

Appendix B-1

Traceability Protocol for Certification of Reference Aerosol Generators

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Executive Summary

A reference aerosol generator (RAG) produces an aerosol by nebulizing a solution of known concentration, at a measured rate, into a measured carrier gas flow to emit aerosols with concentrations traceable to NIST standards. Uncertainties are defined for each input and a total, combined uncertainty value for the generated aerosol concentration is established. The reference aerosol can be used to challenge the accuracy of monitors designed to measure species contained in aerosols. These monitors include metals and particulate matter continuous emissions monitors (CEMS), ambient PM₁₀ and PM_{2.5} beta gauges, and metals continuous fence line monitors (CFLM). Typically gas monitors are challenged using NIST traceable gases, whose concentrations have been established using an unbroken chain of comparisons of a candidate gas standard to a primary NIST gas standard. However, no such primary NIST standards exist for analytes in aerosols. This document outlines the general requirements to certify and evaluate whether an aerosol concentration produced by a reference aerosol generator is traceable to NIST, and provides guidance on establishing uncertainty values for each input as well as the total expanded, combined, uncertainty value. In order to establish NIST traceability for a reference aerosol generator's output, this protocol requires that all measurements required to produce the aerosol are traceable to NIST standards, including using solutions with traceable to NIST standard concentrations, using traceable to NIST standard gas flow meters, and using traceable to NIST standard balances to measure solution loss rate. A total capture or subsample test should be conducted to certify the output concentration of the RAG by verifying the NIST traceable reference value to within 15% of the analytical method. Periodic quality assurance (QA) and recertification protocols should follow as required by the manufacturer or the applicable regulation.

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1. Introduction

A reference aerosol generator (RAG) is a device which produces an aerosol of known concentration of an analyte or analytes of interest. Calibration gases have traditionally been used to establish the accuracy of continuous gas monitors. However, no such primary NIST standards exist for analytes in aerosols. Instead, a reference aerosol generator can be used to establish the accuracy of monitors measuring aerosol analytes. A NIST traceable certified reference aerosol generator is a useful calibration and auditing tool for several types of monitors including particulate matter (PM) continuous emissions monitors (CEMS), multi-metals CEMS, metals continuous fence line monitors (CFLM), and ambient PM_{10} and $PM_{2.5}$ monitors.

Traceability of gas standards are typically established using an unbroken chain of comparisons of a candidate gas standard to a primary National Institute of Standards and Technology (NIST) gas standard. Instead of utilizing direct comparisons to NIST standards, this protocol relies on an approach of establishing traceability to NIST standards for the individual components and measurements of a reference aerosol generator that are critical to establishing the analyte concentration. This is similar to the approach the EPA has taken recently to establish NIST traceability for mercuric chloride ($HgCl_2$) gas generators.¹ This protocol borrows heavily from that document.

This Traceability Protocol for Certification of Reference Aerosol Generators proposes methods for: (1) establishing the initial traceability to NIST standards and performance requirements of the key components of RAGs; (2) determining the uncertainty of each key component; (3) calculating NIST traceable output concentrations and the expanded, combined uncertainty values for the aerosol standards produced by the RAG; and (4) verifying the NIST traceable aerosol concentration with a total capture or subsample test and certifying the output of the RAG. The protocol also makes ongoing quality assurance (QA) recommendations.

Like the Interim EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators (Protocol for $HgCl_2$ Generators), this traceability protocol sets a “target” expanded, combined uncertainty value of 10% for the generated aerosol standards. The NIST traceable RAG output concentration is verified using a total capture or subsample test. This protocol specifies that if the NIST traceable concentration is within 15% of the test results, the output of the RAG is considered certified as a NIST traceable reference aerosol generator. Like the $HgCl_2$ Protocol, this document does not explicitly require assessment of the sample transfer lines or any other measurement system component as they are not considered part of the reference aerosol generator. The total capture or subsample tests are practical tools for verification and certification of RAG output but do not demonstrate NIST traceability.

This protocol could potentially be used to establish NIST traceability and to certify RAGs used in a variety of air quality monitoring capacities as quality assurance and auditing tools for both ambient and source CEMS, but certain aspects of the document are written with respect to Cooper Environmental Services' (CES) Quantitative Aerosol Generator (QAG).

2. Definitions

2.1 *Aerosol*

A suspension of solids and/or liquids in a gas

2.2 *Reference Aerosol Generator (RAG)*

A device which generates an aerosol with an analyte concentration that is traceable to NIST or equivalent standards. This aerosol can then be used to audit or calibrate monitors and/or analytical methods measuring that analyte.

A reference aerosol generator produces an aerosol by nebulizing a solution containing a known analyte concentration, at a measured rate, into a measured flow. All of the inputs can be directly linked to NIST-traceable standards. A reference aerosol generator consists of the following components and modules:

- 1) Solution Delivery Module – This module includes any equipment necessary to contain and deliver the solution to the aerosol generation point. This module will often include a solution reservoir, solution delivery lines, a pump to generate flow, and a balance audited with NIST standards.
- 2) Aerosol Generation System – This system includes all of the equipment required to aerosolize the solution. This could include nebulizers, compressed air, and electronic equipment.
- 3) An Evaporation Zone – This is the zone where the nebulized solution droplets are evaporated to remove liquid water.
- 4) Aerosol Dryer – This system consists of any of the components required to generate, measure, and treat the aerosol carrier gas flow. Key components could often include a pump or a blower, compressed air, flow meters, and valves.
- 5) An Electronic and Data Processing System – This system encompasses the specific electronic configuration of the RAG as well as hardware and software for instrument control and data processing

2.3 *Expanded Uncertainty*

As used in this protocol, expanded uncertainty is defined by two (2) times the total uncertainty or standard deviation

2.4 *Nebulization, aerosolization*

To convert a liquid to a fine spray

2.5 *Operational parameters*

The manufacturer should provide information on the operational range or limitations of the RAG components, including mass flow controllers, mass flow meters, heaters, nebulizer power and frequency, and nebulizer enclosure temperature.

2.6 *Operation, Maintenance and QA*

The manufacturer must provide standard operating procedures for the installation, start-up, operation, maintenance, and quality assurance of the RAG. The manufacturer must also identify the conditions and factors that would automatically require recertification of the RAG, such as known malfunctions, failures, component replacement, recalibrations, etc.

2.7 *Factory Acceptance Test*

The manufacturer of the RAG must develop a report describing the certification testing performed and the accompanying data to demonstrate that the RAG model will generate precise and accurate aerosol over a range of concentrations. The report must also include NIST traceable documentation of the inputs necessary to calculate the aerosol concentration.

2.8 *Traceability to NIST*

A documented procedure by which traceability of measurement results to a respective National Institute of Standards and Technology reference standard is established through an unbroken chain of comparisons, each having stated uncertainties. Comparisons are based on appropriate physical and chemical measurements

2.9 *Total Propagated Uncertainty Equations²*

a)

b)

—

— —

3. Reference Aerosol Generator Traceability, Initial Certification and Uncertainty Equations

This section provides a protocol to establish NIST traceability for a reference aerosol generator by demonstrating traceability to NIST standards of a RAG's key inputs. It also provides the methods and equations necessary to quantify the expanded, combined uncertainty of the RAG's output, as well as instructions for verifying the NIST traceable output of a RAG with a total capture or subsample tests. A RAG that has performed and documented the following procedures and has met or surpassed the acceptance criteria satisfies the NIST traceability and certification requirements.

The basic, key system components of a RAG include:

- (a) A container for the working solution on the balance (reservoir)
- (b) A balance that communicates directly with the on-board computer and establishes a measured solution loss rate
- (c) A flow meter(s) and/or controller(s) to establish the flows of the carrier gas

Initial certification of a RAG requires traceability to NIST standards through a clear, unbroken chain of comparisons for each of the key inputs of the RAG, as well as the determination of the expanded, combined uncertainty of the generated “reference value” concentration. The key inputs include solution concentration, the solution loss rate, and the carrier gas flow. For the solution concentration, NIST traceability is demonstrated through use of commercially available NIST standards or solutions traceable to NIST standards. If no NIST standards or traceable to NIST standards are available, ultra-high purity (>99.95% pure) commercial materials can be utilized. Standard protocols should be followed when diluting the traceable to NIST standard solution. For the solution loss rate and carrier gas flow, NIST traceability is demonstrated through auditing the balance with traceable to NIST standard masses and calibrating the flow meters with traceable to NIST standard flow devices.

A “reference value” of the concentration of each analyte in the aerosol can be calculated using Equation 1.

Equation 1

Where:

- = The concentration of the i^{th} analyte in the reference aerosol (e.g. grams of analyte / dscm)
- = The concentration of the i^{th} analyte in the NIST traceable solution (e.g. grams i^{th} analyte per gram of solution)
- = The solution loss rate (grams per minute)
- = The carrier gas flow for the aerosol, (Total Flow), which is a dry standard flow, (dscm)

NIST traceability for a reference aerosol generator is established through the traceability of the solution concentration, the traceability of the balance used to measure the solution loss rate, and the traceability of the aerosol carrier gas flow.

It is assumed that all of the nebulized analyte within the traceable to NIST standard solution is emitted by the RAG as a NIST traceable aerosol at the “reference value” concentration. This is subsequently verified with a total capture or subsample test before the RAG is certified.

3.1 Solution Concentration

The primary input in generating a NIST traceable aerosol is the traceable to NIST standard solution, which is the basis for the other comparisons. For a RAG to be certified, traceable to NIST standard solutions should be employed. NIST traceable solutions are available commercially for many different types of analytes. These solutions are traceable to NIST standard reference materials (SRM), their concentration expanded uncertainty values are typically known to within $\pm 1\%$ or better, and they are known to be stable for long periods of time (at least a year). Because they are independently produced, well-characterized and widely available, it is best to use these types of solutions whenever possible.

Some NIST traceable solutions may not be available in the concentrations suitable for aerosol generation. Any dilution of a commercially available NIST traceable solution should be done in a manner so that each measurement in the dilution process is traceable to NIST standards. This includes assuring that any gravimetric or volumetric measurements are done using balances and/or glassware that are traceable to NIST standards. Also, all dilutions should be done using deionized (DI) water, with high resistivity (16 mega ohms or higher). If solutions are diluted with acid, they should be high purity and free from contaminants. Generally, acids that are listed as being for use in trace metal analysis are of sufficient purity. Dilutions will also increase the uncertainty of the RAG output. See section 3.1.1. and Equation 3 to calculate the increase in combined uncertainty due to dilution.

NIST traceable solutions may also be made by dissolving NIST traceable SRMs into solution. This process is similar in principle to serial dilution, and each measurement should be traceable to NIST standards. Section 3.1.1 and Equation 3 can be utilized to calculate the combined uncertainty due to dissolving NIST traceable compounds into a solvent.

If NIST standards or solutions traceable to NIST standards are not commercially available for either dilution or dissolution, ultra-high purity (>99.95%) commercial materials can be utilized and the uncertainties in the concentration of the material should be included in the expanded uncertainty calculations defined in this protocol.

3.1.1 Calculating the Uncertainty of the Solution Concentration

If an undiluted, NIST traceable SRM solution is used in the RAG, the uncertainty is equal to the unexpanded uncertainty of the labeled concentration. Most NIST traceable SRM solutions give uncertainty values of about $\pm 1\%$, which represents the expanded uncertainty. To calculate the unexpanded uncertainty of the solution, follow the procedure listed under Equation 3.

If a commercially available solution has to be diluted to create a working solution for the RAG, then the concentration of that working solution may be calculated with Equation 2.

Equation 2

Where:

- = The concentration of the i^{th} analyte in the working solution to be aerosolized
- = Concentration of the i^{th} analyte in the traceable to NIST standard solution
- = The mass of the stock solution
- = The mass of the solution after dilution

However, dilution of the NIST traceable SRM solution increases the combined uncertainty. Combined uncertainty in the working solution is based on the gravimetric and volumetric standard uncertainties as well as the uncertainty in the SRM solution. The uncertainty of the diluted working solution can be calculated using Equation 3:

$$\frac{C_i}{C_i} = \frac{m_i}{m_i} \times \frac{V_i}{V_i} \quad \text{Equation 3}$$

Where:

- = The uncertainty in the concentration of the diluted working solution
 - = The unexpanded uncertainty of the concentration of the i^{th} analyte in the traceable to NIST standard solution
 - = The uncertainty of the aliquot weight or volume
 - = The uncertainty of the final, diluted standard solution weight or volume
- a) The unexpanded uncertainty in the commercial standard C_i is provided by the supplier, and can usually be calculated by removing the coverage factor of the percent accuracy of the solution concentration, which is usually about $\pm 1\%$. Thus, for those solutions with an expanded uncertainty of $\pm 1\%$, the unexpanded value, assuming a coverage factor of 2, would be $\pm 0.5\%$. To define C_i multiply this percentage by the concentration of the analyte in the stock solution.
 - b) The uncertainty of the aliquot weight m_i , as recommended by USEPA, is calculated by multiplying the estimated readability (such as .001 to .00001) of the balance by three and dividing that number by the measured aliquot weight.
 - c) The uncertainty of the final, diluted working solution weight m_i can be estimated by dividing the readability of the balance by three and dividing that number by the measured final aliquot weight.

3.2 Liquid Flow Measurement and Solution Loss Rate

The solution loss rate (aerosolization rate or mass emission rate) is another key factor in controlling RAG output concentration, establishing NIST traceability, and certifying a RAG. For the CES Quantitative Aerosol Generator (QAG), the solution loss rate of the analyte-containing solution is determined using a traceable to NIST standards balance.

CES' QAG utilizes a balance that communicates directly to an on-board computer system. Before operation, the balance can be audited using traceable to NIST standard masses so that the data output of the balance is traceable to NIST standards. Because the balance readings are averaged over one minute intervals, the uncertainty of the balance measurements are determined by the analysis of variance (ANOVA) statistical method, which is the application of t-tests to more than two averages, and assumes that the errors are independent and normally distributed.³

3.2.1 Calibrating a Laboratory Balance and Determining Uncertainty

Zero a three-place (or more accurate) balance and check its calibration against NIST traceable weights in the range of measurement appropriate for each solution loss rate determination. If necessary, calibrate the balance per manufacturer's recommendations.

3.2.2 Solution Loss Rate Equations

Some types of nebulization processes for CES' QAG cause solution evaporation without aerosolization of the salts dissolved in the solutions. This effect is minimized by using carrier gas that is saturated at the same temperature as the nebulization chamber. However this control is not perfect. Also, the nebulization process itself adds heat to the system, so the saturated carrier gas passing through the nebulization zone is heated and therefore can absorb additional water vapor from the NIST traceable source. It is therefore necessary to make a correction to the solution loss rate to account for solution evaporation without aerosolization. For the calculation of vapor loss associated with this process (see Equation 6), it is assumed that the carrier gas achieves total saturation both in the initial saturation phases and after being heated by the nebulizer. The vapor correction is usually less than 5% of the solution loss rate, and the uncertainty of this correction is small relative to the total solution loss rate. The measurements required to account for evaporation should also be traceable to NIST standards and documented in the standard operating procedures for the device.

The equation for the solution loss rate is calculated using Equation 4 – 6 as noted below.

Equation 4

Where:

- = Measured rate of solution reservoir mass loss (solution loss rate), determined as the slope of a linear least squares fit of the reservoir solution mass data over the period of a test or tests (g/min).
- = Rate of vapor loss (converted from mg/min to g/min), calculated from the following equation:

Equation 5

Where:

- = Flow rate of the nebulizer air (slpm)
- = Mass of water lost from the nebulizing air (mg/l), calculated from the following equation:

Equation 6

Where:

- = Mass of water in a liter of air at (mg/l), taken from established NIST certified reference sources⁴;
- = Mass of water in a liter of air at (mg/l), taken from established NIST certified reference sources⁴; where
- = Temperature of the nebulizer air at the aerosol size-selection cone
- = Temperature of nebulizer air at saturation

3.2.2.1 Potential Concentration of the Traceable to NIST standard Solution from Vapor Loss

Represents the mass of water removed from the solution without the entrainment of the salt. Over time, it is possible that this process will concentrate the traceable to NIST standard solution used to generate the aerosol. Typically, the RAG will utilize a single traceable to NIST standard solution for one to three hours, depending on the specifics of the spiking protocol. A typical rate of vapor loss () is, in the high range, around 0.01 grams per minute, and a typical total mass of the traceable to NIST standard solution is around 360 grams. Therefore, for a 3 hour test, approximately 1.8 grams of water could potentially be removed from the NIST solution, which would result in concentrating the solution. As a worst case scenario, after 3 hours of continuous running, the traceable to NIST standard solution may be concentrated 0.5 %, which is within the unexpanded uncertainty range of the original NIST SRM, and for the purposes of this traceability protocol viewed as negligible.

3.2.3 *Solution Loss Rate Uncertainty Calculation*

The uncertainty in the solution loss rate can be determined using standard propagation of error methodologies in respect to Equation 4, and are as follows:

The uncertainty of the solution loss rate can be determined using the following Equations 7 - 9:

$$= \frac{\dots}{\dots} \quad \text{Equation 7}$$

Where:

= the error in the linear regression line that defines the rate of mass loss during aerosol generation, which is calculated using the ANOVA statistical method.

And:

$$= \frac{\dots}{\dots} \quad \text{Equation 8}$$

Where:

= the uncertainty value of the mass flow meter or controller.

And:

$$= \frac{\dots}{\dots} \quad \text{Equation 9}$$

Where:

= the uncertainty of the mass of the water lost from the nebulizing air.

= the uncertainty in the measurement of T_s

= the uncertainty in the measurement of T_n

3.3 Carrier / Dilution Gas Flow Measurement

The carrier gas transports the generated aerosol to the receptor. The RAG utilizes several separate carrier gas flows to facilitate transport and drying of the aerosol, including the saturated nebulizer air flow and a series of heated transport and dilution flows. All carrier gas flows used to calculate the aerosol concentrations should be measured using traceable to NIST standard flow meters or controllers. These flow meters are readily available, usually with specified calibration periods such as annually. An uncertainty value () is provided by the manufacturer. If manufacturer data is not available, gas flow meters can also be calibrated and the uncertainty of the gas flow rate determined by using the procedure listed in steps (a) through (e) of this section.

3.3.1 Calibrating Carrier Gas Flow Meters and Determining Uncertainty

- (a) Install a laboratory standard device for flow meter measurement such as a digital bubble meter or a piston displacement device at the outlet of the calibrator. The flow measurement device must have a NIST traceable calibration and an accuracy of 1.5% or better. Operate the flow measurement device, making sure to follow all the manufacturer's instructions and specifications.
- (b) Operate the RAG according to the manufacturer's instructions and allow the generator to run for enough time to equilibrate.
- (c) Test the gas flow output of the RAG against the traceable to NIST standard flow meter device. For each gas flow level, record the data emerging from the carrier gas flow meter on the RAG and the NIST traceable standard. Record at least ten pairs of readings.
- (d) To determine the uncertainty of the gas flow rate meter () on the RAG, calculate the relative standard deviation (RSD) of the gas flow data pairs at each level. If the RSD is less than or equal to 2%, the gas flow rate determination is considered acceptable.
- (e) In the subsequent use of the flow meter, at each gas flow rate setting, compare the average of the traceable to NIST standard flow measurements to the gas flow reading indicated on the RAG. If the difference of these values exceeds the uncertainty value , a linear correction value can be calculated which can calibrate the indicated gas flow. The linear correction can be: 1) a factor based on the ratio of the actual gas flow to the indicated flow; or 2) a combination of a factor with and adjustment value for zero offset. Record the linear correction, and utilize it until the gas flow measurement device is re-calibrated at the same operating level.

- = The unexpanded uncertainty of the concentration of the i^{th} analyte in the NIST traceable solution (if diluted (Equation 3))
- = The concentration of the i^{th} analyte in the NIST traceable solution (or)
- = The uncertainty in the carrier gas flow
- = The carrier gas flow for the aerosol (Total Flow)

4.2 Acceptance Criteria

Like the Protocol for HgCl_2 Generators, the acceptance criterion for the Traceability Protocol for Certification of Reference Aerosol Generators is targeted at an expanded, combined uncertainty of 10%.

5. Total Capture or Subsample Test Output Verification and Certification

After NIST traceability is established through the use of traceable to NIST standard inputs, calibration of key components and calculation of the combined, expanded uncertainty, a total capture or subsample test can be utilized to certify the output of the RAG by verifying that the generated aerosol concentration is within 15% of the NIST traceable reference value. A 15% performance criterion for the total capture or subsample test is reasonable due to the defined uncertainty of the NIST traceable reference value concentration and the uncertainty of analytical methodology employed by the total capture or subsample test. During a total capture test, a filter, with minimal contaminants, (e.g. stretch Teflon), is placed at the end of the aerosol transport line (at a point as close as possible to the point where the aerosol is introduced into the audited monitor) in such a way that all the aerosols captured on the filter and all flow from the RAG passes through the filter. Alternately, a subsample test samples a quantitatively defined portion of the total flow of the RAG system. The filter material for either test method should match the flow and chemical specifications of the aerosol to ensure complete capture of the particulate. The mass of the analyte on the filter can then be determined using appropriate analytical procedures. If preferred or necessary, an impinger method may also be utilized to trap the aerosol.

Appropriate analysis procedures will depend upon the analyte of interest. A RAG used to generate a particulate matter sample may use gravimetric methods of analysis. Methods for analysis of inorganic constituents may be found in the Compendium of Methods for the Determination of Inorganic Compounds (I.O.) in Ambient Air.⁵ Examples include X-ray Fluorescence (I.O. 3.3), inductively coupled plasma (ICP) spectroscopy (I.O. 3.4), inductively coupled plasma/mass spectrometry (I.O. 3.5), and proton induced X-ray emission (PIXE) spectroscopy (I.O. 3.6). A detailed report that includes documentation of the RAG's NIST traceable inputs as well as the methods and results of the total capture or subsample verification test must be provided and be made available upon request to regulatory officials.

6. Ongoing Quality Assurance and Re-certification

Periodic Quality Assurance (QA) tests should also be conducted, verifying the output of the RAG to within 15% of the NIST traceable reference value, or to the specification set by the applicable regulation. The accuracy of the aerosol generator should be checked over a range of concentration levels, including a zero concentration. This protocol recommends that recertification and calibration of the RAG occur at least annually, as needed, or as specified by the relevant regulations.

7. References

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