Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators

1.0 INTRODUCTION

For regulatory purposes, mercury (Hg) calibration standards of known concentration and known uncertainty are needed to quality assure data recorded by Hg continuous emission monitoring systems (CEMS) and measurements made with instrumental Hg reference test methods. This interim EPA traceability protocol reflects the current state of development of procedures for generating and quantifying elemental Hg calibration standards. The procedures of this interim protocol will be replaced when a final EPA traceability protocol for elemental Hg generators is issued.

This interim traceability protocol focuses on two basic issues. It provides procedures to: (1) establish the quantitative output (i.e., "calibration") of elemental Hg generators; and (2) determine the expanded uncertainty of the gas standards produced by the elemental Hg generators. This protocol specifies the maximum allowable uncertainty for the gas standards. Demonstrating that a particular generator meets the requirements contained in this document establishes that the generator output is traceable to the National Institute of Standards and Technology (NIST) by means of an unbroken chain of comparisons of the generator to a NIST certified reference generator. For CEMS applications, this protocol applies only to Hg monitoring system span values greater than or equal to 5.0 micrograms per cubic meter ($\mu g/m^3$).

Section 2, "Overview," explains the steps in the process leading to elemental Hg generators certification and identifies activities performed by NIST and activities and responsibilities of the generator manufacturer or others. Section 3, "Definitions" presents important definitions related to generator certification and the calculation of uncertainty. Section 4, "Qualification Tests," contains provisions designed to demonstrate the adequacy of a particular generator model for the intended field application(s). Section 5, "Certification," details the specific procedures for the quantitative determination of the candidate generator output. Section 6, "Uncertainty," summarizes the method used to calculate and report the expanded uncertainty of the generator output. Section 7, "Quality Assurance," details approaches for periodic assessments providing assurance of continued acceptable elemental Hg generator performance.

The need for NIST-traceable elemental Hg generators (or lack thereof) in a particular regulatory application depends on the nature of the Hg emission standards that must be met and the associated monitoring and testing requirements. These issues are 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.

2.0 OVERVIEW

In the simplest of terms, elemental Hg generators produce known concentrations of Hg by passing a controlled gas stream through the headspace of a temperature-controlled reservoir containing elemental mercury, and then dynamically blending the mercury-laden gas stream with a controlled dilution gas stream. The temperature of the reservoir, the flow rate of the carrier gas sweeping through the reservoir headspace, the chamber pressure, and the flow rate of the dilution gas stream are carefully monitored and controlled to produce the necessary Hg concentrations. The specific design, configuration, and features of an elemental generator are left to the judgment of the manufacturer and are not constrained by explicit design specifications or EPA requirements.

Qualification tests are required for each elemental Hg generator model. For the purposes of this interim protocol, the tests that are routinely performed by the manufacturer will suffice, provided that the test results demonstrate that the generator model has adequate stability and repeatability and can operate reliably over a stated range of conditions (e.g., back pressures, ambient temperatures, and other applicable factors). These tests may either be performed on each individual generator or on selected generators 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 generator and documents the range of conditions over which reliable generator operation can be expected.

NIST has developed a fundamental analytical method for quantifying the concentration of elemental Hg in gas mixtures to provide traceability to the International System of Units (SI). The method is isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS)[1]. The output of a NIST Prime elemental Hg generator[2], which is maintained at NIST Chemical Science and Technology Laboratory in Gaithersburg, Maryland, has been certified by this method.

NIST uses the NIST Prime generator to certify “Vendor Primes” (which are elemental Hg generators provided by the manufacturers), by direct comparisons of the generator outputs at a series of Hg concentrations.[3,4,5] When a Vendor Prime certification is complete, NIST issues a Report of Analysis to the party submitting the generator. The report describes the experimental procedures used and identifies the specific Vendor Prime set points with the corresponding certified Hg concentrations and expanded uncertainties.

This Interim EPA Traceability Protocol specifies the procedures for establishing the “NIST traceable” quantitative output of elemental Hg generators that are employed in regulatory applications for emission monitoring or testing. These generators may be certified either: (a) at the manufacturer’s facility, prior to shipping, by direct comparison to a certified Vendor Prime; or (b) at the site where the generator will be used (or at another convenient location), by direct comparison to an elemental Hg generator that has been previously certified against a Vendor Prime.

The manufacturer or equipment supplier performing the certifications must maintain documentation of all generator 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.

Following the initial certification of a generator, 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 generator continues to provide accurate and reliable calibration standards. Recertification of a generator 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.

3.0 DEFINITIONS

3.1 Bracketing procedure means an experimental design whereby a measurement system is used to compare the output from a reference standard to the output from a candidate generator.

3.2 Candidate generator means an elemental Hg generator that is being tested for initial certification, recertification, or quality assurance, by comparing its output to that of a reference standard.

3.3 CEMS means continuous emission monitoring system.

3.4 Certified candidate generator output concentration means the arithmetic average of the calculated output concentrations of a candidate generator, when a bracketing procedure is performed at a given concentration level.

3.5 Combined standard uncertainty means an estimate of the standard uncertainty, calculated by propagation-of-error, for measurements that are characterized by multiple sources of uncertainty.

3.6 Control chart means a graphical representation of how the output ratio varies over time, when a series of bracketing procedures (e.g., initial certification and ongoing quarterly performance evaluations) is performed with a particular certified Field Reference generator and a particular User generator.

3.7 Coverage factor means a multiplier used to calculate an expanded uncertainty from a standard uncertainty. A large coverage factor increases the confidence that the "true" value is within the bounds of a stated uncertainty. For a statistical "normal" distribution of measurements, a coverage factor of 2 gives a level of confidence of approximately 95%.

3.8 Detector linearity uncertainty means an uncertainty component related to how closely a detector response approximates a straight line when plotted against known injected Hg concentrations.

3.9 Elemental Hg generator model means a specific configuration identified by the instrument system design, including:

(a) The use of specific gas flow rate measurement/control devices, Hg 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 an elemental Hg generator do not constitute a model change. However, the manufacturer must keep records that document and provide a satisfactory explanation of 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 generator output to generate reference values, operational information, or to activate alarms;
- Substitution or use of new measurement components, provided that the generator manufacturer verifies that the performance of the new components is as good, or better, than the replaced components.

3.10 Expanded uncertainty means a standard uncertainty (or combined standard uncertainty) multiplied by a coverage factor to provide a wider confidence interval within which the “true” value is believed to lie.

3.11 External adjustment means either (1) a physical adjustment to a component of the elemental Hg generator 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 generator. External adjustments are made at the election of the end user but may be subject to various regulatory requirements.

3.12 Field Reference generator means an elemental Hg generator that has been certified by comparing its output to that of a Vendor Prime, using procedures that are more rigorous than those required for certification of a User generator.

3.13 Final certified candidate generator output concentration means the arithmetic average of the calculated output concentrations produced by a candidate generator at a given concentration level, based on data from a bracketing procedure.

3.14 Intrinsic adjustment means an automatic and essential feature of an elemental Hg generator that provides for the internal control of specific components or adjustment of the generator output in a manner consistent with the manufacturer's design of the instrument 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.

3.15 Measurement stability means an uncertainty component related to how much the readings obtained with a measurement device change during a measurement interval.

3.16 NIST means the National Institute of Standards and Technology in Gaithersburg, Maryland.

3.17 NIST Prime means an elemental Hg generator that has been certified by NIST, using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS).

3.18 NIST Traceability means, with respect to elemental Hg gas standards, that either: (a) the concentrations of elemental Hg produced by a generator; or (b) the concentrations of elemental Hg in compressed gas cylinders are traceable to a NIST Prime by an unbroken chain of comparisons.

3.19 Output ratio means the ratio of the output from a candidate generator to the output from a certified reference standard, when a bracketing procedure is performed.

3.20 Reference standard means an elemental Hg generator or other device (e.g., compressed gas cylinder) that is used as the standard for the certification, recertification, or quality assurance of a candidate generator.

3.21 Reference uncertainty means the uncertainty of the traceable reference to which the candidate is being compared. For the purposes of this protocol, this uncertainty comes from the certification of the Vendor-Prime or Field-Reference generator that is used as the reference standard in a bracketing procedure(s).

3.22 Repeatability means an uncertainty component related to successive measurements of the same quantity under the same conditions, based on data collected in a single experiment.

3.23 Reproducibility means an uncertainty component related to successive experiments involving the same measured quantity, but not necessarily under identical conditions.

3.24 Standard uncertainty means the quantitative value of an uncertainty component expressed as the standard deviation of a distribution of measurements.

3.25 Type A uncertainty component means an uncertainty component that is “local” to the measurement process, and is evaluated based on statistical data collected alongside the measurement data.

3.26 Type B uncertainty component means an uncertainty component that is “external” to the measurement process. The statistical data for this type of component is often limited.

3.27 Uncertainty means a statistical predictor of how close measurements are to the true value of the quantity being measured, minus any bias or systematic error.

3.28 **User generator** means an elemental Hg generator that is employed in regulatory applications for emission monitoring or testing.

3.29 **Vendor Prime** means an elemental Hg generator that has been certified by comparing its output to that of a NIST prime.

4.0 QUALIFICATION TESTS

Manufacturers are required to conduct qualification tests to demonstrate the adequacy of each elemental Hg generator model (as defined in Section 3.8). Documentation of the qualification test procedures and results must be available upon request for inspection by EPA and other regulatory officials. Certain other information must be provided to the end user by means of a "Manufacturer's Disclosure" (see Section 4.1) to show that the generator model can operate reliably over the range of conditions that are expected to be encountered in the intended field application(s).

4.1 Manufacturer's Disclosure

As part of each User generator's certification, a "Manufacturer's Disclosure" is required. This disclosure must include documentation and other relevant information for the elemental Hg generator model, in accordance with Sections 4.1.1 through 4.1.4, below. This information shall be provided to each end-user, in the generator manual and/or other documents.

4.1.1 Design Description

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

4.1.2 Range(s)

The manufacturer shall specify the nominal concentration range(s) (minimum and maximum Hg concentrations in units of $\mu g/m^3$) over which the elemental Hg generator 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 Hg concentration values for a specific generator in a particular measurement application.

4.1.3 Operational and Environmental Conditions

The manufacturer shall explicitly state the operational range or limitations within which the generator model can be expected to operate reliably and meet all of the manufacturer's specifications, for such concerns as:

4.1.3.1 Carrier Gas Supply

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

4.1.3.2 Back Pressure

The range of back pressures over which the generator model has been tested and can deliver reliable Hg gas concentrations.

4.1.3.3 Enclosure Temperature Operating Range

The range of ambient temperatures over which the thermal stability of the generator model has been tested and can deliver reliable Hg gas concentrations, and the time required for the generator to equilibrate to a change in ambient temperature.

4.1.3.4 Line Voltage

The acceptable line voltage limits over which the generator can provide reliable Hg gas concentrations.

4.1.4 Operation, Maintenance, and QA

The manufacturer shall provide written procedures for installation, start-up, operation and maintenance, and quality assurance (QA) of the elemental Hg generator. 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 generator, including, as applicable, known malfunctions or failures, exposure to unacceptable operating conditions, component replacements, component recalibrations, or other conditions and/or factors.

4.2 Interim Model-Specific Tests

For the purposes of this interim protocol, the manufacturer shall prepare, keep on file, and make available upon request, a report describing the qualification tests performed to ensure that the elemental generator model (as defined in Section 3.8) will operate reliably and produce stable, repeatable gas concentrations over a stated range of conditions. The report shall indicate whether the qualification tests were performed on each individual generator or on selected generators that are representative of the model, and shall document the results of the tests.

4.3 Standardized Tests

In the final version of this protocol, EPA plans to require all manufacturers to perform and pass a series of standardized qualification tests for each elemental Hg generator model, to evaluate such things as generator stability with respect to time and temperature, set point reproducibility, and the effects of changes in back pressure, supply pressure, and line voltage on generator performance. Sections 4.3.1 through 4.3.5, below, are reserved for these test procedures. Until the final traceability protocol is issued, the interim model-specific qualification tests described in Section 4.2 will suffice for the purposes of initial certification. However, successful completion of the standardized qualification tests is a prerequisite for initial generator certifications that are performed after the standardized qualification tests are incorporated into the final protocol.

4.3.1 Set Point Repeatability Test [Reserved]

4.3.2 Thermal Stability Test [Reserved]

4.3.3 Back Pressure Test [Reserved]

4.3.4 Supply Pressure Test [Reserved]

4.3.5 Line Voltage Variation Test [Reserved]

5.0 CERTIFICATION

The certification protocols described in this document are identical in concept to those used by NIST and are similar in implementation. In order to certify elemental Hg generators, manufacturers must first take steps to have one or more Vendor Primes certified by NIST at specific set points. To date, fifteen (15) certified Hg concentrations within the nominal range from 0.5 to 38 $\mu g/m^3$ have been provided by NIST for this purpose.

There are two options for certifying a User generator and establishing its NIST traceability. The output from the User generator can be compared directly to the output from a certified Vendor Prime at the particular concentrations required by the user, by means of the “bracketing procedure” described in Sections 5.1 through 5.3, below. This approach is used when the manufacturer or equipment supplier can certify the generator prior to shipping it to the user. Alternatively, a User generator can be certified at the field location where it is used, or at another convenient location, by direct comparison with a Field Reference generator that has been previously certified by direct comparison to a Vendor Prime. The Field Reference generator certification procedures, which are presented in Section 5.4, below, are more rigorous than those required for a User generator, in order to minimize the effects of the additional transfer standard.

Within this document, zero-, low-, mid-, and high-level gases are designated as Z, L, M, and H, respectively. The detector (analyzer) responses to the output from each of the generators during the bracketing procedure are identified as follows:

RS* = Reference standard generator
C = Candidate generator
U = User generator
V* = Vendor Prime
FR = Field Reference generator (prior to certification)
FR* = Field Reference generator (after certification)

(*Note*: Generators with * designations have certified outputs)

5.1 Bracketing Procedure

A bracketing procedure is a means of directly comparing the outputs of two elemental Hg gas generators. The purpose of the procedure is to use the output from a certified “reference standard” generator to certify the output of a “candidate” generator. For the purposes of this interim protocol, the certified reference standard is either a Vendor Prime or a certified Field Reference generator. The outputs from the generators are introduced alternately to an analyzer so that each response from the candidate generator is bracketed by a pair of responses from the reference standard generator. At each gas level, the bracketing procedure requires a minimum of four responses from the certified reference standard generator and three responses from the candidate generator. An example of a bracketing procedure injection sequence for a given gas level is provided below in Table 1.

Table 1. Example of Bracketing Procedure Injection Sequence

Generator ID	Response ID
Reference Standard	RS^*_1
Candidate	C_1
Reference Standard	RS^*_2
Candidate	C_2
Reference Standard	RS^*_3
Candidate	C_3
Reference Standard	RS^*_4

5.1.1 Bracketing Procedure for User Generator Certifications

(a) Either a Vendor Prime or a certified Field Reference generator may be used as the reference standard to certify a candidate User generator. At a minimum, the bracketing procedure requires a three by three matrix (3x3) to compare U to V* or FR* (i.e., three comparisons at each of three different concentration levels—see Section 5.3). More than one User generator at a time can be certified using a single Vendor Prime or Field Reference generator. If this approach is followed, sequential responses from each User generator are recorded in-between the Vendor Prime (or Field Reference generator) responses, and linear (time) interpolation of the Vendor Prime (or Field Reference generator) responses is used to correlate with the exact time of each intervening User generator's response.

(b) Table 2 illustrates the bracketing procedure at three typical gas concentrations for a User generator certification, designated as "high", "mid", and "low". In this example, a certified Field Reference generator is used as the reference standard. At the option of the manufacturer, the order of introduction of the three gas concentrations shown in Table 2 (i.e., high, mid, and low) may be reversed.

Table 2. Bracketing Procedure Sequential Steps for User Generator Certification[a]

Z_1
FR^*_{H-1}
U_{H-1}
FR^*_{H-2}
U_{H-2}
FR^*_{H-3}
U_{H-3}
FR^*_{H-4}
FR^*_{M-1}
U_{M-1}
FR^*_{M-2}
U_{M-2}
FR^*_{M-3}
U_{M-3}
FR^*_{M-4}
FR^*_{L-1}
U_{L-1}
FR^*_{L-2}
U_{L-2}
FR^*_{L-3}
U_{L-3}
FR^*_{L-4}
Z_2

(*Note:* In Table 2, and throughout the remainder of this section**, replace FR* with V*** if a Vendor Prime generator is used as the reference standard for the bracketing procedure.)

(c) From these data, an ”output ratio” (R) is calculated for each value of U. The calculation of R is illustrated by Equation 1a, below, for U_{H-1}, the first response to the output from the User generator at the high level.

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[a] The nomenclature for Table 2 is: Z_1= first zero response; FR^*_{H-1}=Field Reference generator, high level, first response; U_{H-1} = User generator, high level, first response; etc.

$$R = \left[\frac{U_{H-1}}{\left(\frac{FR^*_{H-1} + FR^*_{H-2}}{2} \right)} \right] \qquad \text{(Equation 1a)}$$

Where:

R = Output Ratio

U_{H-1} = First response to User generator output at high level (zero corrected, if appropriate)[b]

FR^*_{H-1} = Response to Field Reference generator output, pre U_{H-1} (zero corrected, if appropriate)

FR^*_{H-2} = Response to Field Reference generator output, post U_{H-1} (zero corrected, if appropriate)

(d) The average of the FR^*_{H-1} and FR^*_{H-2} responses in the denominator of Equation 1a provides an estimate of the value of FR^* when U_{H-1} was actually recorded. Note, however, that this equation only applies to equally-spaced measurements when one candidate generator is being certified. If the spacing is not equal or more than one candidate generator is being certified with a single reference standard, a more rigorous, time-interpolated formula in Equation 1b below is used to estimate FR^*.

$$R = \frac{U_{H-1}}{\frac{t_{FR^*_{H-2}} - t_{U_{H-1}}}{t_{FR^*_{H-2}} - t_{FR^*_{H-1}}} \cdot FR^*_{H-1} + \frac{t_{U_{H-1}} - t_{FR^*_{H-1}}}{t_{FR^*_{H-2}} - t_{FR^*_{H-1}}} \cdot FR^*_{H-2}} \qquad \text{(Equation 1b)}$$

The t values in Equation 1b are timestamps associated with the U and FR^* readings. Equations 1a and 1b are mathematically identical when the three t values are equally spaced.

(e) At each calibration gas level, the R values from Equation 1a or 1b (whichever applies) are averaged arithmetically. Then, the value of "Y", i.e., the calculated User generator output, is determined. Equation 2, below, illustrates the calculation of Y for the high level gas. Manufacturers' spreadsheets are generally used to perform this calculation[6,7,8,9]:

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[b] See Section 5.2, below, for a discussion of zero correction

$$Y_H = \left(X^*_{FR_H}\right)\left(\overline{R}_H\right) \qquad \text{(Equation 2)}$$

Where:

Y_H = Calculated User generator output for the high level gas

$X^*_{FR_H}$ = Certified high-level output concentration of the Field Reference generator

$\overline{R}_H$ = Average output ratio for the high level gas

5.1.2 Stepwise Procedures

(a) At each concentration level, perform a minimum of three (3) comparisons as follows:

(1) Turn on all components of the measurement system including the certified reference standard generator,[c] the User generator, the measurement detector (analyzer) and any associated necessary equipment and allow them to reach thermal equilibrium and stable operation with air (or nitrogen) supply connected and carrier gas flowing for both generators. The following procedure is recommended to assess stable operation. Conduct a 15-minute stability check of both generators at the outset. Generator output may be assumed to be stable if no more than 0.10 $\mu g/m^3$ drift is observed over the 15-minute interval.

(2) Ensure that the generator internal data logging functions are properly configured and operational, that the detector internal data logging functions are properly configured and operational, and that any external computers or data logging equipment are properly configured and operational so that complete documentation of the certification test procedures is available for future inspection.

(3) Ensure that the two generators, the analyzer, and any support equipment are operating within the prescribed limits for all key parameters as specified by the manufacturer.

(*Note*: If, at the outset or any other time during the process, test results demonstrate that equilibration is not 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 User generator).

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[c] The certified reference standard generator may either be a Vendor Prime or a certified Field Reference generator.

(4) Set each generator to the first set point (i.e., the high-level or low-level point, as deemed appropriate) and allow all components of the measurement system to attain equilibrium.

(5) If the manufacturer's system utilizes a continuous detector, it shall be calibrated as follows. After equilibrium has been established, zero the detector by injecting zero gas and making any necessary zero adjustments. Once the zero has been set, calibrate the detector by injecting the high-level calibration gas from the reference standard generator and making any necessary span adjustments. Repeat these steps, if necessary, to optimize the analyzer calibration relative to the reference standard generator.

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

(6) Alternatively, the detector may be set up using the manufacturer's standard operating procedure.

(7) Direct the output of the reference standard generator to the detector and obtain a response (V^* or FR^*, as applicable). It is recommended that the recorded response at each test point be based on at least 5 minutes of stable readings for continuous systems, or one reliable batch measurement for gold trap collection systems.

(8) Direct the output of the User generator to the detector and obtain a response (U).

(9) Switch back to direct the output of the reference standard generator to the detector and obtain a response (V^* or FR^*, as applicable).

(10) Repeat steps 7 through 9 two more times to achieve triplicate responses for the User generator at that concentration level.

(11) Repeat steps 7 through 10 for the second and third concentration levels. Be sure to allow system to reach equilibrium before recording any responses. The third concentration level completes the 3x3 matrix.

(12) Check the zero response of the detector, without making any adjustments.

(b) The manner in which the responses are recorded depends on the analyzer (detector). If it is a continuous analyzer, record readings at appropriate set intervals and compute the average over the desired time period. If the analyzer concentrates the sample and an integrated signal is obtained for the generator output, record the result of one analysis cycle or average multiple analysis cycles using all stable measurement system responses. For systems that have two traps ("A" and "B") to concentrate the sample, use the same designated trap (A or B) throughout the sampling procedure.

5.2 Data Processing for User Generator Certifications

To determine the actual output of the User generator, first correct each response for any zero offset of the detector, if appropriate. Zero correction is required only for an instrument that does not perform an automatic baseline correction for every reading. If zero correction is required, calculate the interpolated zero offset based on the time when a specific response was recorded as follows:

$$Z_i = Z_1 + \left[(t_i - t_1) \frac{(Z_1 - Z_2)}{(t_1 - t_2)} \right] \qquad \text{(Equation 3)}$$

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

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

$$U_c = U_i - Z_i \qquad \text{(Equation 4)}$$

Where:
U_c = Response at t_i corrected for zero offset
U_i = Actual response at t_i
Z_i = Zero offset at t_i

(b) The data set in Table 3 provides an example of how each response is corrected for zero offset over the course of a test period.

Table 3. Zero Corrections for an Example Data Set

Time (min)	Zero Response	Interpolated Zero	FR_i* Response[d]	FR_c* Zero-Cor.	U_i Response[d]	U_c Zero-Cor.
0	0.00					
10		0.04	10.00	9.96		
20		0.08			9.85	9.77
30		0.12	10.20	10.08		
40		0.16			9.96	9.80
50		0.20	10.25	10.05		
60		0.24			10.00	9.76
70		0.28	10.40	10.12		
80	0.32					

(c) Next, calculate R, the output ratio for each value of U_c (see Section 5.1.1, above). Table 4, below, illustrates these calculations, for the example data set presented in Table 3.

Table 4. Example Calculation of User Generator Output (With Zero Correction)

Time (min)	FR_i* Response	FR_c* Zero-Cor.	U_i Response	U_c Zero-Cor.	Output Ratio (R)
10	10.00	9.96			
20			9.85	9.77	0.975
30	10.20	10.08			
40			9.95	9.80	0.974
50	10.25	10.05			
60			10.00	9.76	0.968
70	10.40	10.12			

(d) Next, average the three calculated output ratios arithmetically. For this data set, the value of $\overline{R}_H$ is 0.972.

(e) Finally, use Equation 2 in Section 5.1.1, above, to determine Y_H, the calculated candidate (User) generator output concentration at high level. For this example data set, $X^{*}_{FR_H}$, the certified high level output concentration for the Field

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[d] Note that the User and Field Reference generator responses can be in various units of measure (e.g., μg/m^3 , volts, counts, etc.), depending on the exact set up of the measurement system.

Reference generator, is assumed to be 10.0 µg/m^3. Therefore, the value of Y_H from Equation 2 is 9.72 µg/m^3, based on the zero-corrected responses.

(f) Apply the same calculation procedures to each of the other concentration levels. A spreadsheet can be used to perform the calculations.

(g) If zero-correction is not necessary for the detector, use the uncorrected values (FR_i^* and U_i) in the calculations, as shown below in Table 5. For this example data set, the value of Y_H is 9.73 µg/m^3, based on the uncorrected responses.

Table 5. Calculation of User Generator Output (Without Zero Correction)

Time (min)	FR_i* Response	U_i Response	Output Ratio
10	10.00		
20		9.85	0.975
30	10.20		
40		9.96	0.974
50	10.25		
60		10.00	0.969
70	10.40		

(h) For each concentration level ≥ 4.0 µg/m^3, calculate the relative standard deviation (RSD) of the output ratios, using Equation 5.

$$RSD = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n-1}}}{\overline{x}} \ x \ 100 \qquad \text{(Equation 5)}$$

Where:

RSD = Relative standard deviation, percent
$\overline{x}$ = Arithmetic average of the output ratios
x_i = Individual, "ith" output ratio
n = Number of output ratios

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

(j) The calculated RSD values for the output ratios in Tables 4 and 5 are 0.4% and 0.3%, respectively, and are therefore acceptable.

5.3 Selection of Set Points for User Generator Certifications

Field Reference and Vendor Prime generators are certified at specific set points to produce known concentrations of elemental Hg. These generators must be operated at NIST certified concentrations when they are used as reference standard generators. The certified concentrations of a Field Reference generator are established by the manufacturer and are based upon the certified concentrations of a Vendor Prime. The certified concentrations of a Vendor Prime generator are established by an agreement between NIST and the party submitting the generator to NIST.[10] The exact certified concentrations may differ somewhat from the nominal concentrations requested.

The concentration levels that are needed for a User generator may be specified by an applicable regulation. For example, the regulations for a CEMS application may require the user to perform linearity tests at three levels using elemental Hg concentrations of 20 to 30% of span, 50 to 60% of span, and 80 to 100% of span. For practical reasons, it is better to certify the User generator at concentrations near the middle of the specified ranges to provide some working margin to avoid a particular point being either on the cusp of or outside the desired range. Other factors, such as adjustment for calibration gas humidification may also need to be considered. The particular concentrations necessary for certification of a User generator are established by agreement between the user and the equipment supplier.

Any type or model of elemental Hg generator certified as a Vendor Prime or as a Field Reference generator may be used to certify a User generator. The Vendor Prime (or Field Reference generator) and User generators need not be the same type and model. However in practice, equipment suppliers are likely to choose to compare the same or similar models. Furthermore, some generator manufacturers may restrict the parameters that are varied to produce the necessary concentrations for a given span. For example, the Hg reservoir temperature and diluent gas flow rate may vary only between units with different spans, but for a given span, both of these parameters are always held constant and only the flow rate of the carrier gas sweeping through the reservoir headspace is varied. In such cases, the equipment supplier may choose to have the Vendor Prime (or Field Reference) generator certified for various groups of parametric values or combinations of parameter settings.[11] In this situation, the generator manufacturer shall specify the appropriate Vendor Prime (or Field Reference generator) certified concentrations or Vendor Prime (or Field Reference generator) parameter combinations that are selected for certification of User generators in accordance with a written procedure. The written procedure must be available for inspection by regulatory agencies upon request.

After selecting the most appropriate Vendor Prime (or Field Reference generator) certified concentrations for comparison with the User generator, the actual set-points for the User generator can be verified or adjusted to produce the low, mid, and high-level concentrations in the desired ranges. The set points or parameter settings for the User generator are not required to be identical to the set points or parameter settings of the Vendor Prime (or Field Reference generator). However, the certified concentrations of the User generator must either be within ± 30% or ± 0.5 μg/m^3 of the certified Vendor Prime (or Field Reference generator) concentrations (whichever is less restrictive).

5.4 Bracketing Procedure for Field Reference Generator Certifications

When performing a dual-bracketing procedure to certify a Field Reference generator, a Vendor Prime must be used as the reference standard and the Field Reference generator is the candidate generator. Once a Field Reference generator has been certified, it may then be used to certify, recertify, or perform on-going data quality assessments of User generators.

(a) At a minimum, the Field Reference generator certification consists of a three by three bracketing matrix performed in duplicate ((3x3) x 2), comparing the output of the Field Reference generator to the output of the Vendor Prime. Table 6, below, provides a summary of this certification procedure.

(b) Follow all of the steps in Section 5.1.2, above for each 3x3 bracketing matrix. All preparations, precautions, and procedures specified for the certification of User generators also apply to Field Reference generators. If the second 3x3 matrix is commenced immediately after the first one, Z-2, the final zero response from the first matrix, may serve as Z-3, the initial zero response for the second matrix (see Table 6).

Table 6: Field Reference Generator Certification Dual-Bracketing Procedure[e]

Field Reference Generator Bracketing Procedure	
Set 1	**Set 2**
Z-1	Z-3
V*-H-1-1	V*-H-2-1
FR-H-1-1	FR-H-2-1
V*-H-1-2	V*-H-2-2
FR-H-1-2	FR-H-2-2
V*-H-1-3	V*-H-2-3
FR-H-1-3	FR-H-2-3
V*-H-1-4	V*-H-2-4
V*-M-1-1	V*-M-2-1
FR-M-1-1	FR-M-2-1
V*-M-1-2	V*-M-2-2
FR-M-1-2	FR-M-2-2
V*-M-1-3	V*-M-2-3
FR-M-1-3	FR-M-2-3
V*-M-1-4	V*-M-2-4
V*-L-1-1	V*-L-2-1
FR-L-1-1	FR-L-2-1
V*-L-1-2	V*-L-2-2
FR-L-1-2	FR-L-2-2
V*-L-1-3	V*-L-2-3
FR-L-1-3	FR-L-2-3
V*-L-1-4	V*-L-2-4
Z-2	Z-4

(c) Follow the data processing steps in Section 5.2, above, for both the first and second repetitions of the 3x3 bracketing matrix. For each bracketing set where the concentration level is ≥ 4.0 $\mu g/m^3$, calculate the relative standard deviation (RSD) of the output ratios, using Equation 5 in Section 5.2. For any bracketing set where the RSD exceeds 1.0%, that set is invalid and must be repeated.

(d) For detectors that require zero correction, Table 7, below, provides an example of how each response is corrected for zero offset over the course of a test period. Table 7 illustrates the high-level gas injections for the first and second data sets.

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[e] The nomenclature for Table 6 is: Z-1= zero response 1; V*-H-1-1=Vendor Prime, high level, Set 1, response 1; FR-M-2-3 =Field Reference generator, mid level, Set 2, response 3; etc.

Table 7: Zero Corrections for an Example Data Set

Time (min)	Zero Response	Interpolated Zero	V_i* Response	V_c* Zero-Cor.	FR_i Response	FR_c Zero-Cor.
0	0.00					
10		0.02	10.00	9.98		
20		0.04			9.85	9.81
30		0.06	10.20	10.13		
40		0.08			9.96	9.88
50		0.10	10.25	10.13		
50		0.12			10.00	9.88
70		0.14	10.40	10.23		
240	0.48					
250		0.49	10.45	9.96		
260		0.50			10.15	9.65
270		0.51	10.50	9.99		
280		0.52			10.20	9.68
290		0.53	10.48	9.95		
300		0.54			10.22	9.68
310		0.55	10.50	9.95		
360	0.60					

(e) For each matrix, determine the output ratios (R_H) and the calculated Field Reference generator output value (Y_H) using the basic approach shown in Section 5.1.1 (the bracketing procedure for User generator certifications), replacing U with FR (since the Field Reference generator is now the candidate), and replacing FR* with V* (since the Vendor Prime is now the reference standard). Table 8, below, illustrates these calculation procedures for the zero-corrected responses from the example data set presented in Table 7. For this example data set, the certified concentration of the Vendor Prime (Xv_H^*) is assumed to be 10.0 µg/m^3.

Table 8: Example Calculation of Field Reference Generator Output (With Zero Correction)

Time (min)	V_i* Response	V_c* Zero-Cor.	FR_i Response	FR_c Zero-Cor.	Output Ratio
10	10.00	9.98			
20			9.85	9.81	0.975
30	10.20	10.14			
40			9.96	9.88	0.974
50	10.25	10.15			
60			10.00	9.88	0.968
70	10.40	10.26			
250	10.45	9.96			
260			10.15	9.65	0.967
270	10.50	9.99			
280			10.20	9.68	0.971
290	10.48	9.95			
300			10.22	9.68	0.973
310	10.50	9.95			

(f) The final certified candidate (Field Reference) generator output concentration is the arithmetic average of the two calculated Y_H values obtained with Equation 2. For this example data set at the high gas level, the final value of Y_H is 9.71 µg/m^3, based on the zero-corrected responses.

(g) Apply the same calculation procedures to each of the other concentration levels. A spreadsheet may be used to perform the calculations.

(h) If zero-correction is not necessary for the detector, use the uncorrected values (V_i^* and FR_i) in the calculations, as shown in Table 9, below. For this example data set at the high gas level, the final value of Y_H is 9.72 µg/m^3, based on the uncorrected responses.

Table 9: Example Calculation of Field Reference Generator Output (Without Zero Correction)

Time (min)	V_i* Response	FR_i Response	Output Ratio
10	10.00		
20		9.85	0.975
30	10.20		
40		9.96	0.974
50	10.25		
60		10.00	0.969
70	10.40		
250	10.45		
260		10.15	0.969
270	10.50		
280		10.20	0.972
290	10.48		
300		10.22	0.974
310	10.50		

6.0 UNCERTAINTY

This section describes the calculation method that is used to determine the expanded uncertainty of elemental Hg concentrations produced by candidate generators.

6.1 Uncertainty Calculation---General Approach

The first step in the process of determining the uncertainty of a measured quantity is to establish the "standard uncertainty" of each component. For a Type A component where statistical data are available, the standard uncertainty is the standard deviation of a series of repeated measurements related to the component. For a Type B component, standard uncertainty is established based on either (1) statistical data provided by the external source, or (2) a "worst case" estimate converted to a comparable standard deviation.

Once all standard uncertainties are established, they are combined through propagation of error to arrive at a single combined uncertainty value representing the overall uncertainty of the measurement. Finally, the expanded uncertainty is established by multiplying the combined uncertainty by a coverage factor, the magnitude of which depends on the required confidence level. To determine the expanded uncertainty for Hg concentrations produced by elemental mercury generators, a coverage factor of 2 has been selected, approximating a 95% confidence interval for the "true" value.

The uncertainty assigned to the output concentration of an elemental mercury generator is accumulated at each step in a chain of comparisons. The process starts with the primary measurement standard, NIST's Isotope Dilution Induced Coupled Plasma Mass Spectroscopy (ID-ICP-MS) method, which is used to certify the NIST Prime generator and has its own uncertainty. Then, when the NIST Prime generator is compared to a Vendor Prime generator, additional uncertainty components are added, based on NIST's evaluation of its measurement systems and procedures.

The Vendor Prime generator is the starting point for the uncertainty calculations in this protocol. The combined uncertainty of the Vendor Prime generator is one component of the uncertainty for a candidate generator's certification (where a candidate can be either a User generator or a Field Reference generator). This protocol describes how the combined uncertainties of the Vendor Prime and the other components are accumulated to determine the combined uncertainty of the candidate generator's Hg concentrations. When a Field Reference generator is used as a transfer standard between a Vendor Prime and a User generator, the accumulated uncertainties of both comparisons must be taken into account when calculating the User generator concentration uncertainty.

6.2 Uncertainty Components

In addition to the uncertainty of the reference standard, the following four sources of uncertainty have been identified for assigning concentration values to candidate generator setpoints: (1) detector linearity; (2) measurement stability; (3) repeatability; and (4) reproducibility. The first three components apply specifically to a comparison (bracketing) procedure. The reproducibility component applies to the overall process of transferring traceability from the reference gas standard to the candidate.

For the mathematical details of how uncertainty is calculated, refer to the Companion Document to this interim protocol[12]. In practice, these calculations are incorporated into the same spreadsheet files that calculate the certified concentrations. EPA has developed several example spreadsheets, based on the equipment commercially available at the time of this writing. Both the Companion Document and the spreadsheets are available in support of this interim protocol.

6.2.1 Detector Linearity Uncertainty

[Reserved]

6.2.2 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 calculated based on the standard error of the reference and candidate measurement points, assumed to lie on two straight lines when plotted versus time.

6.2.3 Repeatability

Repeatability attempts to quantify, independently of measurement issues such as linearity and stability, the precision of the output ratio determinations within a single bracketing procedure. It is calculated as the difference between (1) the standard deviation of the individual bracket ratios, and (2) the statistical contribution of measurement instability to the standard deviation of the ratios.

6.2.4 Reproducibility

Reproducibility is a measure of how precisely a bracketing procedure’s result can be duplicated. Because of the differences between the certification procedures (as described in Section 5), reproducibility may be estimated differently depending on what type of generator is being certified (i.e., Field Reference generator, or User generator) and how many times the bracketing procedure is repeated.

Field Reference generator certifications must include a calculated reproducibility component in the uncertainty calculation. Either the “statistical” or the “bound on bias” approach may be used, at the analysts discretion, based on guidance provided in Appendix A. For User generator certifications, in addition to these two options, there is a third, i.e., use a Type-B default value equal to 0.5 % of the certified value. The results of field testing have shown that this Type-B reproducibility is routinely achievable.

6.3 Combined and Expanded Uncertainty

Once calculated, all of the individual components (sources) of uncertainty (described above) are combined using propagation of error. First, the combined uncertainty of each bracketing procedure is calculated (assuming zero uncertainty for the reserved linearity component). Then, these uncertainties are combined into a single comparison uncertainty (dimensionless, because it is the uncertainty of the comparison ratio determination). This comparison uncertainty is multiplied by the reference concentration and combined with the reproducibility and reference concentration uncertainties to calculate the overall combined uncertainty in concentration units. The expanded uncertainty is this combined uncertainty multiplied by a coverage factor of 2.

6.4 Uncertainty Acceptance Criteria

At each concentration level, the results of the bracketing certification procedure are acceptable if the expanded uncertainty of the elemental mercury generator concentration, calculated in accordance with Section 6.3 above, does not exceed 5.0 percent of the certified value, or is not more than 2.0 percent above the Vendor Prime uncertainty at the closest set point[f], whichever is less restrictive.

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[f] If the candidate certification setpoint does not exactly match the reference standard setpoint, base the alternative specification on the closest reference standard setpoint.

7.0 QUALITY ASSURANCE

This section specifies: (a) the periodic data quality assessments that are required following initial certification of an elemental Hg generator, to provide assurance of continued acceptable performance; and (b) the required frequency of generator recertification.

7.1 Periodic Data Quality Assessments of Certified User Generators

(a) Periodic data quality evaluations of the generator shall be conducted as follows:

  (1) At least once each calendar quarter, except where otherwise indicated in Section 7.1.2, below; and

  (2) Following any malfunction, repair, or corrective action that may reasonably be expected to affect the generator's output, but does not necessitate recertification of the generator (see Section 7.3, below).

(b) Any of the data quality assessment procedures (Options A through D) described in Sections 7.1.1 through 7.1.4, below, may be used for the performance evaluations.

(c) Except as otherwise provided in Section 7.1.2.1(e), below, if the generator does not meet the acceptable performance criteria, subsequent data from the generator are considered invalid until either:

  (1) Another performance evaluation is successfully completed; or

  (2) The generator is recertified in accordance with the bracketing and data processing procedures in Section 5, above

7.1.1 Option A---Field Reference Generator Comparison

The required performance evaluations of a User generator may be done by direct comparison to a certified Field Reference generator. If this option is selected:

(a) Use the bracketing and data processing procedures described in Sections 5.1 and 5.2, above, except that the performance evaluation is conducted at only one concentration level rather than three. Perform three replicates to provide three output ratios, average the ratios arithmetically, and then calculate Y (see Section 5.1.1, above).

(b) For continuous emission monitoring system (CEMS) applications, perform the comparison with the User generator output set at the certified Hg concentration that is used for daily calibration error checks. The certified set point Hg concentration from the Field Reference generator must be within ± 30% or ± 0.5

µg/m^3 (whichever is less restrictive) of the concentration used for daily calibrations of the CEMS.

(c) The performance of the User generator is acceptable if the Y value obtained from the bracketing procedure is within ± 5.0% or ± 0.5 µg/m^3 (whichever is less restrictive) of the User generator's certified set point concentration.

7.1.2 Option B---Permeation Tube Comparison

Directly compare the User generator output to a permeation device that generates elemental Hg. The manufacturer must demonstrate that any model-specific methodology used for this comparison is consistent with the generic approach described in Section 7.1.2.1.

7.1.2.1 Generic Approach

(a) Use a permeation tube whose output is consistent and predictable over time and under the conditions of its actual operation and use.

(b) Compare the permeation device and the User generator using an Hg analyzer. After taking any system corrective actions or making modifications that would affect the analyzer response to the permeation device or elemental generator, determine an initial ("base") ratio of analyzer responses to the permeation device and to the elemental generator, as described in paragraph (c) of this section, to serve as a reference point for subsequent periodic performance evaluations. It is recommended that the base ratio be established as soon as practicable after initial certification, and re-established as soon as practicable after any subsequent corrective actions or system modifications that may affect the ratio.

(c) To determine the base ratio, make alternating measurements of the output from the permeation tube and the User generator until at least one pair of readings has been obtained.[g] For CEMS applications, perform the comparison procedure at a single concentration level, preferably (but not necessarily) corresponding to the level of the daily calibration error check. Before recording each measurement, allow sufficient time to ensure that a stable analyzer reading is obtained. For each pair of readings, calculate (A_{perm}/A_{gen}), the ratio of the analyzer responses to the output from the permeation device and the elemental generator. If more than one pair of readings is obtained, the base ratio shall be the arithmetic average of the calculated ratios.

(d) For the periodic data quality assessments, repeat the comparison procedure described in paragraph (c). Only one pair of readings is required. Because permeation device will not have EPA traceability and will not have been

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[g] Although one pair of stable readings is the minimum requirement, it is recommended that three pairs be obtained and averaged, to provide a more robust base ratio.

calibrated against a reference method, perform this periodic performance evaluations at least monthly (preferably weekly), for CEMS applications.

(e) The performance of the User generator is acceptable if the calculated value of (A_{perm}/A_{gen}) output ratio of the generator (or the average ratio, if more than one pair of readings is obtained) is within ± 5.0% of the base ratio determined in paragraph (b) of this section. If this performance criterion is not met:

(1) One of the other data quality assessment procedures in Section 7.1 of this protocol may, if available, be used to demonstrate acceptable generator performance[h]. However, if this approach proves to be unsuccessful and it appears that the generator is actually malfunctioning, follow the provisions of Section 7.1(c), above, re-establishing the base ratio, if necessary; or

(2) If none of the other data quality assessment procedures in Section 7.1 of this protocol is available, the permeation tube comparison procedure described in paragraph (c) of this Section may be repeated up to three times over a three-day (72-hour) period, beginning immediately after completing the initial test. If the test is not passed within that 72-hour period, follow the provisions of Section 7.1(c), above, re-establishing the base ratio, if necessary.

7.1.2.2 Model-Specific Methodologies

EPA has reviewed and found the following model-specific methodology for performing periodic QA assessments of User generators with permeation tubes to be sufficient to satisfy the QA requirements of this interim protocol. The procedures are detailed in an April 3, 2008 document prepared by Tekran Instruments[13]. A spreadsheet for the efficient processing of results has been developed and is available[14].

The Agency is persuaded that the internal permeation tube technique developed by Tekran provides meaningful insight into the actual performance of the elemental generator, and is consistent with the generic approach described in Section 7.1.2.1 of this protocol. The viability of this approach has been demonstrated through long term field studies at multiple industrial facilities. All performance requirements in Section 7.1.2.1(e) of this protocol apply to the Tekran-specific procedures.

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[h] Failure to meet the 5.0% performance criterion does not necessarily indicate a generator malfunction. Fouling of the Hg analyzer may be the cause, in which case, performing corrective maintenance on the analyzer is the appropriate follow-up action.

7.1.3 Option C---Sorbent Tube Comparison

Use adsorbent ("sorbent") tubes to sample the User generator effluent. Perform an independent analysis of the samples to confirm the quantity of Hg that is generated.

(a) Conduct the comparison with the User generator producing a certified set point Hg concentration. For CEMS applications, the set point shall be the Hg concentration that is used for daily calibration error checks.

(b) Perform all sorbent tube sampling according to the procedures (including all of the QA procedures) of document No. 14 cited in the "References" section of this interim protocol.[15] Perform a minimum of three replicates of paired samples. Average the three results.

(c) Calculate the difference between the average Hg concentration measured with the sorbent tubes and the generator's certified set point Hg concentration. The performance of the User generator is acceptable if this difference is within ± 5.0% of the certified set point concentration, or if the absolute value of the difference is no greater than 0.5 $\mu g/m^3$ (whichever is less restrictive).

7.1.4 Option D---Cylinder Gas Comparison

Evaluate the performance of a User generator by direct comparison to a compressed calibration gas cylinder having an EPA traceable elemental Hg concentration (see Sections 7.1.4.2 and 7.1.4.3, below). If the analyzer used for the comparisons is sensitive to variation in the oxygen concentration in the sample gas, perform the comparisons only if the oxygen concentrations in the compressed gas cylinder and in the User generator effluent are the same, or are known accurately and precisely so that appropriate corrections can be applied.

7.1.4.1 Comparison Procedure and Criteria

(a) Perform the direct comparison using the procedures for introduction of calibration gas to an elemental Hg analyzer as well as the nesting procedure and data processing described in document No. 15 cited in the "References" section of this interim protocol.[16]

(*<u>Note</u>*: A specially coated regulator (such as a SILTEK coated regulator body, CGA Nipple, and Isolation Valve) should be used with the compressed gas cylinder)

(b) Before proceeding, the following stability check of the output from the cylinder is recommended. Inject cylinder gas and observe the output. The output may be assumed to be stable if no more than 0.10 $\mu g/m^3$ of drift is observed over a period of at least 2-3 minutes.

(c) Perform a bracketing procedure, consistent with Section 5.1.2 and Table 1, above, using the compressed gas cylinder as the reference standard and the User generator as the candidate generator. Perform four replicate cylinder gas injections and three generator gas injections, recording the stable responses of the detector to all injections. Determine three output ratios, average the ratios arithmetically, and calculate the value of Y, in a manner consistent with Section 5.1.1, above.

(d) For CEMS applications, perform the comparison with the User generator producing the certified set point Hg concentration that is used for daily calibration error checks. The certified concentration of the compressed gas cylinder must be within ± 30% of that set point concentration.

(e) Use the average output ratio and the certified cylinder concentration to calculate the average User generator output concentration, in a manner consistent with Section 5.2, above. The performance of the User generator is acceptable if its calculated average output concentration is within ± 5.0% or ± 0.5 $\mu g/m^3$ (whichever is less restrictive) of the certified set point Hg concentration.

7.1.4.2 Protocol Gas Mixtures

After NIST-certified compressed gas mixtures become available to commercial calibration gas suppliers, EPA will revise its traceability protocol for gaseous calibration standards[17], to include procedures for preparing elemental Hg Protocol Gas mixtures. Until such time as the referenced EPA traceability protocol document is revised, the procedures that are used for preparing SO_2 Protocol Gas Mixtures may be followed by the commercial gas suppliers.

7.1.4.3 Hg Compressed Gas Mixtures Certified Relative to a Vendor Prime

Commercial gas suppliers may elect to certify elemental Hg compressed gas mixtures relative to the output of a Vendor Prime elemental Hg generator. If this option is selected, the gas supplier shall develop and maintain a detailed written procedure describing the exact procedures used to certify cylinders relative to a Vendor Prime including all quality assurance measures to ensure the validity of the process, and shall make these procedures available to EPA or other air pollution control agencies upon request.

7.2 Quality Control Procedures for Field Reference Generators

The following quality control (QC) procedures are required for Field Reference generators that are used as reference standards to certify, recertify, or perform periodic QA evaluations of User generators. Each Field Reference generator that is used for these purposes must have a current (non-expired) certification or recertification status.

7.2.1 Preliminaries

Before each use of a Field Reference generator for a certification, recertification, or QA application, ensure that the generator is operating properly. The manufacturer's written procedures and specifications for proper operation and maintenance of the generator must be strictly followed.

7.2.2 Output Ratio Check

The following output ratio check is required on each day that a Field Reference generator is used to certify, recertify, or quality-assure data from a User generator (or generators):

(a) Perform the preliminary procedures described in Section 7.2.1, above. Then, initiate the stepwise bracketing procedure described in Section 5.1.2, above.

(b) Make no additional adjustments to the analyzer after zeroing it and calibrating it with a high-level gas produced by the Field Reference generator (Step (5) in Section 5.1.2).

(c) Prior to, during, or immediately after the bracketing procedure, adjust the output from the Field Reference generator to produce a mid-level gas, and record the analyzer response to the gas.

(d) Calculate the ratio of the high-level and the mid-level gas outputs, from paragraphs (b) and (c), above. Also calculate this output ratio using the certified high-level and mid-level set point concentrations from the initial certification of the Field Reference generator (or, if the generator has been recertified, from its most recent recertification).

(e) If the two ratios calculated in paragraph (d), above, agree to within ± 5.0%, the performance of the Field Reference generator is acceptable. If this criterion is not met:

    (1) Corrective action (which may involve recertification—see Section 4.1.4, above) is required before the Field Reference generator may be used to certify, recertify, or perform quarterly evaluations of User generator(s); and

    (2) If the mid-level gas injection in paragraph (c), above, occurred either during or immediately after a bracketing procedure, the results of that test shall be invalidated.

7.2.3 Use of Control Charts

(a) When a particular Field Reference generator is used to perform a series of bracketing tests on a particular User generator (e.g., the initial certification and subsequent quarterly data quality assessments), a control chart shall be prepared and shall be updated after each test. The control chart is used to track the output ratio of the User and Field Reference generators from one bracketing test to the next. This ratio provides a means of assessing generator stability over the long-term. Significant changes in this ratio[i] indicate possible generator malfunctions.

(b) If, based on an evaluation of a control chart, generator malfunction is suspected:

(1) Investigate the apparent problem. If the control chart evaluation is found to be in error (i.e., a "false positive") and generator malfunction cannot be confirmed, no further action is required.

(2) However, if an actual generator malfunction is discovered:

(i) Corrective action (which may involve recertification of the generator—see Section 4.1.4, above) is required; and

(ii) The bracketing procedure for which the control chart indicated a possible malfunction is invalid and must be repeated, following the corrective action.

(iii) When a malfunction of the Field Reference generator (but not the User generator) is found, data from the User generator are not impacted. However, if a User generator malfunction is discovered, data from that generator are considered invalid from the hour of completion of the invalidated bracketing procedure until the bracketing procedure has been successfully completed.

(c) Control charts are especially useful when a single Field Reference generator is used to assess the data quality of multiple User generators over an extended period of time. For example:

(1) If the output ratios for all of the User generators have changed very little since the previous test, it is likely that the Field Reference generator and the User generators are all operating properly; or

(2) It is likely that a particular User generator is malfunctioning if its output ratio has changed significantly[i] since the last test, but there has been no corresponding change in the other User generator output ratio(s); or

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[i] As a "rule of thumb" if the output ratio changes by more than 5 percent from one test to the next, this is considered significant.

(3) If the output ratios for the User generators have shifted significantly[f] in the same direction since the previous test, the Field Reference generator may be malfunctioning.

7.3 Recertification

Following initial certification, all User generators and Field Reference generators must be periodically recertified to maintain NIST traceability.

(a) User generators shall be recertified:

(1) Whenever any event, condition, or factor that triggers recertification (as identified in the Manufacturer's Disclosure) occurs--see Section 4.1.4, above; and

(2) Once every 8 calendar quarters, if not required for any other reason.

(b) Field Reference generators shall be recertified against a Vendor Prime annually (i.e., once every four calendar quarters), except as otherwise indicated in paragraph (c) of this section.

(c) The interval between required recertifications of a Field Reference generator may be extended, up to a maximum of 8 calendar quarters from the calendar quarter of the last test, as follows:

(1) The recertification test deadline may be extended by one quarter if the 3x3 bracketing procedure described in Sections 5.1 and 5.2, above, is successfully completed in the calendar quarter in which the recertification test is due. In this bracketing procedure, the Field Reference generator is the candidate generator and any available generator that has a current (non-expired) certification may be used as the reference standard. The results of the test are acceptable if, at each gas concentration level (L,M,H), the calculated average output concentration of the Field Reference generator is within ± 5.0% or ± 0.5 g/m (whichever is less restrictive) of the set point concentration from its original certification or from its most recent recertification (as applicable);

(2) Additional one-quarter extensions of the recertification test deadline (up to three) may be obtained, one quarter at a time, by successfully repeating the 3x3 bracketing procedure described in paragraph (c)(1).

(3) As an alternative to extending the recertification test deadline one quarter at a time, as described in paragraphs (c)(1) and (c)(2), the test deadline may be extended by four calendar quarters if the following more rigorous, one-time test is successfully completed in the calendar quarter in which the recertification test is due. Perform the 3x3x2 bracketing procedure described in Section 5.4, above with the Field Reference generator as the

candidate generator. The reference standard shall be a generator that has a current (non-expired) certification and is independent of the Field Reference generator (i.e., its certification was not derived from the Field Reference generator). The results of the test are acceptable if, at each gas concentration level (L,M,H), the calculated average output concentration of the Field Reference generator is within ± 5.0% or ± 0.5 g/m (whichever is less restrictive) of the set point concentration from its original certification or from its most recent recertification (as applicable).

(d) Each elemental generator that is used as the standard for recertification testing must have a current, active (i.e., non-expired) certification or recertification status.

References

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[2] "NIST Prime Certification Points", Spreadsheet provided to US EPA by NIST.

[3] Mitchell, G., Dorko, W., Long, S., "Report of Analysis – Traceability of Mercury Measurements," EPA Reference DW-13-92214701.

[4] Mitchell, G. "Report of Analyses – Quantification of Selected Set-Points for One Thermo and One Tekran Mercury Generator – Numbers 20555 and 3015," August 2008.

[5] Leigh, S., "Memorandum – Uncertainty Calculations for the Certification of Mercury Generator Outputs", 1-14-08.

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[7] Thermo Data Reduction Template-- RMB Consulting & Research, Inc., 08/27/08

[8] McRanie, R. and Roberson, W., "Field Comparison Check of Installed Elemental Hg Calibrator Versus a Reference Calibrator--Tekran Procedure", RMB Consulting & Research, Inc., May 1, 2009.

[9] Tekran Data Reduction Template --RMB Consulting & Research, Inc., 08/27/08

[10] Tentative agreement on these points was reached by all members of the workgroup at the time of the EPRI CEMS Users Conference in Nashville, May 13-14, 2008.

[11] See for example, McRanie, R and Schaedlich, F., "Technical Note Concerning Hg Calibrator Points and Transfer Protocol", May 6, 2008.

[12] Companion Document, "Treatment of Elemental Mercury Gas Generator Certification Data and Calculation of Uncertainty in Support of the Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators"; U.S. EPA; July 2009.

[13] McRanie, R. and Roberson, W., “Using Internal Permeation Source as a Potential QA/QC Check of Installed Elemental Hg Calibrator”, RMB Consulting & Research, Inc., April 2, 2008.

[14] “Tekran Perm Source Ratio Template R01”

[15] Kinner, L.L., “Adsorbent (“Sorbent”) Tube Sampling of Gaseous Mercury Generator/Calibrators and Compressed Gaseous Mercury Cylinders”, Revision 5, Emission Monitoring, Inc., May 26, 2008.

[16] Peeler, J., “Field Evaluation of Hg Compressed Gas Standards”, Emission Monitoring, Inc., June 18, 2008.

[17] “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards”, EPA-600/R-97/121, September 1997.