DRAFT

Standard Operating Procedure for the Analysis of Photochemical Assessment Monitoring Station (PAMS) Volatile Organic Compounds (VOCs) in Ambient Air via the PerkinElmer TurboMatrix TD300 Thermal Desorber with Clarus 580 Auto-Gas Chromatograph with Flame Ionization Detection (Auto-GC-FID)

 EPA Document Number

Effective Date: [DRAFT]

1. **SCOPE AND APPLICABILITY**

This standard operating procedure (SOP) describes the operation of the PerkinElmer (PE) TD300 thermal desorber with Clarus 580 automatic gas chromatography (auto-GC) system for the analysis of volatile organic compounds (VOCs) identified under the EPA’s Photochemical Assessment Monitoring Stations (PAMS) Program to be ozone precursors or relevant to atmospheric ozone formation. Procedures for the setup, calibration, operation, and shut-down are described herein. This SOP is intended to provide instruction for properly trained instrument operators. Monitoring requirements, training requirements, data validation and verification, and data reporting to AQS are outside the scope of this SOP.

1. **SUMMARY OF METHOD**

On an hourly cycle, the PE TD300-Clarus auto-GC system draws in ambient air from the inlet probe to collect and preconcentrate VOCs from the sampled atmosphere and subsequently separate the VOCs for detection via a flame ionization detector (FID). A new sample commences at the beginning of each hour. Ambient atmosphere is drawn into the TD300 sampling inlet by the vacuum supplied by the system’s sampling pump and routed through a two-phase sorbent trap maintained at -30ºC by Peltier cooling. Sample collection occurs for 40 minutes and flow is controlled to 15 mL/minute by a mass flow controller to acquire 600 mL of sample. Sampled atmosphere is routed through a Nafion® dryer to remove moisture prior to passing the sampled atmosphere to the sorbent trap. The permanent gases are unretained and VOCs of interest are captured. At the end of the collection period, the trap is desorbed by quickly heating (40ºC/minute) to 325ºC.

Following desorption, the trap is then backflushed with carrier gas to sweep the desorbed VOCs from the trap for separation. The compounds elute from the BP-1 separation column and are routed through a Deans switch which directs the lighter hydrocarbons (C2-C6) through a subsequent alumina PLOT separation column and the heavier compounds (C6-C12) away from the PLOT column and directly to an FID (FID1). The lighter hydrocarbons (C2-C6) are not appropriately separated by the BP-1 column and must be routed through the PLOT column for separation. These light compounds are detected by a separate FID (FID2) as they elute from the PLOT column. The GC program instructs the Deans switch to route the BP-1 column eluate to the FID1 following the elution of hexane. Compounds are identified by their retention time as they exit the appropriate separation column and are detected by the FID. The voltage responses of the FIDs are converted to a concentration in parts per billion carbon (ppbC) based on the response factor according to the calibration. The response factor is based on the FID response of propane (C2-C6) or benzene (C6-C12). System functions are controlled by a connected personal computer running the TotalChrom software. The TD300-Clarus 580 auto-GC requires additional supplies and support equipment including a zero air generator with support compressor, source of helium carrier gas, source of hydrogen (hydrogen generator or cylinder gas) for FID fuel, and a system to dilute stock standard gases for calibration and ongoing QC checks.

PAMS target VOCs are listed below in Table 1. Priority compounds are those VOCs for which all PAMS sites must report concentrations. Optional compounds are those VOCs that are of interest to the PAMS program but which are not required to be reported. Note there are two compounds in Table 1 that are not assigned by the PAMS program either as priority or optional compounds, but are nonetheless included in the 56-component retention time standard VOCs mix typically analyzed for the PAMS program.

**Table 1: Priority and Optional VOCs for the PAMS Program**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **priority or optional \*** | **compound name** | **# carbons** |  | **priority or optional \*** | **compound name** | **# carbons** |
| o | carbon tetrachloride | 1 |  | o | 2,3-dimethylpentane | 7 |
| p | ethane | 2 |  | o | 2,4-dimethylpentane | 7 |
| p | ethylene | 2 |  | o | n-heptane | 7 |
| o | tetrachloroethylene | 2 |  | o | methylcyclohexane | 7 |
| o | acetylene | 2 |  | o | 2-methylhexane | 7 |
| o | ethanol | 2 |  | o | 3-methylhexane | 7 |
| p | propane | 3 |  | p | 2,2,4-trimethylpentane | 8 |
| p | propylene | 3 |  | p | ethylbenzene | 8 |
| o | 1,3-butadiene | 4 |  | p | m-/p-xylene | 8 |
| p | 1-butene | 4 |  | p | o-xylene | 8 |
| p | cis-2-Butene | 4 |  | p | styrene | 8 |
| p | isobutane | 4 |  | o | 2-methylheptane | 8 |
| p | n-butane | 4 |  | o | 3-methylheptane | 8 |
| p | trans-2-butene | 4 |  | o | n-octane | 8 |
| p | isopentane | 5 |  | o | 2,3,4-trimethylpentane | 8 |
| p | isoprene | 5 |  | p | 1,2,3-trimethylbenzene | 9 |
| o | cyclopentane | 5 |  | p | 1,2,4-trimethylbenzene | 9 |
| p | n-pentane | 5 |  | p | m-ethyltoluene | 9 |
| o | 1-pentene | 5 |  | p | o-ethyltoluene | 9 |
| o | cis-2-pentene | 5 |  | p | p-ethyltoluene | 9 |
| o | trans-2-pentene | 5 |  | o | isopropylbenzene | 9 |
| p | benzene | 6 |  | o | n-nonane | 9 |
| p | n-hexane | 6 |  | o | n-propylbenzene | 9 |
| o | cyclohexane | 6 |  | o | 1,3,5-trimethylbenzene | 9 |
| o | 2,2-dimethylbutane | 6 |  | o | n-decane | 10 |
| o | 2,3-dimethylbutane | 6 |  | o | m-diethylbenzene | 10 |
| x | 1-hexene | 6 |  | o | p-diethylbenzene | 10 |
| o | 2-methylpentane | 6 |  | o | a-pinene | 10 |
| o | 3-methylpentane | 6 |  | o | b-pinene | 10 |
| o | methylcyclopentane | 6 |  | o | n-undecane | 11 |
| p | toluene | 7 |  | x | n-dodecane | 12 |

\* o = optional; p = priority; x = VOC contained in retention time standard but not of interest to PAMS program

1. **DEFINITIONS**

**Absolute pressure**: Pressure relative to complete vacuum, typically expressed in units of: psia, atm, mm Hg, kPa, or in Hg

**Analytical sequence**: List of sample analyses programmed into a sequence table within the CDS.

**Auto-GC**: Automatic gas chromatograph. Gas chromatograph capable of autonomous operation to collect an ambient air sample and to trap, separate chromatographically, identify, and quantitate the VOCs of interest.

**Baseline**: The instrument’s detector background signal in the absence of a substance.

**Carrier gas**: The mobile phase in gas chromatography; the carrier gas is non-reactive to the target analytes. Carrier gas flows at a constant rate through the GC column to carry analytes to the detector. For the PerkinElmer TD300-Clarus 580 system, the carrier gas is helium.

**Chromatographic peak**: The portion of a chromatogram recording the detector response when a compound is eluted from the column. To be considered a true peak for identification purposes, the signal-to-noise ratio must be ≥ 3:1.

**Chromatography Data System (CDS)**: The software program that controls the operation of the GC, acquires raw instrument data, and permits the operator to process collected data. The CDS allows programming of analysis sequences, generation of instrument calibration curves for target analytes, calculation of target analyte concentrations, and post-collection processing of raw instrument data. The CDS for the TD300-Clarus 580 system is PerkinElmer TotalChrom.

**Continuing calibration verification (CCV)**: Quality control sample consisting of a known concentration of target analytes, used to assess the ongoing suitability of the instrument calibration. CCVs are prepared by diluting a stock standard gas to a concentration within the calibration curve range (preferably within the lower 1/3 of the calibration curve range) and analyzed approximately every 24 hours of analysis. CCVs must recover within 30% of the nominal concentration for each analyte. CCVs may also serve as a reference for verifying analyte retention times.

**Data quality objectives (DQO)**: Metrics defined for a project or program which describe or quantify the desired criteria for collected data.

**Deans Switch**: Gas routing device which operates by controlling the flows of subject gas (e.g. column effluent) by adjusting flows of carrier gas through increasing or decreasing auxiliary flow.

**Dilution factor (DF)**: The ratio of a standard gas to the corresponding diluent. Such is needed to calculate the concentration of diluted standard gases.

**Dynamic dilution**: Dilution of a standard gas or gases with a diluent gas by mixing gases together at known flow rates in an inert plenum.

**Flame Ionization Detector (FID)**: Detection device that responds to ions formed during combustion of organic compounds in a hydrogen flame. The production of ions and associated response within the FID is proportional to the concentration of organic compounds in the sample gas stream introduced to the detector. FIDs require a source of both hydrogen (fuel) and oxygen to produce the hydrogen flame.

**Gas chromatograph (GC)**: Analytical chemistry instrument that separates vaporized compounds according to physical or chemical properties by passing the sample through a separation column which serves as the stationary phase.

**Gauge pressure**: Pressure relative to ambient atmospheric pressure. Typically expressed in pounds per square inch gauge (psig). A measurement of 0 psig indicates ambient atmospheric pressure.

**Initial calibration (ICAL)**: Standardization of the instrument area response to known concentrations of a target analyte. Generation of an ICAL typically involves fitting response factors of analyses of several concentration levels via linear regression. The concentration of the target analyte can then be determined by translating its measured area response into a concentration via inversion of the linear regression equation determined from the ICAL.

**Inlet probe**: The opening of the analytical system inlet to the ambient atmosphere. The materials comprising, siting, and configuration of the inlet probe must comply with 40 CFR Part 58 Appendix E.

**Mass flow controller (MFC)**: Device that controls the flow a specific gas by adjusting a flow control valve based on thermal differences within a capillary tube between temperature sensors upstream and downstream from a heater. The difference in temperature between the sensors is translated to set the gas flow to a calibrated known flow via the flow control valve.

**Measurement quality objective (MQO)**: Criteria prescribed for a given measurement or set of measurements, which may entail bias, precision, completeness, frequency, and sensitivity.

**Part per billion carbon (ppbC)**: Concentration unit of measurement equivalent to a ppbv (defined below) multiplied by the number of carbon atoms in the molecule.

**Part per billion volume (ppbv)**: Concentration unit of measurement equivalent to a mixing ratio of 10-9 L (or moles) of a trace gas in 1 L (or mole) of diluent. One ppbv is equivalent to 2.46·1010 molecules cm-3 at 760 mm Hg pressure and 25°C.

**Precision**: The reproducibility of a measurement. Auto-GC precision is determined by evaluating the similarity of the measured concentrations of successive analyses of a CCV on a weekly basis. The relative percent difference of the measurement pair is calculated by taking the absolute difference of the two measurements and dividing by the measurement pair average, expressed as a percentage.

**Raw instrument data**: Signals generated and recorded by the instrument in the process of making measurements. Such data may include instrument area responses, timestamps, flow rates, and other associated recorded instrument events such as valve switching, temperature changes, etc.

**Recovery**: The measured concentration of a target analyte divided by its nominal concentration, expressed as a percentage.

**Relative standard deviation (RSD)**: The standard deviation of a given sample of measurements divided by the mean of the sample measurements, expressed as a percentage.

**Response factor (RF)**: The ratio of the instrument response in area counts to the nominal concentration of the target analyte. The concentration of a given target analyte can be calculated by multiplying the area measured area response?by the response factor determined in the initial calibration.

**Retention time (RT)**: Duration of time following injection of the desorbed trap onto the GC column that a given target analyte takes to reach the detector. Retention times are assigned as the apex of the chromatographic peak.

**Retention time window**: Assigned time range during which a given target analyte is expected to elute from the separation column and reach the detector. Compound identification is determined by whether it elutes within a specified retention time window.

**Retention time standard (RTS)**: A 56-component or 59-component VOCs mixture containing target analytes. This standard is analyzed to confirm the retention times of target analytes.

**Sample**: Aliquot of atmosphere introduced to the inlet of the GC system that is trapped for subsequent separation by the GC. The volume of sample is determined by multiplying the sampling flow rate by the duration of sample collection.

**Second source quality control standard (SSQC)**: A standard gas purchased from a supplier different than the primary standard from which the ICAL is prepared. The standard gas is diluted to within the calibration curve and analyzed immediately following the ICAL. The SSQC independently verifies the quality of each analyte’s calibration curve.

**Signal-to-noise**: The ratio of the detector response to a known substance to the detector response in the absence of the substance.

**Standard temperature and pressure (STP)**: 25ºC and 760 mm Hg absolute pressure

**Static dilution**: Preparation of a standard gas dilution by addition of a standard gas or gases and diluent gas to an evacuated vessel. The absolute pressure of the vessel is measured after the addition of each gas and the dilution factor calculated by dividing the final vessel pressure by the partial pressure of each standard gas.

**System blank (SB)**: Analysis of a humidified zero air blank provided to the instrument through the instrument sampling inlet to ensure the instrument is sufficiently free of contamination.

**Thermal desorption (TD)**: The freeing of molecules from a sorbent by heating the sorbent to a temperature sufficient to release the molecules of interest from the sorbent.

**Ultra High Purity (UHP):** Gas purity ≥ 99.9999%

**Volatile organic compound (VOC)**: Carbon containing compounds with vapor pressure greater than 10-1 Torr at 25ºC and 1 atmosphere pressure

**Zero air**: Ambient air or synthetic air that has been scrubbed of hydrocarbons to achieve a total hydrocarbon content of nominally ≤ 0.05 ppmC.

1. **INTERFERENCES AND CAUTIONS**

Prior to beginning collection of data with the auto-GC system for data reporting, it is strongly recommended that the system be installed and operated for a minimum of two months to ensure proper calibration, stable operation, and that operators are familiarized with the functions and troubleshooting of the instrument. PAMS requirements for Required Network sites as of the time this SOP was written require reporting of PAMS data to AQS for a three-month period annually, starting June 1 and ending August 31. If instruments experience significant downtime between PAMS seasons, there is potential for degradation or failure of components.

Collection and analysis of PAMS VOCs via auto-GC is subject to several interferences. GC/FID identifies compounds solely by retention time, and can be subject to compound misidentification or incomplete chromatographic separation when chromatograms show peaks co-eluting with target analyte peaks. Changes in humidity can impact the trapping efficiency for some of the light hydrocarbon target analytes, and may result in shifts in analyte retention time and subsequent misidentification of analyte peaks.

Higher molecular weight VOCs are susceptible to losses to wetted surfaces of the flow path, whether for sample introduction or connections to standard gases. Where possible, materials comprising the flow path for sample atmospheres and standard gases should consist of chromatographic-grade stainless steel. Where available, it is recommended that the chromatographic-grade stainless steel tubing be deactivated by silica lining.

Operators must be aware of the large amount of data produced by the auto-GC system and the need for frequent contact with the instrument to ensure proper operation. QC sample failure and system failure due to malfunction or power outage, etc. can jeopardize the validity of large amount of data, which could lead to inability to meet the completeness MQO. Operators are encouraged to check in on the system frequently, daily if possible, whether at the site or via remote login, to verify the system is online and collecting data, that QC samples have been analyzed and meet criteria, and that future sample collections are scheduled and queued properly.

The Nafion dryer connections and tubing are delicate and easily damaged. Operators should be aware that rotating the nuts attaching the tee fitting to the drying tube can result in rupture of the drying tube membrane. Use of graphite ferrules to connect the columns or internal tubing to the Deans Switch can result in extrusion of the graphite into the internal flow paths causing blockages in the flow path or adsorption of target compounds. Only graphite/Vespel (15%/85%) ferrules should be installed.

1. **SAFETY**

Refer to the operator instrument manuals for specific safety information for the TD300-Clarus 580 system and support equipment.

The zero air generation system includes an air compressor, which stores air at high pressure in a ballast tank. Ruptures to the tank or connection lines can result in injury to persons in close proximity to the instrument. Instrument components are heavy and require caution when moving.

The FIDs utilize hydrogen gas as fuel. Leaks in the hydrogen delivery system may result in hydrogen build up, which can cause fire or explosion. Instruments should not be operated near open flame and sources of sparks should be eliminated. The shelter in which the instrument is installed should have a hydrogen gas detection/warning system.

Standard gases and support gases are contained within high pressure cylinders. Staff working with high pressure cylinders must be properly trained on the proper handling and operating aspects.

Operators should exercise caution when working on interior components of the instruments as internal components operate at both high temperatures (GC oven, FID, trap during desorption) and very cold temperatures (Peltier cooled trap) which can cause burns to unprotected skin. PerkinElmer recommends waiting minimally 20 minutes for internal parts to cool before handling. Failure to do so could result in severe burns.

1. **APPARATUS AND MATERIALS**

The PerkinElmer TD300-Clarus 580 auto-GC system comprises two main components, the TD300 Thermal Desorber and Clarus 580 GC with dual FID, and several pieces of support equipment. The instrument footprint is approximately 42” wide by 24” deep; however, additional space is required behind and beside the unit for gas and electrical connections and ventilation.

1. PerkinElmer TD300-Clarus 580 auto-GC system

	1. PerkinELmer Clarus 580 GC
		1. Transfer line: length of fused silica-lined column ~2-m length x 0.32-mm inner diameter (ID)
		2. Internal transfer line: length of fused silica-lined column ~ 40 cm length x 0.25 mm ID
		3. Deans Switch
		4. FID – two discrete FIDs (part numbers)
		5. BP-1 Column: 50-m x 0.22 mm with 1-µm film thickness
		6. Porous Layer Open Tubular (PLOT) Column: Al2O3/Na2SO4, 50 m length, 0.32 mm inner diameter, 10 µm film thickness
	2. PerkinElmer TurboMatrix TD300 thermal desorption unit
		1. Preconcentrator trap (part number)
		2. Nafion dryer (part number)
	3. PerkinElmer Network Chromatography Interface (NCI) 900 Series or higher
2. Zero air generator capable of providing air scrubbed to contain ≤ 0.05 ppbC of total hydrocarbons, must have sufficient capacity to provide air for pneumatics operation, purging of the Peltier cooling box, FID air, and dilution gas needs. Zero air employed for purging the Peltier box and FID air must be dried to contain ≤ 1 ppmv of water.
3. Air compressor capable of providing adequate pressure and flow required by the zero air generator
4. PerkinElmer TotalChrom software, version 6.2 or higher
5. Windows PC (cite specifications)
6. Purifying/drying cartridge: for additional clean-up and drying of the helium carrier gas
7. Gas regulators

	1. High purity regulator – stainless steel construction with CGA350 connection fitting. Each standard cylinder will require such a regulator.
	2. CGA 580 regulator(s) for connection to helium cylinder(s)
8. Gas dilution system – Standard gases may be diluted by either dynamic dilution or static dilution.

	1. The dynamic dilution or gas blending system should provide a dilution factor of approximately 5000-fold. This can be accomplished with mass flow controllers capable of flowing at 5 L/minute and 1 mL/minute, respectively, or via a set of flow restrictions that permit flow calculations based on calibrated partial pressures, that can provide such dilution factors.
	2. Static dilutions require a clean, evacuated vessel in which to prepare the dilution and an accurate, highly sensitive pressure gauge to measure the partial pressures of the added standard and diluent gases.
9. Stainless steel sampling canister(s) – Fused silica lined canisters are recommended over SUMMA deactivated canisters due to maximized transfer efficiency of higher molecular weight VOCs. Depending on need, fused silica lined canisters are available in 6-L, 15-L and 33-L from various suppliers.
10. Various lengths of 1/4”, 1/8”, and 1/16” chromatographic-grade stainless steel tubing and associated appropriate Swagelok fittings. It is recommended that all such stainless steel tubing be fused silica lined. Additionally, connections to standard cylinders or canisters should consist of 1/16” tubing to minimize dead volume and potential losses of higher molecular weight VOCs.
11. **REAGENTS AND CHEMICALS**
12. Zero air – Zero air, or hydrocarbon-free air, containing nominally ≤ 0.05 ppbC total hydrocarbons (THC) is provided by the zero air generator. Note that this air must be dried to below 1 ppmv of water to ensure proper TD operation.
13. Calibration stock standard gas – NIST-certified or NIST-traceable certified multi-component blend standard gas containing the target compounds of interest listed in Table 1. Typically, this standard gas is purchased at a concentration of 1000 ppbv for each target compound.
14. Second source stock standard gas - NIST-certified or NIST-traceable certified multi-component blend standard gas containing minimally 15 of the target compounds of interest listed in Table 1. Typically, this standard gas is purchased at a concentration of 1000 ppbv for each target compound.
15. Retention time standard (RTS) – component gas mixture containing the target compounds of interest listed in Table 1. Concentrations of the target compounds range from approximately 8 ppbC to 60 ppbC. While not required, concentrations of propane and benzene, and other compounds, may be NIST-traceable certified.
16. Deionized water (DI) – For use in the hydrogen generator and for humidifying the standard gases. Most laboratory water polishing units provide ASTM Type I water capable of providing water with resistivity ≥ 18 MΩ·cm, which meets specifications for most hydrogen generators.
17. Hydrogen gas: hydrogen generator or cylinder gas – UHP grade – for FID fuel
18. Helium gas: cylinder gas – UHP grade – for carrier gas
19. **SAMPLE COLLECTION AND HANDLING**

Ideally, sample collection begins at the beginning of the hour. Sample collection must commence no earlier than 10 minutes before the top of the hour and no later than 30 minutes after the top of the hour. For example, for sample collection of the 10:00 hour, sample collection must commence between 9:50 and 10:30 for the sample to be valid for that hour. This ensures that at least 30 of the 40 minutes, or 75%, of sample collection occurs during the hour.

The auto-GC permits near real-time analysis of ambient air. Ambient atmosphere is routed through either a standalone inlet dedicated to the auto-GC or to a manifold inlet to which the auto-GC sampling inlet is connected. For the standalone inlet, a length of 1/8” or 1/16” inner diameter (ID) chromatographic stainless steel tubing extends from the instrument sampling inlet through the shelter wall or roof to the inlet probe. Manifold inlets consist of a glass or stainless steel inlet probe outside the shelter extending inside the shelter and connecting to a glass manifold with multiple ports for instrument connections. A blower fan is connected to the manifold to pull ambient air into the manifold at a known rate exceeding two-fold the combined flow demand of all connecting instruments. The blower exhaust is routed outside the shelter away from the inlet probe. The auto-GC sample inlet is connected to the glass manifold via a short length of 1/8” or 1/16” ID chromatographic stainless steel tubing. The length and inner diameter of the stainless steel tubing is selected to ensure the residence time of the sampled atmosphere is 20 seconds or less. The total sampling demand of the PE TD300 instrument is approximately 15 mL/minute. To maintain a residence time of 20 seconds or less at this sampling rate, the lengths of 1/18” or 1/16” ID tubing must be no more than 63 cm or 252 cm, respectively. It is recommended that manifolds and inlet tubing be heated or insulated to prevent condensation as the warmer, more humid ambient air is cooled within the sampling line inside the shelter.

All portions of the inlet pathways must consist of chromatographic-grade stainless steel, glass, PTFE Teflon, or equivalent. Use of rubber, Tygon, or similar materials is prohibited as these materials may behave as sorbents or sources for VOCs, resulting in the loss of VOCs in the sampling train or offgassing VOCs which can contaminate the sampled air stream. The use of copper, brass, or non-chromatographic-grade stainless steel is also prohibited, as such materials contain active sites that can act as catalysts for destructive reactions of target analytes. Sample inlet lines should be cleaned or replaced on a prescribed frequency as particulate matter build-up on the wetted surfaces may also behave as a sink or source of VOCs, biasing measured concentrations.

1. **QUALITY CONTROL**

Quality control (QC) requirements and acceptance criteria are discussed in further detail within the PAMS Technical Assistance Document (TAD) and are summarized in Table 2.

When initially placed into service and prior to reporting data from the system, the method detection limit (MDL) must be determined for each target analyte. The MDL is determined following the procedure described in the PAMS TAD, which is an adaptation of the method update rule (MUR) to the 40 CFR Part 136 Appendix B procedure. The MDL is an estimate of the concentration at which a given analyte can be detected above background 99% of the time. The MDL must be determined initially, following changes to the instrument or method that can reasonably be expected to significantly change the sensitivity of the instrument or method, such as: replacement of the FID, replacement of the trap(s), or change of carrier gas (i.e. from He to H2). Determined MDLs must meet the criteria specified in the PAMS QAPP and TAD. Refer to the PAMS TAD for further instruction for determining MDLs.

QC samples are to be analyzed routinely following the initial calibration (ICAL) to demonstrate continued suitability of the instrument calibration, acceptable levels of target analyte contamination, acceptable reproducibility of measurements, and proper identification of analytes by the chromatography data system. Refer to Section X.C for more information on initial calibration. The frequency for QC sample measurements will be either approximately daily or weekly, depending on the check. Note that such frequency requirements are draft and may be subject to change.

The most frequent QC checks consist of a system blank (SB) and continuing calibration verification, which are to be analyzed approximately daily. These QC checks should be scheduled in the analytical sequence to occur successively (SB followed by CCV) to begin nightly between the hours of 20:00 and 02:00. It is recommended that the starting time for the SB analysis rotate through the hours of 20:00 through 02:00. If the SB/CCV begin at the same time every night, for example, 22:00, no ambient sample data will be collected for the two-hour period between 22:00 and 0:00. An example rotation schedule is included in Figure 1, which demonstrates that the rotation allows approximately four days of ambient collections for each hour each week.

Weekly checks will include the SB/CCV but will also include a precision check consisting of an additional CCV and will be followed by analysis of the SSQC and retention time standard (RTS). Note that if the RTS contains the appropriate target compounds at certified concentrations, this may be analyzed as the SSQC or the CCV. It is recommended that weekly checks be analyzed on weekend (Saturday or Sunday) nights (22:00 to 02:00) in order to maximize the collection of data during the workweek when concentrations are generally higher (and thus have more impact on ozone formation) due to increased traffic and higher traffic density.

The following QC samples are required. Acceptance criteria and additional information are included in Table 2.

1. System blank (SB): This blank sample consists of humidified zero air and is analyzed approximately every 24 hours to demonstrate contamination levels of target analytes are sufficiently low. All target analytes must analyze less than the determined MDL or 0.5 ppbC, whichever is greater (note this specification is subject to change).

2. Continuing calibration verification (CCV): The CCV is analyzed approximately every 24 hours to demonstrate the instrument calibration remains within specification. Target compound response must be within ± 30% difference from the expected nominal concentration.

3. Retention time standard (RTS): The RTS is analyzed weekly to verify the retention time windows assigned to each target analyte are appropriate. If there are shifts in retention times which result in the CDS mis-identifying or missing peaks, the retention time window(s) must be adjusted.

4. Second Source Quality Control Standard (SSQC): The SSQC is analyzed weekly to independently verify the quality of the calibration. Target compound response must be within ± 30% difference from the expected nominal concentration.

1. Precision check: A replicate of the CCV is analyzed weekly to assess the precision of the replicate measurement. Replicate measurements must show precision of ≤ 25% (note this specification is subject to change) relative percent difference (RPD).

**Table 2: Quality Control Parameter and Acceptance Criteria**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **QC Parameter** | **Description** | **Required Frequency** | **Acceptance Criteria**  | **Suggested Corrective Action** |
| Initial calibration (ICAL) | Multi-point calibration of the auto-GC with each compound of interest. Minimum of three concentrations covering approximately 0.5 to 50 ppbC for each compound. | Initially at the beginning of PAMS season, after maintenance to the instrument expected to alter the instrument response, following failing continuing calibration checks, and at the end of PAMS season | For linear regression, must show r2 of ≥ 0.995 and have an x-intercept within ± 0.2 ppbC of the origin. Each standard level evaluated against the calibration curve must be within 30% of the nominal concentration. | Prepare new calibration. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. May require preparation of new calibration standards. |
| System blank (SB) | Analysis of humidified zero air to ensure the system is sufficiently clean for continued analysis. | Prior to ICAL, and approximately daily | All target VOCs must be < the determined MDL or 0.5 ppbC | Analyze another blank, if possible, to investigate potential carryover from high concentration sample. Investigate system for contamination. Potentially qualify all samples for affected compounds since the last passing SB. |
| Continuing Calibration Verification (CCV) | Analysis of a known standard prepared within the calibration curve to demonstrate the instrument calibration remains within tolerance. | Approximately daily following the SB | All target VOCs must recover within 30% of the expected nominal concentration. | Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Potentially qualify all samples for affected compounds since the last passing CCV. |
| Second Source Quality Control Standard (SSQC) | Analysis of a known standard prepared from a stock gas from a supplier different from the stock gas for preparing the ICAL. This check independently verifies the quality of the ICAL. | Immediately following ICAL and weekly thereafter | All target VOCs must recover within 30% of the expected nominal concentration. | Investigate for discrepancy between ICAL and SSQC. Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Potentially qualify all samples for affected compounds since the last passing CCV. |
| Retention Time Standard (RTS) | Analysis of a 56-component blend of VOCs in the ~10-60 ppbC range to verify established retention time windows  | weekly | All target VOCs must be within the established retention time windows.  | Review previous week’s ambient and QC check samples to evaluate events resulting in retention time shift. May require reassignment or adjustment of retention time windows and reprocessing of data collected since the most recent RTS. |
| Precision check | Replicate analysis of the CCV to evaluate the reproducibility of the analysis | weekly | Absolute relative percent difference for each target VOC must be ≤ 25% on a week-to-week basis. | Investigate system for contamination, leaks, or suppression, as indicated by trends in compound behavior. Potentially qualify all samples for affected compounds since the last passing precision check. |
| Method Detection Limit (MDL) | Determination of the estimated concentration where the analyte is detected above the background level 99% of the time. The MDL is an estimate of this concentration and is to be determined following the method update rule (MUR) of the 40 CFR Part 136 Appendix B procedure as described in Section XX of Revision X of the PAMS Technical Assistance Document | Annually or following significant change to the instrument or method which would reasonably be expected to result in a significant change to the instrument sensitivity; such as detector replacement, trap replacement, change in carrier gas (i.e. from He to H2) | MDLs must be determined per the prescribed procedure and be ≤ 0.5 ppbC for each target VOC. | Investigate instrument for carryover or contamination. Verify spiking level for the MDL procedure is appropriate. Adjust spiking level and repeat procedure.  |

1. **PROCEDURE**
2. Installation of the auto-GC system

The manufacturer will typically install the instrument and perform setup when newly purchased. The instrument system must be installed in a shelter maintained between 5 to 40ºC. This required temperature range should be attainable for instruments installed in shelters that also house criteria pollutant monitoring equipment, as the shelter must be maintained within 15 to 33ºC. Note that temperature fluctuations or extended excursions beyond temperature limits may lead to retention time shifts or potential extended GC oven cooling times which may result in failure to begin a sample sequence at the assigned time.

The required power supply for the PE TD300-Clarus 580 instrument is a 20A 110V AC circuit. Additional circuits are necessary to supply power to the zero air generator, compressor, computer, and other support equipment such as a hydrogen generator. Components may be connected to a UPS unit to ensure power is conditioned to 110V and is continually available. The UPS permits the instrument to run uninterrupted during short power outages, the duration of which is dependent on the UPS unit capacity. Note that for instruments connected to a manifold inlet, if the blower motor power is cut during an electrical outage, the instrument will be sampling stale air from the manifold, and not fresh ambient air. In such cases, the associated data must be invalidated.

1. Initial Startup (more information will be included here if deemed necessary by the workgroup)

The initial startup steps are described in detail in the user’s manual. Refer to the instrument manuals for further information, diagrams, and instructions.

1. Calibration (More to be added to this section once calibration conventions are established with the workgroup)

	1. The initial calibration (ICAL) is established prior to performing any sample analysis, following instrument maintenance that would reasonably impact the instrument response (trap change, change or trimming of the column(s), detector change, etc.) and when continuing calibration checks indicate recalibration is necessary (failure or trending of criteria toward failure).
	2. The TD300-Clarus 580 unit is calibrated by challenging the system with minimally three levels of a NIST-traceable certified standard gas diluted with humidified zero air. The calibration curves are modeled by linear regression separately for the two FIDs. Instrument calibration is established using a carbon-based response where concentrations of light hydrocarbons (C2-C6) are determined according the response of propane and concentrations of heavier hydrocarbons (C6-C10) are determined according to the response of benzene. Calibration curves should include a minimum of three concentration levels covering approximately 0.5 ppbC to 50 ppbC.
	3. The calibration curves must demonstrate linearity with a correlation coefficient (r2) ≥ 0.995 and the determined concentration at each level must be within ± 30% difference from the nominal concentration. The resulting average response factors for propane and benzene are applied to the associated light or heavy target compounds, respectively, to define calibration parameters for quantitating target compounds.
	4. Following establishment of the ICAL, a second source quality control (SSQC) standard is analyzed within the calibration curve range to verify the calibration. All target compounds must be within ± 30% difference from the expected nominal concentration.
2. Defining Methods within TotalChrom

TotalChrom requires both instrument methods and process methods to define how a sample, blank, or standard is collected and analyzed.

* 1. Instrument methods define the sample collection parameters and the GC program parameters. These methods prescribe the inlet port, sampling time, and other TD parameters as well as the GC program parameters including gas flows, Deans Switch actuation, and oven program, among others.
	2. Process methods define the parameters for TotalChrom to identify and quantitate the target compounds. These methods prescribe the integration parameters, retention time windows, target compound list, and response factors based on the calibration, among other aspects of data processing.
1. Analysis of Ambient Air

	1. Creating Sequences

	Creating a sequence table requires entry of a list of the combined instrument and process methods into the TotalChrom CDS Navigator. Each hourly sample is a discrete line in the sequence table. Due to the two separate FIDs operating independently, a sequence table must be created for each FID in the respective control window. The sequence editor defines these two different FIDs as Channel A and Channel B. Note that the sample name and instrument method populate across the tables for Channel A and Channel B, however, process methods and corresponding data output filenames must be changed manually for each Channel.

Please refer to Figure 1 for an example sampling schedule including QC samples for a one week period. Note that QC samples are suggested to occur between 20:00 and 02:00 hours (and are highlighted in blue). Ambient samples are noted as “amb” in the figure.



**Figure 1: Example sampling schedule for a 7-day period including approximately daily and weekly QC samples**

In general, the instrument conditions for the individual instrument method designations entered in the sequence table will be identical in most respects with the exception being the instrument port assigned to the various gas streams (whether ambient air, standard gas, system blank, RTS, etc). The analysis parameters for the collection duration, desorb duration and temperature, Deans Switch actuation, and GC temperature program will be identical across these methods. Process methods should be identical for all samples, standards, and blanks.

* 1. Once the sequence tables have been created and saved for each GC-FID, the sequences can be programmed to start at a desired time. Data files are written to the locations specified. More information regarding file naming and file handling will be detailed as this SOP is revised.
1. Evaluating Collected Data (add figures and screenshots to this section)

Refer to the TotalChrom Software Guide for specific instructions for viewing, evaluating, and manipulating collected data.

* 1. Collected sample data may be viewed within the TotalChrom CDS software. This software allows creating overlays of chromatograms in several different viewing configurations. Sample chromatograms can be overlaid with standard or blank chromatograms to investigate retention time shifts, baseline shifts, or carryover of target compounds or interferences.
	2. Post-processing of data is performed with the TotalChrom software. To make adjustments to retention time windows, the operator can adjust these within the process method by clicking and dragging the retention time window. This process method is then saved and data files for affected samples can be reprocessed to ensure compounds were properly identified.
1. **CALCULATIONS AND DATA REPORTING**
	* + 1. Measured concentrations are to be reported in units of ppbC. These are the units to be entered into the system for calibration, therefore the instrument provides results in ppbC and reporting of the concentrations is straightforward. Consult the PAMS TAD and the AQS reporting guide for specific AQS reporting parameters and conventions.
			2. Calculations
	1. Standard dilution concentration via dynamic dilution:

Cd = (Fs·Cs)/(Fs + Fd)

Where:

 Cd = diluted concentration (ppbC)

 Cs = stock standard concentration (ppbC)

 Fs = flow of stock standard gas (standard mL/minute)

 Fd = flow of diluent gas (standard mL/minute)

* 1. Standard dilution concentration via static dilution:

Cd = Ps·Cs

 Pf

Where:

 Cd = diluted concentration (ppbC)

 Cs = stock standard concentration (ppbC)

 Ps = partial pressure of stock standard gas (mm Hg)

 Pf = final pressure of vessel (mm Hg)

* 1. Quantitation of Sample Using Calibration Response Factors:

where: C = concentration of compound measured in ppbC

Ac = integrated peak area of the compound being measured in the sample

Rfc = response factor of the target compound based on the calibration (area/ppbC)

* 1. Relative Standard Deviation (RSD):

RSD = standard deviation x 100

 mean

* 1. Absolute Relative Percent Difference (RPD) is calculated as:

RPD = |result A – result B| x 100

 mean of results A & B

* 1. Absolute Percent Difference (APD) is calculated as:

APD = |result measured – result expected| x 100

 result expected

* 1. Percent Recovery is calculated as:

% recovery = concentration measured x 100

 concentration expected

* 1. Total collected sample volume

 Vs = Fs·Ds·106

Where:

 Vs = collected sample volume (m3)

 Fs = sample flow rate (standard mL/minute)

 Ds = duration of sampling (minutes)

* + - 1. Data Validation and Verification

During review of the ambient concentration data, operators and data reviewers will invariably encounter situations where compounds exhibit interferences, QC checks fail acceptance criteria, and target compound responses are questionable as to the presence or absence. Monitoring organizations must have prescribed procedures to address such issues to ensure they are handled consistently and the decisions are technically justifiable. Refer to the PAMS TAD and PAMS QAPP for further information regarding data validation and validation.

1. **REFERENCES**
	1. Photochemical Assessment Monitoring Stations Required Site Network Quality Assurance Plan (Revision Number and date)
	2. Photochemical Assessment Monitoring Stations Required Site Network Technical Assistance Document (Revision Number and date)
	3. VOC Ozone Precursor Analyzer User’s Manual, Release A, PerkinElmer Instruments LLC, November 2001
	4. TurboMatrix Series Thermal Desorbers User’s Guide, P/N M041-3331, Release E PerkinElmer Instruments LLC, January 2007
	5. Clarus 500/580 GC User’s Guide, PerkinElmer Instruments LLC, 2002
	6. TotalChrom Tutorial for Version 6.3. P/N N515-6021, Release B, PerkinElmer Instruments LLC, November 2004
	7. Nomenclature for chromatography, (IUPAC Recommendations, 1993), PAC, 1993. *65*, 819