to a coeluting interference.

4.3.9.1.2 Labware Cleaning. Labware must be thoroughly cleaned prior to use to eliminate potential interferences and contamination. Regardless of the specific procedures implemented, all method performance specifications for cleanliness must be met. Volumetric labware used for collection of cartridge eluent can show buildup of silica gel residue over time, requiring aggressive physical/manual cleaning methods with laboratory detergent and hot water. The recommended cleaning procedure for labware is to rinse interior surfaces with ACN, wash with hot water and laboratory detergent, rinse with deionized water, rinse with ACN or methanol, and air drying or drying in an oven at no more than 80 to 90°C. Heated drying of volumetric ware at temperatures > 90°C may void the manufacturer volumetric certification.

4.3.9.1.3 Minimizing Sources of Contamination. Several target analytes in this method are typically present in ambient air and may contaminate solvents and react with DNPH reagent on the cartridge media if appropriate preventive measures are not in place. ACN used for sample extraction, standards preparation, and mobile phase preparation must be carbonyl-free HPLC grade or better (as indicated by the supplier or on the COA) and must be stored tightly capped away from sources of carbonyls. DNPH cartridges must be handled properly per Section 4.3.5.2. Laboratories which process environmental samples for organic compounds such as pesticides or herbicides typically employ extraction with acetone or other solvents which may contaminate DNPH cartridge media and carbonyl extraction solvents. Laboratory areas in which cartridges are stored, extracted, and analyzed should be free of contaminating solvent fumes. Carbonyls sample handling areas should have heating, ventilation, and air conditioning (HVAC) systems separate from such laboratory operations.

4.3.9.2 Reagents and Standard Materials

4.3.9.2.1 Solvents. Solvents employed for extraction, preparation of standards solutions, and preparation of mobile phase(s) must be high-purity carbonyl-free, HPLC grade (or better), and shown by analysis to be free of contaminants and interferences. Such solvents include ACN, methanol, and deionized water. Deionized water must be ASTM Type I (resistivity ≥ 18 MΩ·cm).

Analysts should be aware that contamination of solvents with carbonyls will not be evident in HPLC-UV chromatograms unless the contaminated solvent or reagent comes in contact with
DNPH to form carbonyl-hydrazones (target carbonyl compounds do not fluoresce at the UV wavelengths interrogated for this method). Analysis of solvent will typically demonstrate an absence of carbonyl-hydrazones; however, precautions should be taken to prevent dissolution of carbonyls into laboratory solvents employed for this method as they will derivatize upon contact with DNPH within sampling media cartridges.

4.3.9.2.2 Calibration Stock Materials. Calibration source (primary standard) material must be of known high purity and must be accompanied by a COA. Calibration stock standard solutions may be prepared from neat high purity solid stock standards or may be sourced as certified single component or component mixtures of target compounds in an appropriate solvent (i.e., ACN or methanol).

Neat solid material must be weighed with a calibrated analytical balance with the appropriate sensitivity for a minimum of three significant figures in the determined standard mass. The neat material is weighed into the Class A volumetric flask in which the solution will be diluted to final volume or the analyst will weigh into a suitable container and perform a robust method of quantitative transfer (e.g., weighing in a suitable weighing boat, transferring the weighed material to the Class A volumetric flask, and rinsing the weighing boat thoroughly several times with ACN). The calibration of the balance must be verified on the day of use with certified weights bracketing the masses to be weighed. Calibration standard solutions diluted from stock standard solutions must be prepared by delivering stock volumes with mechanical pipettes or calibrated gastight syringes and the volumes dispensed into Class A volumetric labware to which ACN is added to establish a known final dilution volume.

4.3.9.2.3 Second Source Calibration Verification Stock Materials. A second source standard solution must be prepared to verify the calibration of the HPLC on an ongoing basis, minimally immediately following each ICAL. The second source stock standard must be purchased from a different supplier than the calibration stock material or, only if unavailable from a different supplier, may be of a different lot from the same supplier as the calibration material.

4.3.9.2.4 Stock Standard Holding Time and Storage Requirements. Unopened stock materials are appropriate for use until their manufacturer-assigned expiration date provided they are stored per manufacturer requirements. Once opened, stock materials may not be used past the manufacturer recommended period or, if no time period is specified, not beyond six months from the opened date. To use the standard materials past this time period, standards must have been demonstrated to not be degraded or concentrated by comparison to freshly opened standards. Unopened stock materials are to be stored per manufacturer recommendations. Stock and diluted working calibration standard solutions are to be stored at ≤ 4°C in a separate refrigeration unit from sample cartridges and sample extracts. If storage conditions are not maintained appropriately, compare affected standards to standards with appropriate integrity to ensure standard concentrations are < ±15.1%. Data associated with samples analyzed with compromised standard materials will need to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

4.3.9.3 Cartridge Holding Time and Storage Requirements. Field-collected cartridges must be stored at ≤ 4°C and extracted within 14 days of the end of collection. These conditions
similarly apply to laboratory-prepared QC samples, which must be stored at ≤ 4°C and extracted within 14 days of preparation. Extracts are to be analyzed within 30 days of extraction. Results input to AQS must be appropriately qualified (QA Qualifier LJ indicating the value is an estimate) for failure to meet the holding time and/or storage criteria. Note that as of the time this document was prepared the AQS qualifier code related to holding time exceedance was a NULL Qualifier (TS) that invalidates the measurement data. EPA’s preference is that sample data measured with an exceeded holding time be qualified, and not invalidated.

4.3.9.4 Cartridge Extraction. DNPH cartridge extraction is to be accomplished in batches of field samples which comprise associated laboratory QC samples. The guidance that follows presumes a recommended extraction batch size of 20 or fewer field-collected samples (including field QC samples as listed in Section 4.3.8.2), and strongly recommends that extraction batch QC samples be prepared at this frequency, where an additional suite of laboratory extraction batch QC samples be included when the batch incorporates > 20 field-collected samples and this same convention applies for batch sizes including multiples of 20 (e.g., batches including 41 field-collected samples include three suites of laboratory QC samples, and so on).

4.3.9.4.1 Laboratory Quality Control Samples. The following negative and positive laboratory extraction batch QC samples are to be prepared (except LCS/LCSD which must be prepared/analyzed minimally quarterly – recommended with each batch) with each batch of 20 or fewer field-collected samples. As practical, a best practice is to employ cartridge media for preparing QC samples of the same lot as the associated field-collected samples. This simplifies troubleshooting and root cause analysis when acceptance criteria are exceeded.

- Extraction Solvent Method Blank (ESMB): An ESMB is prepared by transferring the extraction solvent into an extract catch flask just as an extracted sample. The purpose of this negative control is to demonstrate that the extraction solvent is free of interferences and contamination and that the labware washing procedure is effective. Analysis must show target compound responses are less than the laboratory MDL_sp for MDLs determined via Section 4.1.3.1 or the s·K portion of the MDL for MDLs determined via Section 4.1.3.2.

- Method Blank (MB): The MB is a negative control sample that may also be referred to as the cartridge blank. The MB is an unopened and unused cartridge (that has not left the laboratory) which is extracted identically to field samples. All target analytes must meet criteria specified in Table 4.3-2.

- Laboratory Control Sample (LCS): The LCS, also referred to as the laboratory fortified blank (LFB), is a positive control sample prepared by spiking a known amount of underivatized or derivatized DNPH-carbonyl target analyte onto a cartridge such that the expected extract concentration is in the lower third of the calibration range. The cartridge is spiked and allowed to sit for minimally 30 minutes to allow the solvent to dry before extraction. The LCS is then extracted with the same extraction solvent and method employed for field samples to assess bias in matrix of the extraction and analysis procedures. Recovery of the LCS must be within 79.9 to 120.1% of theoretical nominal spike for formaldehyde and 69.9 to 130.1% of the theoretical nominal spike for all other target carbonyls.
**Laboratory Control Sample Duplicate (LCSD):** The LCSD is prepared and extracted identically to the LCS. The LCSD assesses precision through extraction and analysis. Recovery of the LCSD must be within 79.9 to 120.1% of the theoretical nominal spike for formaldehyde and 69.9 to 130.1% for all other target carbonyls. The LCS and LCSD results must show RPD of < 20.1%.

All field-collected and laboratory QC samples in a given extraction batch must be analyzed in the same analysis batch (an analysis batch is defined as all samples analyzed together within a 24-hour period).

Laboratories must take corrective action to determine the root cause of laboratory extraction batch QC sample criteria exceedances. Field-collected sample results associated with failing QC results (in the same preparation batch) must be appropriately qualified (QA Qualifier QX indicating QC failure) when input to AQS. Additionally, for extraction batch ESMB and MB exceedances, data for affected target carbonyls for associated samples are to be qualified (QA Qualifier LB indicating lab blank above acceptance limit) when reported to AQS.

### 4.3.9.4.2 Cartridge Extraction Procedures

Field-collected cartridges must be removed from cold storage and allowed to equilibrate to room temperature, approximately 30 minutes, prior to extraction. Cartridges are extracted with carbonyl-free HPLC grade ACN. Cartridges are removed from the foil-lined pouch, the end caps are removed, and the cartridges are installed in a holding rack with the inlet of the cartridge pointed down (preference) to facilitate elution. ASLs have reported that extraction efficiency is equivalent regardless of whether the cartridge is oriented with the cartridge inlet or outlet downward, and some ASLs have reported problems with eluting captured particulates from cartridges when orienting inlets downward. ASLs are encouraged to adopt their preferred orientation and make this standard practice. Field-collected samples and associated field and laboratory extraction batch QC samples discussed in Section 4.3.9.4.1 are to be extracted in the same batch.

Cartridges are extracted with ACN and a minimum 2-mL extraction volume is necessary to ensure complete elution of the target analytes from the sorbent bed. An extraction volume up to 5 mL may be employed, however larger volumes do not increase the extraction efficiency and may unnecessarily dilute the extract. Elution may be performed by gravity or vacuum-assisted methods. The cartridge eluent is collected in a clean volumetric flask or other appropriate volumetrically certified vessel. Once the eluent is collected, the extract is brought to the known final volume with ACN extraction solvent.

Once brought to final volume, the extract is capped and agitated to mix. It is strongly recommended that an aliquot of the extract is transferred to an autosampler vial for analysis and that the remaining extract be stored in a sealed vial with a PTFE-lined lid protected from light (e.g., in an amber glass vial) at ≤ 4°C. The stored extract affords reanalysis if there are problems during analysis (up to 30 days from extraction).

### 4.3.9.5 Analysis by HPLC

Analysis performance criteria for the solvent blank (SB), ICAL, SSCV, and CCV must be met as detailed below for Tier I carbonyls and should be met for non-Tier I carbonyls. If the criteria are not met and sample extracts cannot be reanalyzed with
appropriately acceptable QC results, Tier I carbonyls are to be invalidated (Null qualifier EC indicating critical criteria failure) and non-Tier I carbonyls are to be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS.

4.3.9.5.1 Instrumentation Specifications. For separation of the DNPH-carbonyls by HPLC, the analytical system will have the following components:

- Separations module capable of precise pumping of ACN, methanol, and/or deionized water at 1 to 2 mL/min (note many instruments including UHPLC instruments will be capable of higher flow rates and elevated pressures)
- Analytical column, C18 reversed phase, 4.6 × 50-mm, 1.8-µm particle size, or equivalent
- Guard column
- UV absorbance detector or PDA set to $\lambda = 360$ nm (nearby wavelengths such as 365 nm are also acceptable) or mass selective detector capable of scanning m/z range of 25 to 600
- Column heater capable of maintaining inline temperature of 25 to 35 ± 1 °C
- Degassing unit

4.3.9.5.2 Initial Calibration. On each day that analysis is performed, the instrument must be calibrated (meaning an ICAL must be performed) or the calibration must be verified by analysis of a CCV according to the following guidance.

ICAL of the HPLC must be performed initially, when CCV checks fail criteria, and when there are major changes to the instrument which affect the response of the instrument. Such changes include, but are not limited to: change of guard or analytical column (if analyte RTs or sensitivities change), backflushing of the analytical column (if analyte retention times change), replacement of pump mixing valves and/or seals (if analyte retention times change), replacement of the detector and/or lamp, and cleaning of the MS source (if HPLC/MS).

Working calibration standards are prepared in ACN at concentrations covering the desired working range of the detector, typically from approximately 0.01 to 3.0 µg/mL of the free carbonyl. In order to avoid confusion or error in concentration calculation, it is recommended that all concentrations be expressed as the free carbonyl and not the DNPH-carbonyl. The ICAL must consist of a minimum of five calibration standard levels which cover the desired calibration range.

Prior to calibrating the HPLC, the instrument must be warmed up and mobile phase should be pumped for a time sufficient to establish a stable chromatographic baseline. Solutions to be analyzed must be removed from cold storage and equilibrated to room temperature prior to analysis. A best practice is to agitate the solutions (shake by hand or vortex) prior to placement in the instrument autosampler.
Once a stable baseline is established, minimally one SB (an aliquot of extraction solvent dispensed directly into a vial suitable for the HPLC autosampler, or similar) is to be analyzed to demonstrate the instrument is sufficiently clean, after which analysis of calibration standard solutions may commence. The SB must show target compound responses are less than the laboratory MDL_{sp} for MDLs determined via Section 4.1.3.1 or the \( s \cdot K \) portion of the MDL for MDLs determined via Section 4.1.3.2.

To establish the ICAL, each standard solution must be injected minimally once and preferably in triplicate. The instrument response (e.g., area units) is plotted on the y-axis against the theoretical nominal concentration on the x-axis and the calibration curve is generated by least squares linear regression for each target compound. The calibration curve correlation coefficient must be \( \geq 0.999 \) for linear fits and the curve must not be forced through the origin. The calculated concentration of each calibration solution (the concentration equivalent when the standard area unit response is input into the regression equation) must be \( < \pm 20.1\% \) of its theoretical nominal concentration.

The absolute value of the concentration equivalent to the intercept of the calibration linear regression curve equation (\( \text{intercept/slope} \)) must be less than the laboratory MDL_{sp} for MDLs determined via Section 4.1.3.1 or the \( s \cdot K \) portion of the MDL for MDLs determined via Section 4.1.3.2. When this specification is not met, this indicates contamination or suppression of the target analyte response and the source of the error must be corrected and the calibration curve must be properly established before sample analysis may commence.

RT windows for each target analyte are calculated from the ICAL by determining the mean RT from the analyzed calibration standards for each target compound. For positive identification of a target analyte, the RT of a derivatized carbonyl must be within the greater of three standard deviations (3\( s \)) or \( \pm 2\% \) of its mean RT from the ICAL. Note that heating the column to a constant temperature (\( \pm 1\°C \)) of approximately 25 to 30°C promotes consistent RT response by minimization of column temperature fluctuations.

### 4.3.9.5.3 Second Source Calibration Verification Standard

Following each successful ICAL, a SSCV must be analyzed to verify the accuracy of the ICAL. The SSCV is prepared in ACN at approximately the mid-range of the calibration curve by dilution of the second source stock standard. Alternatively, two or more concentrations of SSCV may be prepared covering the calibration range. Regardless of their concentration, SSCVs must recover within \( \pm 15.1\% \) of the theoretical nominal.

### 4.3.9.5.4 Continuing Calibration Verification

Once the HPLC has met ICAL criteria and the ICAL verified by the SSCV, a CCV is to be analyzed prior to the analysis of samples on days when an ICAL is not performed, and minimally every 12 hours of analysis. The CCV is also recommended to be analyzed after every 10 sample injections and at the conclusion of the analytical sequence. On days when an ICAL is not performed, a SB is to be analyzed prior to the CCV to demonstrate the instrument is sufficiently clean to commence analysis.

At a minimum, a CCV is to be prepared with target analytes at concentrations recommended to be in approximately the mid-range or lower end of the calibration curve. The CCV is typically
diluted from the primary stock or second source stock material; however, if from a third source, the CCV source must be concentration certified. CCVs must recover within ± 15.1% of the theoretical nominal for each target compound. As a best practice, CCVs may be prepared at two or more different concentrations for each target analyte (e.g., lower 1/3 and upper ½ of the calibration range) so as to better cover instrument performance across the calibration range.

Corrective action is to be taken to address CCV failures, including, but not limited to, preparing and analyzing a new CCV, changing the guard or analytical column, backflushing of the analytical column, replacement of the detector and/or lamp (if HPLC/UV), and cleaning of the MS source (if HPLC/MS). Solutions analyzed since the most recent passing CCV will require reanalysis after successfully verifying the instrument calibration.

4.3.9.5.5 Replicate Analysis. For each analytical sequence of 20 or fewer field-collected samples, at least one field-collected sample extract (not a blank such as a FB or TB) should be selected for replicate analysis (as prescribed in the workplan). For sequences containing more than 20 field-collected samples, \( n \) such replicates must be analyzed, where \( n = \text{batch size} / 20 \), and where \( n \) is rounded to the next highest integer. Thus, for batch sizes of 30, two replicate analyses would be performed. Replicate analysis must demonstrate precision of < 10.1% RPD for extracts for which at least one of the extracts measures \( \geq 0.5 \mu\text{g/cartridge} \) (refer to Section 2.1.3.1). Qualify sample data for affected carbonyls (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated) when reporting to AQS (note that this applies to AQS RD transactions and that replicate data reported as an AQS QA transaction cannot be qualified).

For replicate analysis, the ASL will typically assign a convention that the first replicate for a replicate analysis is that which is reported to AQS for the sample result. However, if the first replicate is invalidated for any reason (e.g., as may occur when a coeluting peak significantly interferes with the target peak) and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as described in Section 2.1.3.2.

4.3.9.5.6 Compound Identification. The following criteria must be met in order to positively identify a target compound:

1. The signal to noise ratio of the target compound chromatographic peak must be > 3:1, preferably > 5:1. Refer to Section 4.2.11 for more information on signal to noise ratio.

2. The RT of the compound must be within the acceptable RT window determined from the ICAL average (see Section 4.3.9.5.2).

3. **HPLC-MS only** - The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other). Refer to Section 4.2.11 for more information on co-maximization.

4. **HPLC-MS only** - The abundance ratio of the qualifier ion response to target ion response for at least one qualifier ion must be within ± 30.1% of the average ratio from the ICAL. Refer to Section 4.2.11 for more information on ion abundances.

The signal to noise ratio for each chromatographic peak does not need to be evaluated closely. Rather the interpretation of the experienced analyst should weigh heavily on whether the peak
meets the minimal signal to noise ratio. The assignment and evaluation of RT windows may be automated by the analysis software such that peaks outside this range are not positively identified. Analysts should ensure that RT windows are updated with each ICAL.

If any of these criteria (as applicable) are not met, the compound may not be positively identified. The only exception to this is when in the opinion of an experienced analyst the compound is positively identified, in which case the rationale for such an exception must be documented.

4.3.9.5.7 Data Review and Quantitation. Each chromatogram is to be examined to ensure chromatographic peaks are appropriately resolved and integrated peaks do not inappropriately include peak shoulders or inflections indicative of a coelution. The HPLC method may require modification to employ mobile phase gradient programming or other methods to resolve coeluting peaks. Proper and improper chromatographic peak integration practices are discussed in Appendix D. Analysts should review their own work to ensure documentation is comprehensive, calculations are accurate, and that sample processing practices follow established procedures. ASLs are strongly encouraged to have a peer conduct review of the completed data package for these same aspects and to document this review in the laboratory records. Review of a representative amount of the generated data (e.g., 10%) should be included in routine QA audits to ensure calculation veracity and procedural compliance.

Each chromatogram of an extracted cartridge (MB, LCS, LCSD, or any field-collected sample) is to be examined to ensure a DNPH peak is present. Chromatograms in which the DNPH peak area is < approximately 50% of the typical peak area of the laboratory MBs are to be investigated for potential compound misidentification due to the likely appearance of additional chromatographic peaks as a result of formation of side products from the consumption of the DNPH. This verification can be estimated and should be prescribed within the SOP or similar controlled document. Once sample identification is confirmed, affected target analyte concentration measurements for field-collected samples are to be qualified (QA Qualifier DN indicating DNPH peak is less than 50% of the expected peak area and the value is an estimate) when entered into AQS since depletion of the DNPH to below 50% of typical levels indicates the potential for negative bias in the measured concentrations. Cartridge extracts without a DNPH peak will have the associated measurement data invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

The concentrations of target carbonyls in unknown samples are calculated by relating the area response of the target carbonyl to the relationship derived in the calibration linear regression curve generated in Section 4.3.9.5.2 as follows:

\[
C_t = \frac{(A - b)}{m}
\]

where:

- \(C_t\) = measured concentration of target carbonyl in the extract (µg/mL)
- \(A\) = integrated peak area response of the target carbonyl (area units)
- \(b\) = y-intercept of linear least-squares regression (area units)
- \(m\) = slope of linear least-squares regression (area unit/(µg/mL))
Concentration results which exceed the instrument calibration range must be diluted and analyzed such that peak area response is within the calibration range. The diluted result is to be reported and the associated MDL adjusted accordingly by the dilution factor (the MDL is multiplied by the dilution factor for reporting).

While TO-11A allows for blank subtraction, this is not an acceptable practice for the NATTS Program and results must not be corrected for SB, lot blank, FB, or MB levels. Concentrations exceeding acceptance criteria for these blanks will be a prompt for investigation as to the source of contamination and associated field collected sample results may require qualification to describe the nature of the failure (e.g., field blank exceedance would prompt qualification of ambient sample data with an FB QA Qualifier for reporting to AQS).

4.3.9.5.8 Calculation of In-Air Concentration. For sampling units which do not provide an integrated collected sample volume (i.e., the sampling flow rate is not logged to provide these data at retrieval), the initial and ending flows are averaged and then multiplied by the elapsed sampling time to calculate the collected air volume.

\[
V_A = Q_{\text{avg}} \cdot T_c
\]

where:

\[
V_A = \text{volume of collected air at STP (m}^3\text{)}
\]

\[
Q_{\text{avg}} = \text{average STP flow rate over the sample collection duration (m}^3\text{/minute)}
\]

\[
T_c = \text{sample collection duration (min)}
\]

For computer controlled sampling units, the integrated collected volume is typically available from the data logging system. Sampled air volumes must be expressed in EPA STP conditions of 25°C and 760 mm Hg. Sampling unit flow rates are to be calibrated relative to standard conditions so conversion from local conditions to standard flow rates (and the potential for error) is not necessary.

The air concentration in µg/m³ of each target carbonyl is determined by multiplying the concentration in the extract by the final extract volume and dividing by the collected sample air volume at standard conditions of 25°C and 760 mm Hg:

\[
C_A = \frac{C_t \cdot V_e}{V_A}
\]

where:

\[
C_A = \text{concentration of the target carbonyl in air (µg/m}^3\text{)}
\]

\[
C_t = \text{concentration of the target carbonyl in the extract (µg/mL)}
\]

\[
V_e = \text{final volume of extract (mL)}
\]

\[
V_A = \text{volume of collected air at STP (m}^3\text{)}
\]

Carbonyl concentrations can also be calculated in ppbv by multiplying by a conversion factor based on the molecular weight of the target carbonyl at STP as follows:
\[ CF = \frac{MW}{0.082059 \times 298.15} \]

where:

\[ CF = \text{conversion factor (µg·m}^{-3}\cdot\text{ppbv}^{-1}) \]
\[ MW = \text{molecular weight of the target carbonyl (g/mol)} \]

The air concentration of the target carbonyl in ppbv is then calculated as follows:

\[ C_{A,\text{ppbv}} = \frac{C_A}{CF} \]

where:

\[ C_{A,\text{ppbv}} = \text{concentration of the target carbonyl in air (ppbv)} \]
\[ C_A = \text{concentration of the target carbonyl in air (µg/m}^3\) \]
\[ CF = \text{conversion factor (µg·m}^{-3}\cdot\text{ppbv}^{-1}) \]

4.3.10 Summary of Quality Control Parameters. A summary of QC parameters is shown in Table 4.3-4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Blank (SB)</td>
<td>Aliquot of ACN analyzed to demonstrate instrument is sufficiently clean to begin analysis</td>
<td>Prior to ICAL and daily beginning CCV</td>
<td>Target carbonyls &lt; MDLsp (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2)</td>
</tr>
<tr>
<td>Initial Calibration (ICAL)</td>
<td>Analysis of a minimum of five calibration levels covering approximately 0.01 to 3.0 µg/mL</td>
<td>Initially, following failed CCV, or when changes to the instrument affect calibration response</td>
<td>Linear least squares regression: ( r \geq 0.999 ), the concentration of each target carbonyl at each calibration level (&lt;\pm 20.1% ) of theoretical nominal Y-intercept concentration equivalent &lt; MDLsp (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2)</td>
</tr>
<tr>
<td>Second Source Calibration Verification (SSCV)</td>
<td>Analysis of a second source standard at approximately the mid-range of the calibration curve range to verify curve accuracy</td>
<td>Immediately following each ICAL</td>
<td>Recovery of each target carbonyl &lt; ±15.1% of theoretical nominal</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Details</td>
<td>Required Frequency</td>
<td>Acceptance Criteria</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------</td>
<td>--------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>Analysis of a known standard at approximately the mid-range of the calibration curve to verify ongoing instrument calibration. Concentration of CCV in the lower 1/3 of the calibration curve also recommended</td>
<td>Prior to sample analysis on days when an ICAL is not performed, and minimally every 12 hours of analysis. Recommended following every 10 sample injections, and at the conclusion of each analytical sequence</td>
<td>Recovery of each target carbonyl $\pm 15.1%$ of theoretical nominal</td>
</tr>
<tr>
<td>Extraction Solvent Method Blank (ESMB)</td>
<td>Aliquot of extraction solvent analyzed to demonstrate extraction solvent is free of interferences and contamination</td>
<td>One with every extraction batch of 20 or fewer field collected samples, at a frequency of no less than 5%</td>
<td>Target carbonyls &lt; MDL$_{sp}$ (refer to Section 4.1.3.1) or $s\cdot K$ (refer to Section 4.1.3.2)</td>
</tr>
<tr>
<td>Method Blank (MB)</td>
<td>Unexposed DNPH cartridge extracted as a sample</td>
<td>One with every extraction batch of 20 or fewer samples, at a frequency of no less than 5%</td>
<td>Criteria in Table 4.3-2 must be met</td>
</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>DNPH cartridge spiked with known amount of target analyte at a concentration in approximately the lower third of the calibration curve</td>
<td>Minimally quarterly. Recommended: One with every extraction batch of 20 or fewer field-collected samples, at a frequency of no less than 5%</td>
<td>Formaldehyde recovery 79.9-120.1% of theoretical nominal spike</td>
</tr>
<tr>
<td>Laboratory Control Sample Duplicate (LCSD)</td>
<td>Duplicate LCS to evaluate precision through extraction and analysis</td>
<td>Minimally quarterly. Recommended: One with every extraction batch of 20 or fewer field-collected samples, at a frequency of no less than 5%</td>
<td>Must meet LCS recovery criteria</td>
</tr>
<tr>
<td>Replicate Analysis</td>
<td>Replicate analysis of a field-collected sample extract</td>
<td>Once with every analysis sequence of 20 or fewer field-collected samples, at a frequency of no less than 5% (as required by workplan)</td>
<td>Precision &lt; 10.1% RPD for extracts where minimally one replicate concentration is $\geq 0.5$ µg/cartridge</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>RT of each target compound in each standard and sample</td>
<td>All qualitatively identified compounds</td>
<td>Each target carbonyl within $\pm 3$s or $\pm 2%$, whichever is greater, of its mean ICAL RT</td>
</tr>
<tr>
<td>Lot Blank Evaluation</td>
<td>Determination of the target analyte background concentration of the DNPH cartridge media</td>
<td>Minimum of 3 cartridges or 1% (whichever is greater) for each new lot of DNPH cartridge media</td>
<td>All cartridges must meet criteria in Table 4.3-2. For failure, extract the greater of 3 additional cartridges or 1%. Repeated failure results in rejection of lot for sample collection.</td>
</tr>
<tr>
<td>Bias Qualification Check (zero qualification challenge and known standard qualification challenge)</td>
<td>Collection of humidified zero air and known standard gas on reference cartridges and through the sampling unit to assess target analyte concentration bias</td>
<td>Annually following denuder (and other component) replacement and maintenance, prior to field deployment</td>
<td>Zero qualification will show each target carbonyl in the zero certification $\leq 0.2$ ppbv above reference sample. Known standard challenge sample will be $\leq 15.1%$ of the reference sample.</td>
</tr>
</tbody>
</table>
### Table 4.3-4. Summary of Quality Control Parameters for NATTS
**Carbonyls Analysis (Continued)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field Blank</td>
<td>Blank DNPH cartridge exposed to field conditions for minimally 5 minutes in the primary sampling position</td>
<td>Monthly Recommended with each primary sampling event</td>
<td>Must meet criteria in Table 4.3-3</td>
</tr>
<tr>
<td>Duplicate Sample</td>
<td>Field sample collected through the same inlet probe as the primary sample</td>
<td>Collected as 10% of primary samples for sites performing duplicate sample collection (as required by QAPP)</td>
<td>Precision &lt; 20.1% RPD of primary sample when at least one of the concentrations in the precision pair is ≥ 0.5 µg/cartridge</td>
</tr>
<tr>
<td>Collocated Sample</td>
<td>Field sample collected through a separate inlet probe and with a separate sampling unit from the primary sample</td>
<td>Collected as 10% of primary samples for sites performing collocated sample collection (as required by workplan)</td>
<td>Precision &lt; 20.1% RPD of primary sample when at least one of the concentrations in the precision pair is ≥ 0.5 µg/cartridge</td>
</tr>
<tr>
<td>DNPH peak evaluation</td>
<td>Compare DNPH peak area response in sample chromatograms to the batch MB</td>
<td>Each field collected sample</td>
<td>DNPH peak area in unknown samples ≥ 50% of the MB DNPH peak area</td>
</tr>
</tbody>
</table>

### 4.3.11 References


4.4 PM$_{10}$ Metals Sample Collection and Analysis

Each agency and ASL is to prescribe in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for performing PM$_{10}$ metals sampling, filter digestion, digestate analysis, and data reporting. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.4.12 must be met.

4.4.1 Summary of Method. PM$_{10}$ metals are collected onto a filter by either a low volume or high volume air sampling method. Following completion of either sampling procedure, the collected filter, or portion thereof, is digested to liberate (dissolve) the desired elements by heating in acid, and the digestate is analyzed via ICP/MS per EPA Compendium Method IO-3.5. Briefly, digestates are introduced to the ICP/MS through pneumatic nebulization into a radio frequency argon plasma where the elements in solution are desolvated, atomized, and ionized. The ions are extracted from the plasma by vacuum and separated on the basis of their mass-to-charge ratio by a quadrupole MS, TOF MS, or magnetic field sector MS capable of a resolution of $\leq 1$ amu at 5% peak height. An electron multiplier is applied to the ions’ transmission responses and the resulting signal information recorded and processed by the data system.

The particle-bound metals in the air are collected with a commercially-available standalone air sampler fitted with a size-selective inlet (SSI) such that only PM with a mass median aerodynamic diameter less than 10 µm is captured. Particles are deposited on either 47-mm PTFE Teflon® filter (low volume) or 8 inch × 10 inch QFF media over the 24-hour collection period. The low volume sampling method flow rate is controlled to 16.7 liters per minute (LPM; at local conditions) for a total collection volume of 24.05 m$^3$. The high volume method flow rate is controlled to approximately 1.13 m$^3$/min (at local conditions) for a total collection volume of approximately 1627 m$^3$. For both low volume and high volume sampling methods, the SSIs require a closely-regulated flow rate to ensure PM separation cut points are accurate and temporally stable.

If collected filters are to be analyzed for total PM$_{10}$ concentration, a weighing laboratory will need to measure a tare weight of the unsampled filter prior to field deployment. Such gravimetric total PM$_{10}$ concentration analysis is outside the scope of this TAD and will not be further discussed except for precautions which impact PM$_{10}$ metals analysis. Following the completion of any desired gravimetric measurements for determining total PM$_{10}$ gravimetric concentration, the filters are digested for metals analysis. Following collection, filters should be stored at ambient conditions and are to be digested and analyzed within 180 days of the end of collection.

The target metals of interest to the NATTS Program are listed in Table 4.4-1.
Table 4.4-1. NATTS Program Metals Elements and Associated CAS Numbers

<table>
<thead>
<tr>
<th>Element</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>7440-36-0</td>
</tr>
<tr>
<td>Arsenic</td>
<td>7440-38-2</td>
</tr>
<tr>
<td>Beryllium</td>
<td>7440-41-7</td>
</tr>
<tr>
<td>Cadmium</td>
<td>7440-43-9</td>
</tr>
<tr>
<td>Chromium</td>
<td>7440-47-3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>7440-48-4</td>
</tr>
<tr>
<td>Lead</td>
<td>7439-92-1</td>
</tr>
<tr>
<td>Manganese</td>
<td>7439-96-5</td>
</tr>
<tr>
<td>Nickel</td>
<td>7440-02-0</td>
</tr>
<tr>
<td>Selenium</td>
<td>7780-49-2</td>
</tr>
</tbody>
</table>

*a* NATTS Tier I core analyte  
*b* NATTS PT target analyte

4.4.2 Advantages and Disadvantages of High Volume and Low Volume PM10 Sample Collection. Summarized below are some of the advantages and disadvantages of the high and low volume air sampling for PM10 metals.

4.4.2.1 Low Volume Sampling

Advantages

- Many low volume samplers are already in use at PM monitoring sites to assess compliance with the National Ambient Air Quality Standards and are identical in operation to FRM PM2.5 sampling units ubiquitous at ambient air monitoring sites. As a result, many monitoring agencies are familiar with and have the trained staff and infrastructure (equipment and spare parts) to support low volume PM10 sampling.
- PTFE Teflon® filters, as compared to QFFs, typically have lower background levels of metals such as chromium, nickel, manganese, and cobalt. As a result of this lower background, MBs are cleaner and MDLs are typically lower than those for high volume QFFs.
- Low volume instruments are available which permit the installation of several filters such that the site operator can program several sequential sampling events to occur without operator intervention.
- Electrical power (current draw) for low volume samplers is less than that for high volume samplers (particularly at startup), thereby requiring less robust electrical infrastructure at sites.
- Low volume sampling units sample much lower volumes of ambient air and therefore are permitted to be closer (1 meter) than high-volume samplers (2 m) to other sampling instruments and inlets.

Disadvantages

- The extraction and analysis method must have greater sensitivity (lower detectability) and background contamination must be more strictly limited in order to achieve MDLs equivalent to high volume sampling, due to the lower total sample volume.
collected. A low volume PTFE Teflon® filter collects approximately 1/7 of the mass of a comparable 1 inch x 8 inch filter strip portioned from a collected high volume QFF.

- The entire PTFE Teflon® filter is digested for analysis, thus error in preparation for digestion may require invalidation of results, and it is not possible to prepare duplicate and/or spike duplicate field collected samples for QC purposes.

### 4.4.2.2 High Volume Sampling

**Advantages**

- At the listed flow rates, the high volume sampling method collects approximately 67 times more mass on the filter than low volume sampling, thereby providing greater sensitivity (approximately seven-fold) for metals analysis even after taking into consideration that only a portion (typically approximately 1/9) of the QFF is digested for analysis.
- In the event of loss of the primary sample strip and when assessment of method precision and bias is desirable, additional strips from the collected filter may be portioned to prepare duplicate and spike duplicate samples.

**Disadvantages**

- QFFs typically have higher background levels of target metals, such as chromium, nickel, manganese, and cobalt, which results in elevated MDLs.
- Sequential sampling is not possible with high volume filter sampling instruments, therefore, the site operator must attend to the sampling unit before and after each sample collection event.
- High volume sampling units require a large electrical current draw on startup and require robust electrical infrastructure at monitoring sites. This may limit the ability to collocate another high-volume PM10 sampler at the site.

### 4.4.3 Minimizing Contamination, Filter Handling, and Filter Inspection

**4.4.3.1 Minimizing Contamination of Filter Media and Collected Samples.** Careful handling of the filter media is required to ensure that metals measured on the filter are present as a result of sampling the ambient atmosphere, rather than due to contamination. Additionally, collected filters must be handled carefully to reduce the likelihood of dislodging collected PM from the filter. What follows in this section are practices either that are required or are recommended for adoption into an agency’s and/or ASL’s quality system.

See also Section 4.4.6 for guidance on minimizing contamination during the preparation of labware.

**4.4.3.2 Filter Handling.** Filters should only be handled with gloved hands (new gloves are recommended to avoid contamination as is changing gloves after potentially contaminating
gloves during filter sample handling) or plastic or fluoropolymer-coated forceps, and filter media
must not be manipulated with metal tools. Tools for portioning filter strips must be non-metallic – e.g., ceramic or plastic. Forceps and work areas should be routinely decontaminated using a
dilute nitric acid solution followed by rinses with deionized water. Use of volumetric syringes
with metal needles and/or metallic components that contact solutions must be avoided. Work
areas should be cleaned regularly to eliminate dust that could contaminate field-collected and QC
sample filters.

PTFE Teflon® filter media should be transported to and from the field in Delrin™ (or equivalent)
cassettes which must be kept tightly capped except during installation of filters into sampling
units. Note that support screens for the PTFE filters are typically stainless steel; however, a
robust cleaning and inspection process (refer to Section 4.4.9.3.2) should be established to ensure
the support screens are not damaged (i.e., corroded or exhibit loose plating) to result in transfer
of metallic residue to the PTFE filters. Placement of filters into, and subsequent removal of
filters from cassettes should be performed in the laboratory in a clean area where measures are
taken to control the levels of airborne particulate matter, such as a conditioning room for filter
weighing. Such filter weighing rooms typically employ dust-reduction methods such as high
efficiency particulate air (HEPA) filtration to minimize potential deposition contamination.

QFFs should be placed into, and subsequently removed from, the cassette while the cassette is in
a clean area, one without obvious dust contamination, away from visible sources of PM, and with
minimal air movement (e.g., indoors such as inside a monitoring shelter or vehicle). For
transportation to the field monitoring site, a best practice is to install the QFF into the sampling
cassette and install a snap-fit cover on the cassette to protect the filter exposure surface. If
transportation to the field monitoring site in the cassette is not practical, unsampled filters should
be protected in a manila folder or envelope to avoid dust contamination and prevent folding or
creasing of the QFF. Following removal from the cassette after the conclusion of sampling, the
filter is folded (lengthwise recommended) in half (with gloved hands or within a clean paper or
cardboard template) with the particulate matter inward. The folded filter is then placed into a
glassine envelope to protect the filter from loss of PM or from deposition of dust and then placed
within a protective manila envelope or folder. Sampling unit SSIs should be inspected and
cleaned periodically (recommended minimally annually and more often if the site experiences
high PM concentrations such as occurs in spring with high pollen levels) to ensure gasket
material, corrosion, and/or dust and dirt does not slough onto the collected filter when lifting the
SSI to access the filter.

4.4.3.3 Filter Inspection. New filter media is to be inspected for pinholes, discolorations,
crease, thin spots, and other defects which would make them unsuitable for sample collection.
PTFE Teflon® filters are additionally to be inspected for separation of the support ring. Filters
should be inspected with a light table or similar apparatus which allows diffuse backlighting of
the filter to aid in the identification of defects. Any surface (such as the light table) coming into
contact with the filter media must be decontaminated from dust and residue prior to use with
deonized water and lint-free wipes. Filter handling requirements given in Section 4.4.3.2 are to
be followed. Data for samples collected with damaged or defective filters are to be invalidated
(Null qualifier AJ indicating filter damage) when reported to AQS.
4.4.4 Precision – Sample Collection and Laboratory Processing. Given below are the various types of precision for PM$_{10}$ metals measurements and guidance on how to measure each.

Precision is assessed by calculating the RPD for precision pairs (e.g., collocated samples, QFF digestion batch duplicates, LCS/LCSD, MS/MSD, and replicate analyses). The RPD is evaluated when at least one of the measurements in the precision pair is $\geq 5\times$ MDL and must be $< 20.1\%$. When both measurements in the precision pair are $\geq 5\times$ MDL, the calculation is straightforward. However, for precision pairs for which one measurement is $\geq 5\times$ MDL and the other is $\leq 5\times$ MDL, calculate the precision RPD by substituting the $5\times$ MDL concentration for the measurement $\leq 5\times$ MDL per the convention in Section 2.1.3.1. This calculation of RPD is only for assessment of precision; measured concentrations for the precision pair are to be reported to AQS as measured (not substituted for $5\times$ MDL).

Failure to satisfy the precision criterion will prompt root cause analysis to investigate and correct the failure. If the issue cannot be corrected satisfactorily, the associated sample data are to be qualified when entered into AQS as follows (Refer to Table 3.1-1):

- Collocated precision – both primary and collocated samples qualified (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated)
- QFF digestion batch duplicate filter strips – all samples in the digestion batch qualified (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated)
- MS/MSD – the sample in question qualified (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated)
- LCS/LCSD - all samples in the digestion batch qualified (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated)
- Replicate analyses – all samples in the analysis batch qualified (QA Qualifier QX indicating QC failure and QA Qualifier LJ indicating the value is estimated) unless the batch is reanalyzed with acceptable QC

For replicate analysis, the ASL will typically assign a convention that the first replicate for a replicate analysis is that which is reported to AQS for the sample result. However, if the first replicate is invalidated for any reason and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as the sample result as described in Section 2.1.3.2.

4.4.4.1 Sample Collection Precision. Given that each PM$_{10}$ metals instrument consists of a discrete inlet and sampling pump, collection of duplicate samples is not possible. Thus, evaluation of the precision of the entire PM$_{10}$ metals sampling technique, from collection through extraction and analysis, may only be performed by way of collocated sampling.

For monitoring sites conducting collocated PM$_{10}$ metals sampling, collocated samples are to be collected as minimally 10% of the primary samples collected (as prescribed in the QAPP). This is equivalent to a minimum of six collocated samples for sites conducting one-in-six days.
sampling for a total of 61 primary samples annually. More frequent collocated sample collection provides additional sample collection precision data and is encouraged where feasible.

4.4.4.2 Laboratory Precision

4.4.4.2.1 Low Volume PTFE Teflon® Filter Laboratory Precision. PTFE Teflon® filters are extracted in their entirety, therefore duplicate samples for assessing laboratory precision may not be prepared by subdividing a filter. However, the precision of filter digestion and analysis should be assessed by the preparation and analysis of duplicate LCSs (an LCS/LCSD pair). A sample digestate may be selected with each digestion batch to be analyzed in replicate to determine analytical precision.

- Duplicate LCSs provide precision of filter preparation, digestion, and analysis procedures;
- Replicate analysis of a sample digestate provides precision for the analysis only.

4.4.4.2.2 High Volume QFF Laboratory Precision. Sample processing and analysis precision may be evaluated in several different ways for QFFs. To evaluate the precision of the filter preparation, digestion, and analysis processes, duplicate strips may be portioned from a field-collected QFF and digested separately and duplicate LCSs (and LCS/LCSD pair) may be prepared. Preparation, digestion, and analysis of a matrix spike (MS) and matrix spike duplicate (MSD) pair can additionally be performed to evaluate the precision of filter preparation, digestion, and analysis as well as the matrix effects of field collected samples. Finally, to determine analytical precision, a sample digestate may be analyzed in replicate. To summarize:

- Duplicate sample filter strips and duplicate LCSs provide precision of filter preparation, digestion, and analysis procedures;
- Duplicate MS filter strips provide information on the precision of filter preparation, digestion, and analysis procedures, and include an assessment of potential matrix effects of the selected sample; and
- Replicate analysis of a sample digestate provides precision for the analysis only.

4.4.5 Sampling Schedule, Sampling Duration, and Field QC Blanks

4.4.5.1 Sampling Schedule and Duration. Metals sample collection must be performed on a 1-in-6 days schedule for 24 ± 1 hours beginning at midnight and concluding at midnight of the following day, standard time (unadjusted for daylight savings time), as per the national sampling calendar. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes and mechanical timers are within ±15 minutes of the reference time (cellular phone, GPS, or similar accurate clock).

4.4.5.2 Field QC Blanks. For both high volume and low volume sampling methods, FB samples are to be collected minimally monthly for each primary sampling unit (total of 12 per year for a total of 18% of samples [12 out of 61]). For collocated sampling units, FB samples should be collected minimally twice per year (two out of six) or for 18% of collocated samples collected, whichever is greater.
FBs are collected by installing the FB filter into the sampling unit to simulate a field sample collection. All portions of sample preparation and handling should be identical to routine field sample collection except the sampler pump is not turned on to pull air through the FB filter. After minimally 5 minutes have elapsed (or the duration of sample switching required by the sampling unit, as applicable), the filter is retrieved from the sampler and stored at the field site until the associated field sample can be retrieved for transport to the laboratory.

Target element measurements for FBs are to demonstrate all target elements < MDL. Monitoring agencies should be careful to submit the lot of filter material to the laboratory so the lot blank analysis described in Sections 4.4.9.3.1 and 4.4.10.3.1 can be performed and so the ASL can incorporate the lot of filter material into the MDL determination. Filter lots that have not been incorporated into the MDL procedure or have not been characterized for lot blank analysis risk exceeding the acceptance criterion if the lot of material has a higher background than the filter media used to determine the MDL. When measurements exceed this criterion, monitoring agencies must investigate the root cause of the apparent contamination and take corrective action when a root cause is identified. Measurement data for associated field-collected samples (i.e., those collected on the sampler since the most recent acceptable FB) are to be qualified (QA Qualifier FB indicating field blank value above acceptance limit) when reported to AQS.

An exposure blank is similar to a FB, but is not required, and may be collected via several protocols based on the conditions the monitoring agency intends to characterize. Due to variation in how exposure blanks may be collected, the information they provide also varies. In general, an exposure blank is meant to simulate a field collected sample and to characterize deposition that occurs passively over the period a typical field collected sample remains installed in a sampling unit, in addition to contamination that may occur during installation, handling, and transport. The exposure blank is exposed to the ambient conditions by installation in a sampling unit, and just like a FB, air is not drawn through the exposure blank. The exposure blank filter sample may be installed in the primary sampling unit on non-sample collection days or may be installed in a collocated sampling unit that is not actively sampling during collection of a primary sample. Monitoring agencies should prescribe acceptance criteria befitting the intended purpose of the exposure blank. Given the complexity of the flow path for a PM_{10} sampler, passive deposition of PM on an exposure blank is likely minimal, therefore measured concentrations on exposure blanks would be expected to be in line with those measured on a FB. Therefore, a reasonable exposure blank acceptance criterion is that target elements measure < MDL.

4.4.6 Labware Preparation for Digestion and Analysis. Regardless of the method of filter digestion, labware cleaning is essential to ensure background contamination is minimized. As with other contamination minimization procedures, each ASL is to prescribe in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for effective cleaning and decontamination of labware for PM_{10} metals analysis. Regardless of the procedures adopted, method performance specifications as given in Section 4.4.13 are to be met.

Labware for metals analysis includes equipment employed to contain or transfer standards solutions, concentrated and dilute digestion acids, sample digestates, etc. Examples of which include digestion vessels, pipette tips, volumetric pipettes and flasks, autosampler tubes, and
storage bottles, among others. Labware should be of quartz glass, plastic (polyethylene, polypropylene, etc.), and/or fluoropolymer (e.g., PTFE or FEP Teflon®) composition. As possible, use of glass should be minimized and solutions to be analyzed for Pb should not be stored in glass. Use of borosilicate glass and materials with metallic content are to be avoided due to the leaching of metals into acid solutions. If borosilicate glass materials must be used, solutions and reagents prepared in borosilicate glass labware should be transferred as soon as possible to a suitable (i.e., plastic or fluoropolymer) storage container. Additionally, single-use supplies are available from commercial vendors, and some are available with COAs indicating metals testing performed to document potential contributions to metals digestion and analysis processes. To avoid potential background contamination that may result from single-use supplies, ASLs are encouraged to source supplies and equipment labeled or indicated specifically for trace metals analysis. ²

Labware for digestion employing hot block methods is typically single use; however, laboratories may maintain labware (i.e., not single-use or disposable) for microwave digestion, volumetric solution preparation, and other purposes which must be effectively cleaned before each use. An effective cleaning procedure should involve the following:

- Rinses with tap water to remove the bulk of previous contents and residue
- Soaking minimally overnight (longer is preferred) in a concentrated (e.g., ≥ 10% v/v) HNO₃ aqueous solution
- Rinses (three or more) with deionized water to remove acid and residue followed by inversion for air drying

Alternatively, labware cleaning equipment is commercially available which may be programmed to provide washing, rinsing, and soaking cycles in various detergent and acid solutions.

Volumetric labware (e.g., Class A volumetric flasks or delivery pipettes) must not be heated above 80 to 90°C as high temperature exposure may void the volumetric certification.³ Clean labware should be stored in a contaminant-free area, upside-down or capped to minimize introduction of contaminants. Elevated levels of target elements in calibration blanks (CBs) and digested reagent blanks (RBs) indicate the presence of contamination possibly attributable to labware. Additional cleaning and acid rinsing steps should be considered when such blanks exceed the specified acceptance criteria, and the laboratory procedures updated to reflect the comprehensive labware cleaning process.

Note: Contamination in such CB and RB samples may also indicate contribution from reagents such as acids and deionized water. ASLs may conduct a study to characterize the level of background contaminants in CB and/or RB samples as described in Section 4.4.8.3 and use the results to establish acceptance criteria for RB samples.

4.4.7 Reagents for Metals Digestion and Analysis. Due to the capability of ICP/MS instruments to measure relatively small masses of target elements in the digested air filter matrix, employing high purity reagents and standards is paramount for analyzing air filter samples. Reagents and standards must be certified and traceable with COAs indicating target element concentration thresholds (i.e., maximum tolerances), and it is recommended that all reagents and standards be of the highest purity possible and have minimal background levels of target
elements, as practical. Regardless of the reagents and standards selected, calibration blanks and reagent blanks are to meet method specifications as given in Section 4.4.12.

Reagent water for the preparation of digestion solutions and for dilution of standard materials should be deionized water of ASTM Type I or equivalent (having an electrical resistivity ≥ 17.9 MΩ·cm). Given the volume of deionized water required for preparing reagents and standards and cleaning labware, laboratories will typically employ a water polishing unit for sourcing reagent water. Analysts should carefully maintain water polishing units according to manufacturer prescribed schedules to ensure appropriate water quality. Maintenance and replacement of components are to be recorded in laboratory records.

Acids (nitric and hydrochloric are common, hydrofluoric acid is less commonly used) should be trace metals grade, ACS spectroscopic grade, UHP grade, or equivalent. Further polishing of reagent water and redistillation of acids may be necessary to achieve blank acceptance criteria specified in Section 4.4.13.

4.4.8 Method Detection Limits. MDLs for PM$_{10}$ metals must be determined per the guidance in Section 4.1, which details the MDL determination process generally for the NATTS Program. This section will briefly provide details for determining the MDL for metals measurements by ICP-MS.

The MDL procedure in Section 4.1 prescribes preparing and analyzing MDL spikes and MBs for determining an initial MDL and for collecting ongoing data for MDL verification. MDLs must be determined following the procedure in Section 4.1.3.1 unless there is a sufficient number (n ≥ 7) of MBs in which the specific target analyte has been detected, in which case the procedure in Section 4.1.3.2 may be employed. ASLs should closely review the requirements in Section 4.1.3.1.1.4 to evaluate whether previously collected MDL spike data and MB data meet the requirements for calculating an initial and ongoing MDL. If the previously collected data do not meet the specified criteria, the initial MDL as detailed in Section 4.1.3.1.1 must be redetermined.

As practical, ASLs should include as wide a variety as possible of the available lots of filters for the MDL spiked samples and MBs and select filters for these samples from different boxes/cases. This best characterizes variability of measurements attributable to the variation in filter material. For each of the individual MDL spike and MB measurements, these are to be discrete filters and data from the same filter digestate can only be included in the calculations when analyzed on a separate instrument (when more than one instrument is employed).

Determining metals MDLs will typically involve preparing MDL spiked samples at several concentrations to ensure that metals of different sensitivities are adequately captured. If the ASL employs calibration stock standard solutions containing several elements for spiking MDL spiked samples, several sets of preparations may be necessary. For this reason, ASLs are recommended to use single element standards for preparing the MDL spiked sample spiking solutions so the concentration of each element can be customized. All steps performed in the preparation and analysis of field sample filters are to be included in the MDL procedure.
Determined MDLs for Tier I core analytes must meet (be equal to or lower than) the MDL MQO values listed in the most current workplan template, available on the NATTS area of EPA’s AMTIC (accessed June 2022): https://www.epa.gov/amtic/air-toxics-ambient-monitoring#natts. MDLs must be determined per the guidance provided in Section 4.1. Furthermore, MDLs must be determined with reagents, media, and sample handling techniques identical to those employed for the processing of field samples. Determined MDLs for Tier I core analytes must meet the MQO requirements (MDLs must be less than the specified values) listed in the most recent workplan template.

Aspects unique to PTFE Teflon® filter MDLs and QFF MDLs follow.

4.4.8.1 PTFE Teflon® Filter MDL. The MDL for PTFE Teflon® filters is to be determined by preparing MDL spiked samples and MBs containing one new filter each and taken through all steps of the digestion process, including filtration, centrifugation, etc.

4.4.8.2 QFF MDL. The MDL for QFFs is to be determined by preparing MDL spiked samples and MBs containing one new 1 inch x 8 inch strip (or equivalent strip to the standard field sample filter portion), each from a separate filter (i.e., it is not acceptable to digest multiple strips from the same QFF for this determination). The filter strip MDL spikes and MBs are each taken through all steps of the digestion process, including filtration, centrifugation, etc.

4.4.8.3 Digestion Vessel Lot Background Determination (Optional). Contributions of target analyte background is expected to be modest from reagents and labware, but may result in RBs exceeding the established ASL MDL_{sp} due to background from reagents and labware (particularly from single-use digestion vessels) taken through digestion. Therefore, laboratories may experimentally determine an acceptance criterion for the RB by conducting a study to assess the background of digestion vessel lots and reagents. The RB is a digested sample of digestion solution, equivalent to an MB but omitting a filter. The analyst prepares minimally seven RBs, digests by the established method, and analyzes each. The resulting concentrations are input into the MDL_{b} calculation in Section 4.1.3.1 and this MDL_{b} equivalent represents a defensible acceptance criterion above which an RB is considered to be contaminated.

4.4.9 Low Volume Sample Collection and Digestion

4.4.9.1 Air Sampling Instruments. Low volume sample collection instruments must comply with the low volume PM_{10} FRM requirements as listed in 40 CFR Part 50 Appendix L, i.e., they must operate at the design flow rate of 16.67 L/minute (at local conditions), utilize 47-mm PTFE Teflon® filter collection media, and be fitted with the “pie plate” PM_{10} inlet or the louvered inlet specified in 40 CFR 50 Appendix L, Figures L-2 through L-19, configured as in the PM_{10} reference method. The following instruments are among those that comply with these specifications:

- Andersen Model RAAS10-100
- Andersen Model RAAS10-200
- Andersen Model RAAS10-300
- BGI Incorporated Model PQ100
- BGI Incorporated Model PQ200
Samplers siting requirements are listed in Section 2.4.

4.4.9.2 Sampler Flow Rate Calibration. Sampling unit flow calibration must be performed initially when deployed to the field and after maintenance that reasonably would alter the flow rate calibration of the sampling unit (e.g., replacement of temperature probe(s), barometric pressure probes, sampling pumps, and computer control board components affecting temperature, pressure, or flow control readings or measurements). The PM$_{10}$ FRM sampling instruments control flow rate by measuring ambient temperature and barometric pressure, therefore the temperature and barometric pressure probes are to be calibrated first before the flow rate is calibrated. Temperature, barometric pressure, and flow rate are to be calibrated by reference to a suitable calibrated transfer standard following the manufacturer instructions.

The instrument ambient temperature, barometric pressure, and sampling flow rate calibration are to be verified minimally quarterly, and is recommended monthly, by comparison to a traceably certified transfer standard. These calibration verifications are prescribed in per 40 CFR Part 50 Appendix L, which requires recalibration (adjustment) when the ambient temperature, barometric pressure, or flow rate are not within the following tolerances:

- Ambient temperature measurement within ± 2.1°C of transfer standard
- Barometric pressure measurement within ± 10.1 mmHg of transfer standard
- Indicated flow rate within ± 4.1% of the transfer standard or within ± 4.1% of the design flow rate of 16.7 L/minute

Sample data from samplers failing flow rate calibration verification are to be invalidated (Null qualifier AH indicating sampler flow rate or CV out of limits) back to the most recent acceptable calibration or calibration verification when reported to AQS.

Prior to performing flow rate calibration verification, sampling units should undergo leak check to ensure that flow path integrity is maintained. A leak check is to be performed minimally every five sample collection events. A successful leak check indicates a total flow of less than 80 mL or loss of less than 25 mmHg (manufacturers may prescribe a different, but equivalent acceptance criterion). Samples collected with a failing leak check are to have associated data invalidated (Null qualifier AK indicating filter leak) when reported to AQS.

4.4.9.2.1 Flow Rate Verification and Flow Rate Audit Reporting. Following flow rate calibration verifications and flow rate audits, the results are to be input into AQS. Guidance for
establishing the monitor and flow channels in AQS is described in Appendix E. Monitoring agencies should input these data quarterly and ensure that flow rates are in LC.

4.4.9.3 **PTFE Teflon® Filter Media.** Low volume PM$_{10}$ metals are collected onto a 46.2-mm Teflon® filter substrate with a polypropylene support ring, 2-µm pore size, and a particle deposit area of 11.86 cm$^2$ (this is the filter media specification for the PM$_{2.5}$ monitoring program). Filters are stamped or printed with a unique identifier on either the support ring or on the filter substrate.$^4$ EPA typically provides filter media to monitoring agencies on an annual basis. Data for filter samples collected with incorrect filter media (e.g., a cellulose filter) are to be invalidated (Null qualifier AQ indicating collection error) when reported to AQS.

4.4.9.3.1 **PTFE Teflon® Filter Lot Background Determination.** For each lot of filters, the background concentration of metals in the lot are to be determined by digesting and analyzing minimally five separate filters from a given lot. PTFE Teflon® filters are not typically assigned a lot or batch from the manufacturer. Instead, an allotment of received filters will typically comprise a sequential run of unique filter identifiers (e.g., filter serial numbers), which can be referenced to assign a lot of filters. As EPA typically provides filter allotments once annually, the filters comprising the annual allotment can be assigned as a “lot.” Filters are typically packaged within plastic clamshell boxes that contain 50 filters separated into two individual stacks of 25 filters. The intent of the lot background determination is to characterize the average amount of each target element’s background within the lot. Therefore, filters digested for lot blank background should be selected from different packages (e.g., boxes of 50 filters) within the lot such that variation is maximized. Note the lot blank background can be determined concurrently with determination of the initial MDL as described in Section 4.1.3.1.

While there is not a prescribed threshold for the lot background not-to-exceed concentration for each element, the lot blank concentrations are to be reported to AQS (RB transaction). Note that an earlier version of this TAD permitted monitoring agencies to correct ambient air measurements for the lot blank value provided results were qualified in AQS with the QA data qualifier “CB”; however, lot blank subtraction is not permitted. Guidance for qualifying reported data to AQS is provided in Section 3.3.1.3.15 and Section 7.3.

4.4.9.3.2 **PTFE Filter Handling, Cassette Cleaning, and Field Deployment.** PTFE filters are to be inspected as described in Section 4.4.3.3 prior to field deployment. If PM$_{10}$ sampling for metals also includes gravimetric analysis, filters will require environmental conditioning and weighing prior to subsequent preparation for field deployment (these steps for gravimetric determination are outside the scope of this TAD). Once inspected (and tare weights measured, as needed), filters are to be installed into cassettes compatible with the sampling unit.

Cassettes should be cleaned before use by sonicating the cassettes, support screens, and caps. An effective cleaning regimen established for cassette cleaning for the PM$_{2.5}$ PEP involve two cycles of sonicating the cassette components in deionized water with a small amount of non-residue-forming laboratory-grade detergent (e.g., Liqui-Nox®) for minimally 30 minutes followed by thorough rinsing under flowing deionized water. Following the second rinsing cycle, cassette components are placed on lint-free laboratory wipes in a clean area (e.g., a HEPA-filtered
weighing laboratory) for air drying. When dry, cassette components should be stored in zipseal plastic bags to prevent deposition of dust and contaminants.

In order to minimize filter mixups once filters are installed into cassettes (cassettes typically cover up the printed filter identifier [ID]), cassettes should be uniquely identified (all components labeled with a permanent marker on surfaces that do not contact filters). A best practice is to assign unique identifiers to cassettes and to track and record cassette identifiers in order to aid in troubleshooting in the event of contaminated field QC blanks (i.e., FB and TB). When installing filters into cassettes, technicians will record the unique filter ID (and cassette ID) onto a COC form and package the cassettes for field deployment. Filter cassettes intended for direct installation into a sampler should have cassette caps installed at this time and should be transported in zipseal plastic bags. Filter cassettes for sampling units which employ a canister to hold the cassette (e.g., R&P/Thermo 2025 or similar) should be packaged into the sampling canisters and the canister lids/caps installed. COC/sample collection forms should be attached to the filter cassettes (e.g., rubber banded or inserted in the zipseal plastic bag) for field deployment.

4.4.9.4 Filter Sampling, Retrieval, Storage, and Shipment. Prior to field deployment, PTFE Teflon® filters for PM$_{10}$ low-volume sampling should be installed into sampling cassettes in a clean environment such as at a laboratory or field office (refer to Section 4.4.9.3.2). Prior to installation of cassettes for field sample collection, site operators should complete calibration verifications, as needed. Filter cassettes are to then be installed in the sampling unit per manufacturer procedures, after which the site operator performs a leak check, programs the sampler event timer, and records sample set up details on the COC/sample collection form (sample set up date, leak check results, sample start time, etc.). Prior to departing the site, a best practice is to double-check the sampler program is correct and enabled. If onsite on the sampling date, site operators should verify the sampler is operating as expected.

Sample filters should be retrieved as soon as reasonably possible after end of collection; however, there is not a prescribed time period for sample retrieval (though this period will be less than six days due to the need to collect samples every six days) unless such is prescribed for gravimetric PM$_{10}$ determination. When retrieving sampled filters, instrument performance information including the average temperature, average barometric pressure, average flow, total collected volume, collection duration, and sampler unit-assigned qualifiers (flags) indicating a problem during collection should be recorded on the sample collection form/record and downloaded or, as appropriate, for transfer to the ASL. Following removal from the instrument, the covers are placed back onto the filter cassette or cassette canister, as appropriate. Cassettes not installed in canisters are to be sealed into a zipseal plastic bag for transport. Unless required for gravimetric PM$_{10}$ determination, filters may be transported at ambient temperature. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the ASL. COC documentation is to comply with Section 3.3.1.3.7.

Collected sample filters are to be inspected at the ASL for defects or damage to the filter. If damage or defects are noted, the associated data for affected filters are to be invalidated (Null qualifier AJ indicating filter damage) when reported to AQS.
4.4.9.5 **PTFE Teflon® Filter Digestion**

4.4.9.5.1 **Laboratory PTFE Digestion QC Samples.** PTFE filter digestion is to be accomplished in batches of field samples which comprise associated laboratory QC samples. The guidance that follows presumes a recommended batch size of 20 or fewer field-collected samples (primary samples, collocated samples, and field QC blanks [FB and TB]), and strongly recommends that batch QC samples be prepared at this frequency of one per 20, where an additional suite of laboratory QC samples is included when the batch incorporates > 20 and up to 40 field-collected samples and this same convention applies for batch sizes including multiples of 20 (e.g., batches including 41 to 60 field-collected samples include three suites of laboratory QC samples). The following laboratory QC samples are required with each digestion batch:

- **Negative Control Samples (Blanks), one each:**
  - RB – digestion solution with no filter
  - MB – blank filter with digestion solution

- **Positive Control Samples (Spikes), one each:**
  - Reagent Blank Spike (RBS) – spiked digestion solution with no filter
  - LCS – spiked blank filter with digestion solution
  - LCSD – duplicate spiked blank filter with digestion solution

To the extent possible, ASLs are recommended to use the same lot of filter media for preparing digestion batch QC samples as that of the field-collected samples. If this is not possible, it is recommended that the same lot of filter material be used commonly for the digestion batch QC samples to minimize variables if troubleshooting is necessary.

Optionally, ASLs may additionally include in the digestion batch a positive control sample employing SRM, which can be prepared with or without a filter (e.g., NIST SRM 8785 is one such available SRM at the time this TAD was written). To prepare a digested SRM sample, the analyst weighs a known amount of SRM into a digestion vessel. The theoretical mass of each target element in the SRM sample is then calculated based on the SRM mass weighed for digestion. Recommended acceptance criteria are those prescribed for the LCS/LCSD after correction for RB (if SRM does not include filter) or MB (if SRM includes a filter), where applicable.

Associated sample data in the digestion batch are to be qualified (QA Qualifier LB indicating laboratory blank above acceptance limit and QA Qualifier QX indicating a QC failure) when entered into AQS when RBs and MBs exceed the acceptance criteria specified in Table 4.4-3. Similarly, when RBSs, LCSs, and/or LCSDs exceed acceptance criteria specified in Table 4.4-3 associated data in the batch are to be qualified (QA Qualifier LJ indicating the value is an estimate and QA Qualifier QX indicating a QC failure) when entered into AQS.

Laboratory QC samples must be processed, digested, and analyzed identically to field-collected samples, including, if applicable, filtration and/or centrifugation of digestates.

4.4.9.5.2 **PTFE Teflon® Filter Digestion Procedure.** Filters are digested with one of three possible methods: hot block digestion, microwave digestion, or heated sonication digestion. The three different techniques are described in the following sections.
Digestion of filters requires handling concentrated nitric acid in addition to other potential acids (HF is particularly hazardous). Nitric acid is a known human carcinogen, and its fumes are given off during digestion procedures. All handling of acids (concentrated or dilute) should be in a properly operating fume hood. Digestion equipment (hot block digesters, microwaves, and sonicators) as well as ICP-MS autosampler equipment must also be installed in a fume hood or equivalent properly vented enclosure to minimize analyst exposure to acid fumes. Laboratory staff handling acids should wear appropriate personal protective equipment (PPE) to protect skin and eyes from inadvertent splashing.

4.4.9.5.2.1 Filter Hot Block Digestion

Hot block digestion involves placing a digestion vessel containing the filter (or no filter for the RB, RBS, etc.) and digestion solution into individual wells in a heated digester block which is then heated to a desired temperature. Initially prior to commissioning for use and annually thereafter, the hot block digester well positions are to be checked to ensure each reaches and is able to maintain the target digestion temperature. To do so, the hot block is set to the target temperature (typically 95°C) and, after the temperature has been reached, a digestion vessel filled with deionized water, a temperature blank, is placed into each well. After the temperature stabilizes (approximately 5 minutes), the temperature of the water in each temperature blank is measured. Temperature measured across the block will ideally be uniform to within ± 5°C of the target temperature setting. Notate wells that exceed this range and mark that they not be used.

To perform digestion of PTFE Teflon® filters, each is placed into a separate digestion vessel. To prevent contamination to the filters, handle only with plastic or fluoropolymer-tipped forceps. Single-use certified metals-free digestion vessels with certified volumetric graduations are commercially available for hot block digestions. These are advantageous as they permit digestion and final volume dilution without transfer to suitable volumetric ware. Other suitable vessels may be utilized provided they do not unacceptably contaminate filter digestates, as is demonstrated by meeting the required blank specifications. The lot and manufacturer of the digestion vessels must be documented with each batch and ASLs should maintain COAs and volumetric certificates provided with each lot of digestion vessel. A known and consistent volume of digestion solution is added to each vessel so as to completely submerge the filter. Digestion solutions typically consist of approximately 2% (volume per volume [v/v]) nitric acid (HNO₃) and 0.5% (v/v) hydrochloric acid (HCl), as these concentrations are sufficient to completely digest filters and conserve acids. However, ASLs may employ acid concentrations deemed effective for their processes. To assist in the recovery of antimony, it may be helpful to add 0.1% hydrofluoric acid (HF) to the digestion solution.

The analyst will document the digested filters in a digestion batch log which will include documentation of the reagents used (digestion solution), spiking solutions for positive QC samples, lot(s) of digestion vessels, pipettes or other volumetric delivery devices for spiking samples and adding digestion solution, times vessels were placed into and were taken out of the digester, thermometer or temperature probe identifier for the temperature blank, hot block digester and locations of filters in respective wells, and other observations as needed to fully reconstruct the digestion batch preparation.
The hot block digester is powered on and warmed to the desired temperature (~95°C) prior to placing the digestion vessels into digestion wells. Each digestion vessel should be covered with a precleaned ribbed watchglass and the batch of filters should be digested for a minimum of 30 minutes; however, the digestion duration is strongly recommended to be 2.5 hours (longer durations will ensure more effective digestion). The analyst will document the time the digestion began (when vessels are placed in the heated block). Note that the chosen duration of digestion must be standardized for this method, prescribed in the ASL SOP, and must be consistent from batch to batch. An automatic shutoff timer can ensure consistent digestion duration; however, if manual switching off is required, the time the digestion was stopped is to be recorded in the digestion records. A temperature blank is to be included with each batch to ensure that the proper temperature is reached and maintained within ±5°C of the setpoint during the digestion period. Measurement data for samples in digestion batches that do not reach the intended temperature range are to be qualified (QA Qualifier LJ indicating the value is estimated) when entered into AQS.

Digestion vessels should be observed periodically throughout digestion to ensure none go to dryness and that the filters remain submerged. Deionized water (and not digestion solution, as this alters the concentration of acid in the digestate) should be added to digestion vessels when intervening with digestion vessels trending toward dryness. PTFE filters tend to float in the heated digestion solution and should be resubmerged as possible with a clean plastic or fluoropolymer stirring rod.

Once the digestion heating period has completed, digestion vessels are removed from the block digester and cooled to room temperature (approximately 30 minutes) in a fume hood. Digestion vessels should not be permitted to remain in the warm block digester for extended periods (>10% of the digestion duration) and this duration should not vary from batch to batch. Once cooled, the watchglass and walls of each digestion vessel should be rinsed down with approximately 10 mL of deionized water and the digestates should be allowed to settle for minimally 30 minutes. Following settling, digestates are brought to their final volume with deionized water. The final volume may be measured with the graduations on the volumetrically-certified digestion vessel (if employed) or must be transferred to a Class A volumetric vessel for volumetric standardization of the digestate. To accomplish this quantitative transfer, the digestion vessel is rinsed several times with small (2 to 3 mL) volumes of deionized water (this procedure must be standard [i.e., number and approximate volume of rinses] for each digestion vessel and prescribed in the ASL SOP). The transferred digestates must be then brought to volume with deionized water.

For transfer of aliquots for analysis, filtration or centrifugation is recommended (and may be necessary – though this is typically more of a problem for QFF digestions) to eliminate particulate interference on the ICP/MS. A filtration step can be added during quantitative transfer (if performed) or may be accomplished by employing syringe mounted disc-type filters for transfer to autosampler vials. Alternatively, ASLs may choose to allow an extended settling period for particulates or may centrifuge digestates to accelerate particulate settling. If allowed to settle or centrifuged, analysts should be careful to draw the supernatant liquid and not disturb the settled material. The chosen method for addressing particulates must be standardized for this method for the ASL and prescribed in the ASL SOP. All such processing steps must be
performed on both the field-collected and laboratory batch QC samples. Digestates are to be stored tightly capped to prevent evaporation and potential ingress of dust and contaminants.

4.4.9.5.2.2 Microwave Filter Digestion

Microwave digestion techniques have several advantages over hot block digestion and heated sonication digestion, which include: digestion may be performed more quickly (in approximately 30 minutes), digestions are more reproducible due to the even heating, the sealed digestion vessels ensure no loss of volatile analytes such as mercury and lead and decrease the likelihood of the introduction of external contamination, and digestions are more complete (higher extraction efficiency) as a result of the increased temperature and pressure.

However, microwave techniques have several disadvantages when compared to hot block digestion and sonication digestion. For example, microwave digestion equipment and accessories are expensive. Digestion vessels and associated caps must be thoroughly cleaned and decontaminated after each use. Microwave oven power also requires calibration on a specified, periodic basis to ensure that the digestion energy is appropriate, comparable, and stable from batch to batch, not to vary by more than 10% across batches. ASLs should follow manufacturer recommendations for microwave power calibration; however, may not exceed annual for calibration and are recommended to calibrate approximately every 6 months. To ensure the appropriate amount of heat is imparted to vessels in an incompletely filled digestion rack, blank vessels may need to be added or the microwave power may need to be reduced. Due to the higher pressure and temperature, digestion vessels may overpressurize and rupture, resulting in loss of sample and possible injury to laboratory staff. While such is possible, modern microwave digestion units typically employ temperature and pressure monitoring to adjust the power to reduce the likelihood of vessels rupturing.

To digest air filter samples by microwave digestion the microwave temperature program should permit ramping the temperature to 180°C over 10 minutes and holding at 180°C for 10 minutes followed by a 5-minute cool down. Other programs are also acceptable provided the requisite batch QC acceptance criteria are met. Manufacturers typically offer established program parameters to appropriately digest air filters based on the volume digested and concentration and composition of acids.

To perform digestion of PTFE Teflon® filters, each is placed into a separate digestion vessel. To prevent contamination to the filters, handle only with plastic or fluoropolymer-tipped forceps. It is recommended that microwave digestion vessels be uniquely labeled and the identifier recorded in digestion records to aid in troubleshooting. Additionally, ASLs are recommended to dedicate a set of microwave digestion vessels for air filter digestion if the laboratory also digests soils, sludges, and other matrices with high metals content. A known and consistent volume of digestion solution is added to each vessel so as to completely submerge the filter. Digestion solutions typically consist of approximately 2% (v/v) HNO₃ and 0.5% (v/v) HCl, as these concentrations are sufficient to completely digest filters and conserve acids. However, ASLs may employ acid concentrations deemed effective for their processes. To assist in the recovery of antimony, it may be helpful to add 0.1% HF to the digestion solution.
The analyst will document the digested filters in a digestion batch log which will include documentation of the reagents used (digestion solution), spiking solutions for positive QC samples, unique digestion vessel identifiers (if applicable), pipettes or other volumetric delivery devices for spiking samples and adding digestion solution, microwave oven identifier (e.g., serial number), analytical balance and associated weight set for weighing prepared digestion vessels, and other observations as needed to fully reconstruct the digestion batch preparation.

After the filters and known measured volume of digestion solution is added to each vessel in the batch, the vessel caps and pressure relief valves are installed on the microwave digestion vessels. If determining the loss of digestate volume by mass, the assembled vessels are then weighed on an analytical balance to the nearest 0.01 g. Digestion vessels are then installed in the carousel and placed into the microwave. The microwave digestion program is executed concluding with a cool down which allows pressure to decrease in the vessels. At the end of the program, the microwave operation status should be checked to verify the program completed appropriately and there are not error messages or faults indicated. The digestion vessel carousel is then carefully removed from the microwave oven and allowed to cool in a fume hood.

Once cooled, the analyst assesses the loss of digestate volume by either weighing each vessel or by volumetrically measuring the digestate. Vessels which have lost more than 15% of their volume (assuming that 1 mL ~ 1 g if weighing vessels) are to be invalidated (Null qualifier AR indicating a lab error) when reported to AQS (unless digestion can be repeated such as is possible for portioning a new QFF strip). Once cooled and weighed, vessels may be opened in a fume hood. Caution must be used when opening vessels as the contents may still be under pressure.

After cooling, the walls of the digestion vessel are rinsed down with approximately 10 mL of deionized water and the digestates should then be allowed to settle for minimally 30 minutes. Following settling, digestates are transferred to a Class A volumetric-certified vessel and the digestion vessel is rinsed several times with small (2 to 3 mL) volumes of deionized water to complete the quantitative transfer (this procedure must be standard [i.e., number and approximate volume of rinses] for each digestion vessel and prescribed in the ASL SOP). The transferred digestates must be then brought to volume with deionized water.

For transfer of aliquots for analysis, filtration or centrifugation is recommended (and may be necessary) to eliminate particulate interference on the ICP/MS. A filtration step can be added during quantitative transfer or may be accomplished by employing syringe mounted disc-type filters for transfer to autosampler vials. Alternatively, ASLs may choose to allow an extended settling period for particulates or may centrifuge digestates to accelerate particulate settling. If allowed to settle or centrifuged, analysts should be careful to draw the supernatant liquid and not disturb the settled material. The chosen method for addressing particulates must be standardized for this method for the ASL and prescribed in the ASL SOP. All such processing steps must be performed on both the field-collected and laboratory batch QC samples. Digestates are to be stored tightly capped to prevent evaporation and potential ingress of dust and contaminants.
4.4.9.5.2.3 Acid Sonication Filter Digestion

Acid sonication involves placing racks of digestion vessels containing filters and digestion batch QC samples into a heated sonicator for several hours. Each filter and digestion batch QC sample will have its own digestion vessel. To prevent contamination to the filters, handle filters only with plastic or fluoropolymer-tipped forceps. Single-use certified metals-free digestion vessels with certified volumetric graduations are commercially available for use in such digestions. These are advantageous as they permit digestion and final volume dilution without transfer to suitable volumetric ware. Other suitable vessels may be utilized provided they do not unacceptably contaminate filter digestates, as is demonstrated by meeting the required blank specifications. The lot and manufacturer of the digestion vessels must be documented with each batch and ASLs should maintain COAs and volumetric certificates provided with each lot of digestion vessel. A known and consistent volume of digestion solution is added to each vessel so as to completely submerge the filter and the digestion vessel is loosely capped. Digestion solutions typically consist of approximately 4% (v/v) HNO₃, as this concentration is sufficient to completely digest filters and conserve acids. However, ASLs may employ acid concentrations deemed effective for their processes (as demonstrated by acceptable QC sample recoveries). To assist in the recovery of antimony, it may be helpful to add 0.1% HF to the digestion solution.

The analyst will document the digested filters in a digestion batch log which will include documentation of the reagents used (digestion solution), spiking solutions for positive QC samples, lot(s) of digestion vessels, pipettes or other volumetric delivery devices for spiking samples and adding digestion solution, the time in and out of the water bath, the time the sonicator was started and the duration of sonication, thermometer or temperature probe identifier for the sonication bath, and other observations as needed to fully reconstruct the digestion batch preparation.

The sonication bath is powered on and warmed to the desired temperature (recommended ~69°C) prior to placing the digestion vessels into the bath. When placing the digestion vessels in the sonicator, it is strongly recommended a removeable rack be employed to facilitate insertion and removal. The level of water in the sonication bath is to minimally be at the level of the digestate in the vessels (but minimally 1 inch below the top of the vessel). Once the rack of tubes is inserted in the sonicator bath, the sonicator is activated and digestion should continue for minimally 3 hours. The duration and temperature of the heated bath sonication is to be standardized for this method and prescribed in the ASL SOP. An automatic shutoff timer for the sonicator and waterbath heater can ensure consistent digestion duration; however, the digestion vessels should not remain in the digester for extended periods (> 10% of the sonication duration) and this duration should not vary from batch to batch. If manual switching off is required, the time the digestion was stopped and the digestion vessels removed from the waterbath is to be recorded in the digestion records. Analysts should periodically observe the digestion to ensure that filters remain submerged in the digestion solution, and that the digestion process completes successfully. The temperature of the waterbath is to be measured and recorded approximately mid-way (~90 minutes) through the digestion and should be within ± 5°C of the intended setting. Measurement data for samples in digestion batches that do not reach the intended temperature range are to be qualified (QA Qualifier LJ indicating the value is estimated) when entered into
AQS. PTFE filters tend to float in the heated digestion solution and should be resubmerged as possible with a clean plastic or fluoropolymer stirring rod.

Once the digestion heating period has completed, digestion vessels are removed from the waterbath and cooled to room temperature (approximately 30 minutes) in a fume hood. Once cooled, the walls of each digestion vessel should be rinsed down with approximately 10 mL of deionized water and the digestates should be allowed to settle for minimally 30 minutes. Following settling, digestates are brought to their final volume with deionized water. The final volume may be measured with the graduations on volumetrically-certified digestion vessels (if employed) or must be transferred to a Class A volumetric vessel for volumetric standardization of the digestate. To accomplish this quantitative transfer, the digestion vessel is rinsed several times with small (2 to 3 mL) volumes of deionized water (this procedure must be standard [i.e., number and approximate volume of rinses] for each digestion vessel and prescribed in the ASL SOP). The transferred digestates must be then brought to volume with deionized water.

For transfer of aliquots for analysis, filtration or centrifugation is recommended (and may be necessary) to eliminate particulate interference on the ICP/MS. A filtration step can be added during quantitative transfer (if performed) or may be accomplished by employing syringe mounted disc-type filters for transfer to autosampler vials. Alternatively, ASLs may choose to allow an extended settling period for particulates or may centrifuge digestates to accelerate particulate settling. If digestates are allowed to settle or are centrifuged, analysts should be careful to draw the supernatant liquid and not disturb the settled material. The chosen method for addressing particulates must be standardized for this method for the ASL and prescribed in the ASL SOP. All such processing steps must be performed on both the field-collected and laboratory batch QC samples. Digestates are to be stored tightly capped to prevent evaporation and potential ingress of dust and contaminants.

4.4.10 High Volume Sample Collection and Digestion

4.4.10.1 High Volume Air Sampling Instruments. High volume sample collection instruments will comply with the high volume PM$_{10}$ FRM requirements in 40 CFR Part 50 Appendix J, i.e., they operate at a design flow rate of 1.13 m$^3$ (at local conditions), utilize 8 inch $\times$ 10 inch QFF collection media, and are fitted with the PM$_{10}$ inlet per EPA Reference Method RFPS-0202-141, RFPS-1287-063, or equivalent. The following sampling units are among those that comply with these specifications:

- Ecotech Model 3000
- Graseby Andersen/General Metal Works (GMW) Model 1200
- Graseby Andersen/GMW Model 321-B
- Graseby Andersen/GMW Model 321-C
- Tisch Environmental Model TE-6070 or New Star Environmental Model NS-6070
- Wedding and Associates or Thermo Environmental Instruments Inc. Model 600

Sampler siting requirements are listed in Section 2.4.

4.4.10.2 High Volume Sampler Flow Rate Calibration. Sampling unit flow calibration must be performed initially when deployed to the field and after maintenance that reasonably would
alter the flow rate calibration of the sampling unit (e.g., replacement of temperature probe(s), barometric pressure probes, blower motor and/or blower motor brushes, and computer control board components affecting temperature, pressure, or flow control readings or measurements). The PM$_{10}$ FRM sampling instruments control flow rate by either employing a choked flow venturi designed to flow at a known flow rate of approximately 1.13 m$^3$/minute with a blower motor creating a pressure drop greater than the critical pressure differential for the venturi or by employing an MFC device that measures the ambient temperature and barometric pressure and adjusts blower draw to control flow rate at approximately 1.13 m$^3$/minute. For instruments with a choked flow venturi, the pressure drop across the venturi is measured and related to the flow rate measured by a flow transfer standard. For sampling units controlling flow with an MFC, the computer controlling the motor speed is calibrated against a flow transfer standard after the temperature and barometric pressure probes are to be calibrated. Temperature, barometric pressure, and flow rate are to be calibrated by reference to a suitable calibrated transfer standard.

The flow rate calibration is to be verified minimally quarterly, and this is recommended to be monthly, by comparison to a traceably certified transfer standard. Samplers controlling flow are to have the ambient temperature measurement and barometric pressure measurement verified before verifying the sampling flow rate calibration. These calibration verifications are prescribed in per 40 CFR Part 50 Appendix L, which requires recalibration (adjustment) when the ambient temperature, barometric pressure, or flow rate are not within the following tolerances:

- Ambient temperature measurement within ± 2.1°C of transfer standard
- Barometric pressure measurement within ± 10.1 mmHg of transfer standard
- Indicated flow rate within ± 7.1% of the transfer standard or within ± 10.1% of the design flow rate of 1.13 m$^3$/minute

Sample data from samplers failing flow rate calibration verification are to be invalidated (Null qualifier AH indicating sampler flow rate or CV out of limits) back to the most recent acceptable calibration or calibration verification when reported to AQS.

Prior to performing flow rate calibration verifications, sampling units should be leak checked to ensure air is not leaking around the adapter plate for the flow transfer standard. Leak checks are performed by blocking the flow through the flow transfer standard adapter plate with a flat piece of durable material (e.g., thick polycarbonate). If a high-pitched whistle is heard, there is a leak in the flow path that requires remediation before calibration/calibration verification can be performed. Site operators should perform leak checks carefully and only operate the sampler motor briefly to avoid burning out the motor with the high load. If a leak is indicated, possible leak locations are at the mating surfaces of the blower motor to the venturi throat, venturi throat to the filter holding plate, or the gasket on the filter holding plate. Leak checks are also to be performed periodically as part of the routine sampling setup, and these are described in Section 4.4.10.4. Samples collected with a failing leak check are to have associated data invalidated (Null qualifier AK indicating filter leak) when reported to AQS.

4.4.10.2.1 Flow Rate Verification and Flow Rate Audit Reporting. Following flow rate calibration verifications and flow rate audits, the results are to be input into AQS. Guidance for
establishing the monitor and flow channels in AQS is described in Appendix E. Monitoring agencies should input these data quarterly and ensure that flow rates in LC.

4.4.10.3 Quartz Fiber Filter Media. Sampling media consist of 8 inch × 10 inch QFF substrate with a 2-µm pore size, capable of 99% particle sampling efficiency for particles 0.3 µm in diameter or larger. Filters must be stamped or printed with a unique identifier on the corner of the filter. EPA typically provides QFF media to monitoring agencies on an annual basis.

4.4.10.3.1 QFF Lot Background Determination. For each lot of filters, the background concentration of metals in the lot are to be determined by digesting and analyzing minimally five filter strips portioned from five separate filters from a given lot. QFFs are typically provided by EPA in boxes of 60 QFF 8 inch x 10 inch sheets with the lot identifier labeled on the box. The intent of the lot background determination is to characterize the average amount of each target element’s background within the lot. Therefore, filter strips digested for lot blank background should be selected from QFFs taken from different boxes of 60 filters within the lot such that variation is maximized. Monitoring agencies are to submit filters for lot blank analysis to their ASL for each new lot of QFF media to be placed into use. Note the lot blank background can be determined concurrently with determination of the initial MDL as described in Section 4.1.3.1.

While there is not a prescribed threshold for the lot background not-to-exceed concentration for each element, the lot blank results (the average mass of each target element measured on the lot blank filters) are to be reported to AQS using an AQS RB transaction. Note that an earlier version of this TAD permitted monitoring agencies to correct ambient air measurements for the lot blank value provided results were qualified in AQS with the QA data qualifier “CB”; however, lot blank subtraction is not permitted. Guidance for reporting data to AQS is provided in Section 3.3.1.3.15.

4.4.10.3.2 QFF Handling, Cassette Cleaning, and Field Deployment. QFFs are to be inspected as described in Section 4.4.3.3 prior to field deployment. If PM$_{10}$ sampling for metals also includes gravimetric analysis, filters will require environmental conditioning and weighing prior to subsequent preparation for field deployment (these steps for gravimetric determination are outside the scope of this TAD). Once inspected (and tare weights measured, as needed), filters are to be installed into cassettes compatible with the sampling unit.

Filter media may be installed in a sampling cassette at the laboratory before shipment to the field, or the site operator may be required to install the filter into the cassette. Installation of the filter into the cassette must be performed in a clean (minimal dust) indoor environment, preferably protected from air movement, with the filter identifier oriented downward. A cover should be attached to the top (inlet side) of the cassette to protect the filter sampling surface. Storing the assembled filter and cassette in a sealed plastic bag during transport and storage is a best practice.

Cassettes for 8 inch x 10 inch QFFs should be cleaned periodically by rinsing with deionized water and air drying.
In order to minimize filter mixups once filters are installed into cassettes (cassettes typically cover up the printed filter ID), cassettes should be uniquely identified. A best practice is to assign unique identifiers to cassettes and to track and record cassette identifiers in order to aid in troubleshooting in the event of contaminated field QC blanks (i.e., FB and TB). When installing filters into cassettes, technicians will record the unique filter ID (and cassette ID) onto a COC form.

### 4.4.10.4 Filter Sampling, Retrieval, Storage, and Shipment

Prior to installation of loaded filter cassettes into sampling units for field sample collection, site operators should complete calibration verifications, as needed, per Section 4.4.10.2. To install the cassette in the sampling unit, the cam-lock bolts of the SSI on the sampling unit are loosened to allow the SSI to open on the hinge and the inlet securely propped open. The cassette securing swing bolts on the filter support stage are then loosened and swung downward to allow the assembled cassette and filter to be installed. Installation is to be performed carefully to ensure that the rubber gasket on the base of the sampling unit forms a tight seal around the cassette. The swing bolts are then tightened stepwise in a diagonal pattern to ensure even pressure is applied to the cassette and gasket. Each time a sample is set up, the inside of the SSI, gaskets, and mating surfaces should be visually inspected for loose debris or corrosion which could fall onto the filter. It is common for insects, plant matter, and debris to settle on the protective screen at the outlet of the SSI, and this screen should be serviced periodically to remove such debris. Particular attention should be paid to the gasket attached to the bottom of the SSI that seals to the filter cassette.

Once the cassette is securely installed, the operator should perform a leak check (as required) and address leaks as needed, repeating the leak check until achieving a satisfactory result. A leak check is required every five sampling events, but is recommended for each event. The leak check is performed by covering the installed filter cassette with a piece of flat (clean) stiff material (e.g., polycarbonate), activating the sampler blower briefly, and listening for a high pitched whistle (absence of a whistle is a successful leak check). Leak check remediation is discussed in Section 4.4.10.2. Following successful leak check, the SSI is lowered onto the filter support stage and secured to the body of the sampling unit using cam-lock bolts.

The site operator programs the sampler event timer, and records the following sample set up details on the COC/sample collection form:

- Filter installation date
- Leak check results
- Elapsed time indicator reading (for sampling units without data logging capability)
- Programmed sample start time
- Initial flow rate (for sampling units without data logging capability)

Sampling units that do not incorporate computer controlled flow rate and employ data logging of sample collection data (e.g., start and stop times, temperature, barometric pressure, and integrated sample flow rate data), will require powering on the sampler for minimally five minutes (10 minutes are recommended) and measuring the pressure differential across the venturi with a calibrated manometer (i.e., magnehelic) for determination of the starting sampling
flow rate by cross referencing with the corresponding flow rate calibration regression. Without this starting flow rate, the collected volume cannot be measured and the sample is to be invalidated (Null qualifier EC indicating failure of a critical criterion) when entered into AQS. Prior to departing the site, a best practice is to double-check the sampler program is correct and enabled. If onsite on the sampling date, site operators should verify the sampler is operating as expected.

Sample filters should be retrieved as soon as reasonably possible after end of collection; however, there is not a prescribed time period for sample retrieval (though this period will be less than six days due to the need to collect samples every six days) unless such is prescribed for gravimetric PM$_{10}$ determination.

Upon sample retrieval, the following sample collection details are to be recorded:

- Filter retrieval date
- Leak check results
- Elapsed time indicator reading (for sampling units without data logging capability) and presumed sample stop time
- Ending flow rate (for sampling units without data logging capability)
- Average temperature over the sampling event
- Average barometric pressure over the sampling event
- Qualifiers (flags) or alerts logged in the sampler data

If the sampling unit permits electronic data retrieval, the site operator should transfer the sampler data for transfer to the ASL and archiving. For sampling units without electronic flow control, the sampling unit is powered on and allowed to run for minimally five minutes (ten minutes are recommended) before recording the reading of the pressure drop across the flow venturi as the ending flow rate measurement. Without this ending flow rate, the collected volume cannot be measured and the sample is to be invalidated (Null qualifier EC indicating a critical criteria failure) when entered into AQS. The filter sample cassette is then removed from the sampling unit and the cover placed on the cassette until the filter may be removed from the cassette in a clean area, free of obvious contamination, and with minimal air movement. If filters are to be transported to the laboratory in the cassette, a best practice is to seal the loaded filter cassette into a plastic bag for transport. Filters need not be shipped or stored refrigerated unless required for PM$_{10}$ gravimetric analysis.

When removed from the cassette, the filter is folded in half, lengthwise, with the particulate matter inward. Folding the filter lengthwise ensures that the portioned filter strips include the crease. The folded filter is then placed within a protective manila or glassine envelope.

Filters are to be handled per the procedures in Section 4.4.3.2. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the laboratory. COC documentation is to comply with Section 3.3.1.3.7.
Collected sample filters are to be inspected at the ASL for defects or damage to the filter. If damage or defects are noted, the associated data for affected filters are to be invalidated (Null qualifier AJ indicating filter damage) when reported to AQS.

4.4.10.5 QFF Digestion

4.4.10.5.1 QFF Laboratory Digestion Batch QC Samples. QFF extraction is to be accomplished in batches of field samples which comprise associated laboratory QC samples. The guidance that follows presumes a recommended batch size of 20 or fewer field-collected samples (primary samples, collocated samples, and field QC blanks [FB and TB]), and strongly recommends that batch QC samples be prepared at this frequency, where an additional suite of laboratory QC samples be included when the batch incorporates > 20 up to 40 field-collected samples and this same convention applies for batch sizes including multiples of 20 (e.g., batches including 41 to 60 field-collected samples include three suites of laboratory QC samples). The following laboratory QC samples are required with each digestion batch:

- Negative Control Samples (Blanks), one each:
  - RB – digestion solution only (no filter strip)
  - MB – blank filter strip with digestion solution

- Positive Control Samples (Spikes), one each:
  - RBS – spiked digestion solution only (no filter strip – ensures proper spike recovery without the filter matrix)
  - LCS – spiked blank filter strip with digestion solution (evaluates proper spike recovery with blank filter matrix)
  - LCSD – (optional) duplicate spiked blank filter strip with digestion solution (evaluates precision of proper spike recovery with blank filter matrix)

- Matrix QC Samples, one each:
  - Duplicate Sample Strip – An additional strip cut from a collected field sample (evaluates precision of the sample result and digestion process)
  - Matrix Spike (MS) – An additional strip cut from a collected field sample which is spiked at the same concentration as the LCS (provides information on matrix effects on spike recovery)
  - Matrix Spike Duplicate (MSD) – An additional strip cut from a collected field sample which is spiked at the same concentration as the LCS (provides precision information on matrix effects on spike recovery)

To the extent possible, ASLs are recommended to use the same lot of filter media for preparing digestion batch QC samples as that of the field-collected samples. If this is not possible, it is recommended that the same lot of filter material be used commonly for the digestion batch QC samples to minimize variables if troubleshooting is necessary.

Optionally, ASLs may additionally include in the digestion batch a positive control sample employing SRM, which can be prepared with or without a filter (e.g., NIST SRM 8785 is available at the time this TAD was written). To prepare a digested SRM sample, the analyst weighs a known amount of SRM into a digestion vessel. The theoretical mass of each target element in the SRM sample is then calculated based on the SRM mass weighed for digestion. Recommended acceptance criteria are those prescribed for the LCS/LCSD after correction for...
the RB (if the SRM does not include filter) or MB (if the SRM includes a filter), where applicable.

When RBs and MBs exceed the acceptance criteria specified in Table 4.4-3, associated sample data in the digestion batch are to be qualified (QA Qualifier LB indicating lab blank above acceptance limit and QX indicating QC failure) when entered into AQS. Similarly, when RBSs, duplicate sample strips, LCSs, and/or LCSDs exceed acceptance criteria specified in Table 4.4-3 associated data in the batch are to be qualified (QA Qualifier LJ indicating the value is an estimate and QX indicating QC failure) when entered into AQS. The data for the parent sample for the MS/MSD are to be qualified (QA Qualifier LJ indicating the value is an estimate and QX indicating QC failure) when entered into AQS.

Laboratory QC samples must be processed, digested, and analyzed identically to field-collected samples, including, if applicable, filtration and/or centrifugation of digestates.

4.4.10.5.2 Digestion Procedure. Filters are digested with one of three possible methods: hot block digestion, microwave digestion, or heated sonication digestion. The three different techniques are described in the following sections.

Digestion of filters requires handling concentrated nitric acid in addition to other potential acids (HF is particularly hazardous). Nitric acid is a known human carcinogen, and its fumes are given off during digestion procedures. All handling of acids (concentrated or dilute) should be in a properly operating fume hood. Digestion equipment (hot block digesters, microwaves, and sonicators) as well as ICP-MS autosampler equipment must also be installed in a fume hood or equivalent properly vented enclosure to minimize analyst exposure to acid fumes. Laboratory staff handling acids should wear appropriate PPE to protect skin and eyes from inadvertent splashing.

Prior to digestion, filter samples are to be examined for damage to the filter or other defects (presence of insects, large visible particulates, etc.) which may affect sample integrity or analysis results. Following inspection, the requisite number of filter strips is to be cut from each filter to complete the digestion batch as listed above in Section 4.4.10.5.1.

Sampled 8 inch × 10 inch QFF media have an exposed filter area of 7 inch × 9 inch, leaving a ½-inch wide border of unsampled area around the perimeter of the filter. Strips for digestion should be cut perpendicular to the fold/crease line for filters folded lengthwise as shown in Figure 4.4-1 and must not include the unsampled ½ inch × 8 inch border section at each end (left and right in Figure 4.4-1). This results in a 1 inch × 7 inch (7 in²) exposed section of the filter for each strip, equivalent to 1/9 of the 63 in² exposed filter area. Other conventions for portioning filter strips are acceptable so long as they include at least 7 in² of exposed filter area and a portion of the fold/crease. Portioning filter strips with less than 7 in² of exposed filter area risks having insufficient analyte mass for measurement and elevates detection limits (decreases sensitivity).
Filter sample strips may be digested using one of three methods: hot block digestion, microwave digestion, or heated sonication. Each filter strip is quantitatively transferred into its own separate digestion vessel. Filters may be coiled, folded, subsequently portioned, or other added to the digestion vessel with other suitable mechanical process for ensuring quantitative transfer. The convention chosen should ensure the filter material remains submerged in the digestion solution during digestion.

4.4.10.5.2.1 Hot Block Digestion

Follow procedures as given in Section 4.4.9.5.2.1. Note that HF acid does not improve digestion efficiency and is not recommended for digestion of QFFs.

4.4.10.5.2.2 High Volume QFF Microwave Digestion

Follow procedures as given in Section 4.4.9.5.2.2. Note that HF acid does not improve digestion efficiency and is not recommended for digestion of QFFs.

4.4.10.5.2.3 High Volume QFF Acid Sonication

Follow procedures as given in Section 4.4.9.5.2.3. Note that HF acid does not improve digestion efficiency and is not recommended for digestion of QFFs.
4.4.11 PM₁₀ Metals Analysis by ICP/MS – EPA Method IO-3.5

4.4.11.1 ICP/MS Instrumentation. In order to achieve the necessary sensitivity (detectability) for the masses collected on ambient air filter samples, PM₁₀ metals for NATTS Program work are to be analyzed via ICP/MS. Analysis via ICP-atomic emission spectroscopy (ICP-AES), ICP-optical emission spectroscopy (ICP-OES), graphite furnace atomic absorption (GFAA), and/or flame atomic absorption (FAA) methods are insufficiently sensitive and may not be employed for NATTS Program analyses. ICP/MS instruments may be equipped with quadrupole MS, TOF MS, or magnetic field sector-type detectors. Quadrupole and TOF MS instruments experience similar interferences but can be equipped with collision reaction cells to minimize polyatomic interferences. Magnetic sector field-type detectors are considered to be high-resolution (HR or ‘high-res’) detectors and can differentiate fractions of an amu which allows differentiating between polyatomic and isobaric interferences that can affect quadrupole instruments and, to a lesser degree, TOF instruments. The chosen instrument must have the capability to minimally scan for masses ranging from 7 to 238 amu with resolution of ≤ 1 amu.

4.4.11.1.1 ICP-MS Operation. The ICP-MS sample introduction peristaltic pump tubing should be replaced frequently to ensure proper operation (per manufacturer recommendations). Solutions should be introduced for a defined period of time sufficient to ensure the sample introduction system is properly conditioned/rinsed with the sample to be interrogated, and the autosampler probe and pump tubing introducing the solutions for analysis should be rinsed with a rinse blank for a period sufficient to demonstrate no perceptible carryover from the high calibration standard to a continuing calibration blank (CCB). Each introduced solution should be quantitated for minimally three replicate integrations and these replicates averaged for reporting. The relative standard deviation (RSD) of the replicates should be ≤ 5%; however, should follow manufacturer recommendations.

4.4.11.2 ICP/MS Interferences. ICP/MS instruments are susceptible to interferences which can result in bias or saturation effects which overload the detector and require an extended period to bring detector response back into the acceptable sensitivity range. These are not typically an issue in analyzing ambient air filter samples due to the small masses of elements typically introduced to the instrument during analysis. Such interferences are explained in more detail below.

- Isobaric interferences are caused by isotopes of different elements which have the same mass/charge ratio as a target element. This results in a high bias for the target element, but such biases may be corrected for target elements with standard equations in ICP/MS software, which assess the measured concentration for respective interfering isobaric isotopes and relative ratios to detect and correct for such interferences.
- Polyatomic, or molecular interferences are caused by combination of ions to form molecular ions which have the same mass/charge ratio as a target element. These interferences can result in high or low bias depending on the target element. Use of a collision reaction cell to remove polyatomic interferences upstream of the MS detector can significantly reduce or effectively eliminate the effect of the interference.
Transport interferences are a result of matrix effects which alter aerosol formation and result in changes to solution nebulization at the plasma. These interferences are typically not an issue with air filter analysis as the concentration of dissolved solids in digestates is fairly consistent from sample to sample.

Matrix interferences are due to a chemical component in the solution which causes suppression or enhancement of the measured signal. Matrix interferences can be addressed by utilization of an internal standard (which this method involves) or by diluting the sample digestate to minimize the impact of the interference.

Memory, or carryover, interferences can occur when solutions of very high concentrations are analyzed. The residual material following high concentration solutions may be difficult to effectively rinse from the ICP/MS sample introduction pathway resulting in contamination of subsequent solutions or in the electron multiplier becoming saturated resulting in a “burn in” where response factors of the ICP/MS are affected requiring extended durations for sensitivity to return. Extensive rinsing times, recalibration, and or replacement of torch components may be necessary to resolve such interferences.

For ambient air, collected masses of PM result in low concentrations of interfering elements, therefore, interferences are not generally appreciable for air filter analyses. Analysts accustomed to analyzing water (particularly surface water or wastewater matrices) and/or soils and sediments will note that concentrations of minerals (and their associated interferences) are significantly lower in digestates of metals air filters. The interference demonstration described in Section 4.4.11.7.4 is configured to demonstrate that typical interferences do not unacceptably impact target element analysis for air filters.

4.4.11.3 Preparation of Calibration Standards for ICP/MS Analysis. Due to the instrument sensitivity effects of dissolved solids (notably acid salts), the matrix of standard solutions must exactly match that of the final analyzed digestates. For example, if the final concentrations of acids in the analyzed digestates are 2% (v/v) HNO₃, 0.5% (v/v) HCl, and 0.1% (v/v) HF when samples are brought to volume, these acids’ concentrations in standard solutions must also be 2%, 0.5%, and 0.1%, respectively. Mismatch in acid concentration(s) can result in isotope response differences between mismatched solutions and subsequent concentration reporting errors.

Aliquots of the stock standard solutions must be delivered with a Class A pipette or traceably calibrated mechanical pipettor. All standard solutions must be brought to final volume in a Class A volumetric flask or labware with equivalent volumetric tolerance. Mechanical pipettes employed for delivery of solution are to have the calibration of their volumetric delivery verified periodically (refer to Section 3.3.1.3.4.1).

Stock single element or multi-element solutions may be purchased commercially at certified concentrations in dilute nitric acid (typically 3% v/v) which are conveniently diluted to working concentration levels. Alternatively, stock solutions may be prepared gravimetrically by weighing appropriate amounts of high purity element solids and dissolving them into dilute nitric acid. Preparing stock solutions from neat solid materials is time consuming and requires excellent
technique and hygiene to perform accurately; therefore, ASLs are encouraged to purchase certified standard solutions as these are relatively inexpensive and of high quality.

4.4.11.3.1 Primary Calibration Standards. Multi-element calibration standard solutions are prepared by diluting primary certified stock standard solutions in dilute nitric acid (typically 2% v/v). Due to the linear response of the ICP-MS over several orders of concentration magnitude, standard levels to establish the calibration will minimally include three non-zero concentrations spanning the desired concentration range (typically 0.1 to 250 ng/mL [ppb] although some elements may require a different range), however; five concentration levels are strongly recommended to ensure the diluted calibration standard solutions are accurate and proportional. These standard solutions are analyzed to generate the ICAL.

4.4.11.3.2 Second Source Calibration Verification Standard. A SSCV standard solution, also referred to as the QC sample, is analyzed to independently verify the calibration curve (and by extension the quality of the primary calibration materials and their preparation). The SSCV is prepared by dilution of the second source stock standard solution in dilute nitric acid (typically 2% v/v) to minimally a single concentration approximately at the mid-range of the calibration curve. Preparation of the SSCV at three different concentrations covering approximately the lower third, mid-range, and upper third of the calibration range is a best practice and is recommended. This second source stock standard solution must be purchased from a different supplier than the primary calibration stock standard. The SSCV stock may only be purchased from the same supplier as the primary calibration stock standard if a suitable standard is unavailable from a different supplier, in which case it must be a different lot than the primary calibration stock standard.

4.4.11.4 Internal Standards. ICP/MS analysis must include the evaluation of ISs to monitor ion response of analyzed solutions and to correct for instrumental drift and matrix interferences. A minimum of three IS elements must be co-analyzed with each analyzed solution and are added at the same concentration to all analyzed solutions. Suggested IS elements include Bi, Ge, In, $^{6}$Li, Sc, Tb, $^{69}$Ga, Rh, and Y.

As relative responses of the target elements and IS elements are used to determine the final concentration of the elements in solution, the concentration of the IS must be the same for each analyzed solution. To achieve such, a known volume of the IS at a known concentration may be manually added (using a suitably calibrated pipette) to a known volume of each solution to be analyzed, or the IS may be added to each analyzed solution via a mixing coil on the ICP/MS sample introduction system. Further, IS concentrations should approximate those in the analyzed samples. A concentration of no more than 200 ng/mL is recommended.

As with the calibration stocks, acids, and reagent water, the IS stock solution(s) must be from a high purity source so as to minimize background levels of target elements. IS stock solutions at appropriate concentrations are available from commercial suppliers and can readily be diluted into a proper concentration range for analysis.

IS responses are monitored throughout the analysis and must be within 59.9 to 125.1% of the response of the initial calibration blank (ICB). For samples or solutions which show responses
outside of this range, the instrument should be investigated to ascertain whether the IS response change is due to matrix effects of an individual sample digestate or due to instrument drift. Instrument drift causing failures in IS response requires retuning of the instrument and recalibration (a new ICAL and subsequent QC sample analysis) prior to continuing sample analysis.

There are several conventions for fortifying analyzed solutions with ISs. The ISs may be added after digestion when known volumes of digestate are transferred to autosampler vials for analysis or by employing a mixing tee in the autosampler to mix IS solution with the ingested solutions for analysis. Employing a mixing tee on the autosampler saves analyst time pipetting solutions and verifying pipette operation; however, requires periodic maintenance (pump tubing replacement) to ensure proper volumetric addition of ISs to the analyzed solutions.

**4.4.11.5 Tuning Solutions.** A tuning solution is analyzed to standardize the MS mass calibration and to perform mass resolution checks. The tuning solution(s) will contain elements covering the mass range of interest (approximately 7 to 238 amu); a typical tuning stock solution contains isotopes of Li, Mg, Y, Ce, Tl, and Co at approximately 10 µg/mL (ppm) and is diluted so that final concentrations are approximately 100 ng/mL (parts per billion [ppb]) or less for each element.

**4.4.11.6 ICP/MS Warm Up, MS Tuning, and Setup.** The ICP/MS is to be warmed up for a minimum of 30 minutes, or a duration prescribed by the manufacturer, prior to use. The tuning solution must be analyzed to perform mass calibration and resolution checks, which may be performed during the warmup period (per manufacturer recommendation). The MS tuning is to be optimized to provide a minimum resolution of approximately 0.75 amu at 5% peak height and mass calibration within 0.1 amu of unit mass. Minimally five aliquots of the tuning solution are to be analyzed and must achieve absolute signal RSD for each analyte of ≤ 5%. Manufacturer tuning recommendations, which may differ from those listed here, may also be followed and can usually be accomplished by automated tuning regimens controlled through instrument software.

Standard, blank, and sample solutions should be aspirated for a minimum of 30 seconds to equilibrate the ICP/MS response prior to acquiring data. Accelerated sample introduction systems (e.g., SC-FAST) may lessen this equilibration time. The ICP/MS must be set up such that three replicate integrations are performed for each analyzed solution. The average of the replicate integrations is to be reported for the analysis result.

A rinse blank of 2% nitric acid in deionized water should be used to flush the system between analyzed solutions. The rinse blank solution should be aspirated for a sufficient time to ensure complete return to baseline response levels before the next sample, standard, or blank introduction. Depending on the sample introduction system, this may take up to approximately 60 seconds. Sample introduction systems that increase the rinse blank pumping speed are available to decrease rinse times.

**4.4.11.7 ICP/MS Calibration and Analytical Sequence Batch.** The ICP-MS is to be calibrated each day that analysis is performed and the analysis batch QC samples listed in the following subsections are to be analyzed. Calibration acceptance criteria are given in the
following sections and are summarized in Section 4.4.12. Tier I metals must meet these specified criteria for the ICAL, ICV, and CCV or will be invalidated (Null qualifier EC indicating critical criteria failure) and non-Tier I metals should meet these criteria or will be qualified (QA Qualifier LJ indicating the value is an estimate and QA Qualifier QX indicating QC failure) when reported to AQS.

An example analysis sequence is given in Table 4.4-2.

<table>
<thead>
<tr>
<th>Sequence Number</th>
<th>Solution Analyzed</th>
<th>Sequence Number</th>
<th>Solution Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tuning solution</td>
<td>24</td>
<td>field sample 4</td>
</tr>
<tr>
<td>2</td>
<td>ICB</td>
<td>25</td>
<td>field sample 5</td>
</tr>
<tr>
<td>3</td>
<td>ICAL 1 (lowest concentration)</td>
<td>26</td>
<td>field sample 6</td>
</tr>
<tr>
<td>4</td>
<td>ICAL 2</td>
<td>27</td>
<td>field sample 7</td>
</tr>
<tr>
<td>5</td>
<td>ICAL 3 (highest concentration)</td>
<td>28</td>
<td>field sample 8</td>
</tr>
<tr>
<td>6</td>
<td>ICV</td>
<td>29</td>
<td>field sample 9</td>
</tr>
<tr>
<td>7</td>
<td>ICB</td>
<td>30</td>
<td>field sample 10</td>
</tr>
<tr>
<td>8</td>
<td>ICS A</td>
<td>31</td>
<td>field sample 11</td>
</tr>
<tr>
<td>9</td>
<td>ICS B</td>
<td>32</td>
<td>field sample 12</td>
</tr>
<tr>
<td>10</td>
<td>CCV</td>
<td>33</td>
<td>field sample 13</td>
</tr>
<tr>
<td>11</td>
<td>CCB</td>
<td>34</td>
<td>CCV</td>
</tr>
<tr>
<td>12</td>
<td>RB</td>
<td>35</td>
<td>CCB</td>
</tr>
<tr>
<td>13</td>
<td>MB</td>
<td>36</td>
<td>field sample 14</td>
</tr>
<tr>
<td>14</td>
<td>LCS</td>
<td>37</td>
<td>field sample 15</td>
</tr>
<tr>
<td>15</td>
<td>LCSD</td>
<td>38</td>
<td>field sample 16</td>
</tr>
<tr>
<td>16</td>
<td>field sample 1</td>
<td>39</td>
<td>field sample 17</td>
</tr>
<tr>
<td>17</td>
<td>duplicate (field sample 1)</td>
<td>40</td>
<td>field sample 18</td>
</tr>
<tr>
<td>18</td>
<td>MS (field sample 1)</td>
<td>41</td>
<td>field sample 19</td>
</tr>
<tr>
<td>19</td>
<td>MSD (field sample 1)</td>
<td>42</td>
<td>field sample 20</td>
</tr>
<tr>
<td>20</td>
<td>field sample 2</td>
<td>43</td>
<td>replicate analysis (field sample 16)</td>
</tr>
<tr>
<td>21</td>
<td>field sample 3</td>
<td>44</td>
<td>1:5 serial dilution (field sample 19)</td>
</tr>
<tr>
<td>22</td>
<td>CCV</td>
<td>45</td>
<td>CCV</td>
</tr>
<tr>
<td>23</td>
<td>CCB</td>
<td>46</td>
<td>CCB</td>
</tr>
</tbody>
</table>

### 4.4.11.7.1 Initial Calibration

Once the mass calibration and tuning have met the criteria listed in Section 4.4.11.6, the response of the instrument must be calibrated for the elements of interest over the concentration range of interest. It is recommended that the calibration range encompass a high concentration range minimally 10 to 25% above the highest anticipated field-collected sample concentration to avoid needing to dilute sample digestates for reanalysis. The ICP-MS response is linear over several orders of concentration magnitude, therefore a higher concentration than needed can be employed without much risk to failing to meet calibration acceptance criteria. Analyze the initial calibration blank (ICB, an undigested reagent blank) followed by the calibration standard solutions (minimum of three non-zero levels). The calibration curve must include the ICB as the zero concentration standard. Linear least squares regression is performed on the calibration solution instrument responses and their relative nominal concentrations and must show appropriate linearity with a correlation coefficient (r) of 0.995 or greater for the curve fit. Replicate analyses of the calibration standards must show %RSD < 10.1%. The calibration is verified by analysis of the initial calibration verification (ICV).
4.4.11.7.2 Initial Calibration Verification. Once the calibration curve is established, the SSCV (or QC sample) is analyzed as the ICV and must recover within ± 10.1% of the theoretical nominal value or the calibration is not verified. Analyses following a failing ICV will require reanalysis once the instrument calibration can be properly established.

4.4.11.7.3 Initial Calibration Blank. The ICB is again analyzed following the ICV; all element responses must be less than the laboratory’s established MDLsp for MDLs determined via Section 4.1.3.1 or the portion of the MDL represented by s·K for MDLs determined via Section 4.1.3.2. If the ICB does not meet this criterion, the analysis sequence must be stopped and the source of the contamination found before analysis may continue.

4.4.11.7.4 Interference Check Standards. (Note: This procedure has been completely revised from the procedure described in TAD Revision 3.) ASLs may elect to analyze interference check standard (ICS) solutions with each analytical sequence, but must minimally demonstrate that interferences are sufficiently low on a quarterly basis. Analysis of the ICS solutions allows for the explicit demonstration that known isobaric and/or polyatomic interferences do not impact concentration results. Interferences for ICP-MS are typically due to high concentrations of elements and are typically a problem with water analyses (particularly surface water and groundwater) due to the high dissolved mineral loading. However, for air filter analyses, particularly for ambient air filters, there is comparably very low loading of interfering elements on the filters and the contribution from interferences is almost negligible. When combined with instrument technology that reduces or eliminates interferences (e.g., collision reaction cells, magnetic field sector MS detectors), interferences are unlikely to impact target element measurements in air filter digestates in a meaningful way. For this reason, the ASL is not required to analyze ICS solutions with each analytical sequence and can demonstrate acceptable absence of interferences quarterly.

4.4.11.7.4.1 Interference Demonstration

Once the instrument has been calibrated, the calibration has been verified by analysis of the ICV, and the system has been shown to be free of contaminants by analysis of the ICB, the ICS solutions can be analyzed to demonstrate the instrument system is not unacceptably influenced by interfering substances.

Two types of ICS are to be analyzed, Type A and Type B. Type A ICS solutions contain elements known to be interferants, and Type B ICS solutions contain both the interferants and the target elements subject to interferences from elements in ICS Type A. ICS Type A solutions will contain the elements Al, Ca, Cl, Fe, Mg, Mo, P, K, Na, S, and Ti which are known interferants to target elements As, Cd, Cr, Co, Cu, Mn, Ni, and Se. The purpose of the ICS solutions is to determine whether interferences cause a positive bias in the measurement of target elements when no target elements are present (Type A ICS solutions) and whether interferences cause enhancement (a positive bias) or suppression (a negative bias) in the response of target elements when target elements are present (Type B ICS solutions). The Type A and Type B solutions are identical except that Type B solutions also contain target elements.
ICS solutions are prepared from certified stock solutions and diluted such that the final analyzed solution is acid composition and concentration matrix-matched to the method specification for the standards, QC samples, and field collected samples.

ICS solutions are prepared with concentrations of interferants above those expected on air filter samples (ASLs may measure the interferants on several field collected air filters to characterize this approximate loading). The concentrations of interferants should not be so high that they interfere with IS response and should be commensurate with the expected concentration on a routine air filter sample. A recommended concentration range for the interferants in ICS Type A and Type B solutions is approximately 1 to 1000 µg/mL. The analyst will evaluate whether there is a significant response of target elements of the ICS Type A solution, when no target elements are present, as this indicates a positive bias for those elements demonstrating a significant response. The ICS Type B solutions are then analyzed, the responses of the target elements are corrected for their responses in the ICS Type A solutions, and their recovery of the target elements is evaluated.

ICS Type B solutions are analyzed with concentrations of interferants identical to those in ICS Type A solutions (i.e., above those expected on air filter samples) and concentrations of target elements at approximately the typical concentration measured in ambient air. Target elements should be present in ICS Type B solutions at concentrations of approximately 10 to 100 ng/mL (0.01 to 0.1 µg/mL), or lower concentrations, as appropriate, based on those measured in the supporting monitoring site’s ambient air samples. Note that these concentrations may be much lower than this range if the ASL solely analyzes PTFE low volume filters.

Analysis of ICS Type A solutions should demonstrate that the concentration of each target analyte is less than 3x MDL_{sp} (for MDLs determined by Section 4.1.3.1) or three-fold the portion of the MDL represented by \( s \cdot K \) for MDLs determined via Section 4.1.3.2, however, these criteria are not evaluated for pass/fail, rather are used to correct the measurements of the target elements in ICS Type B solutions. Analysts should be aware that ICS Type A stock standard solutions may contain target analytes at quantifiable concentrations; however, when diluted to the concentration range recommended above, the background contribution may be negligible. Analysts should review COAs for ICS Type A stock standards to determine whether observed concentrations exceeding this criterion may be due to contaminant levels in the ICS Type A solution (and not due to an interference effect).

ICS Type B solutions are evaluated for the target analyte recovery against the theoretical nominal concentration after correction (subtraction) for the concentration in the ICS Type A solution when the ICS Type A solution exceeds the criterion above (3x MDL_{sp} for MDLs determined by Section 4.1.3.1 or three-fold the portion of the MDL represented by \( s \cdot K \) for MDLs determined via Section 4.1.3.2). The ICS Type B solution, corrected for background, must show recovery of target elements of 79.9 to 120.1%. If this range is exceeded after correction for the concentration in the ICS Type A solution, an interference with affected target analytes is indicated.

The interferants to an affected target element should be reduced (e.g., by approximately half) in the ICS Type A and ICS Type B solutions and the ICS demonstration repeated to ascertain
whether the interference was acceptably remediated by dilution of the interferant(s). The ASL should analyze a suite of ambient air sample digestates to demonstrate that the interferant(s) concentration in air filter samples is less than the concentration of the interferant(s) in the ICS solutions.

Data for samples with elements indicating an unacceptable interference resulting in suppression or enhancement are to be qualified based on the direction of bias (QA Qualifier LL indicating low bias or QA Qualifier LK indicating high bias) when reported to AQS.

4.4.11.7.5 Continuing Calibration Verification. At a minimum, a CCV is prepared at a single concentration at approximately the mid-range of the calibration curve and is analyzed prior to the analysis of samples, after the analysis of every 10 digestates, and at the end of the analytical sequence. The CCV is typically prepared from the primary calibration stock standard material, but may be prepared from the SSCV stock standard material or other certified standard material. CCV recovery is to be within 89.9 to 110.1% for each target element. As a best practice, two or more concentrations of CCV may be prepared and analyzed so as to better verify instrument performance across the range of the calibration curve.

4.4.11.7.6 Continuing Calibration Blank. The CCB is from the same solution as the ICB and must be analyzed after each CCV to ensure the instrument background remains acceptably low. A CCB is not required after the CCV concluding the analysis sequence. CCB analysis must show that the absolute value of the instrument concentration response for each target element is less than the laboratory’s established MDLssp for MDLs determined via Section 4.1.3.1 or the portion of the MDL represented by \( s \cdot K \) for MDLs determined via Section 4.1.3.2. If the CCB does not meet this criterion, the analysis sequence must be stopped and the source of the contamination found before analysis may continue. Samples analyzed since the last acceptable CCB require reanalysis. If reanalysis cannot be performed, data for samples since the most recent passing CCB are to be qualified (QA Qualifier LB indicating laboratory blank over limits and QA Qualifier QX indicating QC failure) when reported to AQS.

4.4.11.7.7 Laboratory Digestion Batch Quality Control Samples. Laboratory digestion batch QC samples for low volume PTFE Teflon® and high volume QFF media described in Sections 4.4.9.5.1 and 4.4.10.5.1, respectively, are analyzed with each analysis batch. Laboratory digestion batch QC samples (consisting of RBs, MBs, RBSs, and LCSs) are analyzed after the first CCV and CCB pair and should be analyzed prior to the analysis of field samples in the same digestion batch. Duplicate digested samples, MSs, and MSDs similarly should be analyzed immediately following their parent field sample. In order to minimize reanalysis if more than one digestion batch is included in an analysis batch, each digestion batch should be analyzed altogether and separated by a CCV and CCB prior to analysis of the next digestion batch.

4.4.11.7.8 Serial Dilution. A sample digestate is chosen for each analysis batch for serial dilution to assess matrix effects of the sample digestate. The sample digestate selected for serial dilution should be a field collected sample (i.e., not a QC sample such as a FB or laboratory blank) to increase the likelihood that elements will be measured above five-fold MDL when the digestate is diluted five-fold. Dilute the chosen digestate five-fold with digestion solution (such that the matrix acid concentration is matched to that of the standards, QC samples, and digested...
samples) and fortify with IS (so that the concentrations ISs are the same as in the parent sample). Element concentrations for elements $\geq 5x$ MDL in the serially diluted sample (note this is equivalent to 25-fold MDL in the undiluted parent sample) must recover within 89.9 to 110.1% of the undiluted parent sample. If acceptance criteria are not met, the data for the parent sample are to be qualified (QA Qualifier LJ indicating the value is an estimate and QX indicating QC failure) when entered into AQS.

**4.4.11.7.9 Replicate Analysis.** A replicate of a digestate from a field-collected sample is to be analyzed at the minimum rate of one for every 20 field-collected samples in the analysis batch. Precision of the replicate analysis must be $< 10.1\%$ RPD for elements $\geq 5x$ MDL in at least one of the replicate analyses as detailed in Section 2.1.3.1.

For replicate analysis, the ASL will typically assign a convention that the first result of replicate analyses is reported to AQS as the sample result. However, if the first replicate is invalidated for any reason (e.g., as may occur when a matrix effect results in poor IS recovery) and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as described in Section 2.1.3.2.

**4.4.11.8 ICP/MS Quantitation.** Analyzed solutions are quantitated by relating the instrument element response (e.g., counts per second or similar) to the linear regression equation established for the ICAL in Section 4.4.11.7.1 as follows:

$$C_t = \frac{(A - b)}{m}$$

where:

- $C_t$ = measured concentration of target element in the digestate (ng/mL)
- $A$ = ICP-MS response of the target element (counts or similar unit)
- $b$ = y-intercept of linear least-squares regression (counts or similar unit)
- $m$ = slope of linear least-squares regression (counts or similar unit / (ng/mL))

Analyzed solutions with concentration results exceeding the instrument calibration range are to be diluted and analyzed within the calibration range. The diluted result must be reported and the associated MDL adjusted accordingly by the dilution factor. For example, if a sample is diluted by a factor of two to analyze nickel within the calibration curve, the MDL is multiplied by this dilution factor of 2 when reporting to AQS. While dilution to within the calibration curve is preferable, the analyst may also analyze a standard above the calibration range as may be performed to determine the linear dynamic range (LDR) of the instrument (note that LDR determination is not required for this method but is typically required for water analysis methods). Provided the higher concentration LDR standard measurement is within $\pm 10.1\%$ of the theoretical nominal concentration, associated samples above the calibration curve range can be reported without qualification.

Negative concentration results which exceed the absolute value of the laboratory’s established MDL_{sp} for MDLs determined via Section 4.1.3.1, or the portion of the MDL represented by $s\cdot K$ for MDLs determined via Section 4.1.3.2 indicate the likely existence of contamination problems in the reagents, standards, or labware used to prepare the calibration curve. This can occur when
different reagents or procedures are employed for preparing calibration standards than those employed for sample digestion. In such cases, a source of background in the calibration standards causes enhanced response due to background which typically is evident as an elevated y-intercept for the linear regression. As a result, the absence of this background in analyzed sample digestates with low concentrations of the target element will calculate to negative concentrations when the sample digestate response is input to the calibration regression equation. Negative concentrations should not be qualified as “9” when entered in AQS as this qualifier indicates that negative concentrations were replaced with zero. Overly negative concentrations are further discussed in Section 6.6.1.

4.4.11.9 **Calculation of In-Air Concentration.** The concentration for each field-collected sample must be reported in mass of element per m³ of sampled air (e.g., ng/m³ or µg/m³) in LC. Results may additionally be reported by correction of the sampled air volume to standard atmospheric conditions of 25°C and 760 mm Hg. Conversion of collected volume in local conditions to standard conditions is performed by converting sampled flow rates as follows:

\[
Q_s = \frac{P_a \cdot Q_a \cdot T_s}{P_s \cdot T_a}
\]

where:

- \( Q_s \) = sample flow rate at standard conditions (760 mmHg and 25°C) – (m³/minute)
- \( P_s \) = standard barometric pressure = 760 mmHg
- \( T_s \) = standard temperature in K = 298.15K
- \( Q_a \) = sample flow rate at ambient conditions – (m³/minute)
- \( P_a \) = ambient barometric pressure in mmHg
- \( T_a \) = ambient temperature in K

Collected sample volume in standard conditions is then calculated by multiplying the sample duration in minutes (e.g., 1440) by the standard conditions sample flow rate.

Determined sample results must not be corrected for levels measured in associated CB, MB, FB, or TB. Concentrations exceeding acceptance criteria for these blanks are to prompt investigation as to the source of contamination.

4.4.11.9.1 **Concentration Calculations for Low Volume Sampling.** To calculate the airborne concentration of each element measured on the PTFE Teflon® filter, the ICP/MS measured concentration in µg/mL is multiplied by the sample digestate final volume in mL and by the dilution factor (if dilution of the digestate was performed), and is divided by the sampled air volume (at LC) in m³, as follows:

\[
C_{\text{air}} = \frac{C_{\text{ICP/MS}} \cdot V_{\text{dig}} \cdot DF}{V_{\text{air}}}
\]

where:
To calculate the airborne concentration of each element measured on the QFF, the ICP/MS measured concentration in µg/mL is multiplied by the final digestate volume in mL, by the fraction of the filter digested for analysis, and by the dilution factor (if dilution of the digestate was performed), then is divided by the sampled air volume (at LC) in m³, as follows:

\[ C_{\text{air}} = \frac{C_{\text{ICP/MS}} \cdot V_{\text{dig}} \cdot DF}{V_{\text{air}} \cdot F_f} \]

where:
- \( C_{\text{air}} \) = Concentration of the element in air at local conditions (ng/m³)
- \( C_{\text{ICP/MS}} \) = Concentration measured in the sample digestate (ng/mL)
- \( V_{\text{dig}} \) = Volume of digestate (mL)
- \( DF \) = Dilution factor
- \( F_f \) = Fraction of exposed filter digested
- \( V_{\text{air}} \) = Volume of air sampled at LC (m³)

\(^a\) For a 1 inch × 8 inch strip portioned as described in Section 4.4.10.5, this is equivalent to 1/9 by dividing the exposed area of the portioned strip by the area of the exposed filter. (1 inch × 7 inch = 7 inches²)/(7 inch × 9 inch = 63 inches²) = 1/9

4.4.12 Summary of Method Quality Control Requirements. QC requirements are summarized in Table 4.4-3.
### Table 4.4-3. Method Criteria Parameters for NATTS Metals Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter Holding Time</td>
<td>Duration between end of sample collection and completion of digestion and analysis</td>
<td>All field collected samples</td>
<td>Must not exceed 180 days</td>
</tr>
</tbody>
</table>
| ICP/MS Tuning                 | ICP/MS mass calibration and resolution checks                                           | Analysis of a minimum of five aliquots of the tuning solution each day of analysis prior to ICAL | Absolute signal of five replicates RSD < 5.1% 
Mass calibration within ±0.1 amu of unit mass
Resolution check within ±0.75 amu at 5% peak height
Alternatively, must meet manufacturer tuning criteria |
<p>| Internal Standards Addition   | Elements other than target elements used to monitor instrument performance and correct for matrix effects | Added to each analyzed solution | Recovery within 59.9 to 125.1% of the IS response of the ICB                        |
| Rinse Blank                   | 2% (v/v) HNO₃ (or similar diluted acid concentration) aspirated by the autosampler to eliminate memory effects between analyzed solutions (recommended to be established by analysis of highest ICAL standard followed by CCB) | Before and after each analyzed solution | Duration of aspiration sufficient to eliminate element carryover as evidenced by successful CCVs and CCBs |
| Initial Calibration (ICAL)    | Minimum of three levels covering the desired concentration range for each target element plus the calibration blank (CB) | Each day analysis is performed prior to analyzing samples | Correlation coefficient (r) of linear least squares regression ≥ 0.995 |
| Initial Calibration Verification (ICV) | Second source calibration verification (SSCV) standard analyzed to verify the ICAL (minimally a single concentration at approximately the mid-range of the calibration curve) | Each day of analysis immediately following the ICAL | Recovery within 89.9-110.1% of theoretical nominal for all target elements |
| Initial Calibration Blank (ICB) | Calibration blank analyzed to ensure instrument is sufficiently clean to continue analysis | Each day of analysis immediately following the ICV | All target elements &lt; MDLₜₚ (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2) |
| Interference Check Standard (ICS) A | Solution containing known interferences at concentrations above those anticipated for routine analysis and analyzed to assess the effect of such interferences on target element measurements | Minimally quarterly. Typically analyzed following the ICB | Criteria do not indicate pass/fail. Target elements should be &lt; MDLₜₚ (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2) |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interference Check Standard (ICS) B</td>
<td>Solution containing known interferences at the same concentration as the ICS Type A and target elements at concentrations commensurate with typical measured sample concentrations. Demonstrates interferences do not unacceptably impact routine sample analysis.</td>
<td>Quarterly, following ICS Type A</td>
<td>After correction for ICS Type A target concentrations, recovery within 79.9-120.1% of theoretical nominal for all target elements. Recovery outside these limits indicates an interference for which mitigation or data qualification is needed.</td>
</tr>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>Standard solution containing target analytes at approximately the mid-point of the calibration curve range analyzed to verify instrument calibration</td>
<td>Immediately following the ICB (or ICS, if analyzed), after every 10 samples and at the conclusion of the analysis sequence</td>
<td>Within ± 10.1% of theoretical nominal for all target elements</td>
</tr>
<tr>
<td>Continuing Calibration Blank (CCB)</td>
<td>Analysis of the calibration blank solution to ensure instrument is sufficiently clean to continue analysis</td>
<td>After each CCV except at the conclusion of the analysis sequence</td>
<td>All target elements &lt; MDL&lt;sub&gt;sp&lt;/sub&gt; (refer to Section 4.1.3.1) or &lt;i&gt;s&lt;/i&gt;·&lt;i&gt;K&lt;/i&gt; (refer to Section 4.1.3.2) Alternatively, ASLs can establish acceptance criteria per 4.4.8.3.</td>
</tr>
<tr>
<td>Reagent Blank (RB)</td>
<td>Aliquot of digestion solution taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>All target elements &lt; MDL&lt;sub&gt;sp&lt;/sub&gt; (refer to Section 4.1.3.1) or &lt;i&gt;s&lt;/i&gt;·&lt;i&gt;K&lt;/i&gt; (refer to Section 4.1.3.2)</td>
</tr>
<tr>
<td>Method Blank (MB)</td>
<td>Blank PTFE filter or QFF strip taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>All target elements &lt; MDL</td>
</tr>
<tr>
<td>Reagent Blank Spike (RBS)</td>
<td>Aliquot of digestion solution spiked with known amount of target elements and taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>Recovery within 79.9 to 120.1% of theoretical nominal for all target elements</td>
</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>PTFE filter or QFF strip spiked with a known amount of each target element and taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>Recovery within 79.9 to 120.1% of theoretical nominal for all target elements, Sb recovery 74.9 to 125.1%</td>
</tr>
<tr>
<td>Laboratory Control Sample Duplicate (LCSD)</td>
<td>Duplicate PTFE filter or QFF strip spiked with a known amount of each target element and taken through the digestion process</td>
<td>(Optional) One per digestion batch of 20 or fewer field-collected samples</td>
<td>Recovery within 79.9 to 120.1% of theoretical nominal for all target elements, Sb recovery 74.9 to 125.1%, precision &lt; 20.1% RPD of LCS</td>
</tr>
<tr>
<td>Duplicate Sample Strip (QFF only)</td>
<td>Additional strip from a field-collected QFF taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>Precision &lt; 20.1% RPD for elements ≥ 5x MDL in at least one of the duplicate sample strip digestates</td>
</tr>
<tr>
<td>Matrix Spike (MS) (QFF only)</td>
<td>Strip from a field-collected QFF spiked with a known amount of each target element and taken through the digestion process</td>
<td>Once per analysis batch of 20 or fewer samples</td>
<td>After correction for the parent sample concentration, recovery within 79.9 to 120.1% of theoretical nominal for all target elements, Sb recovery 74.9 to 125.1%</td>
</tr>
</tbody>
</table>
### Table 4.4-3. Method Criteria Parameters for NATTS Metals Analysis (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Matrix Spike Duplicate (MSD) (QFF only)</strong></td>
<td>Additional strip from the same field-collected QFF as the MS, and spiked with the same amount of each target element as the MS, and taken through the digestion process</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>After correction for the parent sample concentration, recovery within 79.9 to 120.1% of theoretical nominal for all target elements, Sb recovery 74.9 to 125.1%, precision &lt; 20.1% RPD of MS</td>
</tr>
<tr>
<td><strong>Collocated Sample</strong></td>
<td>Sample collected from a separate sampling unit concurrently with the primary sample</td>
<td>10% of primary samples for sites conducting collocated sampling (as required by QAPP)</td>
<td>Precision &lt; 20.1% RPD of primary sample for elements ≥ 5x MDL in at least one of the collocated samples</td>
</tr>
<tr>
<td><strong>Serial Dilution</strong></td>
<td>Five-fold dilution of a field-collected filter sample digestate to assess matrix effects</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>Recovery within 89.9 to 110.1% of undiluted sample for elements ≥ 25x MDL in the undiluted parent sample</td>
</tr>
<tr>
<td><strong>Replicate Analysis</strong></td>
<td>Second aliquot of a sample digestate chosen for replicate analysis</td>
<td>One per digestion batch of 20 or fewer field-collected samples</td>
<td>Precision &lt; 20.1% RPD for elements ≥ 5x MDL in at least one of the replicates</td>
</tr>
<tr>
<td><strong>Field Blank (FB)</strong></td>
<td>Filter sample collected by installation in the sampling unit for minimally five minutes</td>
<td>10% of the primary sampling events</td>
<td>All target elements &lt; MDL</td>
</tr>
<tr>
<td><strong>Trip Blank (TB)</strong></td>
<td>Filter sample accompanying field collected samples throughout field sampling and transport activities, but not exposed to the ambient air</td>
<td>Not required, recommended as 10% of primary sampling events</td>
<td>All target elements &lt; MDL</td>
</tr>
<tr>
<td><strong>Lot Blank Determination</strong></td>
<td>Analysis of a lot of filters to determine lot background</td>
<td>minimally 5 filters from each lot</td>
<td>No acceptance criterion. Average value reported to AQS.</td>
</tr>
</tbody>
</table>

### 4.4.13 References


4. Sampling of Ambient Air for PM10 Concentration using the Rupprecht and Patahschnick (R&P) Low Volume Partisol ® Sampler; EPA Compendium Method IO-2.3; *Compendium of Methods*

4.5 Collection and Analysis of PAHs via EPA Compendium Method TO-13A

Each monitoring agency and ASL is to prescribe in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for performing PAHs sampling, media extraction, and extract analysis. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.5.6 must be met.

4.5.1 Summary of Method. PAHs, which are SVOCs, are collected per the guidance given in EPA Method TO-13A ¹ and ASTM D6209.² These two methods are similar and share collection media specifications: utilizing a QFF for particulate filtration/collection and glass thimble containing PUF and styrene-divinylbenzene polymer resin sorbent (XAD-2 or equivalent) to collect PAHs from ambient air. Additionally, the analyte list and instrument complement and configuration for GC/MS separation and quantitation is virtually identical for EPA Method TO-13A (SVOCs in air) and EPA Method 8270E (SVOCs in water, soils, and sediments). EPA Method 8270E was revised (June 2018) since the previous revision of this TAD and includes updates for modern instrumentation compared to EPA Compendium Method TO-13A, which has not been updated since 1999. Therefore, aspects of analysis applicable to air analyses in this TAD are adapted from Method 8270E.³

Approximately 200 to 350 m³ of ambient air is drawn through a QFF and glass cartridge containing a sandwich of PUF-resin-PUF over 24 hours. The sample is retrieved and transported and stored refrigerated until the QFF and contents of the glass cartridge are extracted by way of accelerated solvent extraction (ASE) ⁴ or in a Soxhlet apparatus, and the extract is concentrated (to 1 mL) and analyzed by GC/MS. Concentrations of PAHs in ambient air are generally low (0.02 to 160 ng/m³), thus a large volume of air must be collected to ensure sufficient masses of target analytes are present for quantification with a typical quadrupole MS in SIM mode. Alternative MS detectors can be employed, such as ion trap MS detectors or tandem MS/MS detectors provided performance specifications are met.

The more volatile PAHs, such as naphthalene, are subject to potential loss from the cartridges due to, for example, volatilization and decomposition from exposure to light.⁵,⁶ Thus, PAH samples should be collected from the sampling unit, protected from light, and brought to refrigerated conditions (≤ 4°C) as soon as possible after the end of the sampling period. Shipment and storage at refrigerated temperatures will further minimize evaporative losses of the more volatile PAHs. PAHs with higher volatility may also be lost from the sorbent cartridge during sampling due to migration out of the cartridge outlet (breakthrough) or from volatilization from the QFF, especially during warm weather.⁷,⁸ The PAHs including, but not limited to, those in Table 4.5-1 may be determined by this method.
Table 4.5-1. PAHs and Associated Chemical Abstract Numbers (CAS)

<table>
<thead>
<tr>
<th>Target Compound</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene a</td>
<td>83-32-9</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>208-96-8</td>
</tr>
<tr>
<td>Anthracene b</td>
<td>120-12-7</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>56-55-3</td>
</tr>
<tr>
<td>Benzo(a)pyrene a b</td>
<td>50-32-8</td>
</tr>
<tr>
<td>Benzo[b]pyrene</td>
<td>192-97-2</td>
</tr>
<tr>
<td>Dibenzo(g,h,i)perylene</td>
<td>191-24-2</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>205-99-2</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>207-08-9</td>
</tr>
<tr>
<td>Chrysene</td>
<td>218-01-9</td>
</tr>
<tr>
<td>Coronene</td>
<td>191-07-1</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>53-70-3</td>
</tr>
<tr>
<td>Fluoranthene b</td>
<td>206-44-0</td>
</tr>
<tr>
<td>Fluorene b</td>
<td>86-73-7</td>
</tr>
<tr>
<td>9-Fluorene</td>
<td>486-25-9</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>193-39-5</td>
</tr>
<tr>
<td>Naphthalene a b</td>
<td>91-20-3</td>
</tr>
<tr>
<td>Perylene</td>
<td>198-55-0</td>
</tr>
<tr>
<td>Phenanthrene b</td>
<td>85-01-8</td>
</tr>
<tr>
<td>Pyrene b</td>
<td>129-00-0</td>
</tr>
<tr>
<td>Retene</td>
<td>483-65-8</td>
</tr>
</tbody>
</table>

a NATTS Tier I analyte  
b NATTS PT target analyte

4.5.2 Sample Collection Equipment. A high volume PS-1 style sampler, or equivalent sampler that permits collection of TSP, which is able to maintain a minimum flow rate of 140 L/min over a 24-hour sampling period is required. Such sampling units are commercially available with various conveniences. The most basic units are equipped with an event timer and an elapsed time counter to control and indicate duration of sample collection. Flow rate is controlled by the fan motor speed, ball valve restricting flow through the cartridge and the blower motor, or combination. A manometer (such as a magnehelic) is attached to the ports on a venturi located between the sampling inlet and the fan motor to indicate the pressure differential which correlates to the flow rate by an established flow rate calibration relative to the pressure differential. These basic units employ a mechanical timer to start/stop sampling and an elapsed time counter. More expensive systems employ computerized functions and comprise temperature and barometric pressure sensors. Such computer equipped samplers control the sampling start and stop time and monitor the ambient temperature, barometric pressure, and venturi pressure differential throughout the sampling event to control the sampling flow rate. The events and measurements are logged by the sampler computer and can be downloaded after the sampling event for review.

Each high volume sampler should have an extension hose/tube for the blower motor exhaust to ensure that the sampled atmosphere (which has been scrubbed of PM and PAHs) is not reentrained/resampled. If so equipped, the exhaust hose/tube is to terminate in the predominant downwind direction minimally 3 m away from the unit. Care should be taken to ensure that the blower motor exhaust does not interfere with other sampling units at the site and should be minimally 4 m from the inlet of any sampling instrument and should not interfere with meteorological instruments (i.e., blow on temperature, relative humidity, or precipitation gauge
instruments). The sampling unit inlet (edge) must minimally be 2 m from all other sampling inlets. Sampler siting requirements are listed in Section 2.4.

4.5.2.1 **Sampler Flow Rate Calibration and Verification.** Sampler flow rate must be calibrated initially and when flow verification checks indicate flow rates deviate by > 10.1% from the flow transfer standard flow or design flow. Flow rate calibration verification checks must be performed quarterly and are recommended to be performed monthly. Flow rate calibration verifications are to be performed at approximately the flow rate setting utilized to collect field samples.

Flow rate calibration of a non-mass flow controlled sampler (those without computer control) must be performed with a traceable, calibrated flow transfer standard capable of inducing various backpressures (restrictions) to generate a range of flow rates that bracket the target flow rate. Such may be accomplished with an electronic flow meter, a variable orifice, or a series of fixed plate orifices, or similar. The calibrated flow rates are then correlated to the measured pressure differential manometer readings at the flow venturi and a least squares linear regression prepared to characterize the flow rate at a given pressure differential reading. Computer controlled sampling units are to have the sampling flow rate slope and intercept assigned following the manufacturer instructions, and this is accomplished similarly to non-flow controlled sampling units by inducing different flow rate conditions to establish the sampling unit flow rate calibration curve.

In the event a flow calibration verification check fails acceptance criteria, data for samples collected since the most recent acceptable flow calibration verification check are to be invalidated (Null qualifier AH indicating sample flow rate or CV out of limits) when reported to AQS.

4.5.2.1.1 **Flow Rate Verification and Flow Rate Audit Reporting.** Following flow rate calibration verifications and flow rate audits, the results are to be input into AQS. Guidance for establishing the monitor and flow channels in AQS is described in Appendix E. Monitoring agencies should input these data quarterly and ensure that flow rates are in EPA standard conditions of 760 mmHg and 25°C.

4.5.2.2 **Sampling Unit Maintenance.** Each monitoring agency is to define a maintenance schedule for PAHs sampling units and for sampling modules in which the sampling cartridge and QFF are installed. Sampling unit maintenance items to prescribe in a periodic check include: inspection of sampling unit electrical connections, check of timers for proper operation, replacement of motors and motor brushes, removal of debris from underneath the gable and inside the upper portion of the sampling unit, and inspection of sealing gaskets. Cleaning of the sampling modules should occur ideally after each sample collection event, should not exceed monthly, and may not exceed quarterly. Sampling modules may be cleaned with hot water with laboratory-grade soap and manual brushing and should be rinsed several times in deionized water. After drying, the interior surfaces should be solvent rinsed with an appropriate solvent such as chromatographic grade hexane, acetone, or other suitable solvent and allowed to air dry. Store clean sampling modules in a clean area protected from dust contamination until next use. Use of such solvents should be performed with proper ventilation (e.g., fume hood) and with
proper personal protective equipment (PPE – such as solvent impermeable gloves, lab coat, and safety glasses).

4.5.3 Sampling Media and Sampling Cartridge Preparation

4.5.3.1 Sampling Media Preparation. Each PAH sample must consist of a QFF, two PUF discs/plugs totaling 3 inches in stack height, and 15 ± 0.5 g of resin sorbent. Measurement data for samples collected with alternative media proportions are to be qualified (QA Qualifier LJ indicating the value is an estimate) when reported to AQS.

Particulate filters for sample collection are quartz fiber filters (QFF), 102 to 104-mm diameter with 2-µm pore size. Filters must be inspected on a light table or with a similarly diffuse backlighting for pinholes, discolorations, tears, or other defects such as thin spots. Filters which present these defects are not to be used for sample collection (though may be suitable for laboratory QC samples). After visual inspection, filters should be baked (in a muffle furnace) at approximately 400°C for a minimum of 4 hours to remove potential impurities and interferences. Once cooled, filters should be stored in a sealed container to ensure they do not become contaminated prior to sample collection.

Naphthalene is the most difficult analyte to adequately remove from the sampling media, particularly for PUF substrates. Commercial vendors offer pre-cleaned PUF and resin sorbent; however, in many instances these materials require additional cleaning steps to attain sufficiently low background for use.

PUF plugs are available commercially, or they may be prepared by cutting plugs of the proper diameter (2 3/8 inch) from PUF sheets of 1.5-inch thickness. The total stack height of PUF in a sampling cartridge will total 3 inches (e.g., can consist of one 1 inch thick and one 2 inch thick piece). PUF plugs may be purchased without treatment and cleaned by the laboratory prior to use, or may be purchased precleaned. Precleaned PUF plugs may not meet cleanliness criteria for target analytes or may contain interferences (e.g., phthalates) which require subsequent cleaning procedures prior to use for sample collection. Precleaned PUF plugs are typically shipped with a COA listing the contaminant levels for common PAHs. ASLs are strongly encouraged to extract and analyze precleaned media to assess the background contaminants prior to placing a lot of material into use. Following sample extraction, used PUF plugs may be cleaned for reuse, if so desired. PUF material typically lose substrate after repeated cleaning and may shrink in diameter, not properly sealing into the sampling cartridge.

Styrene-divinylbenzene polymer resin, such as XAD-2, is commercially available and may be purchased with or without precleaning. As with precleaned PUF, some precleaned resins do not meet cleanliness criteria for target analytes or may contain interferences which require subsequent cleaning procedures before use for sample collection. Precleaned resin sorbent is generally shipped with a COA listing the contaminant levels for common PAHs. Following sample extraction, used resin may be recovered and cleaned for reuse. ASLs will need a reserve supply of resin sorbent as only a portion of used resin can be recovered as it physically degrades and disintegrates over time, requiring periodic replenishment.
PUF and/or resin sorbents will be cleaned before reuse with a specialized solvent extraction program that is slightly different than the method by which the QFF, PUF, and resin from a sample cartridge are extracted. A more aggressive solvent or combination of solvents such as methylene chloride (which is not suitable for PUF cleaning), toluene, hexane, and/or acetone should be employed to remove target analytes and interferences from the PUF and resin media for cleaning. To increase the effectiveness of media cleaning, extracts from media cleaning procedures can be reserved, concentrated, and analyzed to ascertain levels of PAHs removed during cleaning (and low measured masses of target analytes or non-detects indicate effective cleaning processes).

Clean sampling media should be stored in sealed containers protected from light (aluminum foil, amber glass, etc.).

4.5.3.2 Sampling Cartridge and Labware Cleaning. To the extent possible, labware employed in PAHs sampling and analysis must consist of metal, glass, or fluoropolymer. The sampling cartridge must consist of glass or metal construction with a stainless steel or brass screen. Plastics must be avoided due to the leaching of phthalates, particularly when wetted with solvent. Phthalates present in extracts and solvents elute in the PAHs chromatogram and can result in large chromatographic peaks that interfere with separation and quantitation of target PAHs. Cartridge thimbles, extraction glassware, and volumetric glassware for preparing standard solutions must be thoroughly cleaned and contaminant-free prior to use such that blank criteria are met as given in Section 4.5.6. Aggressive washing with hot water and laboratory grade soap, tap water rinsing, deionized water rinsing, acid or base rinsing, and solvent (methylene chloride) rinsing may be necessary to ensure that contaminants and interferences are removed from labware prior to use. Non-volumetric glassware may be baked at approximately 400°C for 4 hours. Volumetric glassware must not be heated above 80 to 90°C unless otherwise indicated by the manufacturer as such heating may void the volumetric certification. Following the final solvent rinse, clean labware should be capped or covered (as appropriate) with solvent rinsed foil to prevent contamination with dust, etc.

4.5.3.3 Sampling Cartridge Preparation. Tools contacting sampling media are to be solvent rinsed and technicians must wear powder-free nitrile or equivalent gloves during cartridge preparation. Refer to Figure 4.5-1 below for the configuration of the sampling cartridge. The cartridge thimble is a cylinder (typically glass) with an indent approximately 1 inch from one end for retention of a stainless steel support screen at the outlet end. Glass thimble cartridges with supports constructed of glass frits must not be used as the glass frit provides too large a flow restriction to attain proper sampling flow rate and will result in premature wear on the sampling unit motor and motor brushes. One (typically 1.5-inch thick) PUF plug is placed into the inlet of the cartridge and pushed down to contact the support screen. A 15-gram aliquot of clean resin sorbent is then added to the cartridge on top of the PUF plug and distributed evenly. The second PUF plug is then placed on top of the resin layer to retain the resin layer in place.

The assembled cartridge must include 15 ± 0.5 g of resin sorbent in the assembled cartridge to ensure that more volatile PAHs (such as naphthalene) are collected and retained. Using a smaller or larger mass of resin sorbent alters the potential collection efficiency which will result in
increased variability (and therefore decreased comparability) among NATTS monitoring sites for PAHs measurements.

The PUF plugs should fit snugly in the cartridge which encourages them to stay in place as well as hold the resin in place. PUF plugs that fit loosely may permit resin to escape out of the cartridge during transport and/or sampling, resulting in lower collection efficiencies. PUF plugs that have been used and recleaned several times may shrink over time and fit less securely in glass cartridges. Assembled cartridges should be wrapped in solvent rinsed foil, sealed in a resealable plastic bag or other container, and kept at ≤ 4°C until removed from storage for addition and field surrogates prior to field deployment.

4.5.3.4 Sample Media Batch Blank. Regardless of the source of materials or the specific cleaning procedures each laboratory adopts, the combined contributions of target PAHs to a sample cartridge, i.e., the sum of a QFF, 3 inches of PUF discs, and 15 g of resin sorbent, may not exceed:

- For naphthalene: 200 ng or the equivalent of 10% of the site’s 5th percentile concentration for the previous three years, whichever is higher.
- All other individual target PAHs: 10 ng or the equivalent of 10% of the 5th percentile concentration for the previous three years, whichever is higher.

This demonstration can be made by preparing and extracting a sample media batch blank consisting of a field-deployable PUF/resin sorbent/PUF cartridge with QFF or by extracting equivalent amounts of each individual media component and summing their relative contributions to prepare the equivalent of one sampling cartridge. This is best accomplished by extracting multiple cartridge equivalents at a time (e.g., 45 g of resin sorbent and dividing the measured amount by 3 for the contribution to the sample media batch blank), as might be done when cleaning media before use. The ASL is to define what constitutes a lot of media, for example, if the ASL cleans a large number of PUF plugs or several hundred g of resin sorbent in a batch/lot, that should be considered as a lot for media cleanliness demonstration purposes. Measurement data for samples collected with media exceeding these criteria are to be qualified (QA Qualifier LB indicating laboratory blank above limits) when input into AQS.

4.5.3.5 Field Surrogate Addition. Prior to dispatching sample cartridges to the field, field surrogate compounds are to be added to the sorbent media. The recovery of field surrogate compounds is evaluated to assess the retention of PAHs through the entire sample handling, sample collection, extraction, and analysis procedures.

Field surrogates are added by spiking 1 µg (e.g., 100 µL of a 10 µg/mL solution in acetone, toluene, hexane, or other suitable solvent) of, for example, fluoranthene-d_{10} and benzo(a)pyrene-d_{12} directly into the PUF and resin sorbent. Field surrogates are recommended to be added to cartridges for deployment no sooner than two weeks prior to the scheduled sample collection date; however, studies have shown field surrogates are stable for up to three months on cartridges before deployment. Once field surrogates have been added to cartridges for deployment, they should be stored refrigerated (best practice) until deployed. ASLs should be aware that troubleshooting low field surrogate recoveries is confounded by extended field surrogate holding times and by storing cartridges unrefrigerated once they have been fortified with field surrogates.
4.5.4 PAHs Sampling. Sample media are to be installed into the sampling unit as close to the sampling date as possible to minimize positive bias due to passive sampling of the sorbent media and deposition onto the QFF. It is a best practice to transport the assembled PUF/resin sorbent/PUF cartridge and QFF to the field monitoring site already installed in the sampling module and that the sampling media be sealed in a zipseal plastic bag for transport. Prior to installation, the sampling media should remain in refrigerated storage.

4.5.4.1 Sample Module Assembly. To assemble the sampling module and to install it in the sampling unit, the technician must wear powder-free nitrile or equivalent gloves. Refer to Figure 4.5-1 below for the following procedure for assembling the sampling module.

A bottom gasket is installed in the cartridge holder of the module and the assembled PUF/resin sorbent/PUF cartridge is inserted into the sampling module cartridge holder with the support screen end first. The gasket is then placed onto the top of the cartridge and cartridge holder and the threaded filter holder collar is then installed and securely tightened. The technician then uses clean (i.e., solvent-rinsed) forceps to install the QFF onto the filter support screen then installs the filter gasket and filter retention ring, securing the retention ring with three swing bolts and wing nuts, tightening the bolts evenly in a circular pattern. If the assembled sampling module is to be transported and not installed in the sampling unit immediately, a suitable plug or rinsed foil cover should be installed on the module outlet and a filter cover should be installed on the module inlet (such a cover attaches to the filter retention ring with the three swing bolts).
4.5.4.2 Sample Module Installation and Sampler Setup. To install the assembled module in the sampling unit, the sampling gable roof is opened and secured from accidental closure (which can cause injury if unsecured). A best practice is to install a plug into the PS-1 sampler port when not in use to prevent debris from getting into the motor. Remove any such plug and insert the sampling module outlet male fitting into the sampling unit female fitting and lift the cam-locks to allow the module to fully seat. Swing the cam-locks downward to secure the module in the sampling unit. If performing a leak check, leave the filter cover in place.

To perform a leak check, power on the sampler briefly with the filter cover in place and listen for an audible whistle. The sampling unit blower motor will strain, therefore leak check procedures should only have the motor operating briefly. If a whistle is heard, there is a leak in the flow path that must be corrected before sampling can commence. The filter cover is removed after performing a successful leak check. Leak checks should be performed minimally every five primary sampling events. For samples which were collected with a failing leak check, the data are to be invalidated (Null qualifier AK indicating filter leak) when reported to AQS.

At sample setup following a successful leak check, sampling units without computerized flow rate control are to be powered on and run for minimally five minutes (ten minutes are
recommended) prior to measuring and recording the venturi pressure differential reading that corresponds to the initial flow rate. Computer-controlled sampling instruments continually log the sampling flow rate, therefore do not require this warm-up period at sample setup. For samples which do not have the beginning sample flow rate recorded for non-computer controlled samplers, the data are to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

The site operator programs the sampler event timer, and records the following sample setup details on the COC/sample collection form:

- Sampling module installation date
- Leak check results
- Elapsed time indicator reading (for sampling units without data logging capability)
- Programmed sample start time
- Initial flow rate (for sampling units without data logging capability)
- Ambient temperature
- Barometric pressure

Prior to departing the site, a best practice is to double-check the sampler program is correct and enabled and that the filter cover was not inadvertently left on the sampling module. If onsite on the sampling date, site operators should verify the sampler is operating as expected.

4.5.4.3 Sampling Schedule and Duration. PAHs sample collection must be performed on a 1-in-6 days schedule for 24 ± 1 hours beginning at midnight and concluding on midnight of the following day, local time unadjusted for daylight savings time, per the national sampling calendar. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation are to be checked with each sample event setup and be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.5.4.4 Retrieval and Transport of Sampled Media. The sampled QFF and PUF/resin sorbent/PUF cartridge is to be retrieved as soon as possible after the conclusion of sampling in order to minimize the evaporative loss of the more volatile PAHs (i.e., naphthalene), preferably within 24 hours, but not to exceed 72 hours of the end of collection. Prompt retrieval is particularly important during warm weather to reduce evaporative losses of naphthalene. Measurement data for samples retrieved after 72 hours from the end of collection are to be qualified (QA Qualifier HT indicating sample pickup hold time exceeded) when reported to AQS.

Upon sample retrieval, the following sample collection details are to be recorded:
• Sampling module retrieval date
• Elapsed time indicator reading (for sampling units without data logging capability) and presumed sample stop time
• Ending flow rate (for sampling units without data logging capability)
• Average temperature over the sampling event
• Average barometric pressure over the sampling event
• Qualifiers (flags) or alerts logged in the sampler data

If the sampling unit permits electronic data retrieval, the site operator should transfer the sampler data for transfer to the ASL and archiving. For sampling units without electronic flow control, the sampling unit is powered on and allowed to run for minimally 5 minutes (10 minutes are recommended) before recording the reading of the pressure drop across the flow venturi as the ending flow rate measurement. For samples which do not have the ending sample flow rate recorded for non-computer controlled samplers, the data are to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

The site operator (or properly trained technician) must don powder-free nitrile or equivalent gloves for handling the sampling module including disassembly steps (if disassembly is performed at the site). The operator installs the filter cover over the filter on the inlet, secures the filter cover with the swing bolts, disconnects the sampling module from the sampling unit, and covers the outlet end of the sampling module with foil or a suitable plug. The assembled sampling module is transported to a clean indoor environment, free of obvious PAHs sources, for disassembly. Disassembly should occur essentially immediately (i.e., within 10 minutes) after retrieving the sampling module, otherwise the sampling module assembly should be stored refrigerated until disassembly (typically in a field office or at the ASL). If the sampling module will not be disassembled at the monitoring site, a best practice is to seal the sampling module in a zipseal plastic bag for storage and transport.

For sampling module disassembly, the filter cover is removed and the QFF is carefully retrieved with clean forceps and folded into fourths with the particulate matter inward. The folded filter is then inserted into the glass thimble cartridge with the sorbent media for transport. It is not acceptable to place the folded filter into a secondary container such as a petri dish, as jostling of the filter inside the petri dish may result in irrecoverable loss of PM to the inside of the dish. Storage inside the glass cartridge minimizes disturbance of PM to ensure that PM is either on the filter or within the PUF inside the thimble cartridge where it is available for extraction. The thimble cartridge is removed from the sampling module, wrapped in solvent-rinsed (or muffled) foil, and placed within a protective jar or case for shipment. Monitoring agencies may opt to utilize additional protective devices on the cartridge such as protective caps with sealing gaskets which provide an additional barrier against passive sampling or migration of PAHs to/from the cartridge media.

The protective jar or case containing the sampled cartridge will be stored at ≤ 4°C until shipment to the laboratory. The temperature of the cartridge is to be determined upon receipt at the laboratory and should be ≤ 4°C for overnight shipments. It is imperative that samples be placed
into cold storage for transport as soon as possible after retrieval to retard the migration and volatilization of PAHs from the collected media. Samples which are shipped overnight should be packed with sufficient cold packs or ice in an insulated cooler to ensure they arrive at the laboratory at ≤ 4°C. For transport of samples which are retrieved at a site and delivered to the laboratory on the day of retrieval, it may be difficult to sufficiently cool samples to ≤ 4°C by the time they are received at the laboratory. In such cases where delivery times are short (less than 4 hours from retrieval), the receipt temperature should be ≤ 10°C. If samples are not stored at ≤ 4°C within 72 hours after the end of collection, measurement data for the samples are to be qualified (QA Qualifier LJ indicating the value is estimated) when input into AQS.

The sample COC form is completed and accompanies the collected sample at all times until relinquished to the laboratory. COC documentation will comply with Section 3.3.1.3.7. If cartridges are broken, resin has escaped, or the sampling media are otherwise compromised, the sample is to be voided and the data invalidated (Null Qualifier BI indicating lost or damaged in transit) when reported to AQS.

4.5.4.5 Field Blanks and Exposure Blanks. Field blanks must be collected minimally monthly. A field blank is a complete blank PUF/resin sorbent/PUF cartridge and QFF fortified with field surrogates and assembled in a sampling module identically to a field-collected sample except that the sampling media are not exposed to sample flow. To collect a field blank, the assembled sampling module is installed into the sampling unit (the gable roof is closed) with the filter cover removed for minimally 5 minutes. The field blank is then retrieved as a regularly collected field sample and placed into cold storage until the co-collected field sample is transported/shipped to the laboratory for analysis. Field blanks must show that all target PAHs are ≤ 3x MDL. When measurements exceed this criterion, monitoring agencies must investigate the root cause of the apparent contamination and take corrective action when a root cause is identified. Results for field collected samples associated with the failing field blank and collected since the last acceptable field blank must be appropriately qualified (QA Qualifier FB indicating field blank above acceptable limits) when entered into AQS.

An exposure blank is similar to a FB, but is not required, and may be collected via several protocols. The purpose of the exposure blank is to assess background contamination that may occur during media installation, exposure to sampling conditions, and retrieval. The exposure blank includes exposing the filter and sorbent media to the ambient conditions by installation in a sampling unit, and just like a FB, air is not drawn through the exposure blank sampling module. The exposure blank sample may be installed in the primary sampling unit on non-sample collection days or may be installed in a collocated sampling unit during collection of the primary sample. Exposure blanks should also meet the FB criteria for which all target PAHs are ≤ 3xMDL.

Field blanks and exposure blanks may passively sample ambient air throughout the time of exposure (i.e., when not sealed in the zipseal plastic bag and in cold storage), and as a result may have somewhat higher background levels as compared to batch blanks or laboratory MBs.

4.5.4.6 Collocated Sampling. Collocated samples must be collected at a frequency of 10% of the primary samples for sites conducting collocated sampling (as required by the QFF). A
collocated sample is a second assembled sampling module (PUF/resin sorbent/PUF cartridge and QFF) collected with a separate collocated PAHs sampling unit. The collocated sampling unit inlet must be between 2 to 4 m (measured nearest edge to edge) from the primary sampling inlet.

Collocated samples must demonstrate precision for each target analyte of < 20.1% RPD when at least one of the collocated sample extract concentrations measured on the GC/MS is ≥ 0.5 µg/mL (refer to Section 2.1.3.1). This determination of RPD is solely for assessing precision; the concentrations measured of the precision pair are to be reported to AQS as measured. Root cause analysis must be performed for instances in which collocated samples fail this precision specification and the results of the primary and collocated samples must be qualified (QA Qualifier LJ indicating the value is estimated and QA Qualifier QX indicating QC failure) when entered into AQS.

4.5.5 PAH Extraction and Analysis

4.5.5.1 Reagents and Standard Materials

4.5.5.1.1 Solvents. Solvents employed for extraction and preparation of standard solutions must be high-purity chromatographic grade, and shown by analysis to be free of target analyte contaminants and interferences. Suitable solvents include dichloromethane, n-hexane, methanol, diethyl ether, and acetone.

4.5.5.1.2 Primary Calibration Stock Materials. Calibration source material (primary source) must be of known high purity and must be accompanied by a COA listing the purity (for neat materials) or the certified concentration (for certified solutions). Calibration materials should be neat high purity solids or sourced as certified single component or component mixtures of target compounds in solvent.

When preparing calibration materials from neat solid materials, the neat material is to be weighed with a calibrated analytical balance with the appropriate sensitivity for a minimum of three significant figures in the determined standard mass. The calibration of the balance must be verified on the day of use with certified weights bracketing the masses to be weighed. Neat materials are to be weighed into the Class A volumetric flask (or labware) in which the solution is to be diluted, or weighed into a suitable (glass, metal, or fluoropolymer) weighing dish (non-plastic) and quantitatively transferred into the Class A volumetric flask for solution dilution using several rinses with the dilution solvent to complete the quantitative transfer. Calibration standards diluted from stock standard solutions are to be prepared by delivering stock standard solution volumes with calibrated mechanical pipettes (preferably positive displacement type) or gastight syringes and the volumes dispensed into Class A volumetric glassware to which solvent is added to complete dilution to a known final volume.

4.5.5.1.3 Second Source Calibration Verification Stock Material. The second source stock standard materials (i.e., neat standard materials or certified standard solutions) must be sourced from a different supplier than the calibration primary stock standards. The exception to this supplier requirement is if suitable SSCV stock standard materials are not available from another
in which case the second source standard materials must be from a different lot from the primary standard materials supplier.

4.5.5.1.4 Internal Standards. ISs are added to analyzed solutions to monitor and correct for both short-term variability in GC/MS performance and for potential matrix effects. ISs must be added to all analyzed solutions at the same concentration and their response monitored.

IS compounds should be chemically and chromatographically similar to the target compounds. Deuterated (a hydrogen atom on the molecule is replaced with a deuterium atom) isotopes of target compounds are recommended as ISs. Suggested deuterated isotopes include: naphthalene-d₈, acenaphthene-d₁₀, perylene-d₁₂, phenanthrene-d₁₀, and chrysene-d₁₂. These ISs should be purchased as high purity single or multi-component mixtures in solvent. Note that deuterated standards also contain small amounts of the related target compound which may appear as contamination if the concentration of IS added is too high.

4.5.5.1.5 Surrogate Compounds. Surrogate compounds are compounds chemically similar to target compounds that are added at stages of the sampling media preparation and extraction. Surrogate compounds are required to monitor and assess the retention of PAHs on the adsorbent media and the performance of the sample media handling, extraction, and analysis procedures. Two types of surrogate compounds are prescribed for the subject method, field surrogates and extraction surrogates. As with ISs, deuterated isotopes of target compounds are recommended for surrogate compounds.

4.5.5.1.5.1 Field Surrogate Compounds

Field surrogates are required to be added to sampling media prior to deployment as previously described in Section 4.5.3.3. Fluoranthene-d₁₀ and benzo(a)pyrene-d₁₂ are the recommended field surrogate compounds; however, other suitable surrogates may be added per the laboratory’s discretion. Stock standard solutions of these two surrogate compounds in solvent are commercially available and can be diluted to working concentrations in suitable solvent (i.e., hexane).

4.5.5.1.5.2 Extraction Surrogate Compounds

Extraction surrogate compounds must be added to the sample media just prior to extraction and their recoveries are evaluated to assess the performance of the extraction and analysis procedures. Fluorene-d₁₀ and pyrene-d₁₀ are the recommended extraction surrogate compounds and 1 µg should be added to the media (e.g., 100 µL of 10 µg/mL solution) for each extracted sample (field collected and laboratory QC). Stock standard solutions of these two surrogate compounds in solvent are commercially available and can be diluted to working concentrations in suitable solvent (i.e., hexane).

4.5.5.2 Hold Times and Storage Requirements. Collected samples are to be transported and stored at ≤ 4°C until extraction, and must be extracted within 14 days of collection. Extracts must be stored at ≤ 4°C in amber glass or foil-wrapped vials with PTFE-lined lids; however, storage in a freezer at ≤ -10°C is preferable to minimize potential solvent evaporation. Extracts must be analyzed within 40 days of extraction. Measurement data for samples exceeding these holding
times are to be qualified (QA Qualifier LJ indicating the value is estimated) when entered into AQS.

Working standards and open ampules of stock standards must be stored protected from light at \( \leq -10^\circ C \) in amber vials with PTFE-lined lids in a storage unit separate from sampled cartridges and sample extracts. If storage conditions are not maintained appropriately, compare affected standards to standards with appropriate integrity to ensure standard concentrations are \( < \pm 15.1\% \). Data associated with samples analyzed with compromised standard materials will need to be invalidated (Null qualifier EC indicating critical criteria failure) when reported to AQS.

4.5.5.3 Extraction, Concentration, and Cleanup. Extraction of samples may be performed by Soxhlet or ASE; these techniques are described in more detail below. Laboratory extraction batch QC samples are also described below.

A MB sample is required with each extraction batch containing 20 or fewer field collected samples. A LCS and LCSD are recommended with each extraction batch, but must be prepared and analyzed minimally quarterly. As practical, a best practice is to employ sampling media for preparing laboratory QC samples of the same lot as the associated field-collected samples. This simplifies troubleshooting and root cause analysis when acceptance criteria are exceeded.

Extraction Batch QC samples are prepared as follows and must meet the specified criteria:

- Method Blank (MB): The MB is a negative control sample consisting of a clean prepared field-deployable sample cartridge (with field surrogates) and QFF or the media equivalent of a prepared deployable sample cartridge (15-g resin sorbent, 2 PUF discs, and a QFF). All target analytes must be \( \leq 2 \times \text{MDL} \).

- Laboratory Control Sample (LCS): The LCS is a positive control sample prepared by spiking a known amount of target PAHs onto a prepared field-deployable cartridge or the media equivalent of a prepared deployable sample cartridge (15-g resin sorbent, 2 PUF discs, and a QFF) such that the concentrations of target PAHs in the extract are in the lower third of the calibration range. The LCS is then extracted with the same extraction solvent and method employed for field samples to assess bias in matrix of the extraction and analysis procedures. Recovery of the LCS must be within 59.9 to 120.1\% of theoretical nominal spike for target PAHs.

- Laboratory Control Sample Duplicate (LCSD): The LCSD is prepared and extracted identically to the LCS. The LCSD assesses precision through extraction and analysis. Recovery of the LCSD must be within 59.9 to 120.1\% of the theoretical nominal spike and precision of the LCS and LCSD results must show RPD of \( < 20.1\% \).

All field-collected and laboratory QC samples in a given extraction batch must be analyzed in the same analysis batch (an analysis batch is defined as all samples analyzed together within a 24-hour period).

Laboratories must take corrective action to determine the root cause of laboratory extraction batch QC criteria exceedances. Field-collected sample results associated with failing QC results (in the same preparation batch or analysis batch) must be appropriately qualified (QA Qualifier QX indicating QC failure) when input to AQS.
4.5.5.3.1 Soxhlet Extraction. Prior to extraction, each field-collected sample and extraction batch QC sample is to be fortified with extraction surrogate standards (typically fluorene-d10 and pyrene-d10) and it is recommended that field surrogates also be added. Extraction should be performed by combining the QFF, PUF plugs, and resin sorbent into the Soxhlet extraction vessel and extracting with sufficient 90:10 hexane:diethyl ether (other solvent mixtures are acceptable provided performance metrics are met) to cover the sample media. Extraction should be performed for a minimum of 18 hours and the temperature of the heating mantle should be set such that reflux occurs at a rate of at least three cycles (a cycle is a filling and emptying of the extraction chamber through the siphon tube) per hour. Following completion of the extraction period, the extracts are quantitatively transferred to a concentration apparatus (refer to Section 4.5.5.3.3.1) and concentrated to 1 mL final volume. If extracts are not to be concentrated immediately following extraction, they are to be capped (to prevent evaporation and ingress of contamination), protected from light, and stored refrigerated at ≤ 4°C. When transferring extracts to concentration labware or to alternative labware for storage, pour the extract into the receiving vessel and thoroughly rinse the extraction glassware three times (e.g., three volumes of 10 mL solvent) with extraction solvent to complete quantitative transfer.

4.5.5.3.2 Accelerated Solvent Extraction. To perform ASE, a 100 mL ASE cell should be packed as follows: QFF, top PUF plug, resin, bottom PUF plug, and clean Ottawa sand to fill the remainder of the cell. Prior to extraction, each field sample and extraction batch QC sample is to be fortified with extraction surrogate standards (typically fluorene-d10 and pyrene-d10) and it is recommended that field surrogates also be added. To ensure the cell seals properly, stray resin beads should be removed from the cell threads with a static-free brush or compressed air.

The following procedure should then be followed: install the cells into the extractor, install the clean extract collection bottles, verify that the solvent reservoirs are full, and start the extraction program. A recommended solvent combination for ASE is 2:1 or 3:1 hexane:acetone (v:v). An example ASE program follows:

- temperature: 60°C
- cycles: minimum of 3
- purge: 60 seconds
- static time: 5 minutes
- flush: 50%

If extracts are not to be concentrated immediately following extraction, they are to be capped (to prevent evaporation and ingress of contamination), protected from light, and stored refrigerated at ≤ 4°C. When transferring extracts to concentration labware or to alternative labware for storage, pour the extract into the receiving vessel and thoroughly rinse the extraction glassware three times with extraction solvent to complete quantitative transfer.

4.5.5.3.3 Extract Concentration and Cleanup

4.5.5.3.3.1 Extract Concentration

Refrigerated extracts are to be equilibrated to room temperature prior to concentration. It is recommended that extracts be dried by passage through approximately 10 g of sodium sulfate,
where the eluate is collected into a concentration flask or tube. A drying column can be configured by placing glass wool into a clean glass funnel or chromatography column and adding 10 g of sodium on top of the glass wool. Prior to use, sodium sulfate should be solvent rinsed and placed in an oven at 400°C for a minimum of 4 hours to remove impurities. Muffled sodium sulfate should be cooled and stored in a desiccator to minimize contact with humidity in ambient air. Glass wool should be rinsed with solvent three times before use.

Pour the extract slowly through the sodium sulfate bed and collect the dried extract into a clean concentration flask or other catch flask. Rinse the extraction flask and sodium sulfate/glass wool three times with extraction solvent and collect the rinsate into the concentration vessel/catch flask.

Extracts should be concentrated by either Kuderna-Danish (K-D) or nitrogen blowdown techniques which have been demonstrated to retain the PAHs within the extraction solvent. If K-D methods are employed, ASLs may employ boiling chips (e.g., silicon carbide 10/40 mesh, or equivalent) in the concentration, which should be cleaned before use by series of solvent rinses or extraction. The sample extracts must not be allowed to evaporate to dryness. If extracts are permitted to go to dryness, the analyst can expect low recovery of surrogate compounds and commensurate losses of target PAHs. Concentration data for extracts that have gone to dryness must be qualified (QA Qualifier LL indicating the value is estimated with a low bias) when reported to AQS.

Bring the extract to 1.0 mL final volume via a volumetric syringe, rinsing the concentration tube with n-hexane as the extract is drawn into the syringe. A technique for ensuring a quantitative transfer of the concentrated extract follows:

Pull the extract (should be < 1 mL) into the syringe, invert the syringe, withdraw the plunger slightly to pull extract fully into the syringe barrel. While inverted, push the plunger up to remove air bubbles within the syringe. Invert the syringe and place the needle at the bottom of the concentrator tube. With another syringe containing clean n-hexane, add solvent dropwise to the inside walls of the concentrator tube and to the extract syringe needle to rinse these surfaces. Slowly draw the rinsate into the extract syringe until the total volume in the syringe is 1 mL. Invert the syringe, draw air into the syringe barrel, and invert the syringe to thoroughly mix the extract. The mixed extract can then be dispensed into an autosampler vial for storage or analysis.

Following concentration to 1 mL, the extract is ready for analysis unless further cleanup is required. Extract cleanup is explained in Section 4.5.5.3.3.2.

4.5.5.3.3.1 Concentration via Kuderna-Danish

To concentrate via K-D, attach a Snyder column to the K-D apparatus and concentrate the extract to approximately 5 mL on a water bath set at 30 to 40°C. Rinse the Snyder column and concentrator flask with several mLs of n-hexane and allow the solvent to drain into the concentrator tube. Concentrate to < 1 mL final volume via nitrogen blow-down or via micro-Snyder column.
4.5.5.3.3.1.2 Concentration via Nitrogen Blowdown

Several nitrogen blowdown evaporator concentrator instruments are commercially available. As concentration releases large volumes of solvent detrimental to air quality, systems which capture the evaporated solvent are preferable. The general principle with nitrogen blowdown involves providing a gentle stream of UHP nitrogen to concentrator tubes containing the extracts. The nitrogen stream slowly evaporates the solvent to a small volume, leaving behind the target PAHs and added surrogates in a small solvent volume. The analyst should rinse down the concentrator tube several times (e.g., three times) during concentration and must not allow the extract to go to dryness.

Concentrate the extract to < 1 mL in a water bath set to 30 to 40°C.

4.5.5.3.3.2 Extract Cleanup

A cleanup step may be required in order to clarify cloudy extracts or remove interfering compounds from extracts showing significant chromatographic interferences. Such cloudiness and interferences are not generally an issue with this method of ambient air collection due to the thorough cleaning performed on the sampling media.

To clarify cloudy extracts, they are passed through a packed column of 10 g of silica gel as detailed in EPA Compendium Method TO-13A\(^1\) and ASTM D6209.\(^2\)

4.5.5.4 PAH Method Detection Limits. MDLs for PAHs must be determined per the guidance in Section 4.1, which details the MDL determination process generally for the NATTS program. This section will briefly provide details for determining the MDL for PAHs measurements by solvent extraction and GC-MS.

The MDL procedure in Section 4.1 prescribes preparing and analyzing MDL spikes and MBs for determining an initial MDL and for collecting ongoing data for MDL verification. MDLs must be determined following the procedure in 4.1.3.1 unless there is a sufficient number (\(n \geq 7\)) of MBs in which the specific target analyte has been detected (positively identified and meeting qualitative identification criteria listed in Section 4.5.5.5.7), in which case the procedure in Section 4.1.3.2 may be employed. ASLs should closely review the requirements in Section 4.1.3.1.1.4 to evaluate whether previously collected MDL spike data and MB data meet the requirements for calculating an initial and ongoing MDL. If the previously collected data do not meet the specified criteria, the initial MDL must be determined as detailed in Section 4.1.3.1.1.

As practical, ASLs should employ a variety of lots of media to prepare the MDL spikes and MBs to best characterize variability of measurements attributable to the variation in the media. For each of the individual MDL spike and MB measurements, these are to be discrete sample cartridge equivalents (i.e., 3” PUF, 15-g resin sorbent, and a QFF) and data from the same sample equivalent can only be included in the calculations when analyzed on a separate instrument (when more than one instrument is employed).

Determining PAHs MDLs will typically involve preparing MDL spiked samples at several concentrations to ensure that PAHs of different sensitivities (i.e., the concentration
corresponding to a signal to noise ratio of 5:1) are adequately captured. PAHs standard materials prepared from multi-component stock solutions may require preparing several MDL spiked samples with different PAHs concentrations to adequately characterize all target PAHs, therefore, it may be advantageous to prepare spiking solutions from single-component stock standard solutions.

All steps performed in the preparation, extraction, and analysis of field samples (such as dilution and addition of surrogates) are to be included in the MDL procedure.

Determined MDLs for Tier I core analytes must meet (be equal to or lower than) the MDL MQO values listed in the most current workplan template, available in the NATTS area of EPA’s AMTIC (accessed June 2022): https://www.epa.gov/amtic/air-toxics-ambient-monitoring#natts

4.5.5.5 PAH Analysis via GC/MS

4.5.5.5.1 GC/MS Instrumentation. The GC oven should be capable of temperature programming such that the temperature may be ramped from 25°C to 290°C at a rate of 8°C/minute or faster. A 30- to 50-m by 0.25-mm fused silica capillary column coated with 0.25 µm crosslinked or bonded 5% phenyl methylsilicone film, or equivalent suitable column capable of separating the target analytes, surrogates, and ISs with appropriate resolution and chromatographic quality (e.g., peak shape, peak sharpness, etc.), should be installed in the GC. The carrier gas should be helium or hydrogen. Injector and transfer lines should be capable of maintaining 275-300°C. GC injection volume should be 1.0 µL. Note these parameters are recommended; however, substitutions can be made provided the requisite performance criteria are met.

Quadrupole MS detectors are commonly suited for this method and should be employ EI ionization at 70 eV and the MS should be operated in SIM mode to maximize sensitivity to ions of the target compounds of interest. Alternatively, for instruments which are capable, operation in combination SIM/scan mode is preferred. Spectrometers operating in full scan mode may lack sufficient sensitivity. If full scan is performed, the MS should be capable of scanning from 35-500 amu in ≤ 1 second. MSs should be capable of performing minimally 5 scans, and preferably 10 or more, across each target analyte chromatographic peak.

TO-13A in 1999 and previous versions of this TAD described quadrupole MS detectors and did not include alternative detectors. With the inclusion of method details from EPA Method 8270E3 in this TAD revision, ASLs may also employ ion trap MS or tandem MS/MS detectors for this method.

For use of an ion trap MS, it must be capable generating ion spectra for target analytes comparable to those generated using quadrupole MS with EI ionization (as detailed in the NIST mass spectral library - https://chemdata.nist.gov/) and be capable of axial modulation to reduce ion-molecule reactions. Ion trap MS detectors must be capable of meeting the ion abundance criteria for decafluorotriphenylphosphine (DFTPP) listed in Section 4.5.5.5.2.
Tandem MS/MS detectors offer greater sensitivity and specificity for this method; however, require additional support equipment and staff training to operate and maintain compared to quadrupole MS instruments. MS/MS detectors must be capable of performing transitions in product ion scan mode or SRM mode for the target analytes. Users need to rely heavily on the documentation and instructions from the manufacturer for assigning precursor and product ions for SRM mode and for tuning the MS.

4.5.5.5.2 Tuning of the MS. The MS tune is verified and/or optimized prior to the initial calibration and should be verified every 12 hours of use thereafter (before continuing calibration verification) following the manufacturer instructions. MS tuning for quadrupole MS instruments operated in full scan or SIM/scan mode and ion trap detectors can be accomplished by introducing 5 to 50 ng of DFTPP to the MS and verifying the abundances of the produced ions achieve those listed in Table 4.5-2. If employing hydrogen as carrier gas or detectors other than a quadrupole MS, the abundance criteria in Table 4.5-2 may not be strictly applicable. In such cases, the MS detector manufacturer should be consulted for proper tuning procedures, demonstration, and documentation. Once established, the tuning conditions established are to be maintained and common for all analyzed solutions (calibration standards, QC samples, and field collected samples). Regardless of the type of detector and tuning procedures and criteria followed, the procedures and acceptance criteria must be specified in the ASL SOP for analysis of PAHs.

MS/MS detector instruments must be capable of documenting the tuning performance of both MSs against manufacturer specifications for mass resolution, mass assignment, and sensitivity using an internal calibrant (e.g., perfluorotributylamine [PFTBA]). The performance of the system should be checked at least weekly when instruments are in use. At a minimum, the performance of the system must be checked just prior to the ICAL.

For quadrupole MSs operated solely in SIM mode or for tandem MS instruments the indicated DFTPP ion abundance criteria in Table 4.5-2 do not strictly apply. Tuning for quadrupole MS instruments operated in SIM mode is optimized to maximize the signal for DFTPP masses greater than 150 amu by maximizing the signal for masses 198, 275, 365, and 442 while maintaining unit mass resolution between masses 197, 198, and 199 as well as 441, 442, and 443. For demonstrating tuning of MS/MS detectors, follow the manufacturer recommended procedures and document the demonstration in laboratory records.

### Table 4.5-2. DFTPP Key Ions and Abundance Criteria

<table>
<thead>
<tr>
<th>Mass</th>
<th>Ion Abundance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>30-60% of mass 198</td>
</tr>
<tr>
<td>68</td>
<td>&lt; 2% of mass 69</td>
</tr>
<tr>
<td>70</td>
<td>&lt; 2% of mass 69</td>
</tr>
<tr>
<td>127</td>
<td>40-60% of mass 198</td>
</tr>
<tr>
<td>197</td>
<td>&lt; 1% of mass 198</td>
</tr>
<tr>
<td>198</td>
<td>base peak, assigned 100% relative abundance</td>
</tr>
<tr>
<td>199</td>
<td>5-9% of mass 198</td>
</tr>
<tr>
<td>275</td>
<td>10-30% of mass 198</td>
</tr>
<tr>
<td>365</td>
<td>&gt; 1% of mass 198</td>
</tr>
<tr>
<td>441</td>
<td>present, but &lt; mass 443</td>
</tr>
<tr>
<td>442</td>
<td>&gt; 40% of mass 198</td>
</tr>
<tr>
<td>443</td>
<td>17-23% of mass 442</td>
</tr>
</tbody>
</table>
4.5.5.3 **Initial Calibration of the GC/MS.** All solutions to be analyzed, including calibration standards, should be removed from refrigerated storage for sufficient time (typically one hour) to equilibrate to ambient temperature prior to analysis. Additionally, analysts should examine solutions for precipitate and can warm (by holding in hands) and agitate (shaking, vortexing, or sonicating) the solutions to dissolve the precipitate.

Calibration standard solutions must be prepared at minimally five separate concentration levels in n-hexane covering approximately 0.1 to 2.0 µg/mL and must contain surrogate compounds (field and extraction) at concentrations bracketing those expected in the analyzed sample extracts.

The ICAL must be established initially, when CCV criteria are not met, or when an instrument changes or maintenance (ion source cleaning, column trim or replacement, etc.) may affect instrument calibration (including alteration of retention times). Calibration is recommended every six weeks. Often, responses of IS compounds and/or labile target analytes will show degradation (i.e., decreased area counts) over time and can serve to alert the analyst that a new ICAL may be needed soon.

A SB which is not fortified with IS must be analyzed just prior to calibration to clean the analytical system and to demonstrate the instrument is sufficiently clean to continue analysis. Analysis of the SB must show all target compounds, IS, and surrogate compounds are not detected (i.e., chromatographic peaks show signal-to-noise of < 3:1). For target PAHs failing this criterion, qualify associated data in the analytical sequence (QA Qualifier LB indicating laboratory blank above acceptance limits) when reporting to AQS.

A known volume of each standard should be transferred to a GC analysis vial (small volume inserts are available and recommended for this purpose) and fortified with IS just prior to analysis. A recommended practice is to agitate solutions prior to aliquoting into the analysis vial. Once autosampler vials are punctured, solvent is quickly lost and the integrity of the solution suspect, therefore an individual vial should be prepared for each separate analysis injection. Recommended quantitation and secondary ions are listed in Table 5 of Method TO-13A. Each compound is to be assigned to the IS compound with the nearest RT.

Following data acquisition for the calibration standards, the relative response factor (RRF) of each surrogate and target compound in each calibration level is determined as follows:

\[
RRF = \frac{A_s \cdot C_{IS}}{A_{IS} \cdot C_s}
\]

where:

- \(A_s\) = peak area for quantitation ion of the surrogate or target compound
- \(A_{IS}\) = peak area for quantitation ion of the assigned IS compound
- \(C_s\) = concentration of the surrogate or target compound
- \(C_{IS}\) = concentration of the assigned IS compound
The RSD of the RRFs for each surrogate and target compound inclusive of all standard levels must be < 30.1%, or, alternatively, a calibration curve may be prepared by performing linear or quadratic least-squares regression. Weighting of calibration standard levels (i.e., 1/concentration or 1/concentration$^2$) may better represent the lower third of the calibration curve range when preparing the regression, and is typically an option provided by CDS software packages. The correlation coefficient for linear or quadratic curves must be ≥ 0.995 for target compounds. Irrespective of the curve fit method selected, the calculated concentration of each calibration level must be < ± 30.1% of the theoretical nominal concentration when quantitated against the resulting calibration curve (i.e., the concentration calculated when inputting the $A_S/A_{IS}$ response factor into the generated regression equation) for all Tier I PAHs and non-Tier I PAHs should meet this criterion. Exclusion of calibration standard levels is not permitted unless the rationale for exclusion is technically justified (for example, a known error in standard preparation or the lowest calibration level did not meet signal to noise ratio criteria) and this rationale must be documented. Sample analysis must not be performed, and if performed, results must not be reported when calibration acceptance criteria are not met. Rather corrective action, possibly including recalibration, must be taken and results cannot be reported unless measured with an instrument system demonstrating acceptable calibration.

The absolute value of the concentration equivalent of the intercept of the calibration curve ([intercept/slope] or concentration calculated when inputting zero response into the calibration response equation) must be less than the laboratory MDL for each target analyte. When this specification is not met, the source of contamination or suppression must be addressed and an acceptable calibration curve established before sample analysis may commence.

Target analyte RT windows are to be established with each ICAL. RTs for target analytes for each calibration concentration level must be within ±10 seconds of the mid-point (third standard) calibration standard or the average RT for the target analyte from the ICAL. Alternatively, particularly if RTs of target analytes and ISs exhibit significant RT shifting, analysts may calculate relative retention times (RRTs) for each concentration level of each surrogate and target compound by dividing the RT of the surrogate or target compound by the RT of the assigned IS compound. The RRTs of each surrogate or target compound across the ICAL are then averaged for each target compound to determine the ICAL RRT. If establishing RT windows using RRTs, the RRTs for each compound must be within ± 0.06 RRT units of the ICAL RRT.

Measurement data for samples for Tier I PAHs that do not meet the ICAL acceptance criteria, the SSCV criteria (in Section 4.5.5.5.4), or the CCV acceptance criteria (4.5.5.5.5) are to be invalidated (Null qualifier EC indicating critical criteria failure) and non-Tier I PAHs are to be qualified (QA Qualifier LJ indicating the value is estimated) when reported to AQS.

4.5.5.5.4 Second Source Calibration Verification. Following each successful initial calibration, a SSCV at approximately the mid-point of the calibration range must be analyzed to verify the ICAL. Alternatively, two or more concentrations (e.g., lower third and mid-point) of SSCV may be prepared covering the calibration range. All SSCVs must recover within ± 30.1% of theoretical nominal (for linear or quadratic modeled calibration curves) or demonstrate an
RRF within ± 30.1% of the ICAL average RRF (for average RRF calibration curves) for each target PAH.

4.5.5.5.5 Continuing Calibration Verification. Once the GC/MS instrument has met tuning and calibration criteria, a SB (refer to acceptance criteria in Section 4.5.5.5.3) and a CCV must be analyzed every 12 hours of analysis to verify the calibration curve response for each target analyte. The tuning check is no longer required immediately prior to the CCV; however, proper MS tuning should be demonstrated routinely and it is a best practice to do so prior to the CCV. The CCV must recover within 69.9 to 130.1% of the theoretical nominal (for linear or quadratic modeled calibration curves) or demonstrate an RRF < ± 30.1% of the ICAL average RRF (for average RRF calibration curves) for each target PAH. Corrective action must be taken to address CCV failures, including, but not limited to, preparing and analyzing a new CCV, cleaning or replacing the injector liner, trimming or replacing the column, retuning the MS, or establishing a new ICAL.

4.5.5.5.6 Analysis of Extraction Batch QC Samples and Field Samples. Analysis of laboratory extraction batch QC samples and field samples can commence once the MS tune is demonstrated to be acceptable, the instrument has been demonstrated to be clean by analysis of a SB, the ICAL is established, the ICAL is verified by the SSCV, and after a CCV prior to every 12 hours of analysis. The analyst should aliquot the solutions to be analyzed (small volume inserts are available for autosampler vials and are recommended for this purpose) and fortify with IS just prior to analysis. Removing aliquots in this way reserves the remainder of the solution for reanalysis, if needed (e.g., in the event an error in IS fortification is made). A recommended practice is to agitate solutions prior to aliquoting into the analysis vial. Once autosampler vials are punctured, solvent is quickly lost and the integrity of the solution is suspect (extract will concentrate as solvent evaporates), therefore punctured vials should not be reanalyzed and an individual vial should be prepared for each separate analysis injection.

The following QC samples are required with each analysis sequence:

- Solvent method blank (SMB)
- MB
- Replicate extract analysis

Prior to analysis of laboratory QC samples or field-collected samples, a SMB consisting of an aliquot of the extraction batch extraction solvent fortified with ISs must be analyzed and demonstrate target compounds are not detected (i.e., signal to noise ratio < 3:1). If SMBs exceed this criterion, concentration data for related field-collected samples in the extraction batch are to be qualified (QA Qualifier LB indicating lab blank above acceptable limits) when input to AQS.

Target PAHs must not be present in MBs at concentrations > 2x MDL. If MBs exceed this criterion, concentration data for related field-collected samples in the extraction batch are to be qualified (QA Qualifier LB indicating lab blank above acceptable limits) when input to AQS.

Replicate analysis must demonstrate precision of < 10.1% RPD for target analyte concentrations when measured in at least one of the replicates ≥ 0.5 µg/mL (refer to Section 2.1.3.1). Failure to attain replicate analysis precision must prompt corrective action to remedy the imprecision and it
is recommended the sample sequence be reanalyzed or new aliquots of the replicate extract be prepared and analyzed. This determination of RPD is solely for assessing precision; the concentrations measured of the precision pair are to be reported to AQS as measured.

If imprecision of the replicate analysis cannot be corrected, the associated sample measurement data in the analysis batch will be qualified (QA Qualifier QX indicating a QC failure and QA Qualifier LJ indicating the value is estimated) when reported to AQS. For replicate analysis, the ASL will typically assign a convention that the first result for replicate analyses is reported to AQS as the sample result. However, if the first replicate is invalidated for any reason (e.g., as may occur when a coeluting peak significantly interferes with the target peak) and the second replicate measurement is acceptable, the second replicate measurement should be reported to AQS as the sample result as described in Section 2.1.3.2.

An LCS/LCSD pair is required quarterly and recommended with each extraction batch to monitor recovery and precision of the analysis inclusive of the sampling media matrix. Target PAHs in the LCS and LCSD must recover within 59.9 to 120.1% of nominal and the LCSD must demonstrate precision of < 20.1% RPD for all target PAHs. If these criteria are not met, the associated samples in the extraction batch will be qualified (QA Qualifier QX indicating a QC failure and QA Qualifier LJ indicating the value is estimated) when reported to AQS.

4.5.5.5.7 Target Compound Identification. Four criteria must be met in order to positively identify a surrogate compound or target PAH:

1. The signal to noise ratio of the target ion and qualifier ion chromatographic peaks must be > 3:1, preferably > 5:1.
2. The target ion and qualifier ion chromatographic peaks must be co-maximized (peak apexes within one scan of each other).
3. The RT of the compound must be within ±10 seconds from the mid-point standard in the calibration curve or the most recent CCV. Alternatively, if RT windows are established as ± 0.06 RRT from the ICAL average, the RT of the compound must meet this criterion.
4. The relative qualifier ion abundance percentage of the target ion response for at least one qualifier ion must be within ± 30.1% relative abundance of the average from the ICAL.

For example: For naphthalene, the base peak of m/z 128 is set to 100% and the analyst has assigned m/z 127 and 128 as the qualifier ions. Their relative abundance from the ICAL were 15% and 16% of m/z 128, respectively. Therefore, for a positive identification, m/z 127 must show response within 10.5 to 19.5% and m/z 128 must show response within 10.2 to 20.8% relative abundance.

If any of these criteria are not met, the compound may not be positively identified. The only exception to this is when in the opinion of an experienced analyst, the compound is positively identified. The rationale for such an exception must be documented. For examples of the qualitative identification criteria and calculation of signal to noise ratio, refer to Section 4.2.11.
4.5.5.5.8 **Internal Standards Response.** IS response must be monitored for each injection (except for the SB immediately preceding the initial calibration or CCV). Area responses of the IS must be 50 to 200% of the area responses in the ICAL mid-level standard and they must elute within ±20 seconds (± 0.33 minute) of the mean RT of the ICAL. Extracts which do not meet these response acceptance criteria should be diluted, fortified with additional IS, and the dilution analyzed to examine for matrix interferences. If the IS still does not meet criteria in the dilution, the MS tune should be evaluated for a degradation or enhancement of sensitivity and corrective action taken to address the failure. Sample results calculated from IS criteria failures must be qualified (QA Qualifier LJ indicating the value is estimated) when entered into AQS.

4.5.5.5.9 **Surrogate Evaluation.** Following the ICAL, each analyzed extract should be evaluated to ensure the recovery of each fortified surrogate compound (field surrogate and extraction surrogate) is within 59.9 to 120.1% of the theoretical nominal spiked value. Results which fall outside of these limits indicate potential analyte loss or enhancement through sample collection, sample handling, sample extraction processes, and/or analytical bias (such as might occur if the GC flow path is active and degrades surrogate compounds) and related target analytes must be qualified appropriately when reported to AQS. When surrogate recoveries are low or high, we likewise expect a low bias in associated target compounds. Therefore, qualify associated target analyte concentration data as LL (QA Qualifier indicating the value is estimated with a low bias) for low surrogate recoveries and LK (QA Qualifier indicating the value is estimated with a high bias) for high recoveries when reporting to AQS.

4.5.5.5.10 **Data Review and Quantitation.** Each chromatogram is to be examined to ensure chromatographic peaks are appropriately resolved and integration does not include peak shoulders or inflections indicative of a coelution. Additionally, analysts should review chromatograms to investigate chromatographic peaks that were improperly integrated by the CDS software or target analytes whose peaks may have been overlooked and not properly identified. Additional guidance on chromatographic peak integration can be found in Appendix D.

Quantitation of the target PAH concentration is performed by comparing the peak area response of the selected characteristic target ion (typically the base peak, or most abundant, ion) to the established calibration curve for the target VOC. Characteristic ions are shown in Table 1 of Method 8270E3 and can be found in NIST mass spectral libraries (https://chemdata.nist.gov/).

The concentrations of target PAHs in samples are calculated by relating the area response ratio of the target PAH and assigned IS (A_t/A_IS) in the unknown to the relationship derived in the calibration curve selected in Section 4.5.5.5.3.
Average RRF (RRF):

\[ C_D = \frac{A_t \cdot C_{IS}}{A_{IS} \cdot \overline{RRF}} \]

where:
- \( C_D \) = instrument-detected analyte concentration (ng/mL)
- \( A_t \) = area response of target compound quantitation ion
- \( C_{IS} \) = concentration of assigned IS (ng/mL)
- \( A_{IS} \) = area response of assigned IS quantitation ion
- \( \overline{RRF} \) = average RRF from the ICAL

Linear Regression Calibration Model:

\[ C_D = \frac{(A_t - b) \cdot C_{IS}}{m} \]

where:
- \( C_D \) = instrument-detected analyte concentration (ng/mL)
- \( A_t \) = area response of target compound quantitation ion
- \( C_{IS} \) = concentration of assigned IS (ng/mL)
- \( A_{IS} \) = area response of assigned IS quantitation ion
- \( m \) = slope of linear least-squares regression curve
- \( b \) = y-intercept of the linear least-squares regression curve

Quadratic Regression Calibration Model:

\[ C_D = \frac{-b + \sqrt{b^2 - 4 \cdot a \left(c - \frac{A_t}{A_{IS}}\right)}}{2a} \cdot C_{IS} \]

where:
- \( C_D \) = instrument-detected analyte concentration (ng/mL)
- \( A_t \) = area response of target compound quantitation ion
- \( C_{IS} \) = concentration of assigned IS (ng/mL)
- \( A_{IS} \) = area response of assigned IS quantitation ion
- \( a \) = quadratic coefficient of the quadratic least-squares regression curve
- \( b \) = linear coefficient of the quadratic least-squares regression curve
- \( c \) = constant of the quadratic least-squares regression curve

4.5.5.5.11 Calculation of In-air Concentrations. For sampling units without computerized flow rate control, the beginning and ending flow rates are averaged to calculate the collected air volume. For computer controlled sampling units, the integrated collected volume is recorded by the data logging system. Sampled air volumes must be in standard conditions, STP, 25°C and 760 mm Hg.
The final air concentration of each target PAH is determined by multiplying the concentration in the extract by the final extract volume and dividing by the collected sample air volume at standard conditions of 25°C and 760 mm Hg:

\[ C_A = \frac{C_t \cdot V_e}{V_A} \]

where:

- \( C_A \) = concentration of the target compound in air (ng/m³)
- \( C_t \) = concentration of the unknown sample in the extract (ng/mL)
- \( V_e \) = final volume of extract (mL)
- \( V_A \) = volume of collected air volume at STP (m³)

### 4.5.6 Summary of Quality Control Parameters

A summary of QC parameters is shown in Table 4.5-3.

Table 4.5-3. Summary of Quality Control Parameters for NATTS PAH Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Blank (SB)</td>
<td>Aliquot of solvent (without IS) analyzed to ensure the GC/MS is free of interferences and compounds of interest (target PAHs, internal standards, and surrogates)</td>
<td>Prior to tuning the instrument and prior to each ICAL</td>
<td>No target compound, IS, or surrogates qualitatively detected</td>
</tr>
<tr>
<td>Tune Check</td>
<td>Demonstration of MS tune – according to MS manufacturer procedures and dependent on detector type. This may be accomplished by analysis of DFTPP or PFTBA and adjusting tuning parameters to demonstrate ion abundances.</td>
<td>Prior to initial calibration and periodically (recommended minimally weekly) thereafter. Frequency to be defined in ASL SOP.</td>
<td>Abundance criteria as defined in ASL SOP</td>
</tr>
<tr>
<td>Initial Calibration (ICAL)</td>
<td>Analysis of a minimum of five calibration levels covering the concentration range of interest (approximately 0.1 to 2 µg/mL)</td>
<td>Initially, following retuning of the instrument, unacceptable CCV, or when changes to the instrument affect calibration response. Recommended every six weeks.</td>
<td>Average RRF &lt; 30.1% RSD and each calibration level must be within ± 30.1% of theoretical nominal. For quadratic or linear regression, ( r \geq 0.995 ), each calibration level must be within ± 30.1% of theoretical nominal</td>
</tr>
<tr>
<td>Second Source Calibration Verification (SSCV)</td>
<td>Analysis of an independent second source standard at approximately the mid-range of the calibration curve to verify curve accuracy</td>
<td>Immediately after each ICAL</td>
<td>Recovery within ± 30.1% of theoretical nominal (for linear and quadratic curves) or RRF within ±30.1% of mean ICAL RRF (for average RRF curves)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Details</td>
<td>Required Frequency</td>
<td>Acceptance Criteria</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------------------</td>
<td>--------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td><strong>Continuing Calibration Verification (CCV)</strong></td>
<td>Analysis of a standard solution at approximately the mid-range of the calibration curve to verify ongoing instrument calibration</td>
<td>Once ICAL is established, every 12 hours of analysis. Also recommended at the conclusion of each sample sequence</td>
<td>Recovery within ± 30.1% of theoretical nominal (for linear and quadratic curves) or RRF within ±30.1% of mean ICAL RRF (for average RRF curves)</td>
</tr>
<tr>
<td><strong>Sample Media Batch Blank</strong></td>
<td>A PUF/resin sorbent/PUF cartridge and QFF (or equivalent of a cartridge and QFF) selected for analysis to ensure acceptable background levels in the batch of sampling media prepared for sampling</td>
<td>The equivalent of one sampling cartridge and QFF for each batch of 20 or fewer prepared cartridges</td>
<td>Naphthalene &lt; 200 ng/sample or &lt; 10% of the site’s 5th percentile concentration from the previous 3 years, whichever is greater. All other target compounds each ≤ 10 ng/sample or &lt; 10% of the site’s 5th percentile concentration from the previous 3 years, whichever is greater</td>
</tr>
<tr>
<td><strong>Field Surrogate Compounds</strong></td>
<td>Deuterated PAHs (or other similar PAHs that are not target compounds) added to assembled cartridges before field deployment to assess recovery during sample collection, handling, and analysis</td>
<td>Added to every cartridge prior to field deployment</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal spiked amount</td>
</tr>
<tr>
<td><strong>Internal Standards (IS)</strong></td>
<td>Deuterated PAHs added to all analyzed solutions (except the SB) to assess the impact of and correct for variability in instrument response</td>
<td>All analyzed solutions (calibration standards, QC samples, and field sample extracts) except the SB</td>
<td>Area response within 50 to 200% of the response of the mid-level ICAL standard</td>
</tr>
<tr>
<td><strong>Extraction Surrogate Compounds</strong></td>
<td>Deuterated PAHs (or PAHs similar to, but not target analytes) which assess recovery during sample extraction and analysis</td>
<td>Added to media before extraction</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal spiked amount</td>
</tr>
<tr>
<td><strong>Solvent Method Blank (SMB)</strong></td>
<td>Aliquot of extraction solvent fortified with IS and analyzed to ensure extraction solvent is free of interferences and target compounds</td>
<td>One with every extraction batch</td>
<td>No target compound or surrogate qualitatively detected (signal to noise ratio &gt; 3:1)</td>
</tr>
<tr>
<td><strong>Method Blank (MB)</strong></td>
<td>Blank cartridge and QFF taken through all extraction and analysis procedures</td>
<td>One with every extraction batch of 20 or fewer field-collected samples</td>
<td>Each target analyte ≤ 2x MDL</td>
</tr>
<tr>
<td><strong>Laboratory Control Sample (LCS)</strong></td>
<td>PUF/resin sorbent/PUF cartridge and QFF spiked with a known amount of target analyte in lower 1/3 of calibration curve</td>
<td>Minimally quarterly. Recommended as one with every extraction batch of 20 or fewer field-collected samples</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal spiked amount</td>
</tr>
<tr>
<td><strong>Laboratory Control Sample Duplicate (LCSD)</strong></td>
<td>Duplicate PUF/resin sorbent/PUF cartridge and QFF spiked with a known amount of target analyte in lower 1/3 of calibration curve</td>
<td>Minimally quarterly. Recommended as one with every extraction batch of 20 or fewer field-collected samples</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal spiked amount and precision &lt; 20.1% RPD compared to LCS</td>
</tr>
</tbody>
</table>
Table 4.5-3. Summary of Quality Control Parameters for NATTS PAH Analysis
(Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Details</th>
<th>Required Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicate Analysis</td>
<td>Replicate analysis of a field sample extract</td>
<td>Once with every analysis sequence</td>
<td>Precision &lt; 10.1% RPD when concentration in at least one replicate measurement is ≥ 0.5 µg/mL</td>
</tr>
<tr>
<td>Field Blank (FB)</td>
<td>Blank cartridge and QFF assembly installed in sampling unit and exposed to ambient atmosphere for minimally five minutes</td>
<td>One per month at each monitoring site</td>
<td>Target analyte amounts ≤ 3x MDL</td>
</tr>
<tr>
<td>Collocated Samples</td>
<td>Sample collected concurrently with the primary sample</td>
<td>≥ 10% of primary samples for sites conducting collocated sampling (as required by QAPP)</td>
<td>Precision &lt; 20.1% RPD when concentration in at least one of the collocated pair extracts is ≥ 0.5 µg/mL</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>RT of each target PAH, surrogate compound, and IS</td>
<td>All qualitatively identified compounds</td>
<td>Target analytes and surrogates within ±10 seconds of the ICAL mid-level standard or most recent CCV, alternatively within ± 0.06 RRT units ISs within ±20 seconds of mean ICAL RT</td>
</tr>
</tbody>
</table>
4.5.7 References


5.0: METEOROLOGICAL MEASUREMENTS

A goal of the NATTS network is to leverage existing monitoring sites (such as those conducting criteria pollutant monitoring, PAMS sites, and NCore sites, etc.) to conduct NATTS Program sample collection. Meteorological parameter measurements are conducted at many of the 26 established NATTS sites.

While such site-specific meteorological measurements such as wind speed, wind direction, solar radiation, precipitation, etc. are highly desirable and complement collected NATTS data, only temperature and barometric pressure measurements are required for NATTS sample collection events. If temperature and barometric pressure measurements are not recorded from calibrated temperature and barometric pressure functions on sampling units themselves, they must be recorded from site-specific calibrated meteorological instruments in order to perform conversions between measurements in standard conditions and local conditions. If site-specific meteorological monitoring is not performed, each site must acquire the applicable temperature and barometric pressure from the closest off-site meteorological monitoring station (i.e., National Weather Service [NWS], local airport, etc.). For sites collecting additional meteorological parameters beyond temperature and barometric pressure, please consult EPA’s Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV Meteorological Measurements (Version 2.0) for more information, available at (accessed June 2022):


Additional guidance can be found in the 2019 PAMS TAD (accessed June 2022):

which includes additional guidance and information on upper air measurements by ceilometer as well as measurements for solar and UV radiation, wind direction and wind speed, relative humidity, and precipitation.
6.0: DATA HANDLING

The earlier sections of this TAD address specifics on how to make measurements of ambient air toxics concentrations to be able to assess the NATTS DQO of trends detection. It includes some references on aspects of observations and measurements to record; however, this section summarizes the data handling practices that monitoring agencies and ASLs are to follow to allow reconstruction of activities employed to support concentration measurements entered into AQS. Monitoring agencies and ASLs should prescribe these aspects into policy documents, a quality manual or quality management plan, QAPP, or other similar controlled document for staff to follow.

6.1 Data Collection

Observations, measurements, and information needed to support measurements must be documented in detail sufficient to reconstruct the activities and transformations to generate reported concentration data. Such information minimally includes records of observations, laboratory measurements, and photographs as well as instrument calibration records and COAs. Records related to transformations and calculations of data such as through data reduction spreadsheets, calibration regression curve generation, hand calculations, or calculation regimens handled by a LIMS are to be maintained and documented in sufficient detail so the transformations may be verified.

6.2 Data Backup

Electronic data acquired from laboratory instruments, field instruments, databases, and data manipulation software in support of NATTS Program work must be maintained for a minimum of six years following acquisition. As previously discussed, this six-year period is needed to cover two consecutive three-year periods needed to assess trends for the NATTS DQO. In order to maintain electronic records for this duration, it is necessary to prevent data loss and corruption by ensuring data redundancy.

For data acquisition software systems such as CDSs, ICP-MS control and operation software, and environmental control tracking software systems which are connected via computer network, a best practice is to enable automated nightly backups of data to a separate physical hard drive or server, preferably one at a different physical location. Backing up of data to a separate partition on the same hard drive provides no additional security if the hard drive fails. For software systems which are not networked to a server, a best practice is to manually back up the data after completion of each day’s activities to removable media (thumb drive, external hard drive, etc.) for transfer to a networked computer or server.

These daily backups must be protected from inadvertent alteration and compiled on a regular frequency, recommended weekly but not to exceed monthly, to an archival system such as a tape drive, digital video disc (DVD), additional external server, cloud storage, etc. This archival must be access-limited by password and/or other security means to a select few individuals as deemed responsible by cognizant management.
 Archived electronic data must remain accessible such that retired computer or legacy software systems are to be maintained to access data, or archived data must be converted such that it remains accessible and legible until the archival period has lapsed.

Once archived, data should be reviewed or tested to ensure complete records are maintained and data have not been corrupted. Such a review is recommended every six months, but should not exceed annually.

6.3 Recording of Data

Data generated as in Section 6.1 must be recorded/memorialized so that it is clear who performed the activity, when the activity was performed, and, if applicable, who documented performance of the activity. Monitoring agencies and ASLs should have a policy on data recording covering the following aspects of hand recorded and electronic data.

6.3.1 Paper Records. Data entries created on paper records (hard copy) such as field collection forms, COC forms, or laboratory notebooks, must be recorded legibly in indelible ink and must identify the individual recording the information. Measurements must clearly indicate appropriate units so there is no ambiguity on the magnitude of the measurement. Individuals creating paper data records must be identified by way of signature or initials unique to the individual and in such a manner that unambiguous identification is possible. One method by which such may be accomplished is to create a cross-reference for each staff person that shows each staff person’s printed name, signature, and initials. Original records of data (raw data) are to be maintained and may not be disposed of once copied or transcribed into a more suitable format (e.g., writing a measurement on a paper towel, transcribing the measurement to logbook, and disposing of the paper towel).

6.3.2 Electronic Data Capture. Electronic data recording systems such as electronic logbooks, LIMS, and instrumental data acquisition software generally require a user to log in with a username and password to utilize the system. Each action (entry, manipulation, instrument operation) recorded by such software systems must be attributable to an individual and the corresponding date and time recorded. If so equipped, audit trails must be enabled on software systems in order to record changes made to electronic records.

6.3.3 Error Correction. Changes to recorded data or data manipulation may be required due to calculation errors, incorrectly recorded measurements, or errors noted during data verification and validation. When records are amended, whether paper or electronic, the original record must remain legible or otherwise intact, and the following information must be recorded: the identity of the individual responsible for making the change, the date the change was made and the rationale for the change. For example, hand-written data records may be corrected by a single line through the entry with the correction, the initials of the responsible individual, the date of correction, and the rationale for change documented in close proximity to the correction or identifiable by annotated footnote. For common corrections such as those for incorrect date, illegible entry, calculation errors, etc., a list of abbreviations may be developed to document
change rationale. Any such abbreviations must be defined in a quality systems document such as an SOP, or in the front of a logbook, etc.

6.3.3.1 Manual Integration of Chromatographic Peaks. Automated functions for the integration of chromatographic peaks are included in the chromatography data systems (CDS) that control the GC/MS and HPLC instruments. These integration functions should be configured such that little intervention or correction is needed by the analyst, so as to best ensure that peak integration is as reproducible and introduces as little human error as possible. While these functions ensure consistent integration practices, subtle differences in peak shape, coeluting peaks, and baseline noise may result in inconsistent or incorrect peak integration. Additional information on chromatographic peak integration is detailed in Appendix D.

Analysts must be properly trained to review and adjust peak integration performed by CDS automated functions, and specific procedures must be codified into each agency’s quality system. All manual changes to automated peak integration are treated as error corrections. Typical corrections to peak integration may include: adjustment of the baseline, addition or removal of a vertical drop line, or peak deletion if the requisite compound identification criteria are not met. The identification criteria for the chromatography methods are listed as follows:

- **VOCs:** Section 4.2.11
- **Carbonyls:** Section 4.3.9.5.6
- **PAHs:** Section 4.5.5.5.7

Manual peak deletion, that is, effectively reporting that the compound was not detected, is not permitted in instances in which the specified identification criteria are met. GC and HPLC analysts should be aware of CDS software settings for peak area thresholds and their impact on chromatographic peaks with small area responses. Setting of such thresholds at too high a value will result in the CDS overlooking peaks meeting identification criteria. Analysts should take care to review chromatograms for such overlooked peaks and manually integrate them as necessary when identification criteria are met.

For each adjustment to chromatographic peak integration (manual integration), the record of the original automated integration must be maintained and it is strongly recommended that the adjustment be justified with the documented rationale (signal-to-noise too low, incorrect retention time, incorrectly drawn baseline, etc.), analyst initials, and date.

6.3.4 Data Transcription. Data recorded on paper hard copy forms or within electronic data systems that are transcribed into an electronic data capture system or other hard copy form should be reviewed 100% to ensure errors were not made in the transcription. Such reviews of transcribed data are to be documented.

6.4 Numerical Calculations

Numerous calculations and transformations are necessary to determine the target analyte concentration of a given field-collected sample or QC sample or to determine evaluate whether
data generated during calibration verifications meet acceptance criteria. Calculations should be reviewed to ensure errors were not made and the review documented.

6.4.1 Rounding. Rounding of values must be avoided until the final step of a calculation. Rounding during intermediate steps risks the loss of fidelity of the calculation which may lead to significant calculation error.

EPA Region IV Science and Ecosystem Support Division SESH has developed guidance for rounding which is adopted into the revision of the Volume II of EPA’s QA Handbook. This guidance is included in Appendix C of this TAD.

6.4.2 Calculations Using Significant Digits. Final reported results should be rounded to the correct number of significant digits per the rules below. To the extent feasible, carry the maximum number of digits available through all intermediate calculations and do not round until the final calculated result. Non-significant digits that are carried through calculations may be represented using subscripted numerals. (For example, 2.321 has three significant figures, with the final 1 being non-significant and carried through to avoid unnecessarily introducing additional error into the final result.)

6.4.2.1 Addition and Subtraction. The number of significant digits in the final result is determined by the value with the fewest number of digits after the decimal place. For example:

\[
\begin{align*}
A & \quad 5.6 \\
B & \quad 63.71 \\
C + 9.238 & \quad 78.5
\end{align*}
\]

The final result is limited to one decimal place due to the uncertainty introduced in the tenths place by measurement A.

6.4.2.2 Multiplication and Division. The number of significant digits in the final result is determined by the value with the fewest number of significant digits. For example, acrolein was measured by the GC/MS at a concentration of 2.721 ppbv from a canister that was diluted with zero air resulting in a dilution factor of 1.41. The dilution factor is applied to the measured result to calculate the in air concentration:

\[
\begin{align*}
2.721 \text{ ppbv} \cdot 1.41 & = 3.837 \text{ ppbv} \\
= 3.84 \text{ ppbv}
\end{align*}
\]

The final result is limited to three significant digits due to the dilution factor containing three significant digits.

6.4.2.3 Standard Deviation. Standard deviation in a final result must not display digits in a place that the sample average does not have a significant digit. Take, for example, the following average and standard deviation of the form \( \bar{x} \pm s \):
The standard deviation is rounded to the appropriate least significant digit of the sample average.

6.4.2.4 **Logarithms.** For converting a value to its logarithm, retain as many places in the mantissa of the logarithm (to the right of the decimal point in the logarithm) as there are significant figures in the number itself. For example (mantissa underlined):

\[
\log_{10} 24.5 = 1.389
\]

For converting antilogarithms to values, retain as many places in the value as there are digits in the mantissa of the logarithm. For example (mantissa underlined):

\[
\text{antilog (1.131)} = 13.5
\]

6.5 **In-house Control Limits**

The analysis methods detailed in Section 4 specify acceptance criteria for routine QC samples. These acceptance criteria are the maximum allowable ranges permitted, however, ASLs may find that they rarely or never exceed the acceptance criteria. As each laboratory and the associated analyst, instruments, and processes are unique, development of in-house control limits is recommended to evaluate trends and identify problem situations before exceedances to method acceptance criteria occur.

In-house control limits may be generated to evaluate the bias of quality control samples such as the LCS, CCV, SSCV, and to evaluate precision of LCSD, matrix spike duplicate, etc. Warning limits and control limits are established following acquisition of sufficient data points, generally more than seven, per the guidance in the subsequent sections. Under no circumstances may data be accepted which exceeds method specified acceptance criteria even if in-house warning or control limits have not been exceeded.

6.5.1 **Warning Limits.** Warning limits are established as a window of two standard deviations surrounding the mean (\(\bar{x} \pm 2s\)). Exceedance of the warning limit should prompt monitoring of the parameter for values which remain outside the warning limits. For repeated values exceeding the warning limits, corrective action should be taken to address the trend.

6.5.2 **Control Limits.** Control limits are established as a window of three standard deviations surrounding the mean (\(\bar{x} \pm 3s\)). Corrective action is required when control limits are exceeded.

6.6 **Negative Values**

In general, negative values of small magnitude may be expected from certain analytical platforms in the NATTS program, specifically those which do not apply calibration regressions which are forced through the origin (e.g., calibrations established with average relative response factors). However, depending on the situation, negative numbers can be problematic and
indicative of bias due to faulty sensors, contamination or background in reagents and labware, improper calibration, or calculation errors.

Negative values must be evaluated to ensure that their magnitude does not significantly impact the resulting measurements.

Negative values for all qualitatively identified analytes must be reported to AQS as-is without censoring or replacing with zero. If the value’s magnitude exceeds the negative value threshold, the data are to be invalidated (Null qualifier BR indicating sample value below acceptable range) when reported to AQS.

6.6.1 **Negative Concentrations.** For analysis measurements, a negative concentration result generated by a positive instrument response (i.e., positive area count) must be investigated to ensure that the negative concentration is of small magnitude such that the absolute value of the concentration is less than the MDL_{sp} (for MDLs determined via Section 4.1.3.1) or s·K for MDLs determined via Section 4.1.3.2. Where negative concentrations fail this criterion, corrective action must be taken to determine and remediate the source of the bias.

6.6.2 **Negative Physical Measurements.** For physical measurements such as mass, absolute pressure, and flow, negative values generated by an instrument must be evaluated to ensure they do not adversely impact future measurements.

For example, a VOCs sampling unit pressure transducer reads -0.4 psia upon connection to a canister at hard vacuum. The acceptable canister pressure threshold is 0.5 psia. Since negative absolute pressures are impossible, the -0.4 psia reading is significant, especially when compared to an acceptance criterion of 0.5 psia. Due to the -0.4 psia bias, the pressure in another canister at 0.8 psia would be read 0.4 psia and would incorrectly meet the acceptance criterion for sample collection due to the incorrect calibration of the pressure transducer.
7.0: DATA VALIDATION TABLES

The following tables are a distillation of the general quality control guidance and requirements in Section 3 and of the individual methods described in Section 4. More information on each data validation parameter can be located within the text identified in the reference column. Each parameter is assigned a category of importance. The right-most column in each table indicates the data reporting impact prescribing the data qualification or invalidation treatment for affected target analytes.

The categories of importance, in order of decreasing importance, are:

1. **Critical** – Criteria must be met for reported results to be valid – Samples for which these criteria are not met are invalidated.

2. **MQO** – Required NATTS Measurement Quality Objective which must be attained – Failure to meet these criteria does not necessarily invalidate data, but may compromise data and result in exclusion from trends analysis.

3. **Operational** – Failure to meet criteria does not invalidate reported results; the results are compromised and on a case-by-case basis may require qualification – refer to the rightmost column in the tables for guidance on qualifiers in addition to Section 3.3.1.3.15 for the list of AQS qualifiers

4. **Practical** – Failure to meet criteria does not invalidate reported results; results may be compromised but do not require qualification.
### 7.1 VOCs via EPA Method TO-15A

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<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Canister Cleaning Batch Blank</strong></td>
<td>Minimally one canister selected for analysis from a given batch of clean canisters to ensure acceptable background levels in the batch of cleaned canisters - must represent no more than 8 canisters. Recommended to analyze additional batch blanks and best practice is to analyze each cleaned canister.</td>
<td>Tier I VOCs ≤ MDL MQO and All target VOCs &lt; 3x MDL or 0.030 ppbv, whichever is lower, corrected for concentration at standard ambient pressure of 760 mmHg Preferably all VOCs ≤ 0.020 ppbv</td>
<td>Section 4.2.4.2</td>
<td>Critical for Tier I VOCs, Operational for Tier II VOCs</td>
<td>Associated canisters in cleaning batch qualified as CC and LK</td>
</tr>
<tr>
<td><strong>Canister Viability</strong></td>
<td>All canisters for field or laboratory use (strongly recommended)</td>
<td>Canister use should not exceed 30 days from final evacuation</td>
<td>Section 4.2.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Unit Clock/Timer Check</strong></td>
<td>Verify clock timer date and time accuracy at set up of each sampling event</td>
<td>Clock/timer accurate to ±5 minute of reference for digital timers, ±15 minutes for mechanical timers, set to local standard time Sample collection period verified to be midnight to midnight</td>
<td>Section 4.2.3.4.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Canister Starting Pressure Determination</strong></td>
<td>Measure canister pressure with a calibrated pressure gauge or pressure transducer at sample setup prior to collection for each sampling event</td>
<td>Canister pressure should not exceed 5% (operational) and must not exceed 10% (critical) of ending canister pressure.</td>
<td>Section 4.2.3.4.2</td>
<td>Critical</td>
<td>Invalidate all measurement for sample as AA</td>
</tr>
<tr>
<td><strong>Sample Setup Leak Check</strong></td>
<td>Each canister prior to collection - draw vacuum on canister connection If leak exists and is not verified, canister pressure at retrieval will not be in the correct range</td>
<td>Leak rate &lt; 0.2 psi over 5 minutes</td>
<td>Section 4.2.3.4.2</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Frequency</strong></td>
<td>One sample every six days according to the EPA National Monitoring Schedule</td>
<td>Sample is to be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)</td>
<td>Section 4.2.3.4.1</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Period</strong></td>
<td>All routine primary, duplicate, and collocated samples 1380-1500 minutes (24 ± 1 hr) starting and ending at midnight</td>
<td></td>
<td>Section 4.2.3.4.1</td>
<td>Critical and MQO</td>
<td>Invalidate all measurement for sample as AG</td>
</tr>
<tr>
<td><strong>Pre-Sample Collection Purge</strong></td>
<td>Each sampling event (strongly recommended)</td>
<td>Minimum of ten air changes just prior to sample collection</td>
<td>Section 4.2.3.4.1</td>
<td>Practical</td>
<td>NA</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field-collected Sample Final Pressure</td>
<td>Measure the final sample pressure of all primary, duplicate, and collocated field-collected samples with a calibrated pressure gauge or pressure transducer</td>
<td>Subambient pressure samples must be ≤ the pressure at which sampling flow rate ceases to be constant as described in Section 4.2.3.1.2.1. Pressurized samples should be &gt; ambient barometric pressure.</td>
<td>Section 4.2.3.2.3</td>
<td>Critical for subambient sample collection</td>
<td>Invalidate measurement data for subambient samples as AA</td>
</tr>
<tr>
<td>Chain-of-custody</td>
<td>All field-collected samples including field QC samples</td>
<td>Each canister must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation</td>
<td>Sections 3.3.1.3.7 and 4.2.5</td>
<td>Critical</td>
<td>Invalidate measurement data as EC</td>
</tr>
<tr>
<td>Sample Holding Time</td>
<td>All field-collected samples, laboratory QC samples, and standards</td>
<td>Analysis ≤ 30 days from end of collection (field-collected samples) or preparation (QC samples or standards)</td>
<td>Section 4.2.1 and 4.2.8.3</td>
<td>Operational</td>
<td>Qualify results as LJ</td>
</tr>
<tr>
<td>Canister Receipt Pressure Check</td>
<td>Measurement of primary, duplicate, and collocated field-collected samples with a calibrated pressure gauge or pressure transducer upon receipt at the laboratory. Canisters received at ambient pressure are presumed to have leaked (unless collected as grab samples)</td>
<td>Pressure change should not exceed 0.5 psi (operational) and must not exceed 1.5 psi (critical) from the final pressure at retrieval. Subambient samples may acceptably exhibit lower pressure than the retrieval measurement. Pressurized samples may acceptably exhibit a higher pressure than the retrieval pressure and the pressure must be &gt; ambient barometric pressure.</td>
<td>Section 4.2.5</td>
<td>Critical for subambient sample collection.</td>
<td>For subambient samples, qualify as LJ if pressure is between 0.51 and 1.5 psi higher than retrieval pressure. If receipt pressure is &gt; 1.5 psi higher than retrieval pressure or is at ambient pressure, invalidate as AA. Pressurized samples received at ambient pressure qualified as LJ</td>
</tr>
<tr>
<td>Instrument Blank (IB)</td>
<td>Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean prior to analysis of ICAL or daily beginning CCV (strongly recommended)</td>
<td>Concentration of each target VOC &lt; 3xMDL or 0.030 ppbv, whichever is lower.</td>
<td>Section 4.2.8.6.3.1</td>
<td>Operational</td>
<td>Qualify measurement data as LB</td>
</tr>
</tbody>
</table>

**Sample Receipt**

This section details the required procedures for ensuring the integrity and accuracy of the sample collection process. Each field-collected sample is uniquely identified and accompanied by a valid and legible Chain of Custody (COC) with complete sample documentation. This is critical for ensuring the reliability of the sample analysis.

**GC/MS Analysis**

The GC/MS analysis involves a rigorous process to ensure the cleanliness of the instrument and the concentration levels of each target VOC are below the detection limit. This is achieved by analyzing the instrument blank (IB) and ensuring that the concentration of each target VOC is below the specified limits.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tune Verification</td>
<td>Verification and adjustment of MS tune prior to ICAL and recommended each day of analysis. Follow manufacturer recommendations for establishing and evaluating tune. Quadrupole MS may be tuned and the tune verified by 50 ng injection of BFB prior to ICAL and every 24 hours of analysis thereafter.</td>
<td>Meet manufacturer criteria as prescribed in ASL SOP. BFB tune should meet abundance criteria listed in Table 4.2-2 Analysis cannot continue if proper tune is not demonstrated.</td>
<td>Section 4.2.8.3.3</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td>GC/MS Multi-Point Initial Calibration (ICAL)</td>
<td>Analysis of a minimum of 5 non-zero concentration levels covering approximately 0.03 to 5 ppbv to establish calibration for each target VOC. For quadratic regression, 8 levels are strongly recommended. Initially, following instrument tuning, failed CCV, or when changes to the instrument affect calibration response. Prepared standards must be traceable to calibrated mass flow controllers (dynamic dilution) and/or pressure gauges (static dilution).</td>
<td>Average RRF &lt; 30.1% RSD and each calibration level must be $\leq 30.1%$ of theoretical nominal For least squares regression (with either a linear or quadratic fit), $r \geq 0.995$ and each calibration level must be $\leq 30.1%$ of theoretical nominal. Intercept may not be forced through origin.</td>
<td>Section 4.2.8.5</td>
<td>Critical</td>
<td>Operational for non-Tier I VOCs</td>
</tr>
<tr>
<td>Second Source Calibration Verification (SSCV)</td>
<td>Analysis of a second source standard at the mid-range of the calibration curve to verify ICAL accuracy immediately after each ICAL SSCV must include all Tier I VOCs and a representative VOC of each VOC type. Recommended that the SSCV include all calibrated target VOCs.</td>
<td>Recovery for each target VOC within 69.9-130.1% of the theoretical nominal (linear or quadratic models) or the RRF $&lt;\pm 30%$ of the mean ICAL RRF.</td>
<td>Section 4.2.8.6.1</td>
<td>Critical</td>
<td>Operational for non-Tier I VOCs</td>
</tr>
</tbody>
</table>

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<tr>
<th>Parameter</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuing Calibration Verification (CCV)</strong></td>
<td>Analysis of a known standard in the lower 1/3 of the calibration range to verify ongoing instrument calibration. Analyze each day of analysis prior to analyzing QC or field samples. Recommended after every 10 field samples and concluding the analytical sequence.</td>
<td>Recovery for each target VOC within 69.9-130.1% of the theoretical nominal (linear or quadratic models) or the RRF &lt; ±30% of the mean ICAL RRF</td>
<td>Section 4.2.8.6.2</td>
<td>Critical for Tier I VOCs Operational for non-Tier I VOCs</td>
<td>Invalidate Tier I VOCs as EC Qualify non-Tier I VOCs as LJ, LL (low bias), or LK (high bias) as appropriate</td>
</tr>
<tr>
<td><strong>Internal Standards (IS)</strong></td>
<td>Deuterated isotopes of target VOCs or non-naturally occurring VOCs co-analyzed with all calibration standards, QC samples, and field-collected samples to monitor instrument response and assess matrix effects</td>
<td>Area response for each IS compound &lt;± 40.1% of the average response of the ICAL</td>
<td>Section 4.2.8.4.1</td>
<td>Operational</td>
<td>Qualify sample results as LJ</td>
</tr>
<tr>
<td><strong>Preconcentrator Leak Check</strong></td>
<td>Pressurizing or evacuating each canister connection to the preconcentrator to verify as leak-free prior to analysis</td>
<td>&lt; 0.5 psi change/minute or manufacturer specifications</td>
<td>Section 4.2.10.2.1</td>
<td>Critical</td>
<td>Invalidate as EC</td>
</tr>
<tr>
<td><strong>Method Blank (MB)</strong></td>
<td>Canister filled with clean humidified diluent gas (gas employed for dilution of standards and/or samples) One with every analysis batch (each day of analysis)</td>
<td>Concentration of each target VOC &lt; 3x MDL or 0.030 ppbv, whichever is lower. Preferably all target VOCs are ≤ 0.020 ppbv Tier I VOCs must be ≤ MDL MQO</td>
<td>Section 4.2.8.6.3.2</td>
<td>Operational</td>
<td>Qualify associated sample data as LB</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution Blank (DB)</td>
<td>Canister filled with clean humidified gas used to prepare calibration standards. May also serve as the method blank if shown to be sufficiently clean. With each preparation of calibration standards. If target analytes are measured in the DB at concentrations exceeding 0.020 ppbv, and the contamination is attributable to the gas (and not the canister or other components of the instrument), error in the lower concentration standards is expected (this may be evidenced by low concentration standards exceeding the ±30% criterion from the theoretical nominal). Additional cleanup of dilution gas is strongly recommended to achieve accurate concentration calibration standards.</td>
<td>Concentration of each target VOC &lt; 3x MDL or 0.030 ppbv, whichever is lower. Preferably all target VOCs are ≤ 0.020 ppbv Tier I VOCs ≤ MDL MQO</td>
<td>Section 4.2.8.6.3.3</td>
<td>Operational</td>
<td>No definitive data reporting impact. Examine calibration curves for enhancement or increased errors at low concentration and the origin (e.g., y-intercept)</td>
</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>Canister spiked with known concentration of each target analyte at approximately the lower third of the calibration curve Recommended: One with every analysis batch of 20 or fewer field-collected samples</td>
<td>Recovery of each target VOC 69.9 to 130.1% of its theoretical nominal spiked amount</td>
<td>Section 4.2.7.6</td>
<td>Operational</td>
<td>Qualify associated sample data as LJ, LL (low bias), or LK (high bias) as appropriate</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>RT of each target compound and internal standard for all qualitatively identified compounds and ISs</td>
<td>RT of each target VOC RRT must be within ± 2 seconds of its mean ICAL RT RT of each IS must be within ± 20 seconds of its mean ICAL RT</td>
<td>Sections 4.2.11 and 4.2.8.4.1.1</td>
<td>N/A – see Compound Identification</td>
<td>NA</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

<table>
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<tr>
<th>Parameter</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound Identification</td>
<td>Qualitative identification of each target VOC in each standard, blank, QC sample, and field-collected sample (including field QC samples)</td>
<td>Signal-to-noise ≥ 3:1&lt;br&gt;RT within ± 2 seconds of the ICAL mean RT&lt;br&gt;Relative abundance of at least one qualifier ion &lt; ±30.1% of mean ICAL relative abundance&lt;br&gt;Peak apexes co-maximized (within one scan) for quantitation and qualifier ions</td>
<td>Section 4.2.11</td>
<td>Operational</td>
<td>Report concentration as 0 and qualify as ND</td>
</tr>
<tr>
<td>Replicate Analysis</td>
<td>A single additional analysis of a field-collected canister&lt;br&gt;Once with every analysis sequence (as prescribed in workplan)</td>
<td>Precision &lt; 25.1% RPD for target VOCs for which at concentration for least one of the replicate pair is ≥ 5x MDL</td>
<td>Sections 2.1.3.1 and 4.2.8.6.4.2</td>
<td>Operational</td>
<td>Qualify all results for affected VOCs in analysis sequence as LJ</td>
</tr>
<tr>
<td>Duplicate Sample</td>
<td>Field sample collected through the same inlet probe as the primary sample&lt;br&gt;10% of primary samples for sites performing duplicate sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 25.1% RPD for target VOCs for which at concentration for least one of the duplicate pair is ≥ 5x MDL</td>
<td>Sections 4.2.2.1, 2.1.3.1, and 4.2.8.6.4.1</td>
<td>Operational</td>
<td>Qualify all results for affected VOCs as LJ</td>
</tr>
<tr>
<td>Collocated Sample</td>
<td>Field sample collected through a separate inlet probe as the primary sample&lt;br&gt;10% of primary samples for sites performing duplicate sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 25.1% RPD for target VOCs for which at concentration for least one of the collocated pair is ≥ 5x MDL</td>
<td>Sections 4.2.2.1, 2.1.3.1, and 4.2.8.6.4.1</td>
<td>Operational</td>
<td>Qualify all results for affected VOCs as LJ</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Required Frequency</td>
<td>Acceptance Criteria</td>
<td>Reference</td>
<td>Category</td>
<td>Data Reporting Impact</td>
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<td>-------------------------------------</td>
</tr>
<tr>
<td><strong>Laboratory Readiness and Proficiency</strong></td>
<td></td>
<td></td>
<td></td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td>Method Detection Limit</td>
<td>Determined initially and verified minimally every 13 months thereafter for each target VOC. When method changes are made that alter instrument sensitivity, initial MDL must be redetermined.</td>
<td>MDL determined via 4.1 must be ≤ those listed in Table 4.1-1. These MDL MQOs current as of April 2022. Refer to current workplan template for up-to-date MQOs.</td>
<td>Sections 4.1 and 4.2.9</td>
<td>MQO</td>
<td>Qualify data from expired standards not recertified as LJ. If recertification shows change ≥ ±20%, invalidate as EC. If recertification shows change &lt;±10%, qualify affected data as LL or LK</td>
</tr>
<tr>
<td>Stock Standard Gases</td>
<td>Stock standard gases for use as primary calibration standard, second source calibration verification standard, and IS</td>
<td>Certified and accompanied by certificate of analysis Recertified or replaced annually unless a longer expiration is specified by the supplier</td>
<td>Section 4.2.6.1.3</td>
<td>Operational and may be Critical</td>
<td>Qualify data from expired standards not recertified as LJ.</td>
</tr>
<tr>
<td>Proficiency Testing</td>
<td>Blind sample submitted to each ASL to evaluate laboratory bias Two per calendar year¹</td>
<td>Each target VOC &lt; ± 25.1% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until appropriate bias is demonstrated</td>
<td>Section 2.1.4.1</td>
<td>MQO</td>
<td>After two consecutive failed PTs for a given VOC, qualify data as LL (low bias), or LK (high bias) as appropriate</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Required Frequency</td>
<td>Acceptance Criteria</td>
<td>Reference</td>
<td>Category</td>
<td>Data Reporting Impact</td>
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</tr>
<tr>
<td><strong>Canister Leak Test</strong></td>
<td>Testing of the leak tightness of each canister used for collecting samples or preparing standards or QC samples. New canisters and prior to canister qualification zero check or known standard check. Recommended annually.</td>
<td>Leak rate ≤ 0.1 psi/day, do not use canisters exceeding this rate</td>
<td>Section 4.2.4.1.1</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Canister Zero Check</strong></td>
<td>Introduction of a humidified HCF zero into the canister to verify that the canister does not contribute to positive bias (i.e., exhibit growth) of target VOCs over an approximate 30-day period. Prior to initial use, every three years thereafter, and following major maintenance such as valve replacement. Recommended annually.</td>
<td>At initial and later (e.g., 30-days) timepoints target VOCs ≤ 3x MDL or 0.030 ppbv, whichever is lower, corrected to standard barometric pressure (760 mmHg). Tier I VOCs must also be ≤ MDL MQO.</td>
<td>Section 4.2.4.1.2</td>
<td>Operational until concentration exceeds 5xMDL, then critical</td>
<td>Qualify affected analytes as CF and LK (high bias). Invalidate affected analytes as EC when concentration exceed 5xMDL.</td>
</tr>
<tr>
<td><strong>Canister Known Standard Gas Check</strong></td>
<td>Introduction of a low concentration (recommended approximately 0.1 to 0.5 ppbv) standard diluted in HCF zero air into the canister to verify that the canister does not contribute to positive bias (i.e., exhibit growth) or negative bias (suppression) of target VOCs over an approximate 30-day period. Prior to initial use, every three years thereafter, and following major maintenance such as valve replacement. Recommended annually.</td>
<td>At initial and later (e.g., 30-days) timepoints target VOCs &lt; ±30.1% of the theoretical nominal concentration</td>
<td>Section 4.2.4.1.3</td>
<td>Operational</td>
<td>Qualify affected analytes as CF and either LL (low bias) or LK (high bias).</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<tbody>
<tr>
<td><strong>Sampling Unit Flow Rate Setting</strong></td>
<td>Establishing sampling unit flow rate – may be set by measuring desired flow rate with a flow transfer standard or by collecting a test sample to achieve the desired final canister pressure. Initially and when collected sample pressures deviate from desired final canister pressure or when components affecting flow are adjusted or replaced.</td>
<td>Flow rate set to achieve the desired final canister pressure</td>
<td>Sections 4.2.3.1.2.1 and 4.2.3.1.3.1</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Unit Constant Flow Rate Determination</strong></td>
<td>For subambient sampling, experimentally determining the canister pressure at which the sampler flow control can no longer maintain constant flow – must be performed annually.</td>
<td>No assigned criteria – basis for assigning final sampling canister pressure criterion</td>
<td>Section 4.2.3.1.2.1</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Unit Zero Qualification Check</strong></td>
<td>Verification that the sampling unit does not unacceptably contribute to high bias of target VOCs measurements. Prior to field deployment and annually thereafter, or when flow path components are replaced. Sampling units are subject to a zero check (with humidified HCF zero air) by collection of a reference sample and challenge sample of the HCF zero air.</td>
<td>When corrected for reference sample concentration, target VOCs ≤ 3x MDL or 0.030 ppbv, whichever is lower. Tier I VOCs must be ≤ MDL MQO.</td>
<td>Section 4.2.3.3</td>
<td>Operational until concentration exceeds 5xMDL, then critical</td>
<td>Qualify affected analytes as SB and LK (high bias). Invalidate affected analytes as EC when concentration exceeds 5xMDL.</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

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<tbody>
<tr>
<td>Sampling Unit Known Standard Qualification Check</td>
<td>Verification that the sampling unit does not unacceptably contribute to bias of target VOCs measurements Prior to field deployment and annually thereafter, or when flow path components are replaced Sampling units are subject to a known standard check (with a standard gas with concentration 0.1 to 0.5 ppbv diluted in humidified HCF zero air) by collection of a reference sample and challenge sample of the standard gas</td>
<td>$\pm 15.1%$ of the reference sample</td>
<td>Section 4.2.3.3</td>
<td>Operational</td>
<td>Qualify affected analytes as SB and either LL (low bias) or LK (high bias)</td>
</tr>
<tr>
<td>Sampling Unit Inlet Siting</td>
<td>Verify conformance to requirements Annually</td>
<td>270° unobstructed probe inlet Inlet 2-15 meters above-ground level $\geq 10$ meters from drip line of nearest tree $\geq 2$ m from any high volume sampler Collocated sampling inlets spaced within 4 m horizontally and within 3 m vertically of primary sampling unit inlet</td>
<td>Section 2.4</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
<tr>
<td>Sample Probe and Inlet</td>
<td>Sample probe and inlet materials composition Annually</td>
<td>Chromatographic grade stainless steel or borosilicate glass</td>
<td>Section 4.2.3.1.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td>Sampling Residence Time</td>
<td>Determine the duration from ambient air ingestion to reach the sampling unit inlet Initially and when changes are made to sampling intake flowpath (components change size or flow rates are changed)</td>
<td>$\leq 20$ seconds</td>
<td>Section 4.2.3.2</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
</tbody>
</table>
### 7.1 VOCs via EPA Method TO-15A (Continued)

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<tbody>
<tr>
<td><strong>Sample Inlet Filter</strong></td>
<td>Particulate filter maintenance&lt;br&gt;Minimally annually, more frequently when sampling flow rates are impeded or in locations with high airborne particulate levels</td>
<td>Clean or replace (preference) the sintered stainless steel filter (recommended 2-µm pore size)</td>
<td>Section 4.2.3.1.1.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Inlet and Inlet Line Cleaning</strong></td>
<td>Sample inlet and inlet line cleaning or replacement&lt;br&gt;Minimally annually - More often in areas with high airborne particulate levels</td>
<td>Cleaned with distilled water or replaced</td>
<td>Section 4.2.3.1.1.2</td>
<td>Operational</td>
<td>NA</td>
</tr>
</tbody>
</table>

**Data Reporting**

| **Data Reporting to AQS**                 | Reporting of sample measurement results for a given calendar quarter<br>Quarterly, within 180 days of end of calendar quarter in which the samples were collected<br>Data which are known to be invalid will be reported with NULL Qualifiers. Data which are known to be compromised, but remain valid are to include QA Qualifiers. | Measurements for target VOCs for field-collected samples. Concentration measurements for all detected target VOCs are to be reported, including concentrations less than MDL. Invalidated data are to be reported with appropriate NULL Qualifier Field QC sample and laboratory replicates are to be reported (as required by workplan). | Section 3.3.1.3.15 | Operational | NA                    |
| **AQS Reporting Units**                   | Units must be as specified with each submission to AQS                                            | ppbv                                                                               | Section 3.3.1.3.15    | Critical  | NA                    |
| **Data Completeness**                     | Valid samples as a percentage of scheduled samples                                                  | ≥ 85% of scheduled samples for the calendar year                                   | Section 3.2           | MQO       | NA                    |

Dependent upon EPA contract with PT provider
## 7.2 Carbonyls via EPA Compendium Method TO-11A

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</thead>
<tbody>
<tr>
<td><strong>Collection Media</strong></td>
<td>All field-collected samples and matrix quality control samples</td>
<td>Cartridge containing silica gel solid sorbent coated with DNPH, Waters WAT037500 or Supelco S10, or equivalent (critical)</td>
<td>Sections 4.3.5 and 4.3.5.4</td>
<td>Critical and Operational</td>
<td>Invalidate incorrect cartridge type samples as EC. Qualify affected sample data as LJ when DNPH is &lt; 85% of initial lot value</td>
</tr>
<tr>
<td></td>
<td>Must be used within expiration period defined by manufacturer or demonstrated to be acceptable for use</td>
<td>DNPH peak area cannot be &lt; 85% of the initial lot acceptance value (operational)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Media Handling</strong></td>
<td>All field-collected samples and all quality control samples</td>
<td>Sample retrieval as soon as possible, not to exceed 72 hours post-sampling.</td>
<td>Sections 4.3.5.2, 4.3.5.3, and 4.3.8.1.4</td>
<td>Critical and Operational</td>
<td>Invalidate damaged cartridges as BI. Qualify samples retrieved after 72 hours at HT. Qualify as LJ samples stored above 4°C after 72 hours from retrieval</td>
</tr>
<tr>
<td></td>
<td>Retrieved sample shipped and stored at ≤ 4°C, protected from light until extraction.</td>
<td>Retrieved sample shipped and stored at ≤ 4°C, protected from light until extraction.</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Damaged cartridges (water damage or cracked) must be voided.</td>
<td>Damaged cartridges (water damage or cracked) must be voided.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cartridge Lot Blank Check</strong></td>
<td>Analysis of a minimum of 3 cartridges or 1% of the total lot, whichever is greater, for each new lot</td>
<td>Formaldehyde &lt; 0.15 μg/cartridge, Acetaldehyde &lt; 0.10 μg/cartridge, Acetone &lt; 0.30 μg/cartridge, all other individual target carbonyls &lt; 0.10 μg/cartridge</td>
<td>Section 4.3.5.1 and Table 4.3-2</td>
<td>Critical</td>
<td>Invalidate affected compounds as EC</td>
</tr>
<tr>
<td></td>
<td>Report the lot blank value to AQS for each new lot of cartridge media</td>
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</tbody>
</table>
## 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

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</thead>
<tbody>
<tr>
<td><strong>Sampling Unit Clock/Timer Check</strong></td>
<td>Verified with each sample collection event</td>
<td>Clock/timer accurate to ±5 minute of reference for digital timers and ±15 minutes for mechanical timers, set to local standard time</td>
<td>Section 4.3.8.1.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample collection period verified to be midnight to midnight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sampling Unit Leak Check</strong></td>
<td>Pressurization or evacuation of internal sampler flow paths to demonstrate as leak-free</td>
<td>No indicated flow or manufacturer criteria for passing leak check</td>
<td>Section 4.3.8.1.3</td>
<td>Critical if sampler is so equipped</td>
<td>Invalidate data collected with failing leak check as AQ</td>
</tr>
<tr>
<td></td>
<td>At setup of each sampling event</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Sampling cannot commence if leak check fails. <em>(strongly recommended)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sampling Frequency</strong></td>
<td>One sample every six days according to the EPA National Monitoring Schedule</td>
<td>Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)</td>
<td>Section 4.3.8.1.1</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Period</strong></td>
<td>All routine primary, duplicate, and collocated field-collected samples</td>
<td>1380-1500 minutes (24 ± 1 hr) starting and ending at midnight</td>
<td>Sections 2.1.1 and 4.3.8.1.1</td>
<td>Critical and MQO</td>
<td>Invalidate all measurement for sample as AG</td>
</tr>
<tr>
<td><strong>Pre-Sample Collection Purge</strong></td>
<td><em>(Strongly recommended)</em> with each sampling event</td>
<td>Minimum of ten air changes just prior to sample collection</td>
<td>Section 4.3.8.1.2</td>
<td>Practical</td>
<td>NA</td>
</tr>
</tbody>
</table>

### Sample Receipt

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Chain-of-custody</strong></td>
<td>All field-collected samples</td>
<td>Each cartridge must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation</td>
<td>Sections 3.3.1.3.7 and 4.3.8.1.4</td>
<td>Critical</td>
<td>Invalidate measurement data as EC</td>
</tr>
<tr>
<td><strong>Sample Holding Time</strong></td>
<td>All field-collected samples, laboratory QC samples, and standards</td>
<td>Extraction: 14 days from sample collection (cartridge storage ≤ 4 °C)</td>
<td>Section 4.3.9.3</td>
<td>Operational</td>
<td>Qualify affected data exceeding holding time or storage conditions as LJ</td>
</tr>
<tr>
<td></td>
<td>Analysis: 30 days from extraction (extract storage ≤ 4 °C)</td>
<td>Analysis: 30 days from extraction (extract storage ≤ 4 °C)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### Sample Receipt

- **Chain-of-custody**
  - All field-collected samples
  - Each cartridge must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation
  - Refer to Sections 3.3.1.3.7 and 4.3.8.1.4
  - Critical
  - Invalidate measurement data as EC

- **Sample Holding Time**
  - All field-collected samples, laboratory QC samples, and standards
  - Extraction: 14 days from sample collection (cartridge storage ≤ 4 °C)
  - Analysis: 30 days from extraction (extract storage ≤ 4 °C)
  - Section 4.3.9.3
  - Operational
  - Qualify affected data exceeding holding time or storage conditions as LJ
### 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

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<tbody>
<tr>
<td>Sample Receipt Temperature Check</td>
<td>Field collected cartridges placed in refrigerated storage at retrieval, within 72 hours of end of sample collection. Shipment temperature measured upon receipt at the laboratory</td>
<td>Cartridge temperature ≤ 4°C or Short term shipments (shipments &lt; 4 hours from retrieval) &lt; 10°C</td>
<td>Section 4.3.8.1.4</td>
<td>Operational</td>
<td>Qualify affected data exceeding shipment temperature conditions as LJ</td>
</tr>
</tbody>
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</thead>
<tbody>
<tr>
<td>Solvent Blank (SB)</td>
<td>Prior to ICAL and daily beginning CCV Analysis must not continue if criteria are not met.</td>
<td>All target compounds &lt; MDL_{sp} (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2)</td>
<td>Sections 4.3.9.5 and 4.3.9.5.2</td>
<td>Critical for Tier I carbonyls</td>
<td>Invalidate Tier I carbonyls as EC Qualify non-Tier I carbonyls as LJ</td>
</tr>
</tbody>
</table>

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<tr>
<td>HPLC Initial Multi-Point Calibration (ICAL)</td>
<td>Initially, following failed CCV, or when changes to the instrument affect calibration response Calibration modeled as linear least-squares regression Injection of a minimum of 5 points covering approximately 0.01 to 3.0 μg/mL (concentration range prescribed by ASL)</td>
<td>Correlation coefficient (r) ≥ 0.999; relative error for each level against calibration curve &lt; ±20.1% of theoretical nominal. Absolute value of intercept divided by slope must not exceed MDL_{sp} (MDLs determined by Section 4.1.3.1) or s·K (MDLs determined by Section 4.1.3.2)</td>
<td>Sections 4.3.9.5 and 4.3.9.5.2</td>
<td>Critical for Tier I carbonyls</td>
<td>Invalidate Tier I carbonyls as EC Qualify non-Tier I carbonyls as LJ</td>
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<tbody>
<tr>
<td>Second Source Calibration Verification (SSCV)</td>
<td>Second source standard prepared at the mid-range of the calibration curve, analyzed immediately after each ICAL</td>
<td>&lt;±15.1% difference from theoretical nominal</td>
<td>Sections 4.3.9.5 and 4.3.9.5.3</td>
<td>Critical</td>
<td>Invalidate Tier I carbonyls as EC Qualify non-Tier I carbonyls as LJ</td>
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<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>Once ICAL is established, prior to sample analysis on days when an ICAL is not performed and minimally every 12 hours of analysis; recommended following analysis of every 10 field-collected samples and at the conclusion of each analytical sequence</td>
<td>&lt;±15.1% difference from theoretical nominal</td>
<td>Sections 4.3.9.5 and 4.3.9.5.4</td>
<td>Critical</td>
<td>Invalidate Tier I carbonyls as EC Qualify non-Tier I carbonyls as LJ</td>
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<tr>
<td>Extraction Solvent Method Blank (ESMB)</td>
<td>An aliquot of extraction solvent delivered to a volumetric flask. One with each extraction batch of 20 or fewer field-collected samples.</td>
<td>Each target carbonyl’s concentration &lt; MDL_{sp} (refer to Section 4.1.3.1) or s·K (refer to Section 4.1.3.2)</td>
<td>Section 4.3.9.4.1</td>
<td>Operational</td>
<td>Qualify affected data as LB and QX</td>
</tr>
<tr>
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</tr>
<tr>
<td>Method Blank (MB)</td>
<td>Unexposed DNPH cartridge extracted as a sample One with every extraction batch of 20 or fewer field-collected samples. Recommended that the lot cartridge for the MB match that of co-extracted field samples.</td>
<td>Formaldehyde &lt; 0.15 μg/cartridge, Acetaldehyde &lt; 0.10 μg/cartridge, Acetone &lt; 0.30 μg/cartridge, all other individual compounds &lt; 0.10 μg/cartridge</td>
<td>Section 4.3.9.4.1</td>
<td>Operational</td>
<td>Qualify affected data as LB and QX</td>
</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>DNPH cartridge spiked with known amount of target analyte at approximately the lower third of the calibration curve, minimally quarterly, one recommended with every extraction batch of 20 or fewer field-collected samples</td>
<td>Formaldehyde recovery 79.9-120.1% of theoretical nominal spike All others recovery 69.9-130.1% of theoretical nominal spike</td>
<td>Sections 4.3.3.2 and 4.3.9.4.1</td>
<td>Operational</td>
<td>Qualify affected data as QX</td>
</tr>
<tr>
<td>Laboratory Control Sample Duplicate (LCSD)</td>
<td>Duplicate LCS to evaluate precision through extraction and analysis, minimally quarterly, one recommended with every extraction batch of 20 or fewer samples</td>
<td>Formaldehyde recovery 79.9-120.1% of theoretical nominal spike All others recovery 69.9-130.1% of theoretical nominal spike Precision ≤ 20% RPD of LCS</td>
<td>Sections 4.3.3.2 and 4.3.9.4.1</td>
<td>Operational</td>
<td>Qualify affected data as QX</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>RT windows assigned with each ICAL Every analysis injection.</td>
<td>Each target carbonyl’s RT within ± 3σ or ± 2%, whichever is larger, of its mean ICAL RT</td>
<td>Section 4.3.9.5.2</td>
<td>N/A – see Compound Identification</td>
<td>N/A</td>
</tr>
<tr>
<td>Replicate Analysis</td>
<td>A single additional analysis of a field-collected sample extract (not a FB or TB) Once with every analysis sequence of 20 or fewer samples</td>
<td>Precision &lt; 10.1% RPD for precision pairs for which at least one replicate is ≥ 0.5 μg/cartridge</td>
<td>Sections 2.1.3.1, 4.3.3.1, 4.3.3.2, and 4.3.9.5.5</td>
<td>Operational</td>
<td>Qualify associated data as QX</td>
</tr>
<tr>
<td>Field Blank</td>
<td>Minimally monthly, sample cartridge installed in primary sampling position and exposed to field conditions for minimally 5 minutes</td>
<td>Formaldehyde &lt; 0.30 μg/cartridge, Acetaldehyde &lt; 0.40 μg/cartridge, Acetone &lt; 0.75 μg/cartridge, Sum of all other target compounds &lt; 7.0 μg/cartridge</td>
<td>Section 4.3.8.2.1</td>
<td>Operational</td>
<td>Qualify data for associated samples (since the most recent acceptable FB) as FB</td>
</tr>
</tbody>
</table>

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)
### 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

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</thead>
<tbody>
<tr>
<td>Trip Blank</td>
<td>Recommended, not required. Sample cartridge accompanies sampled cartridges through all handling and transport</td>
<td>Formaldehyde &lt; 0.30 μg/cartridge, Acetaldehyde &lt; 0.40 μg/cartridge, Acetone &lt; 0.75 μg/cartridge, Sum of all other target compounds &lt; 7.0 μg/cartridge</td>
<td>Section 4.3.8.2.2</td>
<td>Operational</td>
<td>Qualify data for associated samples in the shipment as TB</td>
</tr>
<tr>
<td>Collocated Sample Collection</td>
<td>Field sample collected through a separate inlet probe from the co-collected primary sample 10% of primary samples for sites performing collocated sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 20.1% RPD of primary sample when concentration in at least one of the precision pair is ≥ 0.5 μg/cartridge</td>
<td>Sections 2.1.3.1, 4.3.3.1, and 4.3.8.2.3</td>
<td>Operational</td>
<td>Qualify primary and collocated samples as LJ and QX</td>
</tr>
<tr>
<td>Duplicate Sample Collection</td>
<td>Field sample collected through the same inlet probe as the co-collected primary sample 10% of primary samples for sites performing collocated sample collection (as prescribed in QAPP)</td>
<td>Precision &lt; 20.1% RPD of primary sample when concentration in at least one of the precision pair is ≥ 0.5 μg/cartridge</td>
<td>Sections 2.1.3.1, 4.3.3.1, and 4.3.8.2.4</td>
<td>Operational</td>
<td>Qualify primary and duplicate samples as LJ and QX</td>
</tr>
<tr>
<td>DNP Chromatography Evaluation</td>
<td>All field-collected cartridge extracts</td>
<td>DNP area in samples ≥ 50% of the DNP area in the laboratory QC samples</td>
<td>Section 4.3.9.5.7</td>
<td>Critical</td>
<td>Invalidate sample data as EC</td>
</tr>
<tr>
<td>DNP Chromatography Evaluation</td>
<td>All field-collected cartridge extracts</td>
<td>DNPH peak must be present</td>
<td>Section 4.3.9.5.7</td>
<td>Critical</td>
<td>Invalidate sample data as EC</td>
</tr>
</tbody>
</table>

### Laboratory Readiness and Proficiency

| Proficiency Testing                      | Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year | Each target compound ≤ 25.1% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific analyte) must prompt qualification of the analyte in field collected samples until appropriate bias is demonstrated | Section 2.1.4.1 | MQO | After two consecutive failed PTs for a given carbonyl, qualify data as LL (low bias), or LK (high bias) as appropriate |
### 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method Detection Limit</strong></td>
<td>Determined initially and verified minimally every 13 months thereafter for each target carbonyl. When method changes are made that alter instrument sensitivity, initial MDL must be redetermined.</td>
<td>MDL determined via 4.1 must be ≤ those listed in Table 4.1-1. These MDL MQOs current as of April 2022. Refer to current workplan template for up-to-date MQOs.</td>
<td>Sections 4.1 and 4.3.6</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Stock Standards</strong></td>
<td>Purchased stock materials for each target carbonyl for primary calibration and second source calibration verification. For Certified and accompanied by certificate of analysis.</td>
<td>Certificated and accompanied by certificate of analysis.</td>
<td>Section 4.3.9.2.2</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Working Standard Solutions</strong></td>
<td>Storage of all working standards. Analyze standards stored improperly against standards of known proper integrity. Must be &lt; ±15.1%</td>
<td>Stored at ≤ 4°C, protected from light.</td>
<td>Section 4.3.9.2.4</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Unit Testing and Maintenance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Field Sampler Flow Rate Calibration and Calibration Verification</strong></td>
<td>Calibration of sampling unit flow controller. Prior to field deployment and verified quarterly (recommended monthly). Calibration re-established following failure of flow calibration verification. Flow rates calibrated at EPA standard conditions of 760 mmHg and 25°C.</td>
<td>Flow set to match a certified flow transfer standard and verified to be &lt; ±10.1%</td>
<td>Table 3.3-1 and 4.3.7.1.2</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Ozone Denuder/Scrubber Recharge</strong></td>
<td>Replace or recharge ozone scrubber with KI. Prior to field deployment annually Recommend verifying proper operation prior to field deployment and again when retired Examine data generated with failing ozone scrubbers and assess for chromatographic artifacts indicative of ozone breakthrough.</td>
<td>Scrubber capacity sufficient to be effective (ozone removal &gt; 95%) for 12 months of 24-hour sampling every sixth day</td>
<td>Section 4.3.4.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
</tbody>
</table>
### 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Unit Zero Qualification Check</td>
<td>Verification that the sampling unit does not unacceptably contribute to high bias of target carbonyls measurements Prior to field deployment and annually thereafter, or when flow path components are replaced Sampling units are subject to a zero check (with humidified HCF zero air) by collection of a reference sample and challenge sample of the HCF zero air</td>
<td>When corrected for reference sample concentration, target carbonyls ≤ 0.2 ppbv</td>
<td>Section 4.3.7.1.1.1</td>
<td>Operational Until concentration exceeds 5xMDL, then critical</td>
<td>Qualify affected analytes as SB and LK (high bias) Invalidate affected analytes as EC when concentration exceeds 5xMDL</td>
</tr>
<tr>
<td>Sampling Unit Known Standard Qualification Check</td>
<td>Verification that the sampling unit does not unacceptably contribute to bias of target carbonyls measurements Prior to field deployment and annually thereafter, or when flow path components are replaced Sampling units are subject to a known standard check (with a standard gas diluted in humidified HCF zero air at approximately 10 to 15-fold the MDL) by collection of a reference sample and challenge sample of the standard gas (strongly recommended)</td>
<td>&lt; ±15.1 of the reference sample</td>
<td>Section 4.3.7.1.1.2</td>
<td>Operational</td>
<td>Qualify affected carbonyls as SB and either LL (low bias) or LK (high bias)</td>
</tr>
</tbody>
</table>
### 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Site Specifications and Maintenance</strong></td>
<td></td>
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</tr>
<tr>
<td>Sampling Unit Inlet Siting</td>
<td>Verify conformance to requirements&lt;br&gt;Annually</td>
<td>270° unobstructed probe inlet&lt;br&gt;Inlet 2-15 meters above-ground level&lt;br&gt;≥ 10 meters from drip line of nearest tree&lt;br&gt;≥ 2 m from any high volume sampler&lt;br&gt;Collocated sampling inlets spaced within 4 m horizontally and within 3 m vertically of primary sampling unit inlet</td>
<td>Section 2.4</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
<tr>
<td>Sample Probe and Inlet</td>
<td>Sample probe and inlet materials composition&lt;br&gt;Annually</td>
<td>Chromatographic grade stainless steel, PTFE Teflon, or borosilicate glass</td>
<td>Section 4.3.7.2</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
<tr>
<td>Sampling Residence Time</td>
<td>Determine the duration from ambient air ingestion to reach the sampling unit inlet&lt;br&gt;Initially and when changes are made to sampling intake flowpath (components change size or flow rates are changed)</td>
<td>≤ 20 seconds</td>
<td>Section 4.3.7.3</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
<tr>
<td>Sample Inlet Filter</td>
<td>Particulate filter maintenance&lt;br&gt;Minimally annually, if equipped (strongly recommended)</td>
<td>Replace the inline particulate filter (if equipped)</td>
<td>Section 4.3.7.4</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td>Sampling Inlet and Inlet Line Cleaning</td>
<td>Sample inlet and inlet line cleaning or replacement&lt;br&gt;Minimally annually - More often in areas with high airborne particulate levels (strongly recommended)</td>
<td>Replace tubing or clean with deionized/distilled water</td>
<td>Section 4.3.7.4</td>
<td>Operational</td>
<td>NA</td>
</tr>
</tbody>
</table>
## 7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Reporting to AQS</td>
<td>Reporting of sample measurement results for a given calendar quarter Quarterly, within 180 days of end of calendar quarter in which the samples were collected Data which are known to be invalid will be reported with NULL Qualifiers. Data which are known to be compromised, but remain valid are to include QA Qualifiers.</td>
<td>Measurements for target carbonyls for field-collected samples. Concentration measurements for all detected target carbonyls are to be reported, including concentrations less than MDL. Invalidated data are to be reported with appropriate NULL Qualifier Field QC sample and laboratory replicates are to be reported (as required by QAPP).</td>
<td>Section 3.3.1.3.15</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td>AQS Reporting Units</td>
<td>Units must be as specified with each quarterly submission to AQS Reported concentrations for ambient air samples are to be reported with collected volumes at EPA standard conditions of 760 mmHg and 25°C</td>
<td>mass/volume (ng/m³ or µg/m³)</td>
<td>Section 3.3.1.3.15</td>
<td>Critical (does not invalidate data)</td>
<td>NA</td>
</tr>
<tr>
<td>Data Completeness</td>
<td>Valid samples compared to scheduled samples Annually</td>
<td>≥ 85% of scheduled samples</td>
<td>Section 3.2</td>
<td>MQO</td>
<td>NA</td>
</tr>
</tbody>
</table>

1 Dependent upon EPA contract with PT provider
## 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Field Readiness Checks and Collection Activities</strong></td>
<td></td>
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</tr>
<tr>
<td>Collection Media</td>
<td>All field-collected samples and matrix QC samples</td>
<td>Low volume collection: 47-mm PTFE filters with polypropylene support ring and 2-µm pore size</td>
<td>Section 4.4.9.3</td>
<td>Critical</td>
<td>Invalidate data as AQ</td>
</tr>
<tr>
<td>Collection Media</td>
<td>All field-collected samples and matrix QC samples</td>
<td>High volume collection: 8”x10” quartz fiber filter (QFF) filters with 2-µm pore size</td>
<td>Section 4.4.10.3</td>
<td>Critical</td>
<td>Invalidate data as AQ</td>
</tr>
<tr>
<td>Media Inspection</td>
<td>Filters inspected for pinholes, tears, or other imperfections unsuitable for sample collection</td>
<td>Filters with defects must not be used for routine sampling (may be used for matrix QC samples if defects are visual, such as holes, etc.)</td>
<td>Sections 4.4.3.3, 4.4.9.4, and 4.4.10.4</td>
<td>Critical</td>
<td>Invalidate data as AJ</td>
</tr>
<tr>
<td>Media Handling</td>
<td>All field-collected samples and quality control samples, both QFFs and PTFE filters</td>
<td>Plastic or fluoropolymer coated forceps or powder-free gloves</td>
<td>Section 4.4.3.2</td>
<td>Practical</td>
<td>NA</td>
</tr>
<tr>
<td>Lot Background Determination</td>
<td>For each new lot of media:</td>
<td>Low volume: No acceptance criterion</td>
<td>Section 4.4.9.3.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>• As part of the MDL process when determining the initial MDL via Section 4.1.3.1</td>
<td>Lot blank subtraction is not permitted</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>• Five separate filters digested and analyzed</td>
<td></td>
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</tr>
<tr>
<td>Lot Background Determination</td>
<td>For each new lot of media:</td>
<td>High volume: No acceptance criterion</td>
<td>Section 4.4.10.3.1 Io3.1 Table 9</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>• As part of the MDL process when determining the initial MDL via Section 4.1.3.1</td>
<td>Lot blank subtraction is not permitted</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Five separate filters digested and analyzed</td>
<td></td>
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</tr>
</tbody>
</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Unit Clock/Timer Check</td>
<td>Verified with each sample collection event</td>
<td>Clock/timer accurate to ±5 minute of reference for digital timers and within ±15 minutes for mechanical timers, set to local standard time</td>
<td>Table 3.3-1 and Section 4.4.5.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample collection period verified to be midnight to midnight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Unit Leak Check</td>
<td>Verification that sampling flow path is leak tight</td>
<td>Low volume: Leak rate of ≤ 25 mmHg over 30 seconds or 80 mL/min, or equivalent</td>
<td>Section 4.4.9.2</td>
<td>Practical</td>
<td>Samples with failing leak check are invalidated as AK</td>
</tr>
<tr>
<td></td>
<td>Every five sample collection events, recommended with each sampling event</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>If leak is detected, leak must be mitigated before sample collection can commence (strongly recommended)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Unit Leak Check</td>
<td>Verification that sampling flow path is leak tight</td>
<td>High volume: absence of a whistle</td>
<td>Section 4.4.10.2</td>
<td>Practical</td>
<td>Samples with failing leak check are invalidated as AK</td>
</tr>
<tr>
<td></td>
<td>Every five sample collection events, recommended with each sampling event</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>If leak is detected, leak must be mitigated before sample collection can commence (strongly recommended)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sampling Frequency</td>
<td>One primary sample every six days according to the EPA National Monitoring Schedule</td>
<td>Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)</td>
<td>Section 4.4.5.1</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td>Sampling Period</td>
<td>All primary and collocated field-collected samples</td>
<td>1380-1500 minutes (24 ± 1 hr) starting and ending at midnight local standard time</td>
<td>Sections 2.1.1 and 4.4.5.1</td>
<td>Critical and MQO</td>
<td>Invalidate all measurements for sample as AG</td>
</tr>
</tbody>
</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-Sample Collection Warm-up and Sample Starting Flow Measurement</strong></td>
<td>Only for high volume sampling units without computer controlled flow</td>
<td>Minimum of five minutes (ten minutes recommended) after filter installation but before sample collection, record flow rate as starting flow rate</td>
<td>Section 4.4.10.4</td>
<td>Critical (starting flow rate is needed for total volume)</td>
<td>Invalidate as EC</td>
</tr>
<tr>
<td><strong>Post-Sample Collection Warm-up and Sample Ending Flow Measurement</strong></td>
<td>Only for high volume sampling units without computer controlled flow</td>
<td>Minimum of five minutes (ten minutes recommended) before filter retrieval, record flow rate as ending flow rate</td>
<td>Section 4.4.10.4</td>
<td>Critical (ending flow rate is needed for total volume)</td>
<td>Invalidate as EC</td>
</tr>
</tbody>
</table>

#### Sample Receipt

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chain-of-custody</strong></td>
<td>All field-collected samples</td>
<td>Each filter must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation</td>
<td>Sections 3.3.1.3.7, 4.4.9.4 (low volume), and 4.4.10.4 (high volume)</td>
<td>Critical</td>
<td>Invalidate measurement data as EC</td>
</tr>
<tr>
<td><strong>Sample Holding Time</strong></td>
<td>All field-collected samples and laboratory QC samples</td>
<td>Digestion: within 180 days from sample collection or preparation, Analysis: within 180 days from sample collection</td>
<td>Section 4.4.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
</tbody>
</table>

#### Acid Digestion and ICP/MS Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microwave Calibration</strong></td>
<td>Standardization of microwave power output Output calibration not to exceed twelve months; recommended not to exceed 6 months</td>
<td>Level of output should differ by no more than 10% across batches</td>
<td>Section 4.4.9.5.2.2</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Hot Block Temperature Verification</strong></td>
<td>Deionized water blank with thermometer to ensure digestion temperature consistent for all wells Initially and annually thereafter for each well in the hot block digester</td>
<td>Within ± 5°C of desired temperature. Do not use wells that cannot maintain this temperature range.</td>
<td>Section 4.4.9.5.2.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
</tbody>
</table>
7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Block Temperature</td>
<td>Reagent water blank with thermometer to monitor digestion temperature</td>
<td>Within ± 5°C of desired temperature</td>
<td>Section 4.4.9.5.2.1</td>
<td>Operational</td>
<td>Qualify measurement for the batch as LJ</td>
</tr>
<tr>
<td>Batch Check</td>
<td>Each digestion batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sonication Temperature</td>
<td>Temperature measurement of sonication water bath</td>
<td>Within ± 5°C of desired temperature</td>
<td>4.4.9.5.2.3</td>
<td>Operational</td>
<td>Qualify measurement for the batch as LJ</td>
</tr>
<tr>
<td>Batch Check</td>
<td>Each digestion batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICP/MS Warm Up</td>
<td>Warm up of ICP torch and MS detector</td>
<td>Minimum of 30 minutes (or according to manufacturer specifications) prior to performing initial calibration</td>
<td>Section 4.4.11.6</td>
<td>Practical</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Each day of analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICP/MS Tuning</td>
<td>Analysis of tuning solution containing low (e.g., Li), and medium (e.g., Mg, Co), and high (e.g., Pb, Tl) mass elements</td>
<td>Minimum resolution of 0.75 amu at 5% peak height</td>
<td>Section 4.4.11.6</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Each day of analysis during or immediately following warm up</td>
<td>Mass calibration within 0.1 amu of unit mass</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Analysis must not commence if proper MS tuning cannot be demonstrated</td>
<td>Five replicates of tuning solution with %RSD ≤ 5%</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Manufacturer specifications may be substituted</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Calibration Blank (ICAL)</td>
<td>Analysis of undigested reagent blank</td>
<td>ICB following IVC: each target element’s concentration &lt; MDLsp (refer to Section 4.1.3.1) or s · K (refer to Section 4.1.3.2)</td>
<td>Sections 4.4.11.7.1 and 4.4.11.7.3</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Each day of analysis prior to initial calibration (ICAL) and immediately following the initial calibration verification (ICV)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ICP/MS Initial Multi-Point Calibration (ICAL)</td>
<td>Minimum of three standard concentration levels plus ICB covering approximately 0.1 to 250 µg/L</td>
<td>Linear regression correlation coefficient (r) ≥ 0.995</td>
<td>Sections 4.4.11.7. and 4.4.11.7.1</td>
<td>Critical for Tier I metals</td>
<td>Invalidate Tier I as EC</td>
</tr>
<tr>
<td></td>
<td>Each day of analysis, following failed CCV, or retuning of the MS</td>
<td>Replicate integrations RSD ≤ 10%</td>
<td></td>
<td>Operational for non-Tier I metals</td>
<td>Qualify non-Tier I as LJ and QX</td>
</tr>
</tbody>
</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
</table>
| Initial Calibration Verification (ICV) | Analysis of second source calibration verification  
Each day of analysis immediately following ICAL | Within ± 10.1% of theoretical nominal | Section 4.4.11.7.2 | Critical for Tier I metals  
Operational for non-Tier I metals | Invalidate Tier I as EC  
Qualify non-Tier I as LJ and QX |
| Interference Check Standard (ICS) | Analysis of two solutions, ICS Type A contains only interferants at a high concentration and ICS Type B is identical to ICS Type A but also includes target elements at low (e.g., approximately those in ambient air) concentrations. Employed to verify the interferants at a high concentration do not unacceptably bias the ambient air concentration measurements.  
Minimally quarterly, recommended with each day of analysis. Analyzed after the second ICB.  
If interferences are determined to impact target element concentrations, adjust the interferant concentrations in ICS Type A and ICS Type B downward to approximate the concentration in ambient air samples and repeat the process | No criteria for ICS Type A  
ICS Type B: Recovery of target elements 79.9 to 120.1% after correction (subtraction) for measurements in ICS Type B. Correction is not needed unless target element measures ≥ 3x MDL_{sp} (refer to Section 4.1.3.1) or 3x s·K (refer to Section 4.1.3.2) | Section 4.4.11.7.4.1 | Operational | Qualify affected data as LL (low bias) or LK (high bias) as appropriate |
| Continuing Calibration Verification (CCV) | Each day of analysis immediately following the ICS (if analyzed in the sequence) or second ICB, following every 10 sample injections, and at the conclusion of each analytical sequence | 89.9 to 110.1% recovery | Section 4.4.11.7.5 | Critical for Tier I metals  
Operational for non-Tier I metals | Invalidate Tier I as EC  
Qualify non-Tier I as LJ and QX (since the most recent passing CCV) |
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Category</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuing Calibration Blank (CCB)</td>
<td>Each day of analysis immediately after each CCV</td>
<td>all target elements $&lt; \text{MDL}_{\text{sp}}$ (refer to Section 4.1.3.1) or (s \cdot K) (refer to Section 4.1.3.2)</td>
<td>Section 4.4.11.7.6</td>
<td>Operational</td>
<td>Qualify as LB and QX (since the most recent passing CCB)</td>
</tr>
<tr>
<td>Reagent Blank (RB)</td>
<td>Digested reagent blank (digestion solution with no filter)</td>
<td>Low volume: All target elements $&lt; \text{MDL}_{\text{sp}}$ (refer to Section 4.1.3.1) or (s \cdot K) (refer to Section 4.1.3.2)</td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LB and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer samples</td>
<td>High volume: All target elements $&lt; \text{MDL}_{\text{sp}}$ (refer to Section 4.1.3.1) or (s \cdot K) (refer to Section 4.1.3.2)</td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LB and QX (all samples in digestion batch)</td>
</tr>
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<td></td>
<td></td>
<td>Low volume: All target elements $&lt; \text{MDL}$</td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LB and QX (all samples in digestion batch)</td>
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<td></td>
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<td>High volume: All target elements $&lt; \text{MDL}$</td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LB and QX (all samples in digestion batch)</td>
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<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td></td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td></td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
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<td></td>
<td></td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LB and QX (all samples in digestion batch)</td>
</tr>
</tbody>
</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Laboratory Control Sample (LCS)</strong></td>
<td>Low volume: Digested spiked filter</td>
<td>Low volume: Recovery within 79.9-120.1% of theoretical nominal for all target elements</td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LJ and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>High volume: Digested spiked filter strip</td>
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<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer field-collected samples</td>
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</tr>
<tr>
<td><strong>Laboratory Control Sample (LCS)</strong></td>
<td>Low volume: Digested spiked filter</td>
<td>Low volume: Recovery within 79.9-120.1% of theoretical nominal for all target elements</td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LJ and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>High volume: Digested spiked filter strip</td>
<td>High volume: Recovery within 79.9-120.1% of theoretical nominal for all target elements</td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LJ and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer field-collected samples</td>
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</tr>
<tr>
<td><strong>Laboratory Control Sample Duplicate (LCSD)</strong></td>
<td>Low volume: Duplicate digested spiked filter</td>
<td>Low volume: Recovery within 79.9-120.1% of theoretical nominal for all target elements and precision &lt; 20.1% RPD of LCS</td>
<td>Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LJ and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer field-collected samples</td>
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</tr>
<tr>
<td><strong>Laboratory Control Sample Duplicate (LCSD)</strong></td>
<td>High volume: Duplicate digested spiked filter strip</td>
<td>High volume: Recovery within 79.9-120.1% of theoretical nominal for all target elements and precision &lt; 20.1% RPD of LCS</td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify as LJ and QX (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer field-collected samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Duplicate Digested Filter Strip</strong></td>
<td>High volume only Digested duplicate field-collected filter strip</td>
<td>Precision &lt; 20.1% RPD for elements ≥ 5x MDL in at least one in the precision pair</td>
<td>Sections 2.1.3.1, 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify sample as QX and LJ (all samples in digestion batch)</td>
</tr>
<tr>
<td></td>
<td>Once with each extraction batch of 20 or fewer field-collected samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Matrix Spike (MS)</strong></td>
<td>High volume only Digested spiked field-collected filter strip</td>
<td>Recovery within 79.9-120.1% of the theoretical nominal spiked amount for all target elements – 74.9-125.1% for Sb</td>
<td>Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3</td>
<td>Operational</td>
<td>Qualify parent sample as QX and LJ</td>
</tr>
</tbody>
</table>
7.3  Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
</table>
| Matrix Spike Duplicate (MSD) | High volume only Duplicate digested spiked field-collected filter strip  
Once with each extraction batch of 20 or fewer field-collected samples | Recovery within 79.9 to 120.1% of the theoretical nominal spiked amount for all target elements – 74.9 to 125.1% for Sb  
Precision < 20.1% RPD of MS | Sections 2.1.3.1, 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 | Operational     | Qualify parent sample as QX and LJ |
| Serial Dilution            | Five-fold dilution of a field-collected sample digestate  
Once with every analysis sequence of 20 or fewer field-collected samples | Recovery of 89.9 to 110.1% of undiluted sample for elements ≥ 25x MDL in parent sample | Section 4.4.11.7.8 | Operational   | Qualify parent sample as QX and LJ |
| Replicate Analysis         | A single additional analysis of a field-collected sample digestate  
Once with every analysis sequence of 20 or fewer field-collected samples | Precision < 10.1% RPD for concentrations ≥ 5x MDL in at least one in the precision pair | Section 4.4.11.7.9 | Operational   | Qualify sample as QX and LJ (all samples in analysis batch) |
| Internal Standards (IS)     | Non-target elements added to each analyzed solution at the same concentration | 60 to 125% recovery                                                              | Section 4.4.11.4 | Operational   | Qualify sample as QX and LJ (all samples in analysis batch) |
| Field Blank (FB)            | Sample filter installed in primary sampling unit for minimally 5 minutes  
Minimally monthly for primary sampling units, as 18% (approximately 1 out of 5) of collocated samples | All target elements < MDL                                                         | Section 4.4.5.2 | Operational   | Qualify data from affected sites as FB since last acceptable FB |
## 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collocated Sample Collection</td>
<td>Field sample collected with a separate sampling unit within the following distances from primary sampling unit: Low volume 1 to 4 m High volume 2 to 4 m 10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)</td>
<td>Precision &lt; 20.1% RPD of primary sample for concentrations ≥ 5x MDL in at least one in the precision pair</td>
<td>Section 4.4.4.1</td>
<td>Operational</td>
<td>Qualify primary and collocated sample data as LJ and QX</td>
</tr>
</tbody>
</table>

### Laboratory Readiness and Proficiency

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proficiency Testing</td>
<td>Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year¹</td>
<td>Each target element within ± 25.1% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until appropriate bias is demonstrated</td>
<td>Section 2.1.4.1</td>
<td>MQO</td>
<td>After two consecutive failed PTs for a given carbonyl, qualify data as LL (low bias), or LK (high bias) as appropriate</td>
</tr>
<tr>
<td>Method Detection Limit</td>
<td>Determined initially and verified minimally every 13 months thereafter for each target element. When method changes are made that alter instrument sensitivity, initial MDL must be redetermined.</td>
<td>MDL determined via 4.1 must be ≤ those listed in Table 4.1-1. These MDL MQOs current as of April 2022. Refer to current workplan template for up-to-date MQOs.</td>
<td>Sections 4.1 and 4.4.8</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td>Stock Standard Solutions</td>
<td>Purchased stock materials for each target element for primary calibration standards and second source standards</td>
<td>Certified and accompanied by certificate of analysis</td>
<td>Section 4.4.7</td>
<td>Operational</td>
<td>Qualify affected data as LJ</td>
</tr>
</tbody>
</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

<table>
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<tr>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working Standard Solutions</td>
<td>Storage of all working standards</td>
<td>Stored in fluoropolymer or suitable plastic bottles</td>
<td>Section 4.4.7</td>
<td>Practical</td>
<td>NA</td>
</tr>
</tbody>
</table>

**Sampling Unit Testing and Maintenance**

| Sampling Unit Flow Calibration and Calibration Verification | Calibration of sampling unit flow controller Calibrated prior to field deployment and verified quarterly, recommended monthly Low volume and equipped high volume samplers will also require temperature and barometric pressure probes to be calibrated and calibration verified before flow rate calibration or calibration verification | Low volume calibration verification: Within ± 4.1% of certified transfer standard flow and < ± 5.1% of design flow temperature within ± 2.1°C and barometer < ±10.1 mmHg | Section 4.4.9.2, Table 3.3-1 and 40 CFR 58 Appendix A Section 3.3.3 – EPA QA Guidance Document 2.12 | Critical | Invalidate back to most recent passing calibration or calibration verification as AH |

| Sampling Unit Flow Calibration and Calibration Verification | Calibration of sampling unit flow controller Calibrated prior to field deployment and verified quarterly, recommended monthly Low volume and equipped high volume samplers will also require temperature and barometric pressure probes to be calibrated and calibration verified before flow rate calibration or calibration verification | High volume calibration verification: Within ± 7.1% of certified transfer standard flow and within ± 10.1% of design flow If equipped, temperature within ± 2.1°C and barometer < ±10.1 mmHg | Section 4.4.10.2, Table 3.3-1 and 40 CFR 58 Appendix A Section 3.3.3 EPA QA Handbook Section 2.11.7 | Critical | Invalidate back to most recent passing calibration or calibration verification as AH |
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

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</thead>
<tbody>
<tr>
<td><strong>Sampling Unit Siting</strong></td>
<td>Verify conformance to requirements</td>
<td><strong>Site Specifications and Maintenance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Annually</td>
<td>270° unobstructed probe inlet</td>
<td>Section 2.4 40 CFR Part 58 Appendix E</td>
<td>Operational</td>
<td>Qualify affected data as SX</td>
</tr>
<tr>
<td></td>
<td>Low volume and high volume instruments must be no closer than 1 meter and 2 meters, respectively, to any sampling inlet</td>
<td>Inlet 2-15 meters above-ground level</td>
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<tr>
<td></td>
<td></td>
<td>≥ 10 meters from drip line of nearest tree</td>
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<td>Collocated sampling unit inlets measured at nearest edges. Collocated inlets must be within 3m vertically.</td>
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<tr>
<td></td>
<td></td>
<td>Low volume collocated sampling inlets spaced 1-4 meters from primary sampling unit inlet</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>High volume collocated sampling inlets spaced 2-4 meters from primary sampling unit inlet</td>
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</table>
### 7.3 Metals via EPA Compendium Methods IO 3.1 and IO 3.5 (Continued)

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<tbody>
<tr>
<td><strong>Data Reporting to AQS</strong></td>
<td>Reporting of all results a given calendar quarter Quarter, within 180 days of end of calendar quarter in which the samples were collected</td>
<td>Measurements for target elements for field collected samples. Concentrations for all detected target elements are to be reported, including those less than MDL. All data must be in local conditions (LC) and may additionally be reported in standard conditions Field QC sample and laboratory replicates must also be reported (as prescribed in QAPP)</td>
<td>Section 3.3.1.3.15</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td>AQS Reporting Units</td>
<td>Units must be as specified With each quarterly submission to AQS</td>
<td>mass/volume (ng/m³ or µg/m³) in local conditions</td>
<td>Section 3.3.1.3.15</td>
<td>Critical (does not invalidate data)</td>
<td>NA</td>
</tr>
<tr>
<td>Data Completeness</td>
<td>Valid samples compared to scheduled samples Annually</td>
<td>≥ 85% of scheduled samples</td>
<td>Section 3.2</td>
<td>MQO</td>
<td>NA</td>
</tr>
</tbody>
</table>

Dependent upon EPA contract with PT provider
### 7.4 PAHs via EPA Compendium Method TO-13A

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Collection Media</strong></td>
<td>All field-collected samples and matrix quality control samples (sample media batch blank, method blank, laboratory control sample)</td>
<td>Glass cartridge containing two PUF plugs totaling 3 inches in height, 15 ± 0.5 g styrene-divinyl polymer resin, 102 to 104-mm quartz fiber filter with 2-µm pore size</td>
<td>Section 4.5.3.1</td>
<td>Operational</td>
<td>Quality measurement data with alternative media proportions as LJ</td>
</tr>
<tr>
<td><strong>Media Handling</strong></td>
<td>All field-collected samples and laboratory quality control samples</td>
<td>Field collected sample retrieval as soon as possible recommended, preferably within 24 hours, not to exceed 72 hours post-sampling Retrieved samples shipped and all field and QC samples stored refrigerated at ≤ 4°C, protected from light until extraction Damaged sampling media (e.g., leaking resin) are invalidated</td>
<td>Section 4.5.4.4</td>
<td>Critical and Operational</td>
<td>Invalidate damaged cartridges as BI Qualify samples retrieved after 72 hours at HT Qualify as LJ samples stored above 4°C after 72 hours from retrieval</td>
</tr>
<tr>
<td><strong>Sample Media Batch Blank</strong></td>
<td>Analysis of a prepared cartridge and QFF or media equivalent to a prepared cartridge (3-inch PUF plugs, 15 ± 0.5g resin sorbent, and a QFF) prior to deployment of media to demonstrate appropriate media cleanliness – for each lot of cleaned media Minimum of 1 cartridge/cartridge equivalent for each new lot of media</td>
<td>Naphthalene ≤ 200 ng/cartridge or ≤ 10% of the 5th percentile concentration for the site from the previous 3 years, whichever is higher All other individual target PAHs ≤ 10 ng/cartridge or ≤ 10% of the 5th percentile concentration for the previous three years, whichever is higher</td>
<td>Section 4.5.3.4</td>
<td>Operational</td>
<td>Qualify associated sample data as LB</td>
</tr>
</tbody>
</table>
### 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
<th>Acceptance Criteria</th>
<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling Unit Clock/Timer Check</strong></td>
<td>Verified with each sample collection event</td>
<td>Clock/timer accurate to ± 5 minutes of reference for digital timers, within ± 15 minutes for mechanical timers, set to local standard time; Sample collection period verified to be midnight to midnight</td>
<td>Table 3.3-1 and Section 4.5.4.3</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Frequency</strong></td>
<td>One sample every six days according to the EPA National Monitoring Schedule</td>
<td>Sample must be valid or a make-up sample scheduled (refer to Section 2.1.2.1)</td>
<td>Section 4.5.4.3</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Sampling Period</strong></td>
<td>All primary and collocated field-collected samples</td>
<td>1380-1500 minutes (24 ± 1 hr) starting and ending at midnight</td>
<td>Sections 2.1.1 and 4.5.4.1</td>
<td>Critical and MQO</td>
<td>Invalidate all measurement for sample as AG</td>
</tr>
<tr>
<td><strong>Sample Flow Rate</strong></td>
<td>All primary and collocated field-collected samples</td>
<td>0.140 to 0.245 m³/minute for total collection volume of 200 to 350 m³ (at standard conditions of P = 1 atm and T = 25°C)</td>
<td>Section 4.5.1</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Pre-Sample Collection Warm-up and Sample Starting Flow Measurement</strong></td>
<td>Only for sampling units without computer controlled flow</td>
<td>Minimum of five minutes (ten minutes are recommended) after sampling module installation but before sample collection</td>
<td>Section 4.5.4.2</td>
<td>Critical (starting flow rate is needed for total volume)</td>
<td>Invalidate as EC</td>
</tr>
<tr>
<td><strong>Post-Sample Collection Warm-up and Sample Ending Flow Measurement</strong></td>
<td>Only for sampling units without computer controlled flow</td>
<td>Minimum of five minutes (ten minutes are recommended) before sampling module retrieval</td>
<td>Section 4.5.4.4</td>
<td>Critical (ending flow rate is needed for total volume)</td>
<td>Invalidate as EC</td>
</tr>
</tbody>
</table>
## Parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling Unit Leak Check</strong></td>
<td>Verification that sampling flow path is leak tight Every five sample collection events, recommended with each sampling event If leak is detected, leak must be mitigated before sample collection can commence <em>(strongly recommended)</em></td>
<td>Absence of an audible whistle</td>
<td>Section 4.5.4.2</td>
<td>Practical</td>
<td>Samples with failing leak check are invalidated as AK</td>
</tr>
<tr>
<td><strong>Sample Receipt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Chain-of-custody</strong></td>
<td>All field-collected samples including field QC samples</td>
<td>Each cartridge/QFF must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation</td>
<td>Sections 3.3.1.3.7 and 4.5.4.4</td>
<td>Critical</td>
<td>Invalidate measurement data as EC</td>
</tr>
<tr>
<td><strong>Sample Holding Time</strong></td>
<td>All field-collected samples and laboratory QC samples</td>
<td>Extraction: 14 days from sample collection (cartridge storage ≤ 4 °C) Analysis: 40 days from extraction (extract storage ≤ 4 °C)</td>
<td>Section 4.5.5.2</td>
<td>Operational</td>
<td>Qualify measurement data as LJ</td>
</tr>
<tr>
<td><strong>Sample Receipt Temperature Check</strong></td>
<td>Verification of proper shipping temperature for all field-collected samples upon receipt at the laboratory Cartridge temperature ≤ 4°C or Short term shipments (shipments &lt; 4 hours from retrieval) &lt; 10°C Samples must be stored at ≤ 4°C within 72 hours of end of collection</td>
<td></td>
<td>Section 4.5.4.4</td>
<td>Operational</td>
<td>Qualify measurement data as LJ</td>
</tr>
</tbody>
</table>
### 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description and Required Frequency</th>
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<th>Reference</th>
<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MS Tuning</strong></td>
<td>Establishing and verifying the MS tune prior to ICAL and strongly recommended every 12 hours of analysis thereafter (prior to CCV). May be accomplished by analysis of 5 to 50 ng DFTPP or analysis of PFTBA. Analysis must not commence if proper MS tune cannot be demonstrated.</td>
<td>Must demonstrate appropriate tune as prescribed in the ASL SOP. May be established per manufacturer recommendations. DFTPP criteria are listed in Table 4.5-2</td>
<td>Section 4.5.5.5.2</td>
<td>Critical</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Solvent Blank (SB)</strong></td>
<td>Aliquot of solvent analyzed to demonstrate the instrument is sufficiently clean to begin analysis. Prior to ICAL and daily beginning CCV.</td>
<td>All target, surrogate, and IS compounds not qualitatively detected (signal to noise ratio ≤ 3:1)</td>
<td>Section 4.5.5.5.3</td>
<td>Operational</td>
<td>Qualify failing target PAHs as LB for analysis batch</td>
</tr>
<tr>
<td><strong>GC/MS Initial Multi-Point Calibration (ICAL)</strong></td>
<td>Minimum of 5 non-zero calibration concentration levels covering approximately 0.1 to 2.0 μg/mL. Initially, following failed CCV, following failed tune check, or when changes to the instrument affect calibration response.</td>
<td>Average RRF &lt; 30.1% and each calibration level must be within ± 30.1% of theoretical nominal For linear regression (with either a linear or quadratic fit) correlation coefficient (r) ≥ 0.995 and each calibration level within ±30.1% of theoretical nominal</td>
<td>Section 4.5.5.5.3</td>
<td>Critical for Tier I PAHs</td>
<td>Invalidate Tier I PAHs as EC</td>
</tr>
<tr>
<td><strong>Second Source Calibration Verification (SSCV)</strong></td>
<td>Second source standard prepared at the mid-range of the calibration curve, analyzed immediately after each ICAL.</td>
<td>69.9 to 130.1% recovery of theoretical nominal or RRF within ±30.1% of ICAL average RRF</td>
<td>Section 4.5.5.5.4</td>
<td>Critical for Tier I PAHs</td>
<td>Invalidate Tier I PAHs as EC</td>
</tr>
</tbody>
</table>
### 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>Mid-range standard analyzed prior to sample analysis on days when an ICAL is not performed, every 12 hours of analysis following the tuning verification, and at the conclusion of each analytical sequence</td>
<td>69.9 to 130.1% recovery of theoretical nominal or RRF within ±30.1% of ICAL average RRF</td>
<td>Section 4.5.5.5.5</td>
<td>Critical for Tier I PAHs</td>
<td>Invalidate Tier I PAHs as EC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Operational for non-Tier I PAHs</td>
<td>Qualify non-Tier I PAHs as LJ (since most recent acceptable CCV)</td>
</tr>
<tr>
<td>Method Blank (MB)</td>
<td>Unexposed PUF/resin cartridge and QFF extracted as a sample</td>
<td>All target PAHs &lt; 2x MDL</td>
<td>Section 4.5.5.5.6</td>
<td>Operational</td>
<td>Qualify failing target PAHs in the extraction batch as LB</td>
</tr>
<tr>
<td></td>
<td>One with every extraction batch of 20 or fewer field-collected samples</td>
<td></td>
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</tr>
<tr>
<td>Solvent Method Blank (SMB)</td>
<td>Aliquot of extraction solvent analyzed to ensure the solvent does not contribute target PAHs</td>
<td>All target, surrogate, and IS compounds not qualitatively detected (signal to noise ratio ≤ 3:1)</td>
<td>Section 4.5.5.5.6</td>
<td>Operational</td>
<td>Qualify failing target PAHs in the extraction batch as LB</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>Laboratory Control Sample (LCS)</td>
<td>PUF/resin cartridge and QFF spiked with known amount of target analyte at approximately the lower third of the calibration curve</td>
<td>All target PAHs 59.9 to 120.1% recovery of theoretical nominal spike</td>
<td>Section 4.5.5.5.6</td>
<td>Operational</td>
<td>Qualify failing target PAHs for samples in the extraction batch as QX and LJ</td>
</tr>
<tr>
<td></td>
<td>Minimally quarterly; recommended one with every extraction batch of 20 or fewer field-collected samples</td>
<td></td>
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</tr>
</tbody>
</table>
## 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Laboratory Control Sample Duplicate (LCSD)</td>
<td>Duplicate LCS to evaluate precision through extraction and analysis Minimally quarterly, recommended one with every extraction batch of 20 or fewer field-collected samples</td>
<td>All target PAHs 59.9 to 120.1% recovery of theoretical nominal spike Precision &lt; 20.1% RPD of LCS</td>
<td>Section 4.5.5.6</td>
<td>Operational</td>
<td>Qualify failing target PAHs for samples in the extraction batch as QX and LJ</td>
</tr>
<tr>
<td>Internal Standards</td>
<td>Deuterated isotopes of target PAHs added to every injection except beginning SB</td>
<td>50 to 200% of the area response of the mid-level ICAL standard from ICAL For failures, dilute extracts and fortify with IS to investigate matrix effect as cause of IS recovery exceedance</td>
<td>Section 4.5.5.8</td>
<td>Operational</td>
<td>Qualify measurement data for affected samples as LJ</td>
</tr>
<tr>
<td>Field Surrogate Compounds</td>
<td>Deuterated isotopes of target PAHs added to each cartridge before field deployment, also added to cartridges for laboratory and field QC</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal</td>
<td>Sections 4.5.5.1.5.1 and 4.5.5.5.9</td>
<td>Operational</td>
<td>Qualify associated measurement data as LL (low recovery) or LK (high recovery)</td>
</tr>
<tr>
<td>Extraction Surrogate Compounds</td>
<td>Deuterated isotopes of target PAHs added at the time of extraction to each extracted field sample, field QC sample, and laboratory QC sample</td>
<td>Recovery 59.9 to 120.1% of theoretical nominal</td>
<td>Sections 4.5.5.1.5.2 and 4.5.5.5.9</td>
<td>Operational</td>
<td>Qualify associated measurement data as LL (low recovery) or LK (high recovery)</td>
</tr>
<tr>
<td>Retention Time (RT)</td>
<td>Every injection</td>
<td>Target and surrogate compound RT within ± 10 seconds of the mid-level ICAL standard or most recent CCV Internal standard RT within ± 20 seconds of the mean ICAL RT</td>
<td>Sections 4.5.5.5.7 and 4.5.5.5.8</td>
<td>N/A – see compound identification</td>
<td>NA</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Required Frequency</td>
<td>Acceptance Criteria</td>
<td>Reference</td>
<td>Category</td>
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</tr>
<tr>
<td>Replicate Analysis</td>
<td>A single additional analysis of a field-collected sample extract</td>
<td>Precision &lt; 10.1% RPD for samples for which at least one of the replicate concentrations is ≥ 0.5 µg/mL</td>
<td>Sections 2.1.3.1 and 4.5.5.5.6</td>
<td>Operational</td>
<td>Qualify associated data in analysis batch as QX and LJ</td>
</tr>
<tr>
<td></td>
<td>Once with every analysis sequence of 20 or fewer field-collected samples (as required by QAPP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Blank</td>
<td>Assembled blank sample cartridge/QFF module installed in sampling unit for minimally five minutes</td>
<td>All target PAHs ≤ 3x MDL</td>
<td>Section 4.5.4.5</td>
<td>Operational</td>
<td>Qualify measurement data for affected sites since last acceptable FB as FB</td>
</tr>
<tr>
<td></td>
<td>Minimally monthly</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collocated Sample Collection</td>
<td>Field sample co-collected with a separate sampling unit between 2 and 4 meters from primary sampling unit</td>
<td>Precision &lt; 20.1% RPD of co-collected primary sample for target analytes for which at least one of the precision pair is ≥ 0.5 µg/mL</td>
<td>Sections 2.1.3.1 and 4.5.4.6</td>
<td>Operational</td>
<td>Qualify both the primary and collocated measurement data as LJ and QX</td>
</tr>
<tr>
<td></td>
<td>10% of primary samples for sites performing collocated sample collection (as required by workplan)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound Identification</td>
<td>Qualitative identification of each target PAH in each standard, blank, QC sample, and field-collected sample (including field QC samples)</td>
<td>Signal-to-noise ≥ 3:1</td>
<td>Section 4.5.5.5.7</td>
<td>Operational</td>
<td>Report target analytes not meeting criteria as concentration of 0 and qualify as ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RT within ±10 seconds of mid-level ICAL standard or most recent CCV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>At least one qualifier ion relative abundance within ±15% of mean relative abundance from the ICAL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peak apexes co-maximized (within one scan for quadrupole MS) for quantitation and qualifier ions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameter</td>
<td>Description and Required Frequency</td>
<td>Acceptance Criteria</td>
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<td>Data Reporting Impact</td>
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</tr>
<tr>
<td>Proficiency Testing</td>
<td>Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year(^1)</td>
<td>Each target compound within ± 25.1% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.</td>
<td>Section 2.1.4.1</td>
<td>MQO</td>
<td>After two consecutive failed PTs for a given carbonyl, qualify data as LL (low bias), or LK (high bias) as appropriate</td>
</tr>
<tr>
<td>Method Detection Limit</td>
<td>Determined initially and verified minimally every 13 months thereafter for each target carbonyl. When method changes are made that alter instrument sensitivity, initial MDL must be redetermined.</td>
<td>MDL determined via 4.1 must be ≤ those listed in Table 4.1-1. These MDL MQOs current as of April 2022. Refer to current workplan template for up-to-date MQOs.</td>
<td>Sections 4.1 and 4.5.5.4</td>
<td>MQO</td>
<td>NA</td>
</tr>
<tr>
<td>Stock Standard Materials</td>
<td>Purchased stock materials for each target PAH for both primary calibration and second source calibration verification</td>
<td>Certified and accompanied by certificate of analysis</td>
<td>Sections 4.5.5.1.2 and 4.5.5.1.3</td>
<td>Operational</td>
<td>NA</td>
</tr>
<tr>
<td>Working Standard Solutions</td>
<td>Storage of all working standards Analyze standards stored improperly against standards of known proper integrity. Must be &lt; ± 15.1%</td>
<td>Stored at ≤ -10°C, protected from light</td>
<td>Section 4.5.5.2</td>
<td>Critical</td>
<td>Invalidate data as EC</td>
</tr>
</tbody>
</table>
### 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

<table>
<thead>
<tr>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling Unit Testing and Maintenance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
| Field Sampler Flow Rate Calibration and Calibration Verification | Calibration of sampling unit flow controller  
Prior to field deployment and verified quarterly (recommended monthly).  
Calibration re-established following failure of flow calibration verification  
Flow rates calibrated at EPA standard conditions of 760 mmHg and 25°C | Flow set to match a certified flow transfer standard and verified to be within ±10.1% | Table 3.3-1 and 4.5.2.1 | Critical | Invalidate data back to the most recent passing calibration or calibration verification as AH |
| **Site Specifications and Maintenance** | | | | | |
| Sampling Unit Siting | Verify conformance to requirements  
Annually | 270° unobstructed probe inlet  
Inlet 2-15 meters above-ground level  
≥ 10 meters from drip line of nearest tree  
Collocated sampling inlets measured at nearest edges, spaced 2-4 meters horizontally and within 3 meters vertically from primary sampling unit inlet | Section 2.4 | Operational | Qualify affected data as SX |
| **Data Reporting** | | | | | |
| Data Reporting to AQS | Reporting of all results a given calendar quarter  
Quarterly, within 180 days of end of calendar quarter | Measurements for target PAHs for field collected samples. Concentrations for all detected target PAHs are to be reported, including those less than MDL  
All data must be in standard conditions volumes  
Field QC sample and laboratory replicates must also be reported (as prescribed in workplan) | Section 3.3.1.3.15 | Operational | NA |
| AQS Reporting Units | Units must be as specified  
With each quarterly submission to AQS | mass/volume (ng/m³ or µg/m³) at EPA standard conditions of 760 mmHg and 25°C | Section 3.3.1.3.15 | Critical (does not invalidate data) | NA |
### 7.4 PAHs via EPA Compendium Method TO-13A (Continued)

<table>
<thead>
<tr>
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<th>Category</th>
<th>Data Reporting Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Completeness</td>
<td>Valid samples compared to scheduled samples &lt;br&gt; Annually</td>
<td>≥ 85% of scheduled samples</td>
<td>Section 3.2</td>
<td>MQO</td>
<td>NA</td>
</tr>
</tbody>
</table>

1 Dependent upon EPA contract with PT provider
APPENDIX A

FINAL REPORT

ON

ANALYSIS, DEVELOPMENT, AND UPDATE OF THE NATIONAL AIR TOXICS TRENDS STATIONS (NATTS) NETWORK PROGRAM-LEVEL DATA QUALITY OBJECTIVE (DQO) AND ASSOCIATED METHOD QUALITY OBJECTIVES (MQOS)

JUNE 13, 2013
The June 13, 2013 Analysis, Development, and Update of the National Air Toxics Trends Stations (NATTS) Network Program-Level Data Quality Objective (DQO) and Associated Method Quality Objectives (MQOs) Final Report was removed from the TAD and is available on the NATTS area of EPA’s AMTIC site at the following URL (accessed June 2022):

https://www.epa.gov/sites/default/files/2021-03/documents/nattsdqo20130613.pdf
APPENDIX B

NATTS AQS REPORTING GUIDANCE FOR AMBIENT AIR DATA INCLUDING QUALITY ASSURANCE SAMPLES

BLANKS AND PRECISION SAMPLES (COLLOCATED, DUPLICATE, AND REPLICATE REPORTING)
NATTS Pollutant Data Reporting to AQS

NATTS monitoring agencies and associated ASLs will ensure pollutant data are reported to AQS within 180 days of the end of the calendar quarter in which the sampling date occurred. Coding and reporting of meteorological parameter data is outside the scope of this guidance. EPA may update conventions for data reporting to AQS; therefore, users of this document should be aware that the information herein was current as of the publication date.

Staff inputting data into AQS should be familiar with the AQS data input operations and coding, as the audience for this guidance section is intended for users with such experience. Specifically, the coding of data for AQS reporting is performed by creating transactions consisting of a string of characters starting on the left end with a code describing the transaction type. Reporting of data using XML format is outside the scope of this guidance. The required and optional fields for each transaction type are described in the AQS coding manual (which available online as an interactive resource):


Additional guidance on types of AQS transactions formats, querying reports, and data dictionaries can be found on EPA’s AQS Manuals and Guides website:

https://www.epa.gov/aqs/aqs-manuals-and-guides

Monitoring agencies and/or ASLs are to report measurement data for the NATTS Program for measurements for routine primary samples, collocated samples, duplicate samples, and replicate measurements. Additionally, data for field blanks (FBs) are also to be reported to AQS.

Monitoring agencies and/or ASLs should report data for lot blanks to AQS and may report data for trip blanks (TBs), exposure blanks (EBs), and laboratory method blanks (MBs).

Routine primary sampling data and collocated sampling data are reported to AQS with raw data (RD) transactions. Duplicate sampling data and replicate analysis data are reported with quality assurance (QA) transactions. Blanks (lot blanks, FBs, TBs, EBs, and MBs) are reported with raw blank (RB) transactions.

I. GENERAL CODING INFORMATION

Successful upload of data to AQS requires that the coding is performed properly or data input transactions will be rejected. AQS will provide a report after attempted upload detailing individual transactions that were rejected and the reason for rejection.

To ensure that data are input successfully, measurement data coding requires the following:
The AIRS code must be correct and exist in AQS as an established site. This includes the state/tribal indicator (XX), the county code/tribal code (YYY), and site number (ZZZZ). This is the AQS site ID of the following format: XX-YYY-ZZZZ

- The sampling unit, or “monitor,” must be established in AQS and the monitoring begin and ending date (the ending date is not required until a monitor is decommissioned) must temporally bracket sampling dates for data to be reported.

- Each monitor will have a parameter occurrence code (POC) assigned uniquely for the parameter. Each primary and collocated monitor will need a unique POC for the parameter.

- The parameter code, method code, sample duration code, and units must be compatible, i.e., a combination that AQS accepts as valid (e.g., reporting minutes [unit code 106] of benzene [parameter code 45201] by Magee Aethalometer [Method code 864] is not an appropriate combination), or AQS will reject data inputs that do not comply with established business rules.

The AQS transaction formatting descriptions are not repeated in this document. Please refer to the AQS coding manual available on EPA’s web server: (accessed June 2022):


II. ADDITION OF QUALIFIERS

Coding of the RD, RB, and QA transactions is straightforward as defined in the AQS coding manual. Qualifiers can be appended to measurement data to label data with an indication that there was something exceptional about the data collection, but for these 3 transaction types, qualifiers can only be added to RD transactions (currently). Unfortunately, this does not permit the communication channels for RB and QA transactions to indicate data collected under unusual circumstances.

Qualifiers that may be appended to RD Transactions for the NATTS Program include QA Qualifiers, Inform Qualifiers, and Null Data Qualifiers. A combination of up to 10 total QA Qualifiers and Inform Qualifiers can be appended to a single RD transaction. Only one Null Data Qualifier may be appended and it eliminates any appended QA Qualifiers or Inform Qualifiers (AQS will not store the included QA or Inform qualifiers if included in the reported string).

- Quality Assurance (QA) Qualifiers: Descriptive codes added to reported data to describe data collected under unusual circumstances.
- Inform Qualifiers: Descriptive codes added to reported data to describe data that were collected under unusual environmental circumstances
- Null Data Qualifiers: Descriptive codes added to a transaction to indicate why a scheduled sample or measurement was not collected.
III. CODING PRIMARY MONITOR DATA FOR AQS

Coding of primary sampling data requires that the monitor is defined in AQS with an MO transaction and subsequent reporting of measurement data using an RD transaction.

For a primary sample, the monitor must be identified in AQS as the primary monitor using the MO transaction. The following is an example MO transaction for a primary monitor at AQS site ID 11-222-3333, parameter 44444, POC 5, begin date January 1, 2021:

```
MO|I|11|222|3333|44444|5|20210101||
```

Once defined in AQS as the primary monitor, the RD transaction can be created. The following is an example RD transaction for the above primary monitor for a measurement of 0.22 ppb of parameter 44444 for a 24-hour sample with the primary monitor by method 171, collected every 6 days, with a contaminated field blank, with an MDL of 0.11 ppb:

```
RD|I|11|222|3333|44444|5|7|008|171|20210105|00:00|0.22||6|FB|||||||0.11|
```

IV. CODING QUALITY ASSURANCE DATA

A. Blank Sample Reporting

Blank samples that may be reported to AQS for the NATTS program consist of field blanks (FBs), trip blanks (TBs), lot blanks (LBs), laboratory method blanks (MBs), and exposure blanks (EBs). Monitoring agencies are required to report FB, TB, and LB data to AQS. Optionally, monitoring agencies may also report laboratory MBs and EBs.

To report blank data, submit a raw blank (RB) transaction for each blank sample. The Blank Type for the various blanks are:

- Field blank: FIELD
- Trip blank: TRIP
- Lot blank: LOT
- Laboratory Method Blank: LAB
- Exposure Blank: FIELD 24HR

(a) (AQS guidance no longer lists this option but may still accept this blank type in reported data)

To create an RB transaction for a field blank, the Blank Type field is entered as “FIELD” (bold below) as in the following example:

```
RB|I|11|222|3333|44444|9|7|454|888|FIELD|20150101|00:00|0.0463|||0.0001|
```

B. Precision Data Reporting

Precision data measurements in the NATTS program to be reported to AQS consist of the following:
- Collocated Sampling – Sample collected through an inlet probe to the ambient atmosphere separate from the co-collected primary sample
- Duplicate Sampling – Sample collected through a common inlet probe with the co-collected primary sample
- Replicate Analysis – repeat analysis of a prepared sample (e.g., sample digestate, sample extract, or sample canister)

<table>
<thead>
<tr>
<th>Precision Data Type</th>
<th>AQS Transaction</th>
<th>Qualifiers Permitted?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collocated Sample</td>
<td>RD</td>
<td>yes</td>
</tr>
<tr>
<td>Duplicate Sample</td>
<td>QA - Duplicate</td>
<td>no</td>
</tr>
<tr>
<td>Replicate Analysis</td>
<td>QA – Replicate</td>
<td>no</td>
</tr>
</tbody>
</table>

Simplified schematics are included in this article for illustrative purposes and do not address specifics related to different sampling approaches or methodologies. For each

As indicated above in Section II, QA transactions for AQS do not permit the addition of qualifiers to the data strings. Therefore, when QA data are to be invalidated, substitute the measurement value with -999 to indicate that the measurement was made but that the QA measurement does not meet acceptance criteria.

For example, if a duplicate sample analysis resulted in invalidation of one of the measurements and the other was 0.987 ppb, the following QA Duplicate string would be prepared:

`QA|I|Duplicate|333|11|222|3333|44444|5|20210101|1|454|008|0.987|-999|||`
Collocated Samples

Collocated samples are samples collected simultaneously at the same location using two completely separate sampling systems, each with a separate inlet probe to the ambient sampled atmosphere. The allowable distance between inlet probes is defined in regulations or in program guidance. Both of the monitors (each designated by a separate AQS Parameter Occurrence Code - POCs) have been established in AQS already. The samples are collected and analyzed separately. Each is reported as a sample value for the appropriate monitor.

Schematic

![Collocated Samples Diagram](image)

Collocated Sample Reporting Instructions

For AQS to automatically create the ‘precision pair’ for the primary and collocated samples, the monitors must be identified to the system as QA collocated. One monitor must be designated as the QA primary. If using transactions, the Monitor Collocation Period (MJ) transaction is used. (If using the AQS application, the “QA Collocation” tab on the Maintain Monitor form may be used to enter these data). The collocation data must be entered for both monitors, with one indicated as the primary, and the other indicated as the collocated (not the primary). In the example below, the primary monitor is indicated by the bolded ‘Y’ (yes, this is the primary) in the Primary Sampler Indicator in the first MJ string and the collocated monitor by the bolded ‘N’ (no, this is not the primary) in the Primary Sampler Indicator in the second MJ string.

Once the monitors have been identified as collocated this is done, there are no additional reporting requirements; simply report the raw data from each monitor (From the schematic, value ‘a’ from the primary monitor ‘N’ and value ‘b’ from the collocated monitor ‘C’). Once this is done, AQS will know to pair data from these two monitors for the date range specified.

A set of transactions must be created for each time period the monitors are operating together. The transactions have a begin date and end date for the operational period. The end date may be left blank if the collocation period is still active (as indicated in the example below). To define a collocation, submit two MJ transactions (example below with differences bolded and where primary monitor ‘N’ is POC 5 and collocated monitor ‘C’ is POC 9):
Report two Raw Data (RD) transactions for each time sample data are to be reported from both monitors; one for each monitor (POC). (In this example, sample ‘a’ is 0.0463 from monitor ‘N’ (POC 5) and sample ‘b’ from monitor ‘C’ (POC 9) is 0.0458):

Since there are two monitors involved, each sample is reported for its appropriate POC and there will be an RD transaction for every time there is a valid sample from each monitor (e.g., two per day in this scenario). If the sample value from one POC is not available, report a null data code for that monitor (that is, do not report the sample value from the collocated monitor as being from the primary POC).

**Duplicate Samples**

Duplicate samples are two (or more) samples collected simultaneously using one or more sampling units sharing a common inlet probe to the ambient atmosphere and the collected samples are analyzed separately. This simultaneous collection may be accomplished by “teeing” the line from the flow control device (sampling unit) to the media (e.g. canisters), and then doubling the collection flow rate, or may be accomplished by collecting one discrete sample via two separate flow control devices (sampling units) connected to the same inlet probe.

**Schematic**

![Duplicate Samples Diagram](image-url)
Duplicate Sample Reporting Instructions

In this case, there is only one inlet probe involved but with multiple samples. Since only one inlet probe is involved, all data should be reported for the same POC.

First, report the raw data for the primary monitor as you normally would via the RD transaction. Report just one value, the one for the sample obtained through the ‘primary’ hardware (the normal flow path or normal canister, etc. as defined by the monitoring organization convention – typically this would be sample ‘a’). In this case, if sample ‘a’ comes from the primary hardware and has a value of 54.956, you would report:

RD|I|11|222|3333|44444|5|7|454|888|20150101|00:00|54.956|6|0.0001|0.0005

If the primary value is invalidated (with a Null qualifier), the duplicate value may be reported as the sample value for this POC in the RD transaction. In this case, there is not a valid duplicate assessment to report. If both duplicates are invalidated, an RD transaction with no sample measurement value and a Null data code should be reported.

Each of the duplicate sample values is reported via the QA – Duplicate transaction. This transaction has room for up to 5 duplicate sample values. As above, for any measurement that has been invalidated, report -999 to indicate the measurement was invalid. Report the measurements in any order, starting with 1 and proceeding through the number of samples. In the schematic, there are two samples (a ‘primary’ and a ‘duplicate’) so sample value ‘a’ would be reported as Duplicate Value 1 and sample value ‘b’ would be reported as Duplicate Value 2. The same value reported on the Raw Data transaction must be one of the values reported on the QA – Duplicate transaction.

Note that there is no sampling time reported on the QA – Duplicate transaction. Instead, there is an Assessment Date and an Assessment Number. If multiple duplicate samples are performed on the same day, label the first with Assessment Number = 1, the second with Assessment Number = 2, and so on. Also note that all values must be reported in the same units of measure.

Here is an example QA – Duplicate transaction (with sample ‘a’ = 54.956 and sample ‘b’ = 51.443 – Assessment Number ‘1’ bolded):

QA|I|Duplicate|999|11|222|3333|44444|5|20150101|1|454|888|54.956|51.443|
Replicate Analysis

A replicate assessment is a separate analysis or multiple separate analyses of one discrete sample (VOCs) or prepared sample (a sample extract [carbonyls or PAHs] or digestate [PM$_{10}$ metals]) to yield multiple measurements from the same sample.

Schematic

Replicate Sample Reporting Instructions

Again in this case, there is only one AQS monitor (POC) involved and one single sample, however multiple analyses of the sample.

First, report the raw data as you normally would via an RD transaction. Report just one value, according to your laboratory’s convention for reporting replicate data (e.g. the first replicate). In this case, if you have chosen replicate ‘a’ as your raw data value and it has a value of 0.844, you would report:

```
RD|I|11|222|3333|44444|5|7|454|888|20150101|00:00|0.844||6|1|1|1|1|1|1|1|1|1|0.0001|0.0005
```

If the normally reported value is invalidated (null) for some reason, one of the other replicate values must be reported as the sample value for this POC in the RD transaction. If all replicates are invalidated (null), an RD transaction with no sample value and a null qualifier is to be reported for primary and collocated samples. Duplicate sample reporting is to be addressed as listed above under Duplicate sample reporting.

Once the RD transaction is completed, the replicate data are reported via the QA – Replicate transaction. This transaction has room for up to 5 replicate sample values. Report valid replicate measurements as measured and invalidated replicate measurements as -999. Report the replicates in any order, starting with 1 and proceeding through the number of samples. In the schematic above there are three replicates ‘a’, ‘b’, and ‘c’, thus analytical value ‘a’ would be reported as Replicate Value 1, analytical value ‘b’ would be reported as Replicate Value 2, and analytical value ‘c’ would be reported as Replicate Value 3.
Note that there is no sampling time reported on this transaction. Instead, there is an Assessment Date and an Assessment Number. If multiple replicate samples are collected on the same day, label the first with Assessment Number = 1 (indicated below in bold), the second with Assessment Number = 2, and so on. Also note that all values must be reported in the same units of measure.

Here is a sample QA – Replicate transaction (if sample values ‘a’, ‘b’, and ‘c’ are 0.844, 0.843, and invalidated, respectively):

<table>
<thead>
<tr>
<th>QA</th>
<th>I</th>
<th>Replicate</th>
<th>999</th>
<th>11</th>
<th>222</th>
<th>333</th>
<th>44444</th>
<th>5</th>
<th>20210101</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.844</td>
<td>0.843</td>
<td>-999</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Combining Duplicates and Replicate Analysis

It is possible to collect duplicate samples simultaneously and perform replicate analyses of these duplicate samples. This is often referred to as a duplicate/replicate sample. In this case (see schematic below), there are two duplicate samples, ‘1’ and ‘2’. Duplicate Sample ‘1’ has three replicates: ‘a’, ‘b’, and ‘c’. Duplicate Sample ‘2’ has three replicates: ‘d’, ‘e’, and ‘f’.

Schematic

**Duplicate/Replicate Reporting Instructions**

This scenario requires the reporting of an RD transaction, a QA – Duplicate transaction, and a QA – Replicate transaction to AQS.

For the RD transaction, follow the same rules to report the value from the primary (normal) hardware (this would typically be sample ‘1’, replicate ‘a’) and operations procedure path if possible; follow the convention established by the laboratory based on the guidance above if measurements are invalidated (e.g., reporting the valid measurement for the RD transaction). If the normal hardware path yields sample ‘1a’ you would report (in this case the value is represented by the “a” in the appropriate place, with spaces for clarity):

| RD | I | 11 | 222 | 3333 | 44444 | 5 | 7 | 454 | 888 | 20150101 | 00:00 | a | 6 | 0.0001 | 0.0005 |
|----|---|----|-----|------|--------|---|---|----|-----|------|--------|---|   |      |        |
For the QA - Duplicate transaction: select one of the replicate analyses each from the primary and duplicate sample (using the convention established by the laboratory) and report those on the QA – Duplicate transaction. If the values to be reported are ‘1a’ and ‘2d’, the record would look like this (again, values are represented by ‘a’ and ‘d’, spaces added for clarity):

<table>
<thead>
<tr>
<th>QA</th>
<th>I</th>
<th>Duplicate</th>
<th>999</th>
<th>11</th>
<th>222</th>
<th>333</th>
<th>44444</th>
<th>5</th>
<th>20210101</th>
<th>1</th>
<th>454</th>
<th>888</th>
<th>a</th>
<th>d</th>
</tr>
</thead>
</table>

There are only two duplicate samples (one pair) in this case because only two paths were assessed. (That is, you are not allowed to cross-multiply the replicate analyses to create additional duplicate assessments [pairs].)

For the replicate transaction: report this as two assessments. Assessment Number 1 for the day would include the values for replicates ‘a’, ‘b’, and ‘c’. Assessment Number 2 for the day would include values for replicates ‘d’, ‘e’, and ‘f’.

The example transactions, using letters in place of the values:

<table>
<thead>
<tr>
<th>QA</th>
<th>I</th>
<th>Replicate</th>
<th>999</th>
<th>11</th>
<th>222</th>
<th>333</th>
<th>44444</th>
<th>5</th>
<th>20210101</th>
<th>1</th>
<th>454</th>
<th>888</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA</td>
<td>I</td>
<td>Replicate</td>
<td>999</td>
<td>11</td>
<td>222</td>
<td>333</td>
<td>44444</td>
<td>5</td>
<td>20210101</td>
<td>2</td>
<td>454</td>
<td>888</td>
<td>d</td>
<td>e</td>
<td>f</td>
</tr>
</tbody>
</table>

When any of the duplicate or replicate measurements above are invalid, report those measurements as -999 in the QA Duplicate and QA Replicate transactions.

**Combining Collocated Samples and Replicate Analysis**

It is also possible to make replicate analyses of collocated samples. These are sometimes referred to as collocated replicate samples.

**Schematic**

<table>
<thead>
<tr>
<th>Collocated Replicate Samples</th>
<th>It is also possible to make replicate analyses of collocated samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>Two completely separate sampling systems, two different samples analyzed multiple times.</td>
</tr>
</tbody>
</table>

**Collocated Replicate Reporting Instructions**

Since collocated monitors report all data independently, report these data for each monitor (e.g., under its own POC) according to the replicate reporting instructions.
APPENDIX C

EPA ROUNDED GUIDANCE

Provided by EPA Region IV
Rounding Policy for Evaluating NAAQS QA/QC Acceptance Criteria

The following outlines EPA’s Rounding Policy for evaluating Quality Assurance / Quality Control (QA/QC) acceptance criteria. This policy is being provided to air monitoring organizations in order to ensure consistency across the country in the validation of monitoring data that is used for demonstrating compliance with the National Ambient Air Quality Standards (NAAQS).

EPA’s interpretation of standard rounding conventions is that the resolution of the measurement device or instrument determines the significant figures used for rounding. The acceptance criteria promulgated in the appendices of 40 CFR Part 50, or otherwise established in EPA guidance documents, are not physical measurements. As an example, the quality control (QC) acceptance criterion of ±5% stated in the fine particulate matter regulations (40 CFR Part 50, Appendix L, Section 7.4.3.1) is not a measurement and, as such, does not directly contribute to either the significant figures or to rounding. However, the flow rate of the sampler – measured either internally by the flow rate control system or externally with a flow rate audit standard – is a measurement, and as such, will contribute to the significant figures and rounding. EPA’s position is that it is not acceptable to adjust or modify acceptance criteria through rounding or other means.

Example using PM$_{2.5}$ Sampler Design Flow Rate

40 CFR Part 50, Appendix L, Section 7.4.3.1 defines the 24-hour sample flow rate acceptance criterion as ±5% of the design flow rate of the sampler (16.67 liters per minute, LPM). The QC acceptance criterion of ±5% stated in regulation is not a measurement and, therefore, does not contribute towards significant figures or rounding. The measurement in this example is the flow rate of the sampler. PM$_{2.5}$ samplers display flow rate measurements to the hundredths place (resolution) – e.g., 16.67 LPM, which has 4 significant figures. Multiplying the design flow rate (16.67 LPM) by the ±5% acceptance criterion defines the acceptable flow regime for the sampler. By maintaining 4 significant figures – with values greater than 5 rounding up – the computations provide the following results:

- The low range is -5% of the design flow: $0.95 \times 16.67 = 15.8365 \approx 15.84$
- The upper range is +5% of the design flow: $1.05 \times 16.67 = 17.5035 \approx 17.50$

Rounding in this manner, the lower and upper acceptance limits for the flow rate measurement are defined as 15.84 and 17.50 LPM, respectively.

40 CFR Part 58, Appendix A, Section 3.2.1 requires monthly PM$_{2.5}$ flow rate verifications. The verification is completed with an independent audit standard (flow device). The monthly check includes a calculation to ensure the flow rate falls within ±5% of the design flow rate (see
Method 2.12, Section 7.4.7). Therefore, flow rates obtained during monthly flow rate verification checks should measure between 15.84 – 17.50 LPM, as defined above.

Measurements, in general, are approximate numbers and contain some degree of error at the outset; therefore, care must be taken to avoid introducing additional error into the final results. With regards to the PM$_{2.5}$ sampler’s design flow rate, it is not acceptable to round the ±5% acceptance criterion such that any calculated percent difference up to ±5.4% is acceptable – because rounding the acceptance criterion increases the error in the measurement. It is important to note that the PM$_{2.5}$ sampler must maintain a volumetric flow rate of approximately 16.67 LPM in order for its inertial separators to appropriately fractionate the collected ambient air particles. Flow rates greater than 5% of the nominal 16.67 LPM will shift the cut point of the inertial separator lower than the required aerodynamic diameter of 2.5 microns and, thus, block the larger fraction of the PM$_{2.5}$ sample from being collected on the sample filter. Conversely, as the sampler’s flow rate drops below -5% of the nominal 16.67 LPM, the inertial separator will allow particulate matter with aerodynamic diameters unacceptably larger than 2.5 microns to be passed to the sample filter. Therefore, it is imperative that the flow rate of the sampler fall within the ±5% acceptance criterion.

**A Note on Resolution and Rounding**

Measurement devices will display their measurements to varying degrees of resolution. For example, some flow rate devices may show measurements to tenths place resolution, whereas others may show measurements to the hundredths place. The same holds true for thermometers, barometers, and other instruments. With this in mind, rounding should be based on the measurement having the least number of significant figures. For example, if a low-volume PM$_{10}$ sampler displays flow rate measurements to the tenths place (3 significant figures), but is audited with a flow device that displays measurements to the hundredths place (4 significant figures), the rounding in this scenario will be kept to 3 significant figures.

Table 1 below lists some examples of NAAQS regulatory QA/QC acceptance criteria with EPA’s interpretation of the allowable acceptance ranges, as well as a column that identifies results that exceed the stated acceptance limits. Table 1 is not a comprehensive list of ambient air monitoring QA/QC acceptance criteria. Rather, Table 1 is provided to demonstrate how EPA evaluates acceptance criteria with respect to measurement resolution.

The validation templates in the QA Handbook Vol II will be revised to meet this policy.

If you have any questions regarding this policy or the rounding conventions described, please contact your EPA Regional Office for assistance.
### Table 1: Examples of Quality Control Acceptance Criteria

<table>
<thead>
<tr>
<th>Regulatory Method Requirement</th>
<th>Method Acceptance Criteria</th>
<th>Typical Measurement Resolution</th>
<th>Acceptance Range (Passing Results)</th>
<th>Exceeding QA/QC Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shelter Temperature</td>
<td>20 to 30°C or FEM op. range</td>
<td>1 Decimal, 3 SF*</td>
<td>20.0 to 30.0°C or FEM op. range</td>
<td>≤ 19.9°C, ≥ 30.1°C</td>
</tr>
<tr>
<td>PM2.5 Design Flow (16.67 lpm)</td>
<td>±5%</td>
<td>2 Decimal, 4 SF</td>
<td>15.84 to 17.50 lpm</td>
<td>≤ -5.1%, ≥ +5.1%</td>
</tr>
<tr>
<td>PM2.5 Transfer Standard Tolerance</td>
<td>±4%</td>
<td>2 Decimal, 4 SF</td>
<td>Refer to Table 2 below</td>
<td>≤ -4.1%, ≥ +4.1%</td>
</tr>
<tr>
<td>PM2.5 Lab: Mean Temp 24-hr Mean</td>
<td>20 to 23°C</td>
<td>1 Decimal, 3 SF</td>
<td>20.0 to 23.0°C</td>
<td>≤ 19.9°C, ≥ 23.1°C</td>
</tr>
<tr>
<td>PM2.5 Lab: Temp Control SD over 24-hr Mean</td>
<td>±2°C</td>
<td>1 Decimal, 3 SF</td>
<td>±2.0°C</td>
<td>≤ -2.1°C, ≥ +2.1°C</td>
</tr>
<tr>
<td>PM2.5 Lab: Mean RH 24-hr Mean</td>
<td>30% to 40%</td>
<td>1 Decimal, 3 SF</td>
<td>30.0% to 40.0%</td>
<td>≤ 29.9%, ≥ 40.1%</td>
</tr>
<tr>
<td>PM2.5 Lab: RH Control SD over 24-hr Mean</td>
<td>±5%</td>
<td>1 Decimal, 3 SF</td>
<td>±5.0%</td>
<td>≤ -5.1%, ≥ +5.1%</td>
</tr>
<tr>
<td>PM2.5 Lab: Difference in 24-hr RH Means</td>
<td>±5%</td>
<td>1 Decimal, 3 SF</td>
<td>±5.0%</td>
<td>≤ -5.1%, ≥ +5.1%</td>
</tr>
</tbody>
</table>

*SF = Significant Figures

### Table 2: PM2.5 Transfer Standard Tolerance

<table>
<thead>
<tr>
<th>-4% Audit Std (lpm)</th>
<th>Sampler Display (lpm)</th>
<th>+4% Audit Std (lpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>15.84</td>
<td>16.47</td>
</tr>
<tr>
<td>16.00</td>
<td>16.67</td>
<td>17.34</td>
</tr>
<tr>
<td>16.80</td>
<td>17.50</td>
<td>NA</td>
</tr>
</tbody>
</table>
APPENDIX D

BASICS OF CHROMATOGRAPHY
This appendix is intended to assist the gas chromatograph (GC) or high performance liquid chromatography (HPLC) analyst in understanding basic terms and concepts of chromatography as well as proper techniques for data interpretation and processing. It is not meant as an in-depth discussion of chromatographic principles and theory, for which there are numerous available resources.

1. Basic Chromatography Theory

   Briefly, a GC or HPLC separates the substances in an injected sample mixture within a separation column containing a stationary phase which inhibits the substances to be separated as they are carried through the separation column by a mobile phase at a constant rate. The mobile phase does not react with the substances to be separated - a carrier gas for GC and a liquid mobile phase for HPLC. The introduced substances are separated within the column based on their affinity for the stationary phase, and at the end of the column exit, or elute, to a detector – for NATTS work, the HPLC detector will typically be a UV-vis detector and for GC will be a mass spectrometer (MS). For GC separation, the column is contained within an oven to control the temperature of the separation. For HPLC, the column is typically held within a column heater at isothermal conditions. Typically, the GC oven containing the column is heated according to a temperature program to decrease the time it takes for later eluting substances and shorten the overall GC run time. The detector responds to the substance in proportion to the amount (i.e., mass) of substance as a function of time and the detector response and associated time since injection are continually recorded by the data system to prepare a chromatogram.

2. Anatomy of a Chromatogram

   A chromatogram is a plot of the detector response as a function of time for a single injection on the GC or HPLC. The detector response (on the y-axis or ordinate) is typically displayed in units of millivolts (mV), picoamperes (pA), counts per second (cps), or other relevant unit indicative of an electric or electronic change within the detector. Time (on the x-axis or abscissa) is displayed in minutes or seconds which starts at the injection time (the time the sample was injected onto the separation column). There will typically be a time delay for beginning data collection (acquisition) on a chromatogram such that the detector response recording begins just prior to the elution of the first expected target substance. Refer to Figure D-1 for a detailed example chromatogram illustrating basic chromatogram components.
3. Basic Chromatography Terminology

The following basic descriptions correlate to aspects of chromatography and/or chromatograms for which instrument operators must be familiar.

**Baseline:** The detector response to the mobile phase in the absence of a substance (refer to Figure D-1). The baseline should be sufficiently free from noise. Baselines will typically exhibit some level of electronic noise as shown below in Figure D-2. While baseline anomalies, such as dips, rises, or spikes, are common, they may interfere with proper data processing.

**Chromatographic Peak:** The increase and subsequent decrease of the detector response as a substance elutes from the separation column (refer to Figure D-1). Chromatographic peaks for a
single substance are ideally normal Gaussian in profile shape where the peak starts at the baseline, increases to the apex, and decreases to return back to the baseline (refer to Figure D-3). It is common for peaks to be malformed, exhibiting asymmetry.

![Figure D-3. Example Chromatogram Detailing Peak Apex and Baseline](image)

**Coelution:** Simultaneous elution from the separation column of two or more substances resulting in overlapping of their chromatographic peaks where the detector response does not return to baseline between the substances (refer to Figure D-1). Coelutions for which one of the substances is of much smaller magnitude may show as peak shoulders or “riders” (refer to Figure D-4).

![Figure D-4. Chromatogram Showing Three Coeluting Substances (A) and Approximate Reconstruction of the Individual Peaks (B)](image)

**Retention Time (RT):** The time relative to the time of injection that a substance elutes from the column (refer to Figure D-1). The RT is defined at the peak apex (refer to Figure D-3).

**Retention Window:** The range of time in the separation program during which a target analyte is expected to elute (refer to Figure D-1). The instrument operator defines the retention window for a given substance.

**Resolution:** The extent to which the detector response returns to the baseline between chromatographic peaks (refer to Figure D-1). Peaks are considered to be completely resolved when the detector response returns to the baseline between peaks.
**Peak Area**: The defining of the bounds of the region under the detector response curve of a chromatographic peak (refer to Figure D-3). This is defined by drawing a line to represent the baseline at the bottom of the peak and the area within these bounds is the total response of the eluted substance. Coelutions complicate the definition of peak area.

**Peak Integration**: The defining of the boundaries of area under a chromatographic peak. The parameters for defining integration are user-defined and may be accomplished by chromatography data system (CDS) software (automated integration) or by analyst manual manipulation (manual integration).

**Peak Tailing**: Asymmetric chromatographic peak shape for which the majority of the peak’s area occurs after the peak apex and typically exhibits a slow decay of the detector response back to the baseline (refer to Figure D-5). Tailing peaks typically occur due to the substance having a strong affinity to the column stationary phase and/or there is an active site that further inhibits movement of the substance within the separation column or other components in the separation pathway.

![Figure D-5. Examples of Tailing Chromatographic Peaks](image)

4. Chromatographic Peak Integration

Laboratories should develop an SOP that prescribes the appropriate and practices to be implemented for integrating chromatographic peaks.

It is imperative that laboratories define the methods of peak integration to be employed such that integrations are technically justifiable and consistently performed. For example, the chromatogram in Figure D-6 shows a series of four peaks integrated by two different technically justifiable conventions – tangent skim (A) and perpendicular drop (B). The tangent skim convention shown in this example represents the minimum peak area attributable to each peak; however, the perpendicular drop convention attempts to represent the peak areas when taking into account the baseline trend before and after this series of peaks. Given the magnitude of the baseline noise, both conventions are technically justified; however, this is an example for which the monitoring agency SOP must specify the convention preference to avoid ambiguity in justifying the selected convention.
Under no circumstances may peak integration be improperly adjusted in order to enable calibration standards or QC samples (e.g., blanks or calibration checks) to meet acceptance criteria.

Computer CDS software includes refined functions and routines for performing automated integration of chromatograms. The CDS default integration parameter settings typically provide proper and suitable peak integration; however, some configuration adjustments may be needed for target analytes that exhibit a low response, are subject to RT shifts, exhibit coelutions, and/or indicate other interferences.

When setting up a chromatography integration method within the CDS, the analyst should start with a default or known appropriate method and adjust the integration parameters as needed to optimize the method to properly integrate the analytes of interest. If the GC or HPLC separation needs to identify and quantitate many analytes (as with VOCs for NATTS), the analyst may need to optimize the parameters on an analyte by analyte basis instead of assigning parameters for the entire chromatogram retention period. This event-by-event programming for individual target analytes can be tedious but is a worthwhile investment in saving downstream data processing effort to manually reintegrate peaks in dozens of chromatograms when the automated parameters improperly integrate target peaks. The other advantage to properly configuring and optimizing the integration method is that integrations are performed routinely and objectively, eliminating much of the variability and subjectivity inherent in manual integration. While optimized integration methods can save time and increase consistency for integration, the analyst should still review the chromatograms to ensure proper integration. Even the most carefully configured automated integration method can stumble when field-collected samples exhibit unexpected coelutions or other chromatographic artifacts that interfere with the automated regimen.

Regardless of whether analysts manually integrate chromatographic peaks or optimize the CDS to do so, analysts should strive to ensure chromatographic peaks for a given analyte are integrated consistently among the calibration standards, QC samples, and field collected samples to minimize the bias and variability in measurements that result from inconsistent integration techniques. For example, when a target analyte exhibits a similar interfering coelution in the standard and the field sample chromatogram, it is inappropriate to employ a perpendicular drop for the standard and a
A peer reviewer should review manual integrations to ensure they are technically justified, appropriate, and consistent.

**Proper Integration Techniques**

Peak integration is straightforward when chromatographic peaks occur on a stable baseline, have a sufficient (> 20:1) signal-to-noise ratio (signal to noise ratio), and are completely baseline resolved (start and end at the baseline) without coelutions. Integration becomes more difficult to perform properly when these conditions are not met and peaks exhibit a low signal-to-noise ratio, coelutions, and/or the baseline is not stable or is very noisy. In these situations, the CDS automated integration parameters may appropriately integrate the given peak(s); however, may require manual override to integrate properly or according to laboratory policy.

A discussion of proper integration techniques follows:

**Baseline-to-Baseline:** Chromatographic peaks will be normally integrated such that the peak integration baseline start and stop corresponds to the portion of the detector response of the established baseline prior to and after the peak as shown below in Figure D-7.

![Figure D-7. Example Baseline-to-Baseline Integration of a Chromatographic Peak](image)

Coeluting chromatographic peaks result in an elevated detector response due to the contribution by the coeluting substances. There are several methods for integrating the overlapping peaks, including the perpendicular drop and tangent skim.

**Perpendicular Drop:** For situations where the unresolved peaks are relatively similar in magnitude, the peaks can be integrated by drawing a perpendicular line (perpendicular drop) from the bottom of the valley between the peaks to the baseline to define the area of the peaks (refer to Figure D-8).
**Tangent Skim:** For coeluting peaks where one peak is much larger in magnitude, the peak integration can be accomplished by tangent skim. Tangent skim options within the CDS typically permit use of straight line or exponential tangent skimming, as shown in Figure D-9, peaks (A) and (B), respectively.

![Figure D-8. Perpendicular Drop Integration for Coeluting Peaks](image)

![Figure D-9. Examples of Straight Line (A) and Exponential (B) Tangent Skim Techniques](image)
Improper Peak Integration Practices

**Integrating Noise as Target Peak Area:** CDS automated integration parameters may improperly identify and integrate baseline noise as target analyte peaks (refer to Figure D-10). This typically occurs when the peak area reject threshold or peak height reject threshold parameter is set too low. Analysts will over-ride such automated identification and integration of noise as target analyte peaks. Analysts should understand the sensitivity of defining this threshold to strike an appropriate balance between ignoring chromatographic responses clearly representing instrument noise and overlooking suitable chromatographic peaks exhibiting proper signal-to-noise ratios that are suitable for identification and quantitation. Analysts should err on the side of including more responses resulting from noise, as it is a conservative approach to prevent inadvertent omission of identifying and integrating low-response target analyte peaks.

![Figure D-10. Baseline Noise Improperly Integrated as a Target Peak](image)

**Peak Shaving:** Peak shaving is the improper reducing of integrated peak area by improperly drawing baselines and/or perpendiculars. Examples of improper peak shaving integrations are detailed in Figure D-11.

![Figure D-11. Proper Peak Integration (A), Improper Tangent Skim (B), Improper Perpendicular Drops (C), and Improperly Drawn Baseline (D)](image)

**Peak Enhancement:** Peak enhancement is the improper inclusion of peak area that does not belong to a chromatographic peak. Practices that improperly enhance peak area are shown in Figure D-12 and include:

1. including baseline noise or additional unrelated peaks before or after the target peak
2. including additional baseline area
3. including coeluting peaks or shoulders
Figure D-12. Proper Peak Integration (A), Improper Inclusion of Noise (B), Improper Inclusion of Coelutions (C), and Improper Inclusion of Baseline (D)
APPENDIX E

GUIDE FOR REPORTING FLOW RATE VERIFICATION AND AUDIT DATA TO AQS
Instructions for Reporting Cartridge and Filter Sampling Unit Flow Rate Verification and Audit Data to AQS – March 2022

BACKGROUND:

EPA’s ambient air monitoring networks prescribe periodic flow rate checks for sampling units (monitors) that integrate flows over the collection period and require a total collected volume for determining in-air concentrations of pollutants. To verify the collected volumes are accurate to the reported volume for a given sample, the sampler flow rate must be known with certainty and the flow rate control calibration periodically verified. Additionally, monitoring agencies are to periodically conduct independent flow rate audits employing flow rate transfer standards independent from that used for calibrating and verifying calibration of the sampler flow rate. Previously, EPA did not require reporting flow rate data to AQS and relied upon the periodic (e.g., every 3 years) independent audit to assess sampler flow rate bias. Given that monitoring agencies are conducting these verifications and audits approximately quarterly, the EPA will be able to query these data from AQS to determine flow rate bias for various parameters using more data and with increased time resolution. This guide intends to assist monitoring agencies in setting up their cartridge or filter sampling units in AQS and reporting the flow rate calibration verification and audit data.

REFERENCES:


The following instructions assume familiarity with AQS data entry processes.

A. SETTING UP THE SAMPLER (MONITOR) IN AGENCY’S AREA IN AQS

The sampler can be set up by directly entering through the AQS interface or by submitting AD and AE transactions. For the examples below, we are assuming an ATEC 8000 carbonyls sampling unit (has multiple flow channels per sampler), but the instructions also apply to PM$_{10}$ and PAHs sampling units (have a single flow channel per sampler).

1. Entry through the AQS interface using the Maintain menu
   a. Refer to the Add Site Samplers section in the AQS User Guide page 84.
   b. From the Maintain dropdown menu in the AQS interface, select SIte Sampler.
   c. Click the cancel query icon.
   d. Complete the following required fields in the Maintain Site Samplers (AQS User Guide page 106) table:
      i. Sampler Owner Agency
      ii. State Code (2 digit)
      iii. County Code (3 digit)
      iv. Site Number (4 digit)
      v. Sampler ID (e.g., ATEC8000 - ATEC 8000-A)
vi. Begin Date (YYYYMMDD)

vii. Number of channels (e.g., 2)

e. Click the Execute Query icon, which will populate the form and allow the user to verify Sampler Id and Sampler Channels

f. For each Channel (row), enter:
   
   i. Channel Number
   
   ii. Filter Type (leave blank for DNPH and PUF/XAD cartridges – select the appropriate size PTFE for low volume PM$_{10}$ and quartz fiber filter for high volume PM$_{10}$)
   
   iii. Target Flow Rate (e.g., for 1.0 L/minute enter 1.0)
   
   iv. Flow Unit (for L/minute at standard conditions enter 073)
   
   v. Begin Date (YYYYMMDD)


g. If there are more samplers to enter, click the Next Record icon, otherwise, click Save and ensure the status bar indicates the record has been applied and saved.

2. Submitting AD and AE Transactions – these transaction types have been adapted to permit entry of carbonyls, PM$_{10}$, and PAHs samplers.

   a. Create the Site Sampler by constructing the AD transaction
      
      i. Refer to the transaction format table

      ii. The sampler ID (field 6) is a user-assigned unique ID or ID for the sampler at the site. For a primary sampler that is an ATEC 8000, a sampler ID example is: ATEC8000-A

      iii. Enter the Sampler Owner, (i.e., Agency code) for the sampler in field 7.

      iv. The manufacturer and model number are entered in fields 8 and 9, respectively - example field 8 = ATEC and field 9 = 8000

      v. Enter the sampler serial number in field 10 – example 174519

      vi. Enter the channel count in field 11 – this is the number of concurrent samples that can be collected. If the ATEC 8000 has a primary channel and a single duplicate channel, this field would be =2.

      vii. Enter the begin date in field 12. This field is formatted as YYYYMMDD. Example 20210801

      viii. The example transaction string is:

            AD|I|17|031|4201|ATEC8000-A|0513|ATEC|8000|174519|2|20210801|

   b. Create Sampler Channels by constructing the AE transaction(s)

      i. Refer to the transaction format table

      ii. The Sampler ID (field 6) is entered as in 2.a.ii: ATEC8000-A

      iii. The channel Number is entered (in field 7): 1
iv. Filter Type (field 8) is left blank for carbonyls and PAHs samplers (see A.1.f.ii for filter types for PM10)

v. Target Flow Rate (field 9) and Flow Units (field 10) are entered, for example 1.00 L/minute at standard conditions, field 8 = 1.00 and field 9 = 073

vi. Enter the begin date in field 12. This field is formatted as YYYYMMDD. Example 20210801

vii. The example transaction string is:

AE[I][17][031][4201][ATEC8000-A][1][1.00][073][20210801][

viii. Create additional transactions for the remaining sampler channels.

B. SUBMITTING SAMPLER FLOW RATE VERIFICATIONS AND AUDIT DATA TO AQS

Submitting data to AQS will either be for routine flow rate verifications or independent flow rate audits. Both utilize the AQS QA transaction for submission.

1. Submission of routine flow rate verifications is performed using a QA – Speciation Flow Rate Verification transaction
   a. Refer to the transaction format table: https://aqs.epa.gov/aqsweb/documents/codingmanual/html/fromdatabase/Speciation%20Flow%20Rate%20Verification.html
   b. The Assessment Type (field 3) is entered as: Speciation Flow Rate V
   c. The Performing Agency (field 4) is entered as their Agency code
   d. The Sampler ID (field 8) is entered and must exist for the Site in the database
   e. The Channel Number (field 9) is entered and must be defined for the Sampler in the database
   f. The Assessment Date (field 10) is entered in YYYYMMDD format
   g. The Assessment Number (field 11) is a unique number for an assessment performed at the site on that date, and should be 1 unless additional assessments are performed
   h. The Reported Unit (field 12) is entered for both the Sampler Flow Rate and Assessment Flow Rate
   i. The Sampler Flow Rate (field 13) is the flow rate setting or reading from the sampler
   j. The Assessment Flow Rate (field 14) is the flow rate reading from the flow transfer standard
   k. An example transaction string is:

QA[I][Speciation Flow Rate V][0513][17][031][4201][ATEC8000][1][20211114][1][073][0.998][1.012]

2. Submission of independent flow rate audit data is performed using a QA – Speciation Semi-Annual Flow Rate Audit transaction
b. The transaction is coded identically to the Speciation Flow Rate Verification except for the Assessment Type in field 3, which is entered as: Speciation Flow Rate Audit

c. An example transaction string is:

QA|i|Speciation Flow Rate Audit|0513|17|031|4201|ATEC8000-A|1|20211025|1|073|0.963|0.992