

## Interim EPA Traceability Protocol for Qualification and Certification of Oxidized 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 mercuric chloride (HgCl<sub>2</sub>) calibration standards. Mercuric chloride is a form of oxidized mercury.

Traditionally, National Institute of Standards and Technology (NIST) traceability of gas standards used in U.S. Environmental Protection Agency (EPA) programs has been established using an unbroken chain of comparisons of a candidate gas standard to a primary NIST gas standard; in this approach, gas standards are traceable to a measured, not a theoretical, concentration. Currently, there is no established approach for direct measurement of HgCl<sub>2</sub> gas standards and thus, no way to establish a NIST primary gas standard for HgCl<sub>2</sub>. For the interim until a NIST primary gas standard for HgCl<sub>2</sub> can be established, this protocol relies on an approach of establishing NIST traceability for the individual components of HgCl<sub>2</sub> generating systems. Work is currently underway to evaluate a number of methods for direct HgCl<sub>2</sub> measurement which would allow development of a NIST primary gas standard for HgCl<sub>2</sub>. Once a satisfactory direct measurement procedure has been established, this interim protocol will be replaced with a final EPA/Office of Research and Development traceability protocol for HgCl<sub>2</sub> generators.

This interim traceability protocol provides procedures for: (1) establishing the NIST traceability and quantitative performance (i.e., “calibration”) of key components of HgCl<sub>2</sub> generators; (2) determining the uncertainty contributed by each of these components; and (3) calculating certified output concentrations and expanded, combined uncertainty values for the gas standards produced by the generators. This protocol specifies a “target” expanded, combined uncertainty value of 10% for the HgCl<sub>2</sub> standards (see Sections 4.2.7 and 5.3). Demonstrating that a particular HgCl<sub>2</sub> generator meets the requirements of this protocol establishes that the generator output is traceable to NIST standards by means currently acceptable to EPA. For continuous emission monitoring system (CEMS) applications, this protocol applies only to Hg monitoring system span values greater than or equal to 5.0 micrograms per cubic meter (µg/m<sup>3</sup>).

Section 2, “Types of HgCl<sub>2</sub> Generators,” explains the basic operation of two types of HgCl<sub>2</sub> generators and the general approach to their certification. Section 3, “Qualification Tests,” contains provisions designed to demonstrate the adequacy of a particular generator model prior to performing the actual certification tests. Section 4, “Evaporative HgCl<sub>2</sub> Generator Certification,” and Section 5, “Certification of Generators That Convert Elemental Hg to HgCl<sub>2</sub>” detail specific procedures for quantitatively

determining certified output concentrations from each type of generator and for calculating and reporting the expanded, combined uncertainties of the generator outputs. Section 6, "Quality Assurance," details procedures for periodic data quality assessments, which provide assurance of continued acceptable HgCl<sub>2</sub> generator performance.

The technical specifications and requirements for mercuric chloride generators will have to be evaluated for each regulatory application as new Hg 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 mercuric chloride generators should be specified by the responsible agency or organization.

## 2.0 TYPES OF HgCl<sub>2</sub> GENERATORS

Two basic types of mercuric chloride (HgCl<sub>2</sub>) generators are currently in use: (1) an evaporative HgCl<sub>2</sub> generator, which produces gas standards of known concentration by vaporization of aqueous solutions of HgCl<sub>2</sub> and quantitative mixing the resultant vapor with a diluent carrier gas; and (2) a device that converts the output from an elemental Hg generator to HgCl<sub>2</sub> by means of a chemical reaction with chlorine gas. Either one of these HgCl<sub>2</sub> generators is suitable for both CEMS and instrumental testing applications.

Certification of HgCl<sub>2</sub> generators presents many technical challenges, due to the way that the generators work and the fact that most are integrated into a CEMS measurement system. In view of the fundamental differences between the two types of HgCl<sub>2</sub> generators described above, different methods and procedures are used to certify and quality assure them. The certification and quality assurance procedures in this interim protocol have been developed in recognition of how the generators are integrated into measurement systems.

### 2.1 Evaporative HgCl<sub>2</sub> Generators

In an evaporative HgCl<sub>2</sub> generator, a liquid stream containing a known concentration of HgCl<sub>2</sub> 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 systems include a second liquid feed stream to facilitate control of the moisture concentration of the generated calibration gas. It is assumed that all of the HgCl<sub>2</sub> in the feed solution is emitted from the evaporator. A “reference value” or output HgCl<sub>2</sub> concentration, is calculated from the known inputs of the HgCl<sub>2</sub> solution concentration, the liquid feed rate(s), and the carrier gas flow rate (see Section 4.2 for additional information on reference values).

For the purposes of this interim traceability protocol, certification of evaporative HgCl<sub>2</sub> generators requires: (1) traceability to NIST for each of the inputs; and (2) determination of the expanded, combined uncertainty of the generated reference value concentrations. The HgCl<sub>2</sub> concentration of the working liquid feed solution is established through the use of commercially available NIST-traceable HgCl<sub>2</sub> liquid standards and, if necessary, the quantitative dilution of these standards. Liquid feed rates are established by using a balance to gravimetrically calibrate the feed rate meter relative to NIST-traceable mass standards. 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. The expanded, combined uncertainty of the generated HgCl<sub>2</sub> calibration gas standards is calculated as the square root of the sum of the squares of the individual uncertainties (i.e., the uncertainties of the standard HgCl<sub>2</sub> solution, the liquid feed rate(s), and the carrier gas flow rate), with an appropriate coverage factor (see Section 4.2.6 for further information on the calculation of uncertainty).

When an evaporative HgCl<sub>2</sub> generator is used, the resultant gas stream contains a significant amount of moisture (in the %v/v range). The presence of moisture assists in

transporting the gas standards through calibration lines and sample lines (i.e., umbilical) and through other system components upstream of the analyzer. In practice, the  $\text{HgCl}_2$  gas must be transferred by a heated sample line from the evaporator to the CEMS probe or test method probe, to prevent condensation and  $\text{HgCl}_2$  transport losses.<sup>1</sup>

## 2.2 $\text{HgCl}_2$ Generators That Convert Elemental Hg

With this type of generator, known concentrations of elemental Hg gas pass through a reactor or catalyst in the presence of a chlorine source to produce gaseous  $\text{HgCl}_2$  calibration standards. Some systems combine a mixture of chlorine gas ( $\text{Cl}_2$ ) in nitrogen with the elemental Hg standard. The known concentrations of elemental Hg may be produced by a generator that has already been certified in accordance with an EPA traceability protocol for elemental Hg generators, or other certified source. The amount of  $\text{HgCl}_2$  produced is a function of the efficiency of the reactor system.

Transporting dry  $\text{HgCl}_2$  gas without substantial losses is difficult, even with heated sample lines. Humidification of the elemental Hg calibration gas prior to its conversion to  $\text{HgCl}_2$  will generally reduce transport losses. Location of the reactor in close proximity to the sample probe also minimizes the possibility of  $\text{HgCl}_2$  transport losses because the  $\text{HgCl}_2$  travels only a short distance to the point where it is introduced into the sample probe.<sup>2</sup>

For the purposes of this interim traceability protocol, certification of an  $\text{HgCl}_2$  generator that converts elemental Hg to  $\text{HgCl}_2$  is based on the reference values from the certified elemental Hg generator and the uncertainty of those values. The effects of dilution due to the introduction of chlorine gas and, if applicable, humidification, must also be taken into account. Moisture and/or chlorine dilution reduces the concentration of the  $\text{HgCl}_2$  calibration standards. The combined uncertainty of the  $\text{HgCl}_2$  calibration standards is calculated using the uncertainties of the elemental Hg generator output, the water vapor dilution (if applicable) and the chlorine dilution.

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<sup>1</sup> Note: This protocol does not explicitly require assessment of the transfer lines, nor reactions in the calibration lines, nor reactions on the PM filter, nor reactions within the CEMS sample probe, nor reactions in transfer lines to the converter, nor reactions within other measurement system components, as they are not considered part of the  $\text{HgCl}_2$  generator.

<sup>2</sup> It is also recognized that a portion of the generated  $\text{HgCl}_2$  may revert to elemental Hg within the sample probe and other components upstream of the CEMS converter or analyzer; in other cases, elemental Hg may convert to  $\text{HgCl}_2$ . For generators that convert elemental Hg to  $\text{HgCl}_2$ , the measurement system design may constrain measurement of the  $\text{HgCl}_2$  concentration directly at the reactor outlet. If  $\text{HgCl}_2$  is reduced in the process of transfer to a test apparatus, it can result in underestimation of the  $\text{HgCl}_2$  oxidation efficiency.

### 3.0 QUALIFICATION TESTS

Manufacturers are required to conduct qualification tests to demonstrate the adequacy of each HgCl<sub>2</sub> generator model (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. Certain other information must be provided to the end user by means of a “Manufacturers Disclosure” (see Section 3.2) to show that the generator can operate reliably over the range of conditions expected to be encountered in the intended field applications.

#### 3.1 Definitions

**3.1.1 HgCl<sub>2</sub> Generator Model** – A specific configuration identified by the instrument system design, including:

- (a) The use of specific gas flow rate measurement/control devices, HgCl<sub>2</sub> 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 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 generator output to generate reference values, operational information, or to activate alarms; and
- 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 and documents supporting information for all such changes.

**3.1.2 Intrinsic Adjustment** – An automatic and essential feature of an HgCl<sub>2</sub> 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.

**3.1.3 External Adjustment** – 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.

## **3.2 Manufacturer's Disclosure**

As part of each HgCl<sub>2</sub> generator's certification, a "Manufacturer's Disclosure" is required. This disclosure must include documentation and other relevant information for the HgCl<sub>2</sub> generator model, in accordance with subsections 3.2.1 through 3.2.5, below. This information shall be provided to each end-user in the generator manual and/or other documents.

### **3.2.1 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 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 HgCl<sub>2</sub> concentrations in units of µg/m<sup>3</sup>) over which the HgCl<sub>2</sub> 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 HgCl<sub>2</sub> concentration values for a specific generator 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 generator model can be expected to operate reliably and meet all of the manufacturer's specifications for:

### **3.2.3.1 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.

### **3.2.3.2 Back Pressure**

The range of back pressures over which the generator has been tested and can deliver reliable HgCl<sub>2</sub> gas concentrations.

### **3.2.3.3 Enclosure Temperature Operating Range**

The range of ambient temperatures over which the thermal stability of the generator has been tested and can deliver reliable HgCl<sub>2</sub> gas concentrations.

### **3.2.3.4 Line Voltage**

The acceptable line voltage limits over which the generator can provide reliable HgCl<sub>2</sub> 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 HgCl<sub>2</sub> 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.

## **3.2.5 Output Verification and Oxidation Efficiency**

The manufacturer shall provide documentation of laboratory testing and results for verifying the output of the evaporative HgCl<sub>2</sub> generator or the conversion rate (i.e., oxidation efficiency) of a generator that converts elemental Hg to HgCl<sub>2</sub>.

### **3.3 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 HgCl<sub>2</sub> generator model (as defined in Section 3.1.1) 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.

### **3.4 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 HgCl<sub>2</sub> generator model, to evaluate such things as repeatability, thermal stability, effect of changes in supply pressure and line voltage on generator performance as well as more specific procedures for verifying that the output of the generator agrees with the calculated reference values and the conversion or oxidation efficiency of generators that convert elemental Hg to HgCl<sub>2</sub>. Subsections 3.4.1 through 3.4.5, below, are reserved for these test procedures. Until the final traceability protocol is issued, the interim model-specific qualification tests described in Section 3.3 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.<sup>3</sup>

#### **3.4.1 Repeatability Test [Reserved]**

#### **3.4.2 Thermal Stability Test [Reserved]**

#### **3.4.3 Supply Pressure Test [Reserved]**

#### **3.4.4 Line Voltage Variation Test [Reserved]**

#### **3.4.5 HgCl<sub>2</sub> Generator Output Verification Tests [Reserved]**

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<sup>3</sup> Note: Stand-alone HgCl<sub>2</sub> generator models will, in general, be subject to all of the tests in Sections 3.4.1 through 3.4.5, unless it can be shown that one or more of the tests is inapplicable to a particular model. In such cases, an appropriate justification for omitting the test(s) must be included in the qualification documentation. For generators that convert elemental Hg to HgCl<sub>2</sub> using gas from a certified elemental Hg generator, only the tests in Section 3.4.5 will have to be addressed. The tests in Sections 3.4.1 through 3.4.4 will be addressed through the elemental Hg generator certification.

## **4.0 EVAPORATIVE HgCl<sub>2</sub> GENERATOR CERTIFICATION**

### **4.1 Introduction**

For each candidate evaporative HgCl<sub>2</sub> generator, this section provides procedures to determine certified reference values at specific operating conditions and to calculate the expanded, combined uncertainties of the reference values. Documentation that a particular HgCl<sub>2</sub> generator has been evaluated according to these procedures and has met the applicable acceptance criteria satisfies the interim NIST traceability requirements for the generator.

Key components of an evaporative HgCl<sub>2</sub> generator include:

- (a) Devices used to determine the liquid feed rates (i.e., balance and timing device, calibrated pump(s), and/or liquid mass flow meter(s)/controller(s) for the mercury chloride solution, and (if applicable) similar devices for auxiliary water feed rates);
- (b) Gas mass flow meter/controller to determine the flow rates of the carrier gas;
- (c) Nebulizer/evaporator to convert the liquid feed to a gas vapor;
- (d) Connecting tubing and related apparatus; and
- (e) Software or formulas to calculate the generated HgCl<sub>2</sub> concentrations, based on the working solution molarity, liquid feed rates, and carrier gas flow rates.

Commercially available mercury solutions that are traceable to NIST Standard Reference Material (SRM) 3133 must be used to prepare working solutions for evaporative HgCl<sub>2</sub> generators. The calibration of the liquid feed rate measurement device(s) and the carrier gas flow measurement device must be verified by comparison to independent primary laboratory standards with NIST-traceable calibrations, in order to determine the output of the generator.

The calibration of the liquid feed rate and carrier gas flow rate measurement devices may either be performed by the manufacturer or by the end user. Calibration certificates for the carrier gas mass flow meters are generally available from the manufacturer. Calibration of the liquid feed rate measurement devices is also usually performed by the manufacturer, using gravimetric means.

### **4.2 Generic Certification Procedures and Uncertainty Calculations**

For an evaporative HgCl<sub>2</sub> generator, each generated reference value output concentration at specific operating conditions is based upon the feed rate and concentration of the HgCl<sub>2</sub> solution and the associated volumetric diluents, including the contribution from evaporated water. The expanded, combined uncertainty for each reference value is based

on the combined individual standard uncertainties of the  $\text{HgCl}_2$  solution, the  $\text{HgCl}_2$  solution feed rate, additional water feed rate (if any) and the carrier gas volumetric flow rate. A coverage (K) factor of 2 is used in the calculations. Sections 4.2.1 through 4.2.4, below, describe generic test procedures and calculations for certification of candidate evaporative  $\text{HgCl}_2$  generators.

#### 4.2.1 NIST and Commercial $\text{HgCl}_2$ Standards

Working  $\text{HgCl}_2$  feed solutions may be directly provided by commercial manufacturers or prepared by the end user from commercially available standards. Use only commercially available mercury standards that are traceable to NIST Standard Reference Material 3133, and that have certified concentrations, estimates of shelf life, and specified accuracy values. Commercial  $\text{HgCl}_2$  standards that have certified concentrations with an accuracy of  $\pm 1.0\%$  or better should be used. The  $\text{HgCl}_2$  standard must be in a preservative matrix sufficient to ensure long term stability. For example, 0.1 to 1N HCl combined with 0.1 to 1N  $\text{HNO}_3$  has been found to be a very effective preservative.

Commercial laboratories typically dissolve ultra pure  $\text{HgCl}_2$  in an HCl and nitric acid solution. The resulting  $\text{HgCl}_2$  standards are then analyzed relative to NIST SRM 3133 to establish the NIST-traceable concentrations.

A typical concentration available for purchase is 10  $\mu\text{g/ml}$  (as Hg). An example of a commercially available standard:

Actual Hg Concentration as  $\text{HgCl}_2$ : 10.01  $\mu\text{g/mL}$   
Matrix: A mixture of 1.0 N (i.e., 3.7%) HCl and 1.0 N (i.e., 6.3%)  $\text{HNO}_3$   
Density: 1.048  $\text{g/mL}$  @ 22.6 °C.  
Stability: 1 year from date of certification  
Accuracy:  $\pm 1\%$  of the labeled concentration

The commercial standard is guaranteed to be stable and accurate to within  $\pm 1.0\%$  of the actual concentration 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  $\pm 0.5$  to  $1.0\%$  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.)

#### 4.2.2 Working Solution Preparation and Uncertainty

Direct use of a commercially prepared  $\text{HgCl}_2$  standard solution is preferred. However, subsequent dilution of a commercially prepared  $\text{HgCl}_2$  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 HgCl<sub>2</sub> gas concentrations. These target concentrations may be supplied by the generator manufacturer.

- (b) If necessary, prepare each target working solution by diluting the NIST traceable HgCl<sub>2</sub> 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.

#### 4.2.2.1 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 500 mL or 1000 mL volumetric flask.
- c) Add the targeted mass of the standard mercuric chloride 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.

#### 4.2.2.2 Working Solution Concentration (µg/mL)

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

$$C_{ws} = \frac{(W_{std})(C_{std})}{V_{total}} \quad \text{(Equation 1A)}$$

Where:

- $C_{ws}$  = Mercury concentration of the working solution ( $\mu\text{g/mL}$ )  
 $C_{std}$  = Mercury concentration of the standard solution ( $\mu\text{g/g}$ )  
 $W_{std}$  = Weight of standard solution (g)  
 $V_{total}$  = Final total volume of working solution (mL)

$$C_{ws} = \frac{(W_{std})(C_{std})}{(V_{total})(\rho_{std})} \quad (\text{Equation 1B})$$

Where:

- $C_{ws}$  = Mercury concentration of working solution ( $\mu\text{g/mL}$ )  
 $W_{std}$  = Weight of standard solution (g)  
 $V_{total}$  = Final total volume of working solution (mL)  
 $C_{std}$  = Concentration of standard solution ( $\mu\text{g/mL}$ )  
 $\rho_{std}$  = Density of standard solution (g/ml)

#### 4.2.2.3 Molarity of Working Solution

If necessary, calculate the molarity of mercury in the diluted solution according to Equation 2.

$$M_{ws} = 1 \times 10^{-3} \frac{C_{ws}}{(MW)_{Hg}} \quad (\text{Equation 2})$$

Where:

- $M_{ws}$  = Molarity of the working solution (moles/liter)  
 $C_{ws}$  = Mercury concentration of the working solution ( $\mu\text{g/mL}$ )  
 $(MW)_{Hg}$  = Molecular weight of Hg (200.6 g/mole)  
 $1 \times 10^{-3}$  = Conversion factor (g-mL/ $\mu\text{g}$ -liter)

#### 4.2.2.4 Conversion Between $\mu\text{g/g}$ and $\mu\text{g/mL}$

- (a) For working solutions, the concentration units,  $\mu\text{g/g}$  and  $\mu\text{g/mL}$ , may be used interchangeably. A density of 1.000 g/mL can be assumed when calculating grams/minute injected into the evaporator, and when calculating the resultant molarities.
- (b) Most commercially available standard  $\text{HgCl}_2$  solutions have densities that are nearly 1 g/mL  $\pm$  5%. For example, a NIST traceable standard was recently purchased that had a density of 1.048 g/mL. Diluting with water by a factor of 100 changes the density of the resulting working solution to 1.00048 g/mL, which when rounded to the appropriate number of significant figures, is 1.000 g/mL.

#### 4.2.2.5 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.

- The uncertainty of the aliquot weight ( $U_A$ ) is determined by dividing three times<sup>4</sup> the estimated readability of the balance by the measured aliquot weight, and converting the result to a percentage.
- The uncertainty of the final working solution volume ( $U_F$ ) is estimated by dividing the readability of the certified volumetric glassware<sup>5</sup> by the volume of the flask and converting the result to a percentage.
- The uncertainty of the commercial standard solution value is the percent accuracy of the solution concentration, as specified by the supplier.
- The combined standard uncertainty of the working solution is calculated using Equation 3.

$$U_{ws} = \left[ \left( \frac{U_{CS}}{2} \right)^2 + U_A^2 + U_F^2 \right]^{1/2} \quad \text{(Equation 3)}$$

Where:

- $U_{ws}$  = Uncertainty in the concentration of the working solution (%)
- $U_{CS}$  = Expanded uncertainty of the commercial standard, with a coverage factor of 2 (%)
- $U_A$  = Uncertainty of the aliquot weight or volume (%)
- $U_F$  = Uncertainty of the final, diluted standard weight or volume (%)

- Example:* A 10 g aliquot of a standard  $\text{HgCl}_2$  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  $\text{HgCl}_2$  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

<sup>4</sup> 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  $\pm 0.001 \text{ g}$ . Therefore, the uncertainty of measurements made with a 3-place balance is 3 times  $\pm 0.001 \text{ g}$ , or  $\pm 0.003 \text{ g}$ .

<sup>5</sup> For example, the readability of a one-liter Class A volumetric flask is  $\pm 0.40 \text{ mL}$ .

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.

- (f) Equation 3 assumes that a coverage factor value of 1-sigma, is applied. The uncertainty of a commercially available NIST-traceable  $\text{HgCl}_2$  standard is assumed to have a coverage factor of 2. (SRM 3133 has a coverage factor of 2.18.)

#### 4.2.3 Determination of Liquid Feed Rates

Determine the target liquid feed rates<sup>6</sup> that are necessary to generate the desired  $\text{HgCl}_2$  gas concentrations, taking into account the carrier gas flow rates and other applicable factors. The number and level of liquid feed rates to be verified will depend on the application. Calibrate the liquid flow meter(s) according to the procedures in paragraphs (a) through (e) of this section and calculate the uncertainty of the liquid feed rate at each level. Alternatively, manufacturer's calibrations of the liquid flow meter(s) may be used if the results are expressed in terms of percentage uncertainty.

- (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) Prepare and operate the  $\text{HgCl}_2$  generator according to the manufacturer's instructions. Place the  $\text{HgCl}_2$  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.
- (c) Allow the generator to run for a sufficient period of time to equilibrate. (*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.)
- (d) Record the exact combined weight of the solution and reservoir at time "zero." Allow a sufficient period to achieve the desired weight change. Record the time and exact weight at the end of the timing period. Divide the weight loss by the elapsed time to determine the liquid feed rate, in grams per minute. Repeat at least three times at each liquid feed rate level.
- (e) At each level, calculate the average of all valid test runs. The liquid feed rate determination is acceptable if all test runs are within  $\pm 2.0\%$  of the average. Calculate the liquid feed rate uncertainty ( $U_{\text{LFR}}$ ) as follows. Multiply the

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<sup>6</sup> That is, the feed rates of the  $\text{HgCl}_2$  solution and, if humidification is used, the feed rates of the deionized (DI) water.

readability of the balance (in grams) by three<sup>7</sup>, then divide by the weight change (in grams), and convert the result to a percentage.

- (f) In subsequent use of the HgCl<sub>2</sub> generator, at each liquid feed rate level (set point), compare the average experimental result from paragraph (e) above to the indicated liquid feed rate. If the percent difference between these values exceeds U<sub>LFRR</sub>, the recorded uncertainty, derive a linear correction which, when applied to the indicated liquid feed rate, provides the calibrated liquid feed rate. The linear correction may be either: (1) a factor based on the ratio of actual feed rate to indicated feed rate; or (2) a combination of such a factor and an adjustment for zero offset. Permanently record the linear correction. Continue to use it until the liquid feed rate measurement device is re-calibrated at the same operating level, and then use the new value.
- (g) Maintain documentation of the experimental measurements, derivation of the linear correction, and the relative uncertainty at each calibration level.
- (h) *Note*: Practical constraints may necessitate the use of a liquid feed rate other than one of the exact values used in the calibration. Any liquid feed rate within  $\pm 20\%$  of a calibrated feed rate may be used. The liquid feed rate device is expected to be linear and deviations of 20% or less from a calibrated value will have a negligible effect on the accuracy of the calibration. In such cases, use a linear extrapolation from the nearest calibrated liquid feed rate to determine the actual feed rate. The use of liquid flow meters at points more than 20% above the highest calibrated liquid feed rate is subject to the approval of the applicable regulatory agencies.

#### 4.2.4 Determination of the Gas Mass Flow Meter Output

Determine the target carrier gas flow rates that are appropriate for use with the anticipated concentrations of the liquid working solutions, liquid feed rates, and other applicable factors that are necessary to generate the desired HgCl<sub>2</sub> gas concentrations. The number and level of gas flow rates to be verified will depend on the intended application. Calibrate the gas flow meters according to the procedures in paragraphs (a) through (d) of this section and calculate the uncertainty of the gas flow rate at each level. Alternatively, manufacturer's calibrations of the flow meters may be used if the results are expressed in terms of relative uncertainty.

- (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 accuracy 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.

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<sup>7</sup> See footnote 4, above.

- (b) Prepare and operate the HgCl<sub>2</sub> generator according to the manufacturer's instructions. Allow the generator to run for a sufficient period of time to equilibrate and achieve steady operation.
- (c) For each gas flow rate level, record the setting or reading on the carrier gas mass flow meter 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. The gas flow rate determination is acceptable if the RSD is less than or equal to 2.0%. Report the RSD as the gas flow rate uncertainty ( $U_{GFR}$ ) at each level.
- (e) In subsequent use of the flow meter, at each gas flow rate level (set point), compare the average of the NIST-traceable reference measurements to the indicated gas flow rate. If the difference exceeds  $U_{GFR}$ , derive a linear correction which, when applied to the indicated gas flow rate, provides the calibrated gas flow rate. The linear correction may be either: (1) a factor based on the ratio of actual gas flow rate to indicated gas flow rate; or (2) a combination of such a factor and an adjustment for zero offset. Permanently record the linear correction. Continue to use it until the gas flow rate measurement device is re-calibrated at the same operating level, and then use the new value.
- (f) Maintain documentation of the experimental measurements, derivation of the linear correction, and the uncertainty for each calibration level.
- (g) *Note*: Practical constraints may necessitate the use of a gas flow rate other than one of the exact values used during the calibration. Any gas flow rate within  $\pm 25\%$  of a calibrated gas flow rate is acceptable. The gas flow rate meter is expected to be linear and deviations of 25% or less will have a negligible effect on the accuracy of the calibration. In such cases, use a linear extrapolation from the nearest calibration point to determine the actual gas flow rate.

#### 4.2.5 Calculation of the Reference Values

This section addresses calculation of the HgCl<sub>2</sub> reference values (see Section 4.2) from individual operational parameters. The calculation of the reference values is typically done automatically by the generator's microprocessor using the specific software/firmware version and data processing algorithms as implemented by the particular manufacturer. 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 generator output are all correct. The units of the input and output values and the manufacturer's calculation procedures shall be documented in a report.

*Note 1:* The HgCl<sub>2</sub> generator output concentrations must be expressed at EPA standard conditions (20°C, 760 mm Hg). *Note 2:* Until the time that NIST traceability of evaporative generators can be evaluated by direct measurement, users of this interim protocol should be aware that manufacturers of evaporative generators may be using a model-specific factor in their software to adjust the calibrated output of their HgCl<sub>2</sub> generator to correspond with their certified elemental generators. The manufacturer must provide the end user with the exact value of this correction factor and provide instructions for its application. The correction factor must also be backed by supporting data that is available from the manufacturer upon request.

#### 4.2.6 Expanded, Combined Uncertainty of the HgCl<sub>2</sub> Generator Reference Value

Calculate and record the expanded, combined uncertainty of the output of the candidate evaporative HgCl<sub>2</sub> generator. If the generator has only one liquid delivery pump, use the following equation. A coverage (K) factor of 2 is assumed.

$$U_{GEN} = 2 \left[ U_{STD}^2 + U_{LFR}^2 + U_{GFR}^2 \right]^{1/2} \quad (\text{Equation 4})$$

Where:

- U<sub>GEN</sub> = Expanded, combined uncertainty of HgCl<sub>2</sub> generator output (%)
- U<sub>STD</sub> = Uncertainty in the concentration of the HgCl<sub>2</sub> standard solution (%)
- U<sub>LFR</sub> = Uncertainty of the liquid feed rates (%)
- U<sub>GFR</sub> = Uncertainty of the carrier gas flow rate (%)

If the generator has two independent liquid delivery pumps, use Equation 4A to determine the expanded, combined uncertainty:

$$U_{GEN} = 2 \left[ U_{STD}^2 + U_{HgFR}^2 + (Wt_{LiqV} \cdot U_{DIWFR}^2) + (Wt_{DryV} \cdot U_{GFR}^2) \right]^{1/2} \quad (\text{Equation 4A})$$

Where:

- U<sub>GEN</sub> = Expanded, combined uncertainty of HgCl<sub>2</sub> generator output (%)
- U<sub>STD</sub> = Uncertainty in the concentration of the HgCl<sub>2</sub> standard solution (%)
- U<sub>HgFR</sub> = Uncertainty of the standard solution feed rate (%)
- U<sub>DIWFR</sub> = Uncertainty of the deionized water feed rate (%)
- U<sub>GFR</sub> = Uncertainty of the carrier gas flow rate (%)
- Wt<sub>LiqV</sub> = Weighting factor representing the total volumetric contribution of water vapor to the output stream (decimal fraction)
- Wt<sub>DryV</sub> = Weighting factor representing the total volumetric contribution of dry carrier gas to the output stream (decimal fraction)

The volumetric weighting factors are used to better reflect the contributions of the water vapor and carrier gas components to the expanded, combined certainty based on their relative relationship to the total volumetric output stream. For example, if a generator is producing gas with a 6% (v/v) moisture content, the relative proportions of water vapor and dry carrier gas in the output stream, and hence, the weighting factors Wt<sub>LiqV</sub> and

$W_{t_{DryV}}$ , are 0.06 and 0.94, respectively. The relative contributions of the DI water feed rate and carrier gas flow rate uncertainties to the expanded, combined uncertainty are weighted accordingly.

#### **4.2.7 Acceptance Criteria**

For the purposes of this interim protocol, it is sufficient to calculate and record the expanded, combined uncertainties of the  $HgCl_2$  reference values. There is, at present, no specified acceptance criterion for the uncertainty of a  $HgCl_2$  generator. However, a target uncertainty value of 10.0 percent, is believed to be achievable.<sup>8</sup>

### **4.3 Alternative Certification Procedures for Evaporative $HgCl_2$ Generator Models**

It is recognized that the procedures in Sections 4.2.1 through 4.2.4 may be impractical for evaporative generator units already installed in the field. Also, generator manufacturers may develop model-specific procedures for initial generator certifications that are different from, but accomplish the same objectives as, the generic procedures in Sections 4.2.1 through 4.2.4. Sections 4.3.1 and 4.3.2, below describe two acceptable alternatives to the generic certification procedures in Sections 4.2.1 through 4.2.4, for the Tekran Instruments (Tekran) Model 3315  $HgCl_2$  generator. The first is the procedure currently being used by Tekran for initial certifications. The second is a procedure for recertification of  $HgCl_2$  generators in the field that is still under development by Tekran.

#### **4.3.1 Manufacturer-Specific Initial Certification**

The following procedures are currently being used by Tekran to perform initial certifications of their Model 3315  $HgCl_2$  generators. These procedures have been reviewed by EPA and have been found to be sufficient to satisfy the generic requirements of Sections 4.2.1 through 4.2.4 of this protocol for initial certification. EPA's determination is based on the following considerations:

- a) The standard liquid solutions, which are certified to have an uncertainty of 0.5%, are prepared for Tekran by an outside vendor employing a gravimetric procedure using a NIST traceable balance to prepare the solutions. The concentration of every batch of standard solution is cross-checked against NIST 3133 standards using inductively coupled plasma mass spectroscopy (ICP-MS). The solution preparation uncertainty is smaller than the analytical uncertainty of the verification.
- b) The standard solutions are directly used as the working solutions; there are no manual dilution steps (i.e., there are no further gravimetric and volumetric dilutions).

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<sup>8</sup> During the interim period of applicability of this protocol, EPA will collect and evaluate uncertainty data in order to specify an uncertainty limit in the final version of the protocol.

- c) The Model 3315 uses two liquid pumps, each of which is calibrated independently. Calibration may be performed quite rapidly using a five place balance or, alternatively, if a three place balance is used, the sampling intervals are long enough to allow the uncertainty in the weight change determinations to be less than 1%. The uncertainty of the calibrated liquid feed rate is nominally 1.0% when the pump is subsequently operated at the calibration set point. When operated at flow rates widely differing from the initial rate used for calibration, the flow rate uncertainty may increase up to 2% beyond the set point uncertainty.
- d) The gas mass flow meter is calibrated relative to a BIOS reference flow standard having a NIST traceable certification. The BIOS reference standard is recertified annually. The gas mass flow meter is calibrated at ten discrete levels and linear interpolation is applied between the calibration points. The uncertainty of the gas mass flow meter is nominally 1.0%.
- e) The expanded, combined uncertainty can be calculated in accordance with the Equation 4A in Section 4.2.6, above.
- f) The expanded, combined uncertainty is within the range of 2% to 3% for all Model 3315 units that are calibrated in accordance with the manufacturer's written procedures.
- g) Every generator unit undergoes the initial certification procedure before shipment.
- h) All of the calibration results are stored in the instrument's memory and are used in conjunction with the manufacturer's algorithms and software to determine the output of the generator. The user can rely on the indicated output of the Model 3315 generator as the calibrated output.
- i) Tekran, in an attempt to reduce the expanded, combined uncertainty of the output concentrations further, will institute multi-point liquid pump calibrations when this interim traceability protocol goes into effect. Linear interpolations will be used to operate the pump between the set points.

#### **4.3.2 Manufacturer-Specific Field Recertification**

Tekran is in the process of developing a field recertification protocol consisting of multiple replicate calibrations of the two liquid feed pumps using a 3-place balance, coupled with calibration of the mass flow meter relative to a NIST traceable BIOS reference flow standard. The procedure will be virtually identical to the initial certification procedure and is expected to yield combined uncertainties of less than 5% for the three set point variables. Once these procedures are available, EPA will review them and issue a revised version of this section of the interim protocol.

## **5.0 CERTIFICATION OF GENERATORS THAT CONVERT ELEMENTAL Hg to HgCl<sub>2</sub>**

### **5.1 Introduction**

This section provides procedures to determine reference values and expanded, combined uncertainty values for generators that convert elemental Hg to HgCl<sub>2</sub> at specific operating conditions. Documentation that a particular HgCl<sub>2</sub> generator has been evaluated according to these procedures and has met the applicable acceptance criteria satisfies the interim NIST traceability requirements for the generator.

Each candidate HgCl<sub>2</sub> generator must use elemental Hg concentrations from an elemental Hg generator that has been certified in accordance with an EPA traceability protocol to produce the reference HgCl<sub>2</sub> values. The uncertainty of the elemental Hg concentrations is included in the expanded, combined uncertainty of the generated HgCl<sub>2</sub> reference value concentrations.

In addition to the certified elemental Hg generator, other critical elements of generators that convert elemental Hg to HgCl<sub>2</sub> include some or all of the following:

- (a) A device used to oxidize elemental Hg (i.e., a “reactor” or “oxidizer”);
- (b) A method and controls associated with the introduction of chlorine;
- (c) Methods and controls affecting the moisture content of HgCl<sub>2</sub> gas standards; and
- (d) Heated connecting tubing and related apparatus to transport the generated HgCl<sub>2</sub> standards to the point of use and/or analysis

The certification of this type of HgCl<sub>2</sub> generator may either be performed by the manufacturer or by the end user.

### **5.2 Reference Value Determination (Generic Procedures)**

At each concentration level, the HgCl<sub>2</sub> reference value is numerically equal to the certified elemental generator output, corrected for moisture dilution and/or chlorine dilution (as applicable).

#### **5.2.1 Elemental Hg Generator**

Use of an elemental Hg generator that has been certified in accordance with an EPA traceability protocol for elemental Hg generators is required. The generator must be capable of producing known concentrations of elemental Hg with established uncertainties at the levels necessary for the intended application.

### 5.2.2 Water Vapor Dilution

HgCl<sub>2</sub> generators that convert elemental Hg may add water vapor to the gas stream to improve gas transport. This humidification will alter the overall uncertainty of the reference value concentrations due to volumetric dilution. If humidification is used:

- (a) At each concentration level, determine the absolute water vapor concentration to within  $\pm 0.5\%$  H<sub>2</sub>O on a volumetric basis, either:
  - From information provided by the manufacturer characterizing the performance of the humidification device; or
  - From saturated water vapor tables (if applicable); or
  - By sampling the humidified stream for a sufficient period of time to facilitate gravimetric analysis.
- (b) Record the absolute water vapor concentration and uncertainty of the water vapor determination. If no better estimate of the uncertainty is justified, use a default value of 0.5% H<sub>2</sub>O.

### 5.2.3 Chlorine Gas Dilution

If a gas mixture containing chlorine is mixed with the elemental Hg generator standards, determine the elemental Hg generator output flow rate and the chlorine gas flow rate, to correct the elemental Hg concentrations for the effects of chlorine gas dilution.

- (a) Determine the elemental Hg generator output flow rate and the chlorine gas flow rate in accordance with the manufacturer's instructions.
- (b) Alternatively, you may measure the chlorine gas flow rate using an in-line orifice meter, or similar device that has been calibrated under the conditions of its intended use.
- (c) Record the elemental generator output and chlorine gas mixture flow rates, and the uncertainty of the determinations. If no better estimate of the uncertainty is justified, use a default value of 10 % for the chlorine gas flow rate and 2% for the elemental Hg generator output flow rate.

### 5.2.4 Calculation of the Reference Values and Expanded, Combined Uncertainties

At each concentration level, calculate the HgCl<sub>2</sub> generator reference value by adjusting the elemental Hg generator output concentration for water vapor dilution (if applicable) and chlorine dilution.

The chlorine Dilution Factor (DF)<sub>Cl<sub>2</sub></sub> is calculated, using Equation 5.

$$(DF)_{Cl_2} = \frac{(Q_{EL} + Q_{Cl_2})}{Q_{EL}} = 1 + \frac{Q_{Cl_2}}{Q_{EL}} \quad (\text{Equation 5})$$

Where:  $(DF)_{Cl_2}$  = Chlorine dilution factor  
 $Q_{EL}$  = Elemental calibrator output flow rate (cc/min)  
 $Q_{Cl_2}$  = Chlorine gas mixture flow rate (cc/min)

Then, if the effects of water vapor dilution must be considered, the reference value is calculated using Equation 6.

$$C_{REF} = \frac{C_{EL} \left( 1 - \frac{\%H_2O}{100} \right)}{(DF)_{Cl_2}} \quad (\text{Equation 6})$$

Where:

$C_{REF}$  = Reference  $HgCl_2$  concentration ( $\mu g/m^3$ )  
 $C_{EL}$  = Certified concentration of the elemental Hg standard ( $\mu g/m^3$ )  
 $\%H_2O$  = Water vapor content of the combined gas stream, after humidification  
 $(DF)_{Cl_2}$  = Chlorine dilution factor, from Equation 5

However, if the moisture content of the gas stream does not change from the point of generation of the elemental Hg standards to the Hg analyzer, the moisture dilution term “ $(1 - \%H_2O/100)$ ” in Equation 6 is unnecessary, and only a correction for chlorine dilution is required. In this case, use Equation 6A, below, to calculate  $C_{REF}$ .

$$C_{REF} = \frac{C_{EL}}{(DF)_{Cl_2}} \quad (\text{Equation 6A})$$

Next, determine the uncertainty of the  $HgCl_2$  reference value, taking into account the uncertainty of each term in Equation 6 or 6A (as applicable).

The uncertainty of the water vapor dilution term in Equation 6 depends on the moisture content of the combined gas stream and the uncertainty of the moisture determination. For example, assume that the moisture content is 1.25%  $H_2O$  and that the default uncertainty is 0.5%  $H_2O$  (see Section 5.2.2, above). While the uncertainty in the  $\%H_2O$  measurement is very substantial (40% relative), worst-case error propagation shows that the uncertainty in the term “ $(1 - \%H_2O/100)$ ” is small (approximately 0.506%)<sup>9</sup>. If the moisture content is more carefully established by the manufacturer to within  $\pm 0.25\%$

<sup>9</sup> For a default uncertainty of 0.5%  $H_2O$ , the actual  $\% H_2O$  value could be anywhere from 0.75 %  $H_2O$  to 1.75 %  $H_2O$ . Based on the measured value of 1.25 %  $H_2O$ , the term  $(1 - \% H_2O/100)$  is 0.9875. Using worst-case error analysis,  $(1 - \% H_2O/100)$  is 0.9925 based on 0.75 %  $H_2O$  and 0.9825 based on 1.75 %  $H_2O$ ---i.e., 0.0050 on either side of 0.9875. Dividing 0.0050 by 0.9875 and converting the result to a percentage gives an uncertainty value of 0.506%.

H<sub>2</sub>O, then the uncertainty in the water vapor term will be about 0.25%, at the same humidification level.

The uncertainty of (DF)<sub>Cl<sub>2</sub></sub>, the chlorine dilution factor term in Equations 6 and 6A, depends on the gas flow rate from the elemental Hg generator and the flow rate of the chlorine gas mixture. For example, assume that the elemental Hg generator output flow rate (Q<sub>EL</sub> in Equation 5) is 10 liters per minute (10,000 cc/min) and the chlorine gas flow (Q<sub>Cl<sub>2</sub></sub> in Equation 5) is 600 cc/min. Assume large default measurement uncertainty of 10% in the chlorine gas flow rate and a default uncertainty of 2% in the elemental generator flow rate. In this case, while the uncertainties in the two measured flow rates in Equation 5, are substantial, the uncertainty in the dilution factor term “(DF)<sub>Cl<sub>2</sub></sub>” in Equations 6 and 6A is small (i.e., 0.66% based on worst-case error propagation)<sup>10</sup>. As shown by this example, the significance of errors in the chlorine flow rate determination is greatly diminished because the ratio of the chlorine flow to the elemental generator flow is very much less than one.

Using the uncertainty of the elemental Hg generator output concentration together with the uncertainty estimates for the water vapor dilution term (if applicable) and chlorine dilution term, the expanded, combined uncertainty in the HgCl<sub>2</sub> reference value is calculated using Equation 7. A coverage (K) factor of 2 is assumed.

$$U_{Ref} = 2 \left[ \left( \frac{U_{EL}}{2} \right)^2 + U_{WD}^2 + U_{DF}^2 \right]^{1/2} \quad (\text{Equation 7})$$

Where:

- U<sub>Ref</sub> = Expanded, combined uncertainty of the reference HgCl<sub>2</sub> concentration (%)
- U<sub>EL</sub> = Expanded uncertainty of the elemental Hg concentration, with a coverage factor of 2 (%)
- U<sub>WD</sub> = Uncertainty of the water vapor dilution term in Equation 6, if applicable (%)
- U<sub>DF</sub> = Uncertainty of the chlorine dilution factor in Equation 6 or 6A, as applicable (%)

As an example, assume that the expanded, combined uncertainty of the concentration produced by the elemental Hg generator is 2%. Then, using the uncertainty of the water vapor dilution term (0.506%) and the uncertainty of the chlorine dilution factor (0.66%) from the previous examples, the combined uncertainty of the reference value is 2.601%.

<sup>10</sup> For a default uncertainty of 10%, the Cl<sub>2</sub> flow rate could be anywhere from 540 to 660 cc/min. For a 2% default uncertainty, the elemental Hg generator output flow rate could be anywhere from 9,800 to 10,200 cc/min. The term (DF)<sub>Cl<sub>2</sub></sub> is 1.060 based on the measured flow rates. Using worst-case error analysis, (DF)<sub>Cl<sub>2</sub></sub> varies from 1.053 to 1.067, i.e., 0.007 on either side of 1.060. Dividing 0.007 by 1.060 and converting the result to a percentage gives an uncertainty value of 0.66%.

### 5.3 Acceptance Criteria

For the purposes of this interim protocol, it is sufficient to calculate and record the expanded, combined uncertainty of the HgCl<sub>2</sub> reference values. There is, at present, no specified acceptance criterion for the combined uncertainty of the HgCl<sub>2</sub> generator. However, a target uncertainty value of 10.0 percent, though not required for the purposes of this interim protocol, is believed to be achievable.<sup>11</sup>

### 5.4 Alternative Certification Procedures for HgCl<sub>2</sub> Generators Models That Convert Elemental Hg

For initial certification of HgCl<sub>2</sub> generators, manufacturers may develop procedures that are different from, but accomplish the same objectives as, the generic certification procedures described in Section 5.2, above. This section describes an acceptable alternative to the procedures in Section 5.2 for the Thermo-Fisher Scientific (Thermo) HgCl<sub>2</sub> generator that is coupled to their Model 81i elemental Hg generator. This alternative procedure is applicable to field recertifications as well as initial certifications.

The Thermo HgCl<sub>2</sub> generator oxidizes elemental Hg produced by a certified Model 81i elemental Hg generator, to produce HgCl<sub>2</sub> calibration standards. The generator hardware includes an oxidizer/reaction chamber where the elemental Hg standards are mixed with a chlorine-in-nitrogen gas mixture at an elevated temperature to produce HgCl<sub>2</sub>. To minimize transport losses, the oxidizer is integrated into the probe assembly of the Thermo Hg CEMS so that the HgCl<sub>2</sub> travels only a short distance before entering the sample probe. Because the Thermo HgCl<sub>2</sub> generator is fully integrated into the CEMS, it cannot be readily evaluated as a stand-alone device in field applications. In addition, it is recognized that transport losses and/or chemical reactions in the other CEMS components (dilution module, converter, probe components, sample lines, etc.) may adversely affect the apparent HgCl<sub>2</sub> generator performance. The actual generator performance is therefore assumed to be better than the apparent performance in terms of % HgCl<sub>2</sub> produced and true uncertainty of the output values.

The procedures used by Thermo to certify their HgCl<sub>2</sub> generator have been reviewed by EPA and have been found to satisfy the generic requirements of Section 5.2 of this protocol. EPA's determination is based on the following considerations:

- a) Thermo has performed generator output verification tests which demonstrate that the oxidizer in the Thermo HgCl<sub>2</sub> generator model produces high percentages of HgCl<sub>2</sub>. The results of these tests have been submitted to EPA.
- b) The moisture content of the combined gas stream is determined from the manufacturer's look up tables.

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<sup>11</sup> During the interim period of applicability of this protocol, EPA will collect and evaluate uncertainty data in order to specify an uncertainty limit in the final version of the protocol.

- c) The chlorine gas flow rate may be determined from Table 3-1, "Chlorine Pressure and Expected Flows" in the Instruction Manual, provided that the proper orifice is installed on the chlorine regulator outlet.
- d) The elemental Hg generator output flow rate can be determined with sufficient accuracy (i.e.,  $\pm 2\%$ ) from the Model 81i display, in accordance with the manufacturer's Instruction Manual.

## 6.0 QUALITY ASSURANCE

This section specifies: (1) the periodic data quality assessments that are required following initial certification of an HgCl<sub>2</sub> generator, to provide assurance of continued acceptable performance; and (2) the required frequency of generator recertification.

### 6.1 Periodic Data Quality Assessments

- (a) Periodic performance evaluations of each HgCl<sub>2</sub> generator shall be conducted at the following frequency:
  - (1) At least monthly, in conjunction with system integrity checks<sup>12</sup>; 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 6.2, below).
- (b) If the HgCl<sub>2</sub> generator does not meet the acceptable performance criteria, suspend the generator certification until either:
  - (1) Another performance evaluation is successfully completed, or
  - (2) The generator is recertified in accordance with the procedures in Section 4 or Section 5.

#### 6.1.1 HgCl<sub>2</sub> Generator Performance Evaluations for Hg CEMS

The quality assurance procedures in Sections 6.1.1.1 and 6.1.1.2, below, assess certain HgCl<sub>2</sub> generator parameter(s) that are indicative of potential performance deterioration for each type of generator. For evaporative HgCl<sub>2</sub> generators, the performance evaluation assesses the mass flow meters and/or mass flow controllers while for HgCl<sub>2</sub> generators that convert elemental Hg to HgCl<sub>2</sub>, oxidation efficiency is the key area of focus.

Most Hg emissions monitoring regulations require Hg CEMS to pass daily calibration error tests using elemental Hg gas standards produced by certified generators. Weekly system integrity checks are also required, using HgCl<sub>2</sub> gas standards produced by certified generators.

For a CEM system with an HgCl<sub>2</sub> generator that is independent from the elemental Hg generator (e.g., a CEMS with an evaporative HgCl<sub>2</sub> generator), the calibration error test and the system integrity check provide a comparison of the two independently certified generators. The acceptance criterion for this comparison is that the calibration error and

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<sup>12</sup> Most current Hg emissions monitoring regulations require regular (typically weekly) "system integrity checks" of Hg CEMS. These system integrity checks involve the introduction of a known level of HgCl<sub>2</sub> calibration gas into the CEMS upstream of all sample conditioning components and a determination of recovery, in order to assess oxidized mercury transport and conversion.

system integrity check specifications prescribed by the applicable regulation are met. When an Hg CEMS is properly calibrated to respond to a certified and quality assured elemental Hg generator, a failure of the system integrity check may be due to a malfunction of the HgCl<sub>2</sub> generator, a failure of the CEMS converter, or excessive transport losses of HgCl<sub>2</sub> within the measurement system.

For CEMS with generators that convert elemental Hg to HgCl<sub>2</sub>, it is most important to evaluate the continued oxidation (conversion) efficiency. This can be accomplished by means of calibration error tests and system integrity checks, as described in Section 6.1.1.2.

#### **6.1.1.1 Evaporative HgCl<sub>2</sub> Generators**

- (a) Perform the following tests using all components of the CEMS and under normal operating conditions.
- (b) First, perform a calibration error test, using a zero gas and a certified upscale elemental Hg gas standard. If the test is passed<sup>13</sup>, initiate a the system integrity check in accordance with the manufacturer's written procedures. Determine conformance with the system integrity check specification based on the total vapor phase mercury (Hg<sup>T</sup>) response. If the performance is unacceptable, initiate corrective action and repeat the system integrity check until acceptable performance is achieved.
- (c) The HgCl<sub>2</sub> generator performance evaluation results are acceptable if the result is within the applicable system integrity check specification prescribed by the applicable regulation<sup>14</sup>.

#### **6.1.1.2 HgCl<sub>2</sub> Generators That Convert Elemental Hg**

- (a) Perform the following tests using all components of the Hg CEMS and under normal operating conditions. Do not disconnect the reactor outlet tubing or connect other devices.
- (b) Ensure that the Hg CEMS is operating in the speciating mode and that both the Hg<sup>T</sup> and Hg<sup>0</sup> channels produce the correct response (i.e., within the applicable calibration error specification)<sup>15</sup> to the zero gas and to the upscale elemental Hg calibration standard, before conducting the system integrity check.

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<sup>13</sup> In the absence of a specific regulatory requirement, use a default calibration error specification of 5.0% of the monitor span value, with an alternative specification of 1.0 µg/m<sup>3</sup> absolute difference between the reference value and the analyzer response.

<sup>14</sup> In the absence of a specific regulatory requirement, use a default system integrity error specification of 10.0% of the reference value, with an alternative specification of 0.8 µg/m<sup>3</sup> absolute difference between the reference value and the analyzer response.

<sup>15</sup> See footnote 13, above.

- (c) Conduct a system integrity check in accordance with the manufacturer's written procedures. **Determine conformance with the system integrity check specification based on the Hg<sup>T</sup> response.** If the performance is unacceptable, initiate corrective action and repeat the system integrity check until acceptable performance is achieved<sup>16</sup>.
- (d) Record the Hg<sup>0</sup> response concurrent with the final Hg<sup>T</sup> response recorded during the successful system integrity check. Calculate the apparent HgCl<sub>2</sub> concentration and the apparent percent conversion of Hg<sup>0</sup> to HgCl<sub>2</sub>, using Equations 8 and 9, below.

$$\text{Apparent concentration of HgCl}_2 = \text{Hg}^T - \text{Hg}^0 \quad (\text{Equation 8})$$

$$\text{Apparent \% Conversion to HgCl}_2 = [(\text{Hg}^T - \text{Hg}^0) / \text{Hg}^T] \times 100 \quad (\text{Equation 9})$$

- (e) Compare the apparent % conversion of Hg<sup>0</sup> to HgCl<sub>2</sub> for the current check with all similar checks during the previous three months, to identify changes in the HgCl<sub>2</sub> generator performance or changes in the CEMS performance.
- (f) The HgCl<sub>2</sub> generator performance evaluation results are acceptable if the apparent % conversion of Hg<sup>0</sup> to HgCl<sub>2</sub> is greater than 50%. If the 50% criterion is not met, then consider corrective action and repeat the system integrity check QA procedure until acceptable performance is achieved.

*Note:* If the HgCl<sub>2</sub> generator is fully integrated into the Hg CEMS (i.e., it is a component or sub-assembly of the probe or other device and is not designed to operate as an independent device), it is evaluated as part of the entire system rather than as a stand-alone device. It is recognized that the necessity of involving other CEMS components (i.e., probe filter, dilution module, converter, other probe components, and sample lines) in the performance evaluation may lower the apparent %HgCl<sub>2</sub> generator output.

## 6.2 Recertification

Following initial certification, all HgCl<sub>2</sub> generators must be periodically recertified to maintain NIST traceability. At a minimum, HgCl<sub>2</sub> generators shall be recertified at least once every 8 calendar quarters in accordance with the procedures in Section 4 or 5.<sup>17</sup> HgCl<sub>2</sub> generators shall also be recertified: (a) whenever any event, condition, or factor that triggers recertification (as identified in the Manufacturer's Disclosure) occurs---see

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<sup>16</sup> See footnote 14, above.

<sup>17</sup> Note: Recertifications of generators that convert elemental Hg will generally involve recertification of the elemental Hg generator coupled with recalculation of the expanded, combined uncertainty, using estimates of the uncertainty introduced by dilution with chlorine gas and moisture.

Section 3.2.4, above; and (b) when generator performance is suspected to be the cause of a CEMS RATA failure.

### References

1. "Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators"; U.S. EPA; July 2009.
2. Roberson, W.R.; "Weekly System Integrity Check Guidance, Procedure for Calculating System Integrity Check Measurement Error and HgCl<sub>2</sub> Generator Oxidizer Efficiency"; report prepared by RMB Consulting and Research, Inc. for Electric Power Research Institute; June 2009.