DRAFT

EPA Traceability Protocol
for
Qualification and Certification of Evaporative HCl Gas Standards
and
Humidification of HCl Gas Standards from Cylinders

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1.0 INTRODUCTION

For regulatory purposes, hydrochloric acid (HCl) calibration gas standards of known concentration and known uncertainty are needed to quality-assure data recorded by HCl continuous emission monitoring systems (CEMS) and measurements made with instrumental HCl reference test methods. This EPA traceability protocol reflects the current state of development of procedures for quantifying hydrochloric acid (HCl) concentrations from gas/vapor blending devices designed to produce HCl calibration standards.

This traceability protocol provides procedures for: (1) establishing the NIST traceability and quantitative performance (i.e., “calibration”) of key components of HCl gas/vapor blending devices; (2) determining the uncertainty contributed by each of these components; (3) calculating certified output concentrations and expanded, combined uncertainty values for the gas standards produced by the devices, and (4) verifying the output concentrations of the evaporative through comparison to a NIST traceable gaseous HCl reference standard. This protocol assumes a minimum “target” expanded, combined uncertainty value of 5% for HCl gas/vapor blending devices (see Section 4.7) unless otherwise specified in the applicable regulations. Demonstrating that a particular HCl gas/vapor blending device meets the requirements of this protocol establishes that the device output is traceable to NIST standards by means currently acceptable to EPA.

Section 2, “Overview,” discusses the different approaches to delivering HCl gas standards, explains the certification process for gas/vapor blending devices, and describes the two types of blending devices that are used for HCl gas standards. Section 3, “Qualification,” contains provisions designed to demonstrate the adequacy of a particular model prior to performing the actual certification tests. Section 4, “Certification,” explains specific procedures for quantitatively determining certified output concentrations from each type of device and for calculating and reporting the expanded, combined uncertainties of the HCl output concentrations. Section 5, “Verification,” shows how the certified device output is verified based on measurements of the actual output concentration. Section 6, “Quality Assurance,” details procedures for periodic data quality assessments, which provide assurance of continued acceptable HCl gas/vapor blending device performance.

The technical specifications and requirements for HCl calibration gases will have to be evaluated for each regulatory application as new HCl emission standards and their associated monitoring and testing requirements are developed. These issues may be addressed during formal rulemaking processes or by the regulatory agency responsible for implementing the standards, and are not addressed in this or other EPA traceability protocols. Therefore, for each regulatory application, the maximum acceptable uncertainty (if needed) and other implementation requirements and/or alternatives for devices should be specified by the responsible agency or organization.
2.0 OVERVIEW

There are essentially three ways to deliver HCl gas standards currently in use: (1) direct delivery of bottled dry gas of NIST-traceable HCl concentration, (2) a device that quantitatively blends a bottled dry gas with water vapor or humidified zero gas, and (3) an evaporative HCl standard, which produces gas standards of known concentration by vaporization of aqueous solutions of HCl and quantitatively blending the resultant vapor with a diluent carrier gas. The first option, delivery of a dry HCl gas standard, is outside the scope of this document. The second option was developed as a way to cope with the technical challenges of delivering dry HCl gases without losses and response lags. The third option delivers a humidified gas standard without the need of a NIST-traceable bottled gas. Any of these options is suitable for both CEMS and instrumental testing applications.

The latter two options listed above are essentially variations of a gas/vapor blending device, and are described in more detail below. The specific design, configuration, and features of any HCl gas/vapor blending device are left to the judgment of the manufacturer and are not constrained by explicit design specifications or EPA requirements. In order for the output concentration of a device to be NIST-traceable, however, all of the inputs must be calibrated using NIST-traceable standards, and the uncertainties of these inputs must be combined to calculate the uncertainty of the resulting gas standard.

Qualification tests are required for any blending device that is designed to produce NIST-traceable gas standards. For the purposes of this protocol, the tests that are routinely performed by the manufacturer will suffice, provided the test results demonstrate that the specific model has adequate stability and repeatability and can operate reliably over a stated range of conditions (e.g., line voltages, back pressures, ambient temperatures, delivery back pressures, and other applicable factors). These tests may either be performed on each individual device or on selected devices that are representative of the model. The manufacturer must provide the end user with a statement of disclosure that explains proper set-up and use of the device and documents the range of conditions over which reliable operation can be expected.

This EPA Traceability Protocol specifies the procedures for establishing the NIST traceable quantitative output of HCl gas/vapor blending devices. These devices may be certified either: (a) at the manufacturer’s facility, prior to shipping, or (b) at the site where the device will be used (or at another convenient location). The manufacturer or equipment supplier performing the certifications must maintain documentation of all certifications. The test date, certified Hg concentrations, and uncertainties must be provided in writing to the user. All certification test records must be available for inspection by regulatory officials.

The final step in the process of establishing the acceptability of a blending device as a calibration standard is to verify that the measured output concentration agrees with the calculated and certified concentration. This verification step is essentially a confirmation that everything feeding into the device is being delivered to the outlet undeterred and unaltered; it is a pass/fail test which does not result in any change to the certified output concentrations.
Following the initial certification of a blending device, it can be used in accordance with the manufacturer’s written instructions and operational specifications for regulatory applications in emission monitoring or testing. Periodic quality assurance (QA) checks and/or quality control (QC) procedures are required to verify that the device continues to provide accurate and reliable calibration standards. Recertification of a device is required periodically to maintain NIST traceability. Recertification may also become necessary when certain malfunctions, operating conditions, or other factors identified by the user or manufacturer occur.

2.1 Moisture Blending with Bottled HCl Gas Standards

The presence of moisture assists in transporting HCl gas standards through calibration lines and sample lines (i.e., umbilical) and through other system components upstream of the analyzer. As such, for using bottled HCl gas standards it may be advantageous, if not necessary, to introduce some moisture into the gas stream. There are several technologies for introducing moisture into a gas stream, and describing them is beyond the scope of this protocol.

Since introducing any additional flow into a gas stream dilutes it, the output HCl concentration of any gas/vapor blending device must be calculated based on the measured inputs: the flow rates of any liquid and gas streams that are added, and flow rate and concentration of the original HCl gas standard. For purposes of certifying the output concentration of the blending device, the input measurements must be NIST-traceable. The HCl gas standard should come with its certificate of analysis, providing the certified concentration and uncertainty. Liquid feed rates are established by using a balance to gravimetrically calibrate the feed rate meter relative to NIST-traceable mass standards. The HCl gas standard flow rate, along with any carrier gas flow rate associated with the vapor delivery, is established by calibrating the gas flow rate meter(s) relative to a reference standard that has a NIST-traceable calibration (see Sections 4.2 and 4.7.1).

2.2 Evaporative HCl Standard

In an evaporative HCl standard, a liquid stream containing a known concentration of HCl is metered and then dynamically mixed with a known flow rate of a carrier gas. The liquid feed is nebulized into small droplets, evaporated in a heated chamber, and then diluted with the carrier gas. Some devices may include a second liquid feed stream to facilitate control of the moisture concentration of the generated calibration gas. This principal of operation assumes that all of the HCl in the feed solution is emitted from the evaporator without re-condensing or reacting chemically with any of the device components or other feed streams. The output HCl concentration is calculated from the measured inputs: the HCl solution concentration, the liquid feed rate(s), and the carrier gas flow rate (see Section 4.2).

Certification of evaporative HCl standards requires NIST-traceability for the inputs listed above. The HCl concentration of the working liquid feed solution is established through the use of commercially available NIST-traceable HCl liquid standards and, if necessary, the quantitative dilution of these standards. Like the simpler blending devices described in Section 2.1 above, liquid feed rates are established by using a balance to gravimetrically calibrate the feed rate meter relative to NIST-traceable mass standards, and the carrier gas flow rate is established by
calibrating the gas flow rate meter relative to a primary laboratory standard that has a NIST-traceable calibration.

2.3 Uncertainty

In addition to the mass balance calculations that establish the certified concentration(s) from HCl gas/vapor blending devices (as a function of input parameters), the certification must also include the expanded, combined uncertainty of the certified HCl concentration(s). Combined uncertainty is a function of (1) the uncertainties of the input parameters, as included in the mass balance, and (2) the mathematical sensitivity of the output concentration to changes in each input parameter. A detailed discussion of propagation of uncertainty is outside the scope of this protocol. Equations are provided in Section 4 for all of the expected combinations of gas flows, liquid flows, and gas or liquid concentrations of HCl. Expanded uncertainty is simply the combined uncertainty multiplied by a coverage factor (k=2) to represent the required confidence level.

3.0 QUALIFICATION

Manufacturers are required to evaluate and specify the range of operating conditions over which the device can operate reliably and deliver the certified concentration(s). Information about the limitations of the device must be provided to the end user by means of a “Manufacturers Disclosure” (see Section 3.2) defining the limits of the environmental conditions and operating parameters which must not be exceeded. Manufactures shall conduct qualification tests to demonstrate the adequacy of each gas/vapor blending device (as defined in Section 3.1) prior to undertaking actual certification tests. Documentation of the qualification test procedures and results must be available upon request for inspection by EPA and other regulatory officials.

3.1 Definitions

3.1.1 Blending Device Model – A specific configuration identified by the instrument system design, including:

(a) The use of specific gas flow rate measurement/control devices, evaporation chamber, temperature controllers, temperature or pressure measurement and compensation devices, and other components;

(b) The physical arrangement of principal components;

(c) The specific electronics configuration and signal processing; and

(d) The specific software/firmware version and data processing algorithms, as implemented by a particular manufacturer and subject to an identifiable quality assurance system.
Note: The following changes to a gas/vapor blending device do not constitute a model change. However, the manufacturer must document all such changes:

- Minor changes to software, firmware, or data outputs that do not affect data processing algorithms or status outputs;
- Software installed on external devices, (including external computer systems), and used for processing of the device output to generate reference values, operational information, or to activate alarms; and
- Substitution or use of new measurement components, provided that the device manufacturer verifies that the performance of the new components is as good, or better, than the replaced components and documents supporting information for all such changes.

3.1.2 **Intrinsic Adjustment** – An automatic and essential feature of a gas/vapor blending device that provides for the internal control of specific components or adjustment of the device output in a manner consistent with the manufacturer's design and its intended operation. Intrinsic adjustments are either non-elective or are configured according to factory recommended procedures; they are not subject to change by the user.

3.1.3 **External Adjustment** – Either (1) a physical adjustment to a component of the gas/vapor blending device that affects its output or performance, or (2) an adjustment applied by the data acquisition system (for example, mathematical adjustment to compensate for drift) that is external to the device. External adjustments are made at the election of the end user but may be subject to various regulatory requirements.

3.2 **Manufacturer’s Disclosure**

As part of each gas/vapor blending device’s certification, a “Manufacturer’s Disclosure” is required. This disclosure must include documentation and other relevant information for the blending device model, in accordance with subsections 3.2.1 through 3.2.5, below. This information shall be provided to each end-user in the operation manual and/or other documents.

3.2.1 **Design Description**

The gas/vapor blender manufacturer shall provide a description of the blender design and operation in sufficient detail to afford users with a factual basis to assess the parameters that can reasonably be expected to affect performance. The description must identify the critical components, features for the control or compensation for changes in external influences, alarms or fault indicators, and necessary external devices or connections.

3.2.2 **Range(s)**

The manufacturer shall specify the nominal concentration range(s) (minimum and maximum HCl concentrations in units of ppm) over which the blending device model has been
demonstrated to meet all of the manufacturer’s specifications. The description of the range should explain the parameter values that must be changed or selected by the user to establish the effective operating range and/or HCl concentration values for a specific device in a particular measurement application.

3.2.3 Operational and Environmental Conditions

The manufacturer shall explicitly state the operational range or limitations within which the device model can be expected to operate reliably and meet all of the manufacturer’s specifications for:

3.2.3.1 Line Voltage

The acceptable line voltage limits over which the device can provide reliable HCl gas concentrations.

3.2.3.2 Gas Supply

The minimum and maximum supply pressure of air, nitrogen, or dry HCl gas standard, the allowable variation in supply pressure, the required gas flow rate, and the quality of carrier or HCl gas required.

3.2.3.3 Enclosure Temperature Operating Range

The range of ambient temperatures over which the thermal stability of the device has been tested, and can deliver reliable HCl gas concentrations.

3.2.3.4 Back Pressure

The range of back pressures over which the device has been tested, and can deliver reliable HCl gas concentrations.

3.2.4 Operation, Maintenance, and QA

The manufacturer shall provide written procedures for installation, start-up, operation and maintenance, and quality assurance (QA) of the HCl gas/vapor blending device. The manufacturer shall identify those activities and/or QA check/maintenance intervals, or other factors, that may need to be adjusted based on site-specific conditions or other application factors. The manufacturer shall also identify the specific conditions and factors that require recertification of the device, including, as applicable, known malfunctions or failures, exposure
to unacceptable operating conditions, component replacements, component recalibrations, or other conditions and/or factors.

### 3.3 Qualification Tests

Manufacturers shall perform and pass a series of standardized qualification tests for each HCl gas/vapor blending device model. These tests will assess the repeatability of the delivery concentration, and evaluate the effect of changes in line voltage, supply pressure, ambient temperature, and delivery back pressure. The tests will require an HCl detector or measurement system capable of accepting, either under positive pressure or by pulling a sample at its own rate, the output gas from the HCl gas/vapor blending device. The HCl detector need not be precisely calibrated with NIST-traceable gases, but must be capable of drift-free operation and generate a continuous, linear signal proportional to the HCl concentration.

#### 3.3.1 Repeatability Test

Prior to all other qualification tests, the repeatability of the gas/vapor blending device must be assessed over the range of possible delivery concentrations and operating conditions. Table 1 shows an example list of test conditions, representing an evaporative HCl standard feeding a 0.00555 M solution of HCl.

**Table 1: Repeatability Test Conditions**

<table>
<thead>
<tr>
<th>Concentration, ppm</th>
<th>Liquid Flow, mg/min</th>
<th>Gas Flow, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 (minimum)</td>
<td>100 (minimum)</td>
<td>10000 (maximum)</td>
</tr>
<tr>
<td>18 (maximum)</td>
<td>350 (maximum)</td>
<td>2000 (minimum)</td>
</tr>
<tr>
<td>4.2 (mid-range)</td>
<td>350 (maximum)</td>
<td>10000 (maximum)</td>
</tr>
<tr>
<td>4.2 (mid-range)</td>
<td>210 (mid-range)</td>
<td>6000 (mid-range)</td>
</tr>
</tbody>
</table>

To conduct the repeatability test, both the gas/vapor blending device and the HCl measurement system must be operational and stabilized in a controlled environment (e.g., no recent temperature changes or power interruptions).

(a) Use the blending device’s user interface to set one of the test conditions and activate. Verify that the device is calculating and displaying the expected concentration.

(b) Continue feeding until the HCl measurement response stabilizes and an average response is recorded. Proceed to the next test condition, and repeat until a response is recorded for each condition.

(c) After the first set of responses is recorded, repeat from the beginning to record a second set of responses. For each matched pair of responses \((x_1, x_2)\), calculate a relative percent difference.
\[ RPD = \frac{|x_1 - x_2|}{(x_1 + x_2)/2} \times 100\% \]

(d) If the relative percent difference is greater than 2% for any of the test conditions, take corrective action and conduct a new repeatability test for the full set of conditions.

### 3.3.2 Line Voltage Test

Since HCl measurement equipment often operates in an industrial environment which can be prone to electricity voltage sags and surges, the operation of gas/vapor blending devices must be verified over a range of supply voltages. These tests may be conducted under controlled laboratory conditions using a simple variable transformer (e.g., Variac®) to adjust the line voltage up and down from its nominal value. Like the repeatability test, the output concentration of the gas/vapor blending device will be measured with a suitable detector during the test. The high and low voltage test conditions may be set based on the manufacturer’s disclosure, but must include the range shown in Table 2. If the device is designed to be switchable between the two nominal voltages shown, this test must be conducted at each setting.

**Table 2: Line Voltage Test Conditions**

<table>
<thead>
<tr>
<th>Nominal Line Voltage</th>
<th>Highest Line Voltage</th>
<th>Lowest Line Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 VAC</td>
<td>126 VAC</td>
<td>110 VAC</td>
</tr>
<tr>
<td>240 VAC</td>
<td>252 VAC</td>
<td>220 VAC</td>
</tr>
</tbody>
</table>

The line voltage test may be conducted at the same settings that were used for the repeatability test, or a subset thereof, but must include conditions at the high and low limits of each flow measurement (gas and liquid) that is incorporated into the device.

(a) Plug the device into the variable transformer set to 100% (no change from line voltage), turn on and allow to stabilize.

(b) Use the blending device’s user interface to set one of the test conditions and activate. Verify that the device is calculating and displaying the expected concentration.

(c) Continue feeding until the HCl measurement response stabilizes and an average response is recorded for this nominal voltage.

(d) Slowly adjust the variable transformer to the lowest voltage corresponding to the nominal voltage in Table 2. Allow at least 5 minutes for any shifted response to stabilize, and record an average response for this voltage.

(e) Slowly adjust the variable transformer to the highest voltage corresponding to the nominal voltage in Table 2. Allow at least 5 minutes for any shifted response to stabilize, and record an average response for this voltage.
(f) Using the highest and lowest response averages \( (x_{\text{highest}} \text{ and } x_{\text{lowest}}) \), from among the three recorded responses), calculate a relative percent difference.

\[
RPD = \frac{x_{\text{highest}} - x_{\text{lowest}}}{\left(\frac{x_{\text{highest}} + x_{\text{lowest}}}{2}\right)} \times 100\%
\]

(g) Proceed to the next operating condition on the gas/vapor blending device, allow the response to stabilize, and cycle through the voltage settings in any order, making sure to allow at least 5 minutes for responses to shift before recording the response. Calculate a RPD for this condition.

(h) Once all operating conditions have been tested, review the RPD values. If the value is greater than 3% for any of the operating conditions, take corrective action and conduct a new line voltage test.

### 3.3.3 Supply Pressure Test

The supply pressure test may be conducted under controlled laboratory conditions using a pressure regulator, assuming the supply pressure to that regulator is at least as high as the maximum pressure provided on the manufacturer’s disclosure. Like the other tests, the output concentration of the gas/vapor blending device will be measured with a suitable detector during this test. The high and low pressure test conditions must be set based on the manufacturer’s disclosure, if a range is given. If the manufacturer documentation provides specific warnings against overpressure, the high pressure may be set as much as 10% below the maximum. If the manufacturer only provides a nominal value for input pressure with no range, use pressures of 10% above and below the nominal value for the high and low pressure settings. Table 3 shows some examples of manufacturer pressure specifications, and acceptable ranges for this pressure supply test.

**Table 3: Example Ranges for Pressure Supply Test**

<table>
<thead>
<tr>
<th>Manufacturer Spec.</th>
<th>High Supply Pressure</th>
<th>Low Supply Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-6 bar</td>
<td>6 bar</td>
<td>2 bar</td>
</tr>
<tr>
<td>50-150 psig</td>
<td>135 psig</td>
<td>50 psig</td>
</tr>
<tr>
<td>30 psig</td>
<td>33 psig</td>
<td>27 psig</td>
</tr>
</tbody>
</table>

The pressure supply test may be conducted at the same settings that were used for the repeatability test, or a subset thereof, but must include conditions at the high and low limits of each flow measurement (gas and liquid) that is incorporated into the device.

(a) Connect the device to an air supply or bottled gas that can deliver at least the high supply pressure that will be used for this test. Ensure that the supply includes a regulator that can bring that pressure down to the low supply pressure, and that there is a gauge to read the pressure supplied to the gas/vapor blending device. Set the pressure regulator for the low supply pressure.
(b) Use the blending device’s user interface to set one of the test conditions and activate. Verify that the device is calculating and displaying the expected concentration.

(c) Continue feeding until the HCl measurement response stabilizes and an average response is recorded for this supply pressure.

(d) Slowly adjust the pressure regulator to the high supply pressure. Allow at least 5 minutes for any shifted response to stabilize, and record an average response for this supply pressure.

(e) Using the response averages for the high and low pressure settings \( (x_{\text{high}P}, x_{\text{low}P}) \), calculate a relative percent difference.

\[
RDP = \left( \frac{x_{\text{high}P} - x_{\text{low}P}}{x_{\text{high}P} + x_{\text{low}P}} \right)^2 \times 100\%
\]

(f) Proceed to the next operating condition on the gas/vapor blending device, allow the response to stabilize, and record responses at the high and low supply pressure settings, making sure to allow at least 5 minutes for responses to shift, if they do.

(g) Once all operating conditions have been tested, review the RPD values. If the value is greater than 3% for any of the operating conditions, take corrective action and conduct a new supply pressure test.

3.3.4 Thermal Stability Test

The thermal stability test requires an environmental chamber or enclosure large enough to contain all components of the gas/vapor blending device, with penetrations for electrical and tubing connections. This chamber must be able to maintain temperatures at the high and low extremes listed on the manufacturer’s disclosure. Similar to other tests, the output concentration of the gas/vapor blending device will be measured with a suitable detector or measurement system located in a climate controlled laboratory space or control room outside of the environmental chamber. For this test, because it takes longer to perform, the detector may need to be calibrated or adjusted for drift before each measurement.

The high and low temperature test conditions must be set based on the manufacturer’s disclosure, if a range is given. If no range is specified, set the high temperature to 40°C, and the low temperature to 5°C. The thermal stability test may be conducted at the same settings that were used for the repeatability test, or a subset thereof, but must include conditions at the high and low limits of each flow measurement (gas and liquid) that is incorporated into the device. Ideally, these test conditions will be pre-programmed into the device, or activated remotely, in order to minimize intrusions into the environmental chamber during the test.

(a) Place the device into the environmental chamber, routing the HCl gas output and all power and signal wires outside the chamber as necessary. Set the chamber to a
representative ambient temperature (e.g., 20-25°C). If the chamber has humidity controls, set them to a dewpoint temperature below the low temperature condition.

(b) Use the blending device’s user interface to set one of the test conditions and activate. Verify that the device is calculating and displaying the expected concentration.

(c) Continue feeding until the HCl measurement response stabilizes and an average response is recorded on the HCl detector. Without disturbing the environmental chamber settings, switch the blending device to the next test condition, allow the reading to stabilize for at least 5 minutes, and repeat until a response is recorded for each test condition.

(d) Change the environmental chamber controls to the low temperature setting (i.e., 5°C or the low end of the manufacture-specified range, whichever is lower). Allow at least 4 hours for the device to equilibrate at this temperature.

(e) Perform any necessary calibrations or drift adjustments to the HCl detector to assure that its responses will be comparable to the earlier measurements. Set the gas/vapor blending device to each of the test conditions, as before, and record the detector responses to each test condition.

(f) Change the environmental chamber controls to the high temperature setting (i.e., 40°C or the high end of the manufacture-specified range, whichever is higher). Allow at least 4 hours for the device to equilibrate at this temperature.

(g) Perform any necessary calibrations or drift adjustments to the HCl detector to assure that its responses will be comparable to the earlier measurements. Set the gas/vapor blending device to each of the test conditions, as before, and record the detector responses to each test condition.

(h) Process the detector response data. For each gas/vapor blending device operating condition, identify the lowest and highest response average ($x_{\text{highest}}$ and $x_{\text{lowest}}$, from among the three recorded response averages), and calculate a relative percent difference.

$$RPD = \frac{x_{\text{highest}} - x_{\text{lowest}}}{(x_{\text{highest}} + x_{\text{lowest}})/2} \times 100\%$$

(i) If the relative percent difference is greater than 3% for any of the test conditions, take corrective action and conduct a new temperature stability test.

3.3.5 Delivery Back Pressure Test

The delivery back pressure test may require some modification of the tubing connection between the gas/vapor blending device and the HCl measurement system. By inserting one or more valves or back pressure regulators into the detector and/or vent lines, create a system where the back pressure at the HCl gas/vapor blending device outlet may be varied and maintained.
independently of the device operating conditions (e.g., outlet flow rate). As always, any portion
of the connections leading to the detector must be designed to not alter the delivered
concentration of HCl.

Unless the manufacturer’s disclosure specifies otherwise, the low back pressure test condition
will be ambient pressure, or whatever the minimum back pressure is that will deliver adequate
sample to the detector. The high back pressure test condition should be specified in the
manufacturer’s disclosure; if not, the high back pressure test condition will be 28 kPa. If the
manufacturer documentation provides specific warnings against too much back pressure, the
high back pressure test condition may be set as much as 10% below the manufacturer-specified
maximum. The delivery back pressure test may be conducted at the same HCl gas/vapor
blending device settings that were used for the repeatability test, or a subset thereof, but must
include conditions at the high and low limits of each flow measurement (gas and liquid) that is
incorporated into the device.

(a) Connect the device, through the back pressure arrangement, to the HCl measurement
system. Adjust the back pressure arrangement to the low back pressure setting.

(b) Use the blending device’s user interface to set one of the test conditions and activate.
Verify that the device is calculating and displaying the expected concentration.

(c) Continue feeding until the HCl measurement response stabilizes and an average response
is recorded for this delivery back pressure.

(d) Slowly adjust the back pressure arrangement to the high setting. Allow at least 5 minutes
for any shifted response to stabilize, and record an average response for this delivery
back pressure.

(e) Using the response averages for the high and low back pressure settings \( (x_{\text{highBP}}, x_{\text{lowBP}}) \),
calculate a relative percent difference.

\[
RDP = \frac{|x_{\text{highBP}} - x_{\text{lowBP}}|}{(x_{\text{highBP}} + x_{\text{lowBP}})/2} \times 100\%
\]

(f) Proceed to the next operating condition on the gas/vapor blending device, allow the
response to stabilize, and record responses at the high and low delivery back pressure
settings, making sure to allow at least 5 minutes for responses to shift, if they do.

(g) Once all operating conditions have been tested, review the RPD values. If the value is
greater than 3% for any of the operating conditions, take corrective action and conduct a
new delivery back pressure test.

3.3.6 Other Tests

The manufacturer’s disclosure may include operating ranges for other critical component
parameters (e.g., evaporator temperature for an evaporative calibration gas standard). Qualification tests for these parameters shall be structurally similar to the other tests in this section. The tests may be conducted at the same HCl gas/vapor blending device settings that were used for the repeatability test, or a subset thereof, but must include conditions at the high and low limits of each flow measurement (gas and liquid) that is incorporated into the device.

4.0 CERTIFICATION

4.1 Introduction

For each candidate HCl gas/vapor blending device, this section provides procedures and calculations to determine certified reference values at specific operating conditions and to calculate the combined, expanded uncertainties of those reference values. Documentation that a particular HCl gas/vapor blending device has been evaluated according to these procedures, and has met the applicable acceptance criteria, satisfies the NIST traceability requirements for the device.

4.2 Device Calculations

HCl gas/vapor blending devices calculate and report the delivered concentration using simple algebraic functions. The inputs to these functions are flow measurements, concentrations, and conversion factors. The functions themselves will vary based on the type of device and what it measures. Table 4 shows four device designs, and the associated expressions to calculate outlet concentration in ppm.

Table 4: HCl Gas/Vapor Blending Device Designs

<table>
<thead>
<tr>
<th>Bottled HCl Gas Humidifier</th>
<th>Evaporative HCl Gas Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct</strong></td>
<td><strong>Inert Gas Carrier</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{dry} \cdot V_{dry}$</td>
<td>$C_{dry} \cdot V_{dry}$</td>
</tr>
<tr>
<td>$0.01244 \cdot \dot{m}<em>w + V</em>{dry}$</td>
<td>$0.01244 \cdot \dot{m}<em>w + V</em>{dry} + V_{add}$</td>
</tr>
<tr>
<td>$C_{dry}$  Concentration of dry HCl gas, ppm</td>
<td>$M_{ws}$  Working solution Molarity, mol/liter</td>
</tr>
<tr>
<td>$V_{dry}$  Flow rate of dry HCl gas, liters/min</td>
<td>$V_{sol}$  Working solution flow, µl/min$^a$</td>
</tr>
<tr>
<td>$\dot{m}_w$  Flow rate of liquid water, mg/min</td>
<td>$\dot{m}_{sol}$  Working solution flow, mg/min$^a$</td>
</tr>
<tr>
<td>$V_{add}$  Flow rate of inert carrier gas, liters/min</td>
<td></td>
</tr>
<tr>
<td>$0.01244$ liters/mg  Specific volume of water vapor at standard conditions (0°C, 1 atm)</td>
<td></td>
</tr>
<tr>
<td>$22.414$ liters/mol  Molar volume of ideal gas at standard conditions  (0°C, 1 atm)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ For both water and working solutions, a density of 1.000 g/mL can be assumed for purposes of calculating µl/min injected into the evaporator when the actual measurement is based on mass. See 4.4.1.4.
There are essentially three types of inputs to the concentration calculation: (1) HCl feedstock (gas or liquid) concentration, (2) gas flow rate(s), and (3) liquid feed rate(s). The feedstock concentration is provided by the supplier or the laboratory, and is provided as an input parameter to the blending device. The gas flow and liquid flow rates, however, must be measured in real time and used by the device to calculate the expected HCl concentration. In order to translate an expected concentration into a NIST-traceable concentration, the calculation inputs must be NIST-traceable, and the uncertainties must be propagated through all calculations to the final “certified” HCl concentration and uncertainty. These final calculations may be performed internally or externally to the device’s firmware or software.

4.3 **Dry HCl Gas Concentration**

The NIST-traceability of dry HCl gas standards is beyond the scope of this protocol. For the purpose of certifying devices that use these gas standards as feedstock, it is assumed that NIST-traceable standards are commercially available, and that the certificate of analysis reports the certified concentration and an uncertainty. Unless the certificate states otherwise, the reported uncertainty will be assumed to have a coverage (K) factor of 2, so this number will be divided by 2 to get the standard (K=1) uncertainty which will be used in subsequent calculations of combined uncertainty.

4.4 **Working Solutions for Evaporative HCl Standards**

Working HCl feed solutions may be directly provided by commercial manufacturers or prepared by the end user from commercially available standards. Commercial HCl standards that have certified concentrations with an uncertainty of ± 0.5% or better should be used.

The commercial standard is guaranteed to be stable and accurate up to the expiration date, provided that the solution is kept tightly capped and stored under normal laboratory conditions.

*Note:* Standards with accuracy specifications of ± 0.1 to 0.5% are available. For calculation purposes, the guaranteed accuracy is considered to be the expanded uncertainty of the commercial standard. (The assumed coverage factor is 2.0.)

4.4.1 **Working Solution Preparation**

Direct use of a commercially prepared HCl standard solution is preferred. However, subsequent dilution of a commercially prepared HCl solution to prepare a working solution is permissible, when necessary.

(a) Determine the target concentrations of the working solutions that are appropriate for the anticipated liquid feed rates, gas dilution flow rates, and other applicable factors that are necessary to generate each of the desired HCl gas concentrations. These target concentrations may be supplied by the device manufacturer.
(b) If necessary, prepare each target working solution by diluting the NIST traceable HCl solution to the target concentration using the procedure in Section 4.2.2.1, below, or a similar procedure.

(c) **Note:** The preparation of working solutions described in Section 4.2.2.1 should be performed by qualified persons who are knowledgeable and experienced with the use of proper laboratory procedures and equipment.

### 4.4.1.1 Gravimetric/Volumetric Preparation

This approach offers considerable flexibility while maintaining suitable working solution uncertainties and combines gravimetric and volumetric preparation techniques. An aliquot of the commercial stock solution is added to a tared volumetric flask, weighed using a balance, and then brought to volume. The required precision of the balance depends on the mass of the stock solution aliquot. For aliquots 5g and greater, either a 3-place or a 4-place balance may be used. For aliquots less than 5g, a 4 place balance is required. Stock solution aliquots less than 0.5 g are not recommended.

- **a)** Prepare a 3- or 4-place balance capable of reading in the desired range by zeroing it and then weighing NIST-traceable weights in the range of measurement necessary to prepare each target working solution concentration.

- **b)** Tare an empty Class A volumetric flask (e.g., 100 mL to 1000 mL).

- **c)** Add the targeted mass of the standard HCL solution to the flask (e.g., a 10 mL aliquot will weigh approximately 10 g). Record the total weight. Subtract the tare weight of the flask from the total weight to determine the exact weight of the aliquot.

- **d)** Dilute with deionized (DI) water to the exact mark on the volumetric flask.

### 4.4.1.2 Working Solution Concentration (mg/liter)

(a) Calculate the concentration of the working solution using Equation 1A or Equation 1B, depending on the units of the commercial standard solution:

\[
C_{ws} = 1 \times 10^3 \times \frac{C_{std} W_{std}}{V_{total} \rho_{std}}
\]  

(Equation 1A)

Where:
- \(C_{ws}\) = HCl concentration of the working solution (mg/liter)
- \(C_{std}\) = HCl concentration of the standard solution (g/liter)
- \(W_{std}\) = Weight of standard solution (g)
- \(V_{total}\) = Final total volume of working solution (mL)
- \(\rho_{std}\) = Density of standard solution (g/ml)
- \(1 \times 10^3\) = Conversion factor (mg/g)
\[ C_{ws} = 1 \times 10^3 \times \frac{(W_{std})(N_{std})(MW_{HCl})}{(V_{total})(\rho_{std})} \]  
(Equation 1B)

Where:
- \( N_{std} \) = Normality of HCl working solution (mol/liter)
- \( MW_{HCl} \) = Molecular Weight of HCl (g/mol)

### 4.4.1.3 Molarity of Working Solution

Calculate the molarity of HCl in the diluted solution according to Equation 2.

\[ M_{ws} = 1 \times 10^{-3} \frac{C_{ws}}{MW_{HCl}} \]  
(Equation 2)

Where:
- \( M_{ws} \) = Molarity of the working solution (mol/liter)
- \( 1 \times 10^{-3} \) = Conversion factor (g/mg)

### 4.4.1.4 Conversion Between mg and µl of Working Solution

For dilute HCl working solutions in general, and for gravimetric feeding in particular, the units of mg and µl may be used interchangeably. A density of 1.000 g/mL can be assumed when calculating µl/minute injected into the evaporator. Similarly, in considering alternatives to the gravimetric/volumetric dilution procedure of 4.4.1.1, the final “volume” of the working solution may be determined by weight by substituting grams for ml in the equation of 4.4.1.2.

Commercially available standard HCl solutions ≤ 0.1N, have densities that are nearly 1.00 g/mL.

### 4.4.2 Uncertainty of the Working Solution

The gravimetric and volumetric standard uncertainties are combined with the stock solution standard uncertainty to derive the combined, standard uncertainty of the working solution concentration.

(a) The uncertainty of the aliquot weight \((U_A)\) is determined by dividing three times\(^b\) the estimated readability of the balance by the measured aliquot weight, and converting the result to a percentage.

(b) The uncertainty of the final working solution volume \((U_F)\) is estimated by dividing the readability of the certified volumetric glassware\(^c\) by the volume of the flask, and converting the result to a percentage.

---

\(^b\) Based on guidance from EPA metrology experts, the uncertainty of weights determined using a balance can be estimated based on the readability of the balance and a multiplier of 3. For example, for a 3-place balance, the readability is ± 0.001 g. Therefore, the uncertainty of measurements made with a 3-place balance is 3 times ± 0.001 g, or ± 0.003 g.

\(^c\) For example, the readability of a one-liter Class A volumetric flask is ± 0.40 mL.
(c) Alternatively, the uncertainty of the final working solution weight \((U_F)\) is determined by dividing three times the estimated readability of the balance by the final flask weight, and converting the result to a percentage.

(d) The uncertainty of the commercial standard solution value is the percent accuracy of the solution concentration, as specified by the supplier.

(e) The combined standard uncertainty of the working solution concentration is calculated using Equation 3.

\[
U_{WS} = \sqrt{\left(\frac{U_{CS}}{2}\right)^2 + U_A^2 + U_F^2}
\]

(Equation 3)

Where:
- \(U_{WS}\) = Uncertainty in the concentration of the working solution (%)
- \(U_{CS}\) = Expanded uncertainty of the commercial standard, with an assumed \(k=2\) coverage factor (%)
- \(U_A\) = Uncertainty of the aliquot weight or volume (%)
- \(U_F\) = Uncertainty of the final, diluted standard weight or volume (%)

(f) **Example:** A 10 g aliquot of a standard HCl solution is weighed using a 3-place balance. The exact weight of the aliquot is 10.015 g. The aliquot is diluted to 1.0 liter using a Class A volumetric flask. The specified accuracy of the standard solution is \(\pm 1.0\%\). Calculate the uncertainty of the working HCl solution.

The uncertainty of the aliquot weight \((U_A)\), is \((0.003 \text{ g}/10.015 \text{ g}) \times 100\), or 0.03\%. The uncertainty of the final solution volume \((U_F)\) is \((0.40 \text{ mL}/1000 \text{ mL}) \times 100\), or 0.04\%. The uncertainty of the commercial standard solution \((U_{CS})\) is equal to its specified accuracy, i.e., 1.0\%. Substituting the values of \(U_A\), \(U_F\), and \(U_{CS}\) into Equation 3 gives a combined uncertainty for the working solution of 1.0012\%, which rounds to 1.00\%. For this example, the preparation of the working solution adds negligible additional uncertainty. The uncertainty of the diluted working solution is dominated by the uncertainty of the commercial standard solution.

(g) Equation 3 calculates the uncertainty with a coverage factor value of 1-sigma, which is appropriate for an intermediate uncertainty that will be subsequently combined with other uncertainties and expanded. The uncertainty of a commercially available NIST-traceable HCl standard is assumed to have a coverage factor of 2.

**4.5 Gas Flow Rates**

Every gas/vapor blending device, regardless of configuration, must measure one or more gas flows to calculate its output concentration. This measurement can be made many ways, but is commonly provided by an electronic mass flow controller (MFC). This controller accepts input from the blending device firmware or software to establish its setpoint flow. Using its own internal feedback control loop, the MFC attempts to maintain the flow at the setpoint, and
delivers a signal (analog or digital) indicating the *as delivered* flow. For a NIST-traceable HCl gas/vapor blending device, it is this *as delivered* flow signal that is used to calculate the device’s expected concentration.

Many blending devices use quadratic or even 3rd order curves to linearize both the *setpoint* and the *as delivered* signals, as displayed and recorded by the blending device software. The use of these curves can significantly reduce the uncertainty of the gas flow measurement, but require considerable expertise to ensure that the correct factors are stored in the blending device. Simple mistakes like using the wrong units (e.g., liters/min versus ml/min) to calculate the curve coefficients or applying the wrong curve (e.g., the *setpoint* curve versus the *as delivered* curve), can cause huge errors related to the MFC operation and measurements. Since the internal function of blending device firmware/software is beyond the scope of this protocol, it will simply be assumed that any linearization curves are applied transparently to the operator and the recorded data stream. The linearity of the blending device’s gas flow measurements will be verified as part of the certification process, and any residual non-linearity (i.e., after any *as delivered* curve is applied) will become part of the uncertainty.

4.5.1 Gas Flow Rate Comparison to NIST-Traceable Reference Standard

The number and level of gas flow rates to be measured will depend on the intended application. The range of flows should cover the expected operating range of the device, and the number of flows (no less than 3) should be sufficient to minimize the impact of interpolation uncertainty for in-use flows that don’t exactly match the measured flows. Measure the gas flow from the device according to the procedures in paragraphs (a) through (e) of this section. As noted in the final step, this measurement process must include at least 2 independent experiments (on different days, to assess reproducibility uncertainty), each covering all of the flow rates that will be used to calculate certified concentrations. Alternatively, if the flow device manufacturer’s certification includes uncertainty data for the full range of flows, it may be used as one of the independent experiments for purposes of calculating reproducibility.

(a) Install a primary laboratory standard device for flow rate measurement at the outlet of the calibrator (e.g., a digital bubble meter, piston displacement device, or other device). The device must have: (1) an uncertainty of 1.0% or better; and (2) a NIST-traceable calibration. Operate the reference flow rate measurement device in accordance with the manufacturer’s instructions. Make sure that the reference device is used within its specified operating range and conditions.

(b) Prepare and operate the HCl gas/vapor blending device according to the manufacturer’s instructions. The operating conditions should match the conditions under which the device will be certified, but with the liquid flow(s) and any other gas flow disabled. For each operating condition, allow the device to run for a sufficient period of time to equilibrate and achieve steady operation.

*Note: If the design of the blending device prevents the disabling of other liquid or gas flows, the NIST-traceable reference standard may be inserted into the blending device’s
gas feed upstream of where it mixes with the other flows, provided the device’s hardware is accessible for this purpose.

(c) For each gas flow rate level, record the expected reading of the device’s gas flow measurement (i.e., the as delivered flow after processing through the device’s linearization curve, if used), and the concurrent output of the NIST-traceable reference standard. Record at least ten pairs of readings. If applicable, adjust the reference flow rate measurements to standard temperature and pressure conditions.

(d) Calculate the relative standard deviation (RSD) of the gas flow rate determination replicates at each level. If any RSD value is greater than 2.0%, take corrective action and repeat those pairs of readings. Record the RSD as the first-day gas flow uncertainty ($U_{ν1}$) at each level.

(e) Shut down the HCl gas/vapor blending device according to the manufacturer’s instructions. On another day, repeat the measurement experiment and record the RSD at each level as $U_{ν2}$. The experiment may be repeated more than once, provided all data are recorded, and should result in lower uncertainty.

4.5.2 Combining Data and Correlating Expected to Certified Values

Once the comparison measurements are done, the dataset will consist of a number ($I ≥ 10$) of data points, for each of $J$ flow conditions, each compared on a number ($K>1$) of days. The single-day/single-flow averages ($ν_{jk}$) have already been calculated as part of the RSD check during the comparisons.

$$\nu_{jk} = \frac{1}{I} \sum_{i=1}^{I} \nu_{ji} \quad \text{and} \quad U_{νjk} = \text{RSD} = \sqrt{\frac{\sum_{i=1}^{I} (\nu_{ji} - \nu_{jk})^2}{(I-1)}}^\times 100\% / \nu_{jk}$$

Calculating one reference number for each flow condition means simply averaging the $\nu_{jk}$ values, while the single-flow uncertainty ($U_{νj}$) involves a combination of averages and uncertainties at various levels of the comparison process.

$$ν_j = \frac{1}{K} \sum_{k=1}^{K} ν_{jk} \quad \text{and} \quad U_{νj} = \sqrt{\left(\frac{U_{RFS}}{2}\right)^2 + \frac{K-1}{K^2} \sum_{k=1}^{K} \left(\frac{U_{νjk}}{100\%}\right)^2 + \frac{K}{(K-1)ν_j^2} \sum_{k=1}^{K} (ν_{jk} - ν_j)^2} \times 100\%$$

where $U_{RFS}$ is the uncertainty of the reference flow standard with an assumed coverage factor of $k=2$. If the blending device is properly applying its linearization curves, the single-day/single-flow averages ($\nu_{jk}$) should correlate well with the corresponding expected flow values ($\nu_{jk}$) as recorded by the blending device. To verify this, derive a linear equation which, when applied to the expected gas flow rate, predicts the corresponding reference flow rate. This linear equation may be either: (1) a factor based on the ratio of actual gas flow rate to indicated gas flow rate.
\[ a = \frac{\sum v_{jk}}{\sum x_{jk}} \quad \text{(\(\Sigma\) without bounds denotes all \(v_{jk}\) and \(x_{jk}\) averages are included)} \]

or (2) a combination of such a factor and an adjustment for zero offset.

\[
a = \frac{JK \cdot \sum v_{jk} - \sum x_{jk} \cdot \sum v_{jk}}{JK \cdot \sum x_{jk}^2 - (\sum x_{jk})^2} \quad \text{and} \quad b = \frac{\sum v_{jk}^2 - \sum x_{jk} \cdot \sum v_{jk}}{JK \cdot \sum x_{jk}^2 - (\sum x_{jk})^2}
\]

The term \(JK\) is, in fact, the product of the number of comparison test days with the number of test conditions, and represents the total number of data points for the correlation (usually expressed as \(N\) in a typical least-squares formula). After determining the correction equation, the data points should be compared to the line. If any point is more than 2% above or below the line, take corrective action and repeat the comparisons.

### 4.5.3 Interpolation

As a practical matter, the delivered flow during operation will rarely match one of the calibrated points exactly. In order have a continuum of certified points over the full range of operation, interpolation is necessary. The formula for linear interpolation is straightforward.

\[
v_{gas} = v_{j} + (x_{gas} - x_{j}) \left( \frac{v_{gas} - v_{j}}{x_{gas} - x_{j}} \right) \approx v_{j} + (x_{gas} - x_{j}) \left( \frac{v_{j+1} - v_{j}}{x_{j+1} - x_{j}} \right)
\]

where \(x_{j}, v_{j}\) is the certified point nearest the \(x_{gas}\) value to be interpolated, and \(x_{j+1}, v_{j+1}\) is an adjacent certified point chosen so that \(x_{gas}\) is between, \(x_{j}\) and \(x_{j+1}\). The uncertainty arising from this calculation is primarily related to the assumption that the point \(x_{gas}, v_{gas}\) lies on a straight line between \(x_{j}, v_{j}\) and \(x_{j+1}, v_{j+1}\). This line, along with the correction equation used in 4.5.2 to verify response linearity, defines an estimated uncertainty envelope for interpolation slope.

\[
\left( \frac{v_{gas} - v_{j}}{x_{gas} - x_{j}} \right)_{\text{Max}} = \frac{\max(v_{j+1} - v_{j}, v_{j+1} - (a \cdot x_{j} + b), a \cdot (x_{j+1} - x_{j}) - v_{j}, a \cdot (x_{j+1} - x_{j}))}{x_{j+1} - x_{j}}
\]

\[
\left( \frac{v_{gas} - v_{j}}{x_{gas} - x_{j}} \right)_{\text{Min}} = \frac{\min(v_{j+1} - v_{j}, v_{j+1} - (a \cdot x_{j} + b), a \cdot (x_{j+1} - x_{j}) - v_{j}, a \cdot (x_{j+1} - x_{j}))}{x_{j+1} - x_{j}}
\]

These maximum and minimum values define an uncertainty component related to the linear interpolation.
For any interpolated point within the range of gas flow measurements, the combined uncertainty, including the uncertainty of interpolation, is

\[
U_{\text{vb}} = \left( \frac{V_{\text{gas}} - V_j}{x_{\text{gas}} - x_j} \frac{1}{x_{\text{gas}} - x_j} \right)_{\text{Max}} \left( \frac{V_{\text{gas}} - V_j}{x_{\text{gas}} - x_j} \frac{1}{x_{\text{gas}} - x_j} \right)_{\text{Min}} 12 \times 100\%
\]

As an alternative approach to interpolation, the linear equation from 4.5.2 may be applied as a correction equation to all points within the range of gas flow measurements.

\[
U_{\text{gas}} = \sqrt{U_{\text{vb}}^2 (x_{\text{gas}} - x_j)^2 + U_{\text{vj}}^2 v_j^2}
\]

\[
v_{\text{gas}} = a \cdot x_{\text{gas}} + b
\]

\[
U_{\text{gas}} = \sqrt{\left( \frac{JKb^2 + a^2 \Sigma x_j^2 + 2 \cdot (ab \Sigma x_j v_j - b \Sigma x_j v_j - a \Sigma x_j v_j)}{JK - 2} \right)} \times 100\%
\]

Note: While this alternative does simplify the algorithm for calculating the certified output, it may yield a higher uncertainty than interpolation, particularly at the low end of the flow range.

Whichever calculation is used, interpolation or the linear correction, must be permanently recorded and incorporated into the device’s calculation of its expected output HCl concentration. Maintain documentation of the experimental measurements, derivation of the linear correction and interpolation equations, if used, and the uncertainty determinations for both the compared flow points and the interpolated/corrected points.

### 4.6 Liquid Feed Rates

The liquid feed function of gas/vapor blending devices varies significantly in implementation. Where bottled gas humidification devices may use some type of reservoir with continuous on-demand replenishment, an evaporative HCl standard usually has some type of variable-speed pump. Regardless of design, all devices must measure one or more liquid flows to calculate the output concentration. Like the gas flows, it is the *as delivered* flow that is important, not the *setpoint*. For liquid flows, these are less easily confused, because any component that attempts to set the flow (e.g., a positive displacement pump) is usually separate and distinct from how the flow is measured. Some devices do have a factor (e.g., a “tube factor” for a peristaltic pump) that is used to predict how much flow will result from a given pump setting, but these factors tend to change over time, resulting in dramatic changes to the relationship between *setpoint* and *as delivered* flow (hence the importance of an independent flow measurement to calculate the output concentration).
Like the gas flow, the gas/vapor blending device might use a quadratic or 3\textsuperscript{rd} order curve to linearize the as delivered liquid flow signal(s), as displayed and recorded by the device software. It is assumed that, if used, these curve coefficients are properly calculated and applied, and that the application of the curve(s) is transparent to the operator and the recorded data stream. The linearity of the blending device’s liquid flow measurements will be verified as part of the certification process, and any residual non-linearity will become part of the uncertainty.

4.6.1 Liquid Flow Rate Comparison to NIST-Traceable Reference Standard

Based on the expected output moisture content and (for evaporative HCl standards) the solution concentration, determine the range of liquid feed rates that are necessary to generate the required output concentrations, taking into account the carrier gas flow rates and other applicable factors. The number and level of liquid feed rates to be verified (no less than 3) will depend on the application. The range of flows should cover the expected operating range of the device, and the number of flows should be sufficient to minimize the impact of interpolation uncertainty for in-use flows that don’t exactly match the measured flows. Measure the liquid flow from the device according to the procedures in paragraphs (a) through (k) of this section. As noted in the final step, this measurement process must include at least 2 independent experiments (on different days, to assess reproducibility uncertainty), each covering all of the flow rates that will be used to calculate certified concentrations. Alternatively, if the flow device manufacturer’s certification includes uncertainty data for the full range of flows, it may be used as one of the independent experiments for purposes of calculating reproducibility.

(a) Zero an appropriate three-place (or more accurate) balance and then check its calibration against NIST-traceable weights in the range of measurement necessary for each liquid feed rate determination.

(b) Connect the balance to a data logging device that is capable of recording its reading in real time with an accurate timestamp corresponding to each reading. Software that plots the readings, and even the rate of change, would be very useful for these comparisons. It would also be beneficial to assure that the logging device clock is synchronized with the blending device.

(c) Set up the HCl gas/vapor blending device according to the manufacturer’s instructions, allowing all temperatures to equilibrate. Place the HCl working solution (or DI water, as applicable) in a reservoir on the balance. Position the liquid uptake or delivery tube in such a manner that it does not affect the weighing process.

(d) Operate the HCl gas/vapor blending device according to the manufacturer’s instructions. The operating conditions should match the conditions under which the device will be certified, including a representative gas flow. Allow the device to run for a sufficient period of time to equilibrate and achieve steady operation.

Note: A significant period may be required for systems with peristaltic pumps to ensure that all gas bubbles are removed from the apparatus and steady operation is achieved.
(e) Once steady operation is indicated, allow the device to run for at least 5 minutes while
the balance readings are being logged (more time generates more data points, which
lowers uncertainty). Change to the next operating condition, making sure the exact time
of the change is recorded (either in a notebook or by a flag or comment in the balance
logging file). Allow the blending device to equilibrate at the new flow setting(s).

(f) Continue operating the device at different operating conditions, recording at least 5
minutes of balance data after each condition stabilizes. For each condition, record the
expected reading of the device’s liquid flow measurement (i.e., the as delivered flow
after processing through the device’s linearization curve, if used), and the matching
timestamps from the balance logging.

(g) Shut down the HCl gas/vapor blending device according to the manufacturer’s
instructions. Shut down the balance logging and retrieve the data file.

(h) Parse the balance data into segments of time \( t \) and mass \( m \) readings, each
representing a single operating condition as recorded after stable operation. Calculate
least-squares linear slope, intercept, and standard error of slope for each data segment.

\[
\dot{m}_{jk} = a = \frac{N \cdot \sum_{seg} t_j m_{jk} - \sum_{seg} t_j \cdot \sum_{seg} m_{jk}}{N \cdot \sum_{seg} t^2_{jk} - \left( \sum_{seg} t_{jk} \right)^2} \text{ g/min} \\
b = \frac{\sum_{seg} m_{jk} \cdot \sum_{seg} t^2_{jk} - \sum_{seg} t_{jk} \cdot \sum_{seg} t_{jk} m_{jk}}{N \cdot \sum_{seg} t^2_{jk} - \left( \sum_{seg} t_{jk} \right)^2} \text{ grams}
\]

\[
\text{stderr}_{ajk} = \sqrt{N \left( \sum_{seg} m^2_{jk} + Nb^2 + a^2 \sum_{seg} t^2_{jk} + 2 \cdot \left( ab \sum_{seg} t_{jk} \cdot \sum_{seg} m_{jk} - b \sum_{seg} t_{jk} \cdot \sum_{seg} m_{jk} - a \sum_{seg} t_{jk} m_{jk} \right) \right) - \left( N - 2 \right) \left( N \cdot \sum_{seg} t^2_{jk} - \left( \sum_{seg} t_{jk} \right)^2 \right)}} \text{ g/min}
\]

where the indexes \( j \) and \( k \) identify the specific operating condition out of \( J \) total, and the
comparison day (out of \( K > 1 \)), similar to the gas flow comparisons in 4.5.1.

(i) Calculate the relative standard error \( (U_{ajk}) \) of each liquid flow rate determination

\[
U_{mjk} = \frac{\text{stderr}_{ajk}}{\dot{m}_{jk}} \times 100\%
\]

(j) If any \( U_{mjk} \) value is greater than 1.0\%, take corrective action and repeat the affected
operating conditions. If no operational problem is detected, consider increasing the
interval for recording balance readings.

(k) On another day, repeat the entire comparison experiment, and record the \( U_{ajk} \) for all test
conditions. The experiment may be repeated more than once, provided all data are
recorded, and should result in lower uncertainty.
4.6.2 Combining Data and Correlating Expected to Certified Values

Once the comparison measurements are done, calculating one reference number for each flow condition means simply averaging the $\dot{m}_{jk}$ values, while the single-flow uncertainty ($U_{\dot{m}_{jk}}$) involves a combination of averages and uncertainties at various levels of the comparison process.

$$
\dot{m}_j = \sum_{k=1}^{K} \frac{\dot{m}_{jk}}{K}
$$

$$
U_{\dot{m}_j} = \sqrt{\frac{K-1}{K} \sum_{k=1}^{K} \left( \frac{U_{\dot{m}_{jk}}}{100\%} \right)^2 + \frac{1}{(K-1)} \sum_{k=1}^{K} (\dot{m}_{jk} - \dot{m}_j)^2} \times 100\%
$$

If the blending device is properly applying its linearization curves, the single-day/single-flow averages ($\dot{m}_{jk}$) should correlate well with the corresponding expected flow values ($x_{jk}$) as recorded by the blending device. To verify this, derive a linear equation similar to the gas correlation in 4.5.2. After determining the linear equation, the data points should be compared to the line. If any point is more than 2% above or below the line, take corrective action and repeat the comparisons.

4.6.3 Interpolation

During normal operation, the delivered liquid flow, to an even greater extent than the gas flow, will rarely match one of the calibrated points exactly. As such, linear interpolation is one of the two options for having a continuum of certified points over the full range of operation.

\begin{equation}
\dot{m} = \dot{m}_j + (x_{\text{liq}} - x_j) \left( \frac{\dot{m}_{\text{liq}} - \dot{m}_j}{x_{\text{liq}} - x_j} \right) = \dot{m}_j + (x_{\text{liq}} - x_j) \left( \frac{\dot{m}_{j\pm1} - \dot{m}_j}{x_{j\pm1} - x_j} \right)
\end{equation}

making sure that point $x_j$, $\dot{m}_j$ is the certified point nearest the $x_{\text{gas}}$ value to be interpolated, and $x_{j\pm1}$, $\dot{m}_{j\pm1}$ is an adjacent certified point chosen so that $x_{\text{gas}}$ is between, $x_j$ and $x_{j\pm1}$. The uncertainty calculation for this approach is similar to section 4.5.3.

$$
\left( \frac{\dot{m}_{\text{liq}} - \dot{m}_j}{x_{\text{gas}} - x_j} \right)_{\text{Max}} = \text{Max}(m_{j\pm1} - \dot{m}_j, m_{j\pm1} - (a \cdot x_j + b), (a \cdot x_{j\pm1} + b) - \dot{m}_j, a \cdot (x_{j\pm1} - x_j))
$$

$$
\left( \frac{\dot{m}_{\text{liq}} - \dot{m}_j}{x_{\text{gas}} - x_j} \right)_{\text{Min}} = \text{Min}(m_{j\pm1} - \dot{m}_j, m_{j\pm1} - (a \cdot x_j + b), (a \cdot x_{j\pm1} + b) - \dot{m}_j, a \cdot (x_{j\pm1} - x_j))
$$

$$
U_{\text{liq}} = \sqrt{\frac{\left( \frac{\dot{m}_{\text{gas}} - \dot{m}_j}{x_{\text{gas}} - x_j} \right)_{\text{Max}} - \left( \frac{\dot{m}_{\text{gas}} - \dot{m}_j}{x_{\text{gas}} - x_j} \right)_{\text{Min}}}{12}} \times 100\%
$$
\[ U_{\text{liq}} = \sqrt{\frac{U_{\text{mb}}^2 (x_{\text{liq}} - x_j)^2 + U_{\text{ml}}^2 \cdot V_j^2}{V_{\text{liq}}^2}} \]

where \( \dot{m} \) can be either \( m_{\text{sol}} \) or \( m_{\text{w}} \) (for working solution injection or DI water injection).

The alternative approach of applying the linear equation from 4.6.2 as a correction equation, within the range of liquid flow measurements, is also available.

\[ \dot{m}_{\text{liq}} = a \cdot x_{\text{liq}} + b \]

\[ U_{\text{liq}} = \sqrt{\left( \sum m_{\text{jk}}^2 + JKb^2 + a^2 \sum x_{\text{jk}}^2 + 2 \cdot \left( ab \sum x_{\text{jk}} - b \sum \dot{m}_{\text{jk}} - a \sum x_{\text{jk}} \dot{m}_{\text{jk}} \right) \right) \times 100\% \}

Note: It bears repeating that this alternative may yield a higher uncertainty than interpolation, particularly at the low end of the flow range.

Whichever calculation is used, interpolation or the linear correction, must be permanently recorded and incorporated into the device’s calculation of its expected output HCl concentration. Maintain documentation of the experimental measurements, derivation of the linear correction and interpolation equations, if used, and the uncertainty determinations for both the compared flow points and the interpolated/corrected points.

### 4.7 Calculation of Certified HCl Concentrations and Uncertainties

Section 4.2 describes how HCl gas vapor blending devices calculate and report the expected output concentration. These calculations are typically done automatically by the device’s microprocessor using the specific software/firmware version and data processing algorithms as implemented by the particular manufacturer. When certifying or using any blending device model for the first time, the calculations should be checked independently, according to standard engineering practices, to verify that the units of all inputs, the formulas used, and the units of the device output are all correct.

Defining the certified output concentrations, however, is a process that may or may not be readily and fully incorporated into the device itself. If the device software/firmware is robust enough to incorporate the algorithms of sections 4.6 and 4.7, it is likely that it can be configured to actually report the certified concentration as its expected concentration. Otherwise, an accessory program or macro will be needed to import raw or processed data from the device and calculate the certified concentration for use in calibrating or otherwise quality-assuring emissions measurement equipment.

#### 4.7.1 Bottled HCl Gas Humidifier

The certified output concentration of a bottled HCl gas humidifier is calculated by one of two formulas, depending on whether there is a carrier gas stream (\( v_{\text{add}} \)) used to deliver the moisture.
\[ C_{\text{wet}} = \frac{C_{\text{dry}} \cdot v_{\text{dry}}}{.001244 \cdot \dot{m}_w + v_{\text{dry}}} \quad \text{and} \quad C_{\text{wet}} = \frac{C_{\text{dry}} \cdot v_{\text{dry}}}{.001244 \cdot \dot{m}_w + v_{\text{dry}} + v_{\text{add}}} \]

Where

- \( C_{\text{wet}} \equiv \text{output HCl concentration, ppm} \)
- \( C_{\text{dry}} \equiv \text{HCl concentration of dry gas standard, ppm} \)
- \( v_{\text{dry}} \equiv \text{volumetric flow rate of dry HCl standard, liter/min} \)
- \( v_{\text{add}} \equiv \text{volumetric flow rate of inert carrier gas (if used), liter/min} \)
- \( \dot{m}_w \equiv \text{mass flow rate of humidification water, mg/min} \)

\( C_{\text{dry}} \) comes straight from the bottled gas certificate of analysis, where \( v_{\text{dry}} \) and \( v_{\text{add}} \) are each determined by the procedures in section 4.5, and \( \dot{m}_w \) follows section 4.6. The combined uncertainty incorporates these values and their uncertainties.

\[
U_{C_{\text{wet}}} = \sqrt{\left( \frac{v_{\text{dry}}}{2} \left( \frac{C_{\text{dry}} - C_{\text{wet}}}{C_{\text{wet}}} \right)^2 + \frac{U_{C_{\text{dry}}}}{2} \left( \frac{C_{\text{dry}}}{v_{\text{dry}}} \right)^2 + U_{v_{\text{add}}}^2 \left( v_{\text{add}} \right)^2 + U_{\dot{m}_w}^2 (0.001244 \dot{m}_w)^2 \right)}
\]

Where

- \( U_{v_{\text{dry}}} \) comes from the section 4.5 \( U_{\text{gas}} \) calculation, %
- \( U_{C_{\text{dry}}} \) comes from the dry gas standard certificate of analysis, %
- \( U_{v_{\text{add}}} \) comes from the section 4.5 \( U_{\text{gas}} \) calculation, %
- \( U_{\dot{m}_w} \) comes from the section 4.6 \( U_{\text{gas}} \) calculation, %

4.7.2 Evaporative HCl Gas Standard

The certified output concentration of an evaporative HCl gas standard is calculated by one of two formulas, depending on whether there is an additional liquid stream of deionized or distilled water (\( \dot{m}_w \)).

\[
C_{\text{wet}} = \frac{22.414 \cdot M_{\text{ws}} \cdot v_{\text{sol}}}{.001244 \cdot \dot{m}_{\text{sol}} + v_{\text{add}}} \quad \text{and} \quad C_{\text{wet}} = \frac{22.414 \cdot M_{\text{ws}} \cdot v_{\text{sol}}}{.001244 \cdot (\dot{m}_{\text{sol}} + \dot{m}_w) + v_{\text{add}}}
\]

where

- \( C_{\text{wet}} \equiv \text{output HCl concentration, ppm} \)
- \( M_{\text{ws}} \equiv \text{molarity of HCl working solution, mol/liter} \)
- \( v_{\text{sol}} \equiv \text{volumetric flow rate of HCl working solution, } \mu\text{l/min} \)
- \( \dot{m}_{\text{sol}} \equiv \text{mass flow rate of HCl working solution, mg/min} \)
- \( \dot{m}_w \equiv \text{mass flow rate of additional water, mg/min} \)
- \( v_{\text{add}} \equiv \text{volumetric flow rate of inert carrier gas, liter/min} \)

\( M_{\text{ws}} \) comes either from the solution provider’s certificate of analysis, or from section 4.4 if the solution was prepared from a more concentrated standard solution. Values for \( \dot{m}_{\text{sol}} \) and \( \dot{m}_w \) are each determined by the procedures in section 4.6, which also provides that \( v_{\text{sol}} = \dot{m}_{\text{sol}} \) because the
working solution density is 1.000 mg/µl. The value of $\nu_{\text{add}}$ comes from section 4.5. The combined uncertainty incorporates these values and their uncertainties.

$$U_{\text{corr}} = \sqrt{U_{\text{add}}^2 + m_{\text{add}}^2 (22.414 \cdot M_{\text{w}} - 0.001244 \cdot C_{\text{corr}})^2 + U_{\text{gas}}^2 + m_{\text{gas}}^2 (22.414 \cdot \nu_{\text{sol}})^2} \pm \frac{(0.001244 \cdot m_{\text{sol}} + m_{\text{gas}} + \nu_{\text{add}})^2}{2}$$

Where $U_{\text{add}}$ comes from the section 4.6 $U_{\text{liq}}$ calculation, $\%$

$U_{\text{gas}}$ comes from the section 4.4 $U_{\text{gas}}$ calculation, $\%$

$U_{\nu_{\text{add}}}$ comes from the section 4.5 $U_{\text{gas}}$ calculation, $\%$

$U_{\text{gas}}$ comes from the section 4.6 $U_{\text{liq}}$ calculation, $\%$

Note: If a commercially available working solution is used instead of diluting a more concentrated commercial standard, look for the uncertainty on the certificate of analysis and divide this number by an assumed coverage factor of $k=2$ to get the value of $U_{\text{gas}}$.

### 4.7.3 Expanded Uncertainty

The performance specification for uncertainty will be based on expanded uncertainty. To calculate this quantity, multiply the combined uncertainty value from 4.7.1 or 4.7.2 by a coverage factor. Unless specified otherwise in the applicable regulation, a coverage factor of $k=2$ should be used.

### 4.8 Alternative Approach: Direct Comparison to a Traceable Reference Gas Standard

As an alternative to relying on the calculations of section 4.7 to determine certified output concentrations, a blending device may instead undergo a *bracketing procedure* that provides a direct comparison to a certified gas standard. In a *bracketing procedure*, the outputs from two sources (in this case, a gas/vapor blending device and a certified gas standard) are introduced alternately to a measurement system or detector so that each response from the *candidate* (blending device) is bracketed by a pair of responses from the reference (certified gas standard). At each concentration, the bracketing procedure requires a minimum of four responses from the *reference* and three responses from the *candidate*. An example of a bracketing procedure injection sequence, as performed at a single output concentration, is provided in Table 5.

<table>
<thead>
<tr>
<th>Source</th>
<th>Response ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Standard</td>
<td>RS1</td>
</tr>
<tr>
<td>Candidate</td>
<td>C1</td>
</tr>
<tr>
<td>Reference Standard</td>
<td>RS2</td>
</tr>
<tr>
<td>Candidate</td>
<td>C2</td>
</tr>
<tr>
<td>Reference Standard</td>
<td>RS3</td>
</tr>
<tr>
<td>Candidate</td>
<td>C3</td>
</tr>
<tr>
<td>Reference Standard</td>
<td>RS4</td>
</tr>
</tbody>
</table>

Table 5: Example of Bracketing Procedure Injection Sequence
In addition to the minimum of three candidate injections as shown above, the bracketing procedure must be performed at a minimum of three concentrations (covering the blending device’s usable range), for a 3x3 or larger bracketing matrix. Also, this entire comparison sequence must be repeated at least once on a different day after the blending device has been shut down and restarted by the manufacturer’s recommended procedures. The bracketing comparisons are used to calculate an average concentration ratio between the candidate and reference gases, and the repetition of the 3x3x2 (or larger) certification matrix (see Table 6) is used to assess the repeatability and reproducibility of the certification results.

Table 6: Example Bracketing Certification Matrix

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Day 1</th>
<th>Day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>1Z₁</td>
<td>2Z₁</td>
</tr>
<tr>
<td>High</td>
<td>1H-RS₁</td>
<td>2H-RS₁</td>
</tr>
<tr>
<td>High</td>
<td>1H-C₁</td>
<td>2H-C₁</td>
</tr>
<tr>
<td>High</td>
<td>1H-RS₂</td>
<td>2H-RS₂</td>
</tr>
<tr>
<td>High</td>
<td>1H-C₂</td>
<td>2H-C₂</td>
</tr>
<tr>
<td>High</td>
<td>1H-RS₃</td>
<td>2H-RS₃</td>
</tr>
<tr>
<td>High</td>
<td>1H-C₃</td>
<td>2H-C₃</td>
</tr>
<tr>
<td>High</td>
<td>1H-RS₄</td>
<td>2H-RS₄</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-RS₁</td>
<td>2M-RS₁</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-C₁</td>
<td>2M-C₁</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-RS₂</td>
<td>2M-RS₂</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-C₂</td>
<td>2M-C₂</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-RS₃</td>
<td>2M-RS₃</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-C₃</td>
<td>2M-C₃</td>
</tr>
<tr>
<td>Mid</td>
<td>1M-RS₄</td>
<td>2M-RS₄</td>
</tr>
<tr>
<td>Low</td>
<td>1L-RS₁</td>
<td>2L-RS₁</td>
</tr>
<tr>
<td>Low</td>
<td>1L-C₁</td>
<td>2L-C₁</td>
</tr>
<tr>
<td>Low</td>
<td>1L-RS₂</td>
<td>2L-RS₂</td>
</tr>
<tr>
<td>Low</td>
<td>1L-C₂</td>
<td>2L-C₂</td>
</tr>
<tr>
<td>Low</td>
<td>1L-RS₃</td>
<td>2L-RS₃</td>
</tr>
<tr>
<td>Low</td>
<td>1L-C₃</td>
<td>2L-C₃</td>
</tr>
<tr>
<td>Low</td>
<td>1L-RS₄</td>
<td>2L-RS₄</td>
</tr>
<tr>
<td>Zero</td>
<td>1Z₂</td>
<td>2Z₂</td>
</tr>
</tbody>
</table>

4.8.1 Stepwise Bracketing Procedure

(a) Turn on all components of the HCl gas/vapor blending device, the HCl measurement system (analyzer), and any associated equipment; allow them to reach thermal equilibrium and stable operation.

(b) While awaiting warm-up, check that all data acquisition and logging systems associated with the blending device and the analyzer are operational and properly configured to record data at a sufficient time and concentration resolution, so that complete documentation of the certification test procedures is available for future inspection.

(c) After equilibrium has been established, inject zero gas and make any necessary adjustments to the zero response. Then, calibrate the detector by injecting the high-level
reference gas standard and making any necessary span adjustments. Repeat these steps as necessary to optimize the analyzer calibration relative to the reference standard.

*Note: Adjusting the analyzer to provide the correct responses to the reference gas standard is considered to be a valuable diagnostic technique to detect changes in the measurement system that can adversely affect the bracketing procedure.*

(d) Before beginning the bracketing procedure, ensure that the blending device, the analyzer, and any support equipment are operating within the prescribed limits for all key parameters as specified by the respective manufacturers.

(e) Set the blending device to the first set point (i.e., the high-level or low-level point, as deemed appropriate) and allow the device operation and output to stabilize.

(f) Turn on the reference gas standard that is closest in concentration to the blending device output, and feed this gas standard to the analyzer inlet and obtain a response (RS₁). It is recommended that the recorded response at each test point be based on at least 5 minutes of stable readings.

(g) Shut off the reference gas standard and direct the output of the HCl gas/vapor blending device to the analyzer. Allow the HCl measurements to stabilize and record an average response (C₁), again based on at least 5 minutes of stable readings.

(h) Switch back to feeding the reference gas standard to the analyzer and record an average response (RS₂).

(i) Repeat steps (g) and (h) at least two more times at this concentration to provide three or more candidate responses, each preceded and followed by a reference standard response.

*Note: If, at any time during the process, test results demonstrate that equilibration is not being achieved, or that any key parameter is not within acceptable limits, stop the experiment, investigate and correct the problem. Valid data collected up to that point in the test may be retained. Discard all data collected at non-equilibrium conditions or with any key parameter outside of prescribed limits; such data are not valid and may not be used for certification of the blending device.*

(j) Repeat steps (e) through (i) for at least two more concentrations. Be sure to allow the blending device to reach equilibrium at each new setting before recording any responses.

(k) Inject the zero gas to the analyzer and record an average response without making any adjustments.

(l) Shut down the HCl gas/vapor blending device according to the manufacturer’s instructions. Also shut down all data logging and any other equipment that is not designed to be left on overnight.
(l) On another day, repeat steps (a) through (k). The bracketing procedure may be repeated more than once, provided all data are recorded, and should result in lower uncertainty.

4.8.2 Bracketing Data Processing

Determining the certified output of the blending device starts with correcting each response for any zero offset of the analyzer. For each test day, calculate the interpolated zero offset based on the time when a specific response was recorded as follows:

\[
Z_i = Z_1 + \left[ (t_i - t_1) \frac{(Z_2 - Z_1)}{(t_2 - t_1)} \right]
\]

(Equation 4)

Where:
- \(Z_i\) = Calculated zero offset at \(t_i\)
- \(Z_1\) = Initial zero response
- \(Z_2\) = Final zero response
- \(t_i\) = Time of response to be zero corrected
- \(t_1\) = Time initial zero response was recorded
- \(t_2\) = Time final zero response was recorded

Then, correct the response at \(t_i\) for the zero offset using the following equation:

\[
Y_{ci} = Y_i - Z_i
\]

(Equation 4)

Where:
- \(Y_{ci}\) = Response at \(t_i\) corrected for zero offset
- \(Y_i\) = Response at \(t_i\) as recorded during bracketing
- \(Z_i\) = Zero offset at \(t_i\)

The data set in Table 7 provides an example of how each response is corrected for zero offset over the course of a test period.

**Table 7: Zero Corrections for an Example Data Set**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Zero Response</th>
<th>Interpolated Zero</th>
<th>(RS_i) Response</th>
<th>(RS_{ci}) Zero-Cor.</th>
<th>(C_i) Response</th>
<th>(C_{ci}) Zero-Cor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>10.00</td>
<td>9.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.08</td>
<td>10.00</td>
<td>9.85</td>
<td>9.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.12</td>
<td>10.20</td>
<td>10.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.16</td>
<td></td>
<td>9.96</td>
<td>9.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.20</td>
<td>10.25</td>
<td>10.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.24</td>
<td></td>
<td>10.00</td>
<td>9.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.28</td>
<td>10.40</td>
<td>10.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Next, for each zero-corrected value of $C_{Ci}$, calculate the output ratio $R_i$, using the formula shown in Equation 5 for the first candidate injection response.

$$R_i = \left[ \frac{C_{Ci}}{\frac{RS_{C1} + RS_{C2}}{2}} \right]$$

(Equation 5)

Where: $R_i$ = Output ratio for first candidate device injection  
$C_{Ci}$ = First response to candidate device, zero corrected  
$RS_{C1}$ = First response to reference gas standard, zero corrected  
$RS_{C2}$ = Second response to reference gas standard, zero corrected

Table 8 illustrates these calculations for the example data set presented in Table 7.

**Table 8: Example Calculation of Output Ratio**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$RS_i$ Response</th>
<th>$RS_{ci}$ Zero-Cor.</th>
<th>$C_i$ Response</th>
<th>$C_{ci}$ Zero-Cor.</th>
<th>Output Ratio ($R_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.00</td>
<td>9.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>9.85</td>
<td>9.77</td>
<td>0.975</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>10.20</td>
<td>10.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>9.95</td>
<td>9.80</td>
<td>0.974</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>10.25</td>
<td>10.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>10.00</td>
<td>9.76</td>
<td>0.968</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>10.40</td>
<td>10.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For each of $J \geq 3$ concentrations on each of $K \geq 2$ days, calculate the average ratio $R_{jk}$ and the relative standard deviation (RSD) of the individual output ratio measurements.

$$R_{jk} = \frac{\sum_{i=1}^{I} R_i}{I}$$

$$U_{R_{jk}} = RSD = \sqrt{\frac{I}{(I-1)} \left( \frac{\sum_{i=1}^{I} (R_i - R_{jk})^2}{I} \right)} \times \frac{100\%}{R_{jk}}$$

Where: 
RSD = Relative standard deviation, percent  
$R_{jk}$ = Arithmetic average of the output ratios  
$R_i$ = Individual, “ith” output ratio  
$I$ = Number of output ratio measurements

*Note: The RSD is also the bracketing “repeatability” uncertainty, which will be later combined with other components to calculate the overall uncertainty of the output concentration. The RSD must not exceed 1.0%. If the RSD value is exceeded, the test at that concentration is invalid and must be repeated. The calculated RSD value for the output ratios in Table 8 is 0.4%, and is therefore acceptable.*
Finally, the output concentration is calculated by averaging the $R_{jk}$ ratios at each concentration and multiplying those averages by the corresponding concentration of the certified reference gas.

$$R_j = \frac{\sum_{k=1}^{K} R_{jk}}{K} \quad C_j = R_j \times C_{jref}$$

Where:
- $R_j$ = Overall average ratio for concentration $j$ bracketing
- $R_{jk}$ = Average ratio measured at concentration $j$ on day $k$
- $K$ = Number of days of bracketing experiments
- $C_j$ = Certified concentration from blending device
- $C_{jref}$ = Certified concentration of reference gas used during bracketing at concentration $j$

### 4.8.3 Concentration Uncertainty from Bracketing

When using bracketing to certify calibration gases, the calculation of uncertainty is complicated by the fact that bracketing is an inherently indirect comparison (i.e., the analyzer cannot measure both outputs at the same time, so it must function as an intermediate). Appendix A of this document (which is based on another protocol that uses bracketing) shows all of the uncertainty components and how they are combined to calculate overall concentration uncertainty.

### 4.8.4 Operational Monitoring Requirement

As a condition of using this alternative approach to certification, the operational parameters of the device must be continuously monitored for shifts that could impact the output concentration. These operational parameters include, minimally, all gas and liquid flows, each of which must remain within ±2.0% of the value recorded during certification. Because the bracketing certification values are related specifically to the original operating conditions, any shift in those operating conditions outside of the ±2.0% allowance triggers the need to recertify and reverify the device output.

### 5.0 VERIFICATION

To verify the output of the device, perform a direct comparison of the output to compressed gas cylinders containing HCl with NIST-traceable concentrations. The comparison measurements must be done by an HCl measurement system or detector that is subject to regular QA/QC activities to verify its stable operation.

### 5.1 Comparison Concentrations

This verification will be done at two different output concentrations from among those routinely used by the device in operation. One of the two concentrations must have the blending device operating at its most-used operating condition, which for CEMS applications will likely be the concentration used for daily calibration error checks. One of the bottled HCl gas standards needs
to be within ±30% of that concentration. The other gas standard may be higher or lower, but must have a concentration between 40% and 250% of the first bottle in order to assess the response linearity of the HCl measurement system. Both bottled HCl gas standards must have an uncertainty of ±2.0% or better.

5.2 Verification Setup

Assemble a manifold for the HCl measurement system inlet that allows easy switching between the gas/vapor blending device and the compressed HCl gas standards. This manifold design must ensure that

- There are no changes in manifold pressure or flow to the detector when switching valves.
- Output flow from the gas vapor blending device is unrestricted, even when the manifold valve from that device is closed.
- There is no leakage through the valves when they are closed, even if the bottled gases exert pressure against their valves.
- Materials of construction are inert to HCl gas.

The manifold may also include a valve for zero gas, and may use solenoid valves for automated switching.

5.3 Stepwise Verification Procedure

(a) Inject zero gas to the HCl measurement system, and make necessary adjustments to bring the response to zero.

(b) With the measurement system connected to the switching manifold, inject the higher of the two compressed gases, and make necessary adjustments to make the response match the certified concentration.

(c) Inject the other compressed gas, and check that the response matches the certified concentration within ±2.0% of the higher gas value. If this tolerance is exceeded, take corrective action and repeat from step (a).

(d) Switch the manifold to the gas/vapor blending device operating at its most used operating condition. Allow at least one minute for the response to begin changing, and wait for it to stabilize at the new value. Record the average stable response.

(e) Switch back to the bottled gas whose concentration is closest to the blending device concentration. Allow at least one minute for the response to begin changing, then wait for a stable response before recording the average value.

(f) Continue alternating between the bottled gas and the blending device until at least three blending device responses have been recorded, each one immediately preceded and followed by a bottled gas response (i.e., a minimum of four bottled gas responses).
(g) For each blending device response average, divide this response by the average of the two adjacent bottled gas responses (i.e., before and after) and to get a response ratio.

\[ R_i = \frac{\bar{m}_{\text{Device}}}{(\bar{m}_{\text{Bottle-Before}} + \bar{m}_{\text{Bottle-After}})/2} \]

(h) After calculating all of these ratios, calculate the relative standard deviation of the ratios.

\[ RSD = \sqrt{\frac{\sum_{i=1}^{I} (R_i - \bar{R})^2}{I-1}} \times 100\% \]

Where:
- \( RSD \equiv \) Relative standard deviation, percent
- \( \bar{R} \equiv \) Arithmetic average of the output ratios
- \( R_i \equiv \) Individual output ratio
- \( I \equiv \) Number of output ratios (\( \geq 3 \))

(i) The RSD must not exceed 1.0%. If the RSD value is exceeded, the test is invalid and must be repeated.

(j) Use the average response ratio to calculate a verification value

\[ C_{\text{Verification}} = \bar{R} \times C_{\text{Bottle}} \]

(k) Switch to the other bottled gas, and record a stable response as before.

(l) Select the routinely-used device operating condition that produces an output closest to the bottle concentration, and repeat the procedure from step (d) to get a verification value.

5.4 Verification Tolerance

For each of the two verified points, calculate the verification tolerance as the combined uncertainty of the device output and the verification value (ignoring the uncertainty of the response ratio, which should be small).

\[ \text{Tolerance} = 2 \times \sqrt{U^2_{\text{Verification}} + \bar{R} \times U^2_{\text{Bottle}}} \]

Where \( U_{\text{Verification}} \) is the device output uncertainty calculated in section 4.7.1 or 4.7.2, and \( U_{\text{Bottle}} \) is the bottle concentration uncertainty (divided by its coverage factor). If the difference between the device’s certified output concentration and the verification value exceeds this tolerance, take corrective action and repeat the verification.
6.0 QUALITY ASSURANCE

This section specifies: (1) the periodic data quality assessments that are required following initial certification of an HCl gas/vapor blending device, to provide assurance of continued acceptable performance; and (2) the required frequency of device recertification.

6.1 Periodic Data Quality Assessments

Periodic performance evaluations of each blending device shall be conducted at the following frequency:

(a) At least once each calendar quarter; and

(b) Following any malfunction, repair, or corrective action that may reasonably be expected to affect the device’s output, but does not necessitate recertification of the device (see Section 6.2, below).

Any of the data quality assessment procedures (Options A through C) described in Sections 6.1.1 through 6.1.3 below, may be used for the performance evaluations.

If the HCl gas/vapor blending device does not meet the acceptable performance criteria, suspend the device certification until either:

(a) Another performance evaluation is successfully completed, or

(b) The device is recertified in accordance with the procedures in Section 4, and the output is verified by the procedure in Section 5.

6.1.1 Option A: Single-Point Verification of Inputs

For periodic performance evaluations that are not precipitated by a device malfunction, the evaluation may take the form of a simple check of the input measurements that are used to calculated the certified output. Where a device malfunction has occurred, this option is only to be used when the malfunction was confined to one of the measurement components (i.e., gas flow or liquid flow), and that component has been recertified (or replaced and recertified) using the process in Section 4.5 or 4.6.

This check will be done with the device operating at the condition that is used most often by the measurement system(s) to which the blending device is connected. For CEMS applications, this will likely be the HCl concentration that is used for daily calibration error checks.

(a) For bottled HCl gas humidifiers, measure each of the gas and liquid flow rates with ±1% NIST-traceable flow standards.
For evaporative HCl gas standards, perform the checks in (a) above, then collect a sample of the HCl feed solution from the input reservoir, and have the sample analyzed for HCl concentration by an independent laboratory.

The acceptable performance criterion for each of the measurements is a difference \( \leq 2.0\% \) of the reference value.

6.1.2 Option B: Operational Envelope Linearity Verification

For devices where the liquid and gas flows can be independently set and maintained without substantially limiting each other’s range, acceptable performance may be verified by exercising the blending device near the boundaries of its operational envelope (i.e., the maximum and minimum liquid and gas flows recommended by the manufacturer). The evaluation metric will be the linearity of the output HCl, as determined by the connected measurement system, its detector (i.e., without the sample conditioning and delivery system), or another HCl detector that is subject to regular QA/QC activities to verify its response linearity.

Like Option A above, this option is not to be used when the performance evaluation is precipitated by a device malfunction, unless the malfunction is confined to one of the measurement components (i.e., gas flow or liquid flow), and that component has been recertified (or replaced and recertified) using the process in Section 4.5 or 4.6.

For this check, define an operating envelope consisting of the highest and lowest settings that each flow measurement can maintain without imposing limits on the range of the other flow measurement(s) beyond the manufacturer’s specifications.

(a) With the liquid flow at its highest setting within the operating envelope, operate the blending device such that the gas flows at its highest, lowest, and at least one intermediate setting (nominally equally spaced between the highest and lowest settings), all within the operating envelope, while the liquid flow remains constant.

(b) Allowing the HCl detector response to stabilize at each condition, record the average response and the reported HCl concentration from the blending device at each operating condition, resulting in at least three pairs of data points.

(c) Calculate a best-fit line for the data points collected in step (b). If any point is more than 3% above or below the line, take corrective action and repeat the check.

(d) Adjust the blending device so that the liquid flow is at its lowest setting within the operating envelope, and repeat steps (a) through (c) at this setting.

(e) If the device uses a second gas flow, repeat steps (a) through (d) for that measurement.

(f) Choose one or more intermediate liquid flow rates, and operate the blending device such that the gas flow is at its highest and lowest setting within the operating envelope.
(g) Similar to before, allow the HCl detector response to stabilize at each condition, and record the average response. Combine these data points with the highest and lowest liquid and gas flow points from step (b), so there are at least three highest gas flow conditions, and three lowest gas flow conditions.

(h) Calculate two best-fit lines from the step (g) data points, each representing the reported HCl versus measured HCl at a constant gas flow and variable liquid flow (one for all the highest gas flow points, and one for all the lowest gas flow points), where the blending device output varies solely due to differences in the liquid flow. If any point is more than 3% above or below the line, take corrective action and repeat the check.

(i) If the device uses a second liquid flow (e.g., to control moisture independently of HCl), repeat steps (f) through (h) for that measurement, but include the highest and lowest liquid flows in step (f) so that the check includes the full range of liquid flows.

(j) For evaporative HCl gas standards, perform all of the checks above, then collect a sample of the HCl feed solution from the input reservoir, and have the sample analyzed for HCl concentration by an independent laboratory.

6.1.3 Option C: Comparison to a Dry Bottled HCl Gas Standard

Evaluate the performance of a gas/vapor blending device by direct comparison to a compressed gas cylinder containing HCl with a NIST-traceable concentration. Like Option B above, the comparison measurements may be done by the connected measurement system, its detector (i.e., without the sample conditioning and delivery system), or another HCl detector that is subject to regular QA/QC activities to verify its response linearity.

Similar to Option A above, this check will be done with the blending device operating at its most-used operating condition, which for CEMS applications will likely be the concentration used for daily calibration error checks. In order to have an effective comparison, the bottled HCl gas standard needs to be within ± 30% of that concentration, and have an uncertainty ≤ ±2.0%.

(a) Connect the blending device and the bottled gas to a manifold similar to the one used for verification in section 5. Connect this manifold to the measurement system or detector in a way that does not restrict the output flow or allow air in-leakage.

(b) Feed bottled gas through the manifold to the measurement system/detector. Allow the response to stabilize and record the average stable response.

(c) Switch the manifold to the gas/vapor blending device. Allow at least one minute for the response to begin changing, and wait for it to stabilize at the new value. Record the average stable response.

(d) Continue alternating between the bottled gas and the blending device until at least three blending device responses have been recorded, each one immediately preceded and followed by a bottled gas response (i.e., a minimum of four bottled gas responses).
(e) For each blending device response average, divide this response by the average of the two adjacent bottled gas responses (i.e., before and after) and to get a response ratio.

\[ R_i = \frac{m_{Device}}{(m_{Bottle-Before} + m_{Bottle-After})/2} \]

(f) After calculating all of these ratios, calculate the relative standard deviation of the ratios.

\[ RSD = \sqrt{\frac{\sum_{i=1}^{I}(R_i - \bar{R})^2}{I-1}} \times 100\% \]

Where:
- \( RSD \) ≡ Relative standard deviation, percent
- \( \bar{R} \) ≡ Arithmetic average of the output ratios
- \( R_i \) ≡ Individual output ratio
- \( I \) ≡ Number of output ratios (≥ 3)

(g) The RSD must not exceed 1.0%. If the RSD value is exceeded, the test is invalid and must be repeated.

(h) Multiply the average ratio by the certified HCl concentration of the bottled gas to get the reference concentration. If the reported concentration from the blending device software differs from this reference concentration by more than the concentration uncertainty limit from the applicable regulation (or 5.0%, whichever is less), take corrective action and repeat the test.

6.1.4 Option D: Comparison to Another Certified HCl Gas/Vapor Blending Device

This option is functionally similar to Option C, except instead of a bottled gas, a field reference blending device is used. In order to qualify for field reference applications, a device must be annually recertified to an uncertainty of ≤ ±2.0%, and undergo the same quarterly quality assurance checks as an in-service device connected to a measurement system.

6.2 Recertification

Following initial certification, all HCl gas/vapor blending devices must be periodically recertified to maintain NIST traceability. At a minimum, devices shall be recertified at least once every 8 calendar quarters in accordance with the procedures in Sections 4 and 5. Devices shall also be recertified whenever (1) any event, condition, or factor that triggers recertification (as identified in the Manufacturer’s Disclosure) occurs, or (2) device performance is suspected to be the cause of a CEMS RATA failure.
6.2.1 Full Recertification

Any recertification that involves full implementation of the procedures in Sections 4 and 5 is a full recertification, which resets the “once every 8 calendar quarters” interval.

6.2.2 Cumulative Certification

If, during the first day of flow comparisons for the recertification procedure (see Sections 4.5.1 and 4.6.1), it becomes clear that the HCl gas/vapor blending device performance compares very well to the most recent certification, there is an option to simply incorporate the day’s data with the data from the previous comparisons for purposes of calculating reproducibility. For a very stable device, this could substantially improve the overall uncertainty, and reduce the level of effort to maintain certification. If, however, using the old comparison data causes excess reproducibility uncertainty, that data may be abandoned in favor of a full recertification with an additional day (or more) of comparison tests. Regardless of whether a cumulative or full recertification is performed, the process must include the Section 5 verification process.

6.2.3 Partial Recertification

If a recertification is triggered by a malfunction or other event that is identified in the Manufacturer’s Disclosure, and the cause is confined to one specific measurement component, a partial recertification may be performed. In this type of recertification, the Section 4 procedures are only performed on the affected measurement component, and the traceable concentrations from the previous certification are recalculated with the new data substituted. This partial recertification does not change the expiration of the earlier certification (i.e., no resetting of the “once every 8 calendar quarters” interval), and it does require a Section 5 verification process.

7.0 REFERENCES

Appendix A – Concentration Uncertainty from Bracketing Alternative

When assigning concentration values to blending device operating conditions by bracketing, five sources of uncertainty have been identified:

- Calibration Linearity
- Measurement Stability
- Repeatability
- Reproducibility
- Reference Uncertainty

The first three uncertainty components apply specifically to a bracketing procedure. The other two components apply to the overall process of transferring traceability from the reference gas(es) to the candidate.

A.1 Calibration Linearity

[Reserve]

A.2 Measurement Stability

The measurement stability uncertainty calculation applies a statistical test to the assumptions that are built into the bracketing technique (e.g., no non-linear drift, wavering responses, or excessively “noisy” measurements). This uncertainty component is quantified in terms of the residual error estimate for these two lines:

\[
SE_{\text{Cand}} = \sqrt{\frac{\sum (m_{\text{Cand}} - \bar{m}_{\text{Cand}})^2 - \left[\sum (m_{\text{Cand}} - \bar{m}_{\text{Cand}})(t_{\text{Cand}} - \bar{t}_{\text{Cand}})\right]^2}{(n_{\text{Cand}} - 2)}}
\]

\[
SE_{\text{Ref}} = \sqrt{\frac{\sum (m_{\text{Ref}} - \bar{m}_{\text{Ref}})^2 - \left[\sum (m_{\text{Ref}} - \bar{m}_{\text{Ref}})(t_{\text{Ref}} - \bar{t}_{\text{Ref}})\right]^2}{(n_{\text{Ref}} - 2)}}
\]

where \(t_{\text{Cand}}\) and \(t_{\text{Ref}}\) are the timestamps associated with the candidate and reference measurements. The \(t\) units and the \(t = 0\) origin can be anything, as long as they are consistent within each standard error calculation. The bold \(m\) and \(n\) values refer to all of the points of the regression lines. The standard errors for these lines are used to calculate the standard error of the mean of each individual measurement interval.
where $\bar{m}$ is the mean for just that measurement interval, and \( n \) is the number of individual measurements in that interval. The subscript notations (i.e., Ref-B, Cand, and Ref-A) relate to the before-candidate reference measurement, the candidate measurement, and the after-candidate reference measurement (respectively). For each ratio calculation, these standard errors are used to calculate a combined stability uncertainty for this ratio

\[
R_i = \frac{t_{\text{Ref-A}} - t_{\text{Cand}} \cdot \bar{m}_{\text{Cand}}}{t_{\text{Ref-A}} - t_{\text{Ref-B}} \cdot \bar{m}_{\text{Ref-B}} - t_{\text{Ref-B}} \cdot \bar{m}_{\text{Ref-A}}}
\]

\[
u_{1\sigma}(R_i)_{\text{stability}} = R_i \times \left( \frac{SE(\bar{m}_{\text{Ref-B}})}{t_{\text{Ref-A}} - t_{\text{Ref-B}} \times \bar{m}_{\text{Ref-B}}} \right)^2 + \left( \frac{SE(\bar{m}_{\text{Cand}})}{t_{\text{Ref-A}} - t_{\text{Cand}} \times \bar{m}_{\text{Ref-B}}} \right)^2 + \left( \frac{SE(\bar{m}_{\text{Ref-A}})}{t_{\text{Ref-A}} - t_{\text{Ref-B}} \times \bar{m}_{\text{Ref-A}}} \right)^2
\]

where $R_i$ is the measured ratio for one of \( I \geq 1 \) individual brackets performed at concentration \( j \) on day \( k \) (out of \( K \geq 1 \) days).

Measurement stability is one of three uncertainty components (the first being detector linearity) that relate only to a single bracketing procedure, with average ratio

\[
R_{jk} = \frac{\sum_{i=1}^{I} R_i}{I}
\]

and measurement stability uncertainty

\[
u_{1\sigma}(R_{jk})_{\text{stability}} = \sqrt{\frac{1}{I} \sum_{i=1}^{I} u^2(R_i)_{\text{stability}}}
\]

where \( I \) is the number of brackets in this \( j^{th} \) set.

Note: Whenever a “\( jk \)” subscript appears in this appendix, the term represents an average for the \( j^{th} \) concentration on the \( k^{th} \) bracketing day. When the “\( j \)” subscript appears alone, the term represents the average for the \( j^{th} \) concentration, inclusive of all test days.

### A.3 Repeatability

The most straightforward way to calculate repeatability is a simple standard deviation of the individual bracket ratios.
This approach, however, creates the possibility of “double-counting” where measurement instability contributes to imprecision. To allow for this, the experiments are structured as a 3-level nested design (see chapter 2 of NIST’s “Engineering Statistical Handbook” http://www.itl.nist.gov/div898/handbook/mpc/section4/mpc433.htm), as follows:

Level 1: Individual ratio uncertainty
Level 2: Repeatability within set (sometimes called “within day” uncertainty)
Level 3: Set reproducibility (sometimes called “between day” uncertainty)

In a nested experimental design, standard errors are pooled at each level, and the level-specific contributions to uncertainty are computed from these pooled standard errors. Starting with the pooled level-1 standard error

\[
s_{1R} = \sqrt{\frac{1}{I} \sum_{i=1}^{I} u^2 (R_i)_{\text{stability}}} \quad \text{(subscript R denotes a Ratio uncertainty component)}
\]

and the level-2 standard deviation

\[
s_{2R} = \sqrt{\frac{\sum_{i=1}^{I} (R_i - R_{jk})^2}{(I-1)}}
\]

The repeatability uncertainty of the ratio measurements is computed using

\[
u_{\sigma} (R_i)_{\text{repeatability}} = \sqrt{\text{Max} \left[ 0, \ s_{2R}^2 - \frac{1}{L} \times s_{1R}^2 \right]} = \sqrt{\text{Max} \left[ 0, \ \frac{\sum_{i=1}^{I} (R_i - R_{jk})^2}{(I-1)} - \frac{\sum_{i=1}^{I} u^2 (R_{jk})_{\text{stability}}}{I \times L} \right]}
\]

where \( L \) represents the average number of individual detector readings used in each measurement average and ratio determination

\[
L = \frac{1}{I} \sum_{i=1}^{I} (n_{\text{Ref-B,i}} + n_{\text{Cand,i}} + n_{\text{Ref-A,i}})
\]

The uncertainty of the set-average ratio is

\[
u_{\sigma} (R_{jk})_{\text{repeatability}} = \frac{1}{\sqrt{I}} u_{\sigma} (R_i)_{\text{repeatability}} = \frac{1}{\sqrt{I}} \times \sqrt{\text{Max} \left[ 0, \ \frac{\sum_{i=1}^{I} (R_i - R_{jk})^2}{(I-1)} - \frac{\sum_{i=1}^{I} u^2 (R_{jk})_{\text{stability}}}{I \times L} \right]}
\]
The “Max” function holds this term at zero when short-term precision uncertainty is dominated by measurement instability.

A.4 Reproducibility

Reproducibility is an uncertainty term applied to the calculated candidate concentrations \( C_{jk} = R_{jk} \times C_{j\text{ref}} \). It may be estimated differently depending on what type of device is being certified or how many times the bracketing procedure is repeated.

A.4.1 Statistical Approach

A 3-level nested design\(^2\) assumes that the ratio measurement is done \( I > 1 \) times on each of \( K > 1 \) days. Using the same technique as for the repeatability uncertainty

\[
 u_\sigma(C_{jk})_{\text{reproducibility}} = \sqrt{\text{Max}\left[0, \frac{s_{3C}^2}{I} - \frac{1}{K} \times s_{2C}^2\right]}
\]

where

\[
 s_{3C} = \sqrt{\frac{1}{K-1} \sum_{k=1}^{K} (C_{jk} - C_j)^2} \quad \text{(subscript C denotes Concentration uncertainty)}
\]

\[
 C_j = \frac{\sum_{k=1}^{K} C_{jk}}{K}
\]

and \( s_{2R} \) values (from A.3) are converted to \( C_{jk} \) errors and pooled as follows

\[
 s_{2C} = \sqrt{\frac{1}{\Sigma I_k - K} \sum_{k=1}^{K} (I_k - 1) \times (C_{jk,\text{ref}} \times s_{2R})^2}
\]

As with the repeatability uncertainty, the “Max” function holds this term at zero when the deviation among sets is dominated by short-term effects. The reproducibility uncertainty of the mean candidate concentration is

\[
 u_\sigma(C_j)_{\text{reproducibility}} = \frac{1}{\sqrt{K}} \sqrt{\text{Max}\left[0, \frac{s_{3C}^2}{I} - \frac{1}{K} \times s_{2C}^2\right]}
\]

A.4.2 Bound on Bias (BOB) Approach

When the number of bracketing data sets are few (\( \leq 5 \) sets), a shorthand approach, described in detail elsewhere\(^3\), can be used to compute the reproducibility standard error. This is necessary because small sample sizes don’t provide a lot of information about population distribution. The BOB approach assumes a uniform distribution (as opposed to a normal distribution), and sets the bounds at the highest and lowest \( C_{jk} \) values among the data at each concentration. The estimated standard deviation for a uniform distribution is
where $a$ is half the width of the distribution. Applying this formula to all the bracketing data yields

$$u_{i\sigma}(C_j)_{\text{reproducibility}} = \frac{\text{Max}(C_{jk}) - \text{Min}(C_{jk})}{2\times \sqrt{3}} = \frac{\text{Max}(C_{jk}) - \text{Min}(C_{jk})}{\sqrt{12}}$$

### A.5 Combined Uncertainty

Once calculated, all of the uncertainties are combined using propagation of error. First, the combined uncertainty of each day’s bracketing procedure is calculated

$$u_{i\sigma}(C_{\text{resultant}}) = u_{i\sigma}(R_{jk}) = \sqrt{\left[ u(R_{jk})_{\text{linearity assumed}} \right]^2 + u(R_{jk})_{\text{stability}}^2 + u(R_{jk})_{\text{repeatability}}^2}$$

Then, these uncertainties are combined into a single comparison uncertainty

$$u_{i\sigma}(C_j)_{\text{comparison}} = \sqrt{\frac{1}{K^2} \sum_{k=1}^{K} [C_{jk,.ref} \times u_{i\sigma}(R_{jk})]^2}$$

The reference gas uncertainty component is calculated based on the comparison ratio and the reported uncertainty of the reference gases.

$$u_{i\sigma}(C_j)_{\text{reference}} = \sqrt{\frac{1}{K} \times \sum_{k=1}^{K} [R_{jk} \times u_{i\sigma}(C_{jk,.ref})]_{\text{certification}}^2}$$

Note: In cases where there is no change of reference gas from one bracketing day to the next, the above pooling formula reduces to the quadratic mean of the day-average comparison ratios times the reference gas uncertainty.

The overall combined uncertainty for the candidate gas certification is

$$u_{i\sigma}(C_j)_{\text{combined}} = \sqrt{\left[ u_{i\sigma}(C_j)_{\text{comparison}} + u_{i\sigma}(C_j)_{\text{reference}} + u_{i\sigma}(C_j)_{\text{reproducibility}} \right]^2}$$

and the expanded certification uncertainty (k=2) is

$$u_{i\sigma}(C_j)_{\text{expanded}} = k \times u_{i\sigma}(C_j)_{\text{combined}} = 2 \times u_{i\sigma}(C_j)_{\text{combined}}$$