Performance Specification XX: Performance Specifications for a Quantitative Reference Aerosol Generator

June 9, 2005

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Submitted to:

The Environmental Protection Agency
Research Triangle Park, NC

Prepared by:

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Executive Summary

This performance specification describes the criteria that a Quantitative Reference Aerosol Generator (QRAG) must meet to be considered valid for EPA compliance and/or other regulatory applications. A QRAG should be capable of generating an aerosol containing an analyte whose concentration is traceable to the National Institute of Standards and Technology (NIST) or other equivalent reference. It quantitatively combines solids and/or liquids with a carrier gas to form a stable flow of aerosol with known reference concentration. Before it can be used with regulatory applications, it must be certified according to the requirements of PS-XX. To be certified, you are required to do the following on an annual basis:

- You must ensure that all key components of the QRAG and the analyte standard are process traceable to NIST or other equivalent reference.
- You must test the stability of the QRAG, which is measured by the percent relative standard deviation (PRSD) over a 12-hour test period. The PRSD must be less than 5%.
- You must determine the concentration of the QRAG's generated aerosol with a reference method that measures the concentration of the emissions over the proposed applicable concentration range. The generated aerosol concentration and the reference method measured concentration must have a correlation coefficient (*r)* greater than 0.95, a slope equal to 1.00 ± 0.15, and an intercept less than $1/10^{th}$ of the applicable regulated concentration.

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List of Symbols

b_0	=	The y intercept
b_1	=	Slope
$PRSD$	=	Percent relative standard deviation (given as a percent)
r	=	The correlation coefficient
SD	=	Standard deviation
x	=	Data set for the QRAG generated aerosol concentrations
x_i	=	Value of the i^{th} data point for variable x
$\bar{x}$	=	Average of the values in data set x
y	=	Data set for the reference method aerosol concentrations
y_i	=	Value of the i^{th} data point for variable y
$\bar{y}$	=	Average of the set of values of variable y

1.0 Using PS-XX

1.1 What is the purpose and applicability of Performance Specification XX?

The purpose of Performance Specification XX (PS-XX) is to establish the initial performance requirements for evaluating the acceptability of a quantitative reference aerosol generator (QRAG) prior to using the aerosol it generates as a reference for compliance or other regulatory applications. Such applications may include, (1) instrument, method or procedure calibration, (2) evaluation or certification for initial acceptance, and (3) continuing quality assurance audits or other applications.

1.1.1 Application

PS-XX applies to you if you will be using a QRAG to validate an instrument, method or procedure that will be used in a compliance or other regulatory application.

1.1.2 Compliance

You must comply with PS-XX prior to using any equipment that depends on the QRAG for calibration and/or validation.

1.1.3 Other Data

All components of the QRAG must be certified as NIST-traceable or equivalent; you must obtain the necessary documents of NIST or equivalent certification before using the QRAG.

1.2 What is PS-XX?

This performance specification describes the criteria that a QRAG must meet to be considered valid for use in a compliance or other regulatory application. It should be capable of generating an aerosol of known analyte concentration. A QRAG combines solids and/or liquids with a carrier gas to form an aerosol stream with a NIST-traceable or equivalent analyte concentration that is stable over extended periods.

1.2.1 Basic Requirements

You must have your QRAG certified according to the requirements of PS-XX before its aerosol emissions can be used in a compliance or other regulatory application. To be certified, you are required to do the following on an annual basis:

- You must ensure that all key components of the QRAG and standards are process traceable to NIST (Subsection 4.1.1).
- You must test the stability of the QRAG, which is measured by the percent relative standard deviation (PRSD) of a 12-hour test run. The PRSD must be less than 5% (Subsection 4.1.2).

- You must determine the concentration of the QRAG's generated aerosol with a reference method over a range of concentrations that exceeds the range over which it will be used (Subsection 3.3). The generated aerosol concentration and the reference method measured concentration must have a correlation coefficient (*r)* greater than 0.95, a slope equal to 1.00 ± 0.15, and an intercept less than $1/10^{th}$ of the applicable regulated or compliance concentration (Subsection 4.1.3).

1.3 What special definitions apply to PS-XX?

Aerosol: A suspension of solids and/or liquids in a gas.

Analyte: A species (element, metal, etc.) of interest in an analytical method.

Analytically NIST Traceable Parameter: A parameter whose value is traceable to NIST through a measurement that is NIST traceable[1].

Applicable Concentration Range: The range of concentrations over which a QRAG must be able to produce an aerosol of NIST-traceable or equivalent analyte concentration to be used for a given application.

Certified Concentration Range: The range of concentrations for which the QRAG is certified.

Key Component: A piece of equipment or instrument that measures any parameter used to determine the generated aerosol concentration.

Linearity: The degree to which two parameters are linearly related as determined by the value of the slope and correlation coefficient of a least squares regression analysis.

NIST: The National Institute of Standards and Technology, Gaithersburg, MD.

Particulate: A particle of solid or liquid matter.

Process NIST Traceable: A parameter whose value is traceable to NIST through a procedure, the steps of which are each NIST traceable[1].

Quantitative Reference Aerosol Generator (QRAG): An aerosol generator which emits an aerosol of known analyte concentration that is NIST or equivalent traceable.

Sampling System: A collection of integrated components designed to collect a portion of an aerosol that accurately represents an analyte concentration.

Stability: Percent relative standard deviation of a value measured over an extended period of time.

Standard: Something established by authority, custom, or agreement for use as a rule or basis for comparison in measurement.

Standard deviation: A parameter that indicates the way in which a probability function or a probability density function is centered around its mean and that is equal to the square root of the moment in which the deviation from the mean is squared.

Traceability: A property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties[2].

Traceability to NIST: A documented procedure by which a measured response is related to a standard with an accuracy defined by and certified by the National Institute of Standards Technology (NIST).

Transport/Interface Component: That portion of a test arrangement that connects a QRAG to the point where the aerosol will be evaluated.

Uncertainty: An indication of the degree of reliability of a value usually expressed statistically (probability) as a multiple of the standard deviation of a set of measurements. Unless otherwise stated, the uncertainty in a mean value of a series of measurements will be the standard deviation. In the case of values based on calculations, the uncertainty in the value is equal to the propagated uncertainty based on the uncertainties in the parameters used in the calculations.

2.0 Interferences, Safety, and Equipment Requirements

2.1 Are there any potential interferences for my QRAG?

There are no interferences in this procedure.

2.2 What do I need to know to ensure the safety of persons using PS-XX?

People using PS-XX procedures may be exposed to hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing these procedures. You must consult your QRAG manual and adhere to its specific safety precautions.

2.3 What equipment and supplies do I need?

Your QRAG must be able to continuously emit an aerosol of predictable concentration. You should select a QRAG and a transport system that is appropriate for your specific application. The PS-XX requires that you include, at minimum, the equipment described in subsections 2.3.1-2.3.2.

2.3.1 The QRAG System

A QRAG consists of the following five major components:

- **Analyte Control:** This component quantitatively transports the analyte and/or analyte containing carrier to the point of aerosolization, controls the conditions within which it is delivered, and determines the rate at which it is delivered.
- **Gas Control:** This component quantitatively transports the aerosolizing and/or carrier gas to the point of aerosolization, controls the conditions within which it is delivered, and determines the rate at which it is delivered
- **Aerosolization:** This component combines the analyte and/or analyte carrier with the aerosolizing gas to form a particulate and gas mixture or aerosol under quantitatively controlled conditions.
- **Particulate Size Separator:** This component separates small particulates more likely to have high transport efficiency from larger particles. The separator quantitatively recycles the large particulates that are removed from the aerosol and controls the conditions under which this process takes place.
- **Total Flow Control:** This component controls the total flow rate of the aerosol emerging from the particulate size separator component and controls the conditions under which the final QRAG aerosol is emitted.

2.3.2 Reference Measurement System

For the purpose of certifying the QRAG emissions, you must use either an EPA method or an approved alternative or conditional method. It must be capable of measuring the concentration of analyte in the QRAG emissions over the certified concentration range and test period with an accuracy and precision adequate to evaluate the accuracy and precision of the candidate QRAG.

2.4 What reagents and standards do I need?

2.4.1 Analyte Standard

The QRAG generates an aerosol with NIST-traceable or equivalent accuracy based on the accuracy of the analyte-containing standard. An adequate supply of standard required by a test plan should be prepared prior to testing. The primary requirements of these standards are that (1) the accuracy of the analyte concentrations be NIST-traceable (2) the standards be stable over the period of their use.

2.4.2 Gas

You must select a gas to use for creating the analyte aerosol. The chosen gas must not react with the analyte or with any component in the aerosol that would generate either analyte or analyte interferants.

3.0 Performance Evaluation and Documentation Procedures

3.1 What pre-test performance evaluation procedures do I follow?

3.1.1 Installation

You must install your QRAG according to the manufacturer's written instructions and in a manner that allots an appropriate amount of space for the QRAG to be connected to the reference method measurement system.

3.1.2 Operation

You must operate your QRAG according to the manufacturer's written instructions and specifications.

3.2 How do I monitor and document my QRAG's performance?

You must monitor you QRAG's performance according to the instructions written by the manufacturer, with special attention given to safety precautions. You must also document the QRAG's performance in accordance with the manufacturer's instructions.

3.3 What concentration range must my linearity tests span?

To satisfy the linearity criteria, your tests must span the full applicable concentration range by meeting the following requirements:

- 25% of the data points must be within the upper 66% of the applicable concentration range
- 35% of the data points must be between 33% and 66% of the applicable concentration range.
- 15% of the data points must be within bounds of the lower 33% of the applicable concentration range

You must run linearity tests at a minimum of 4 different concentrations, including a blank. You must ensure that aerosol concentrations required for testing are within (1) the detectable concentration range of the equipment to be calibrated or evaluated and (2) the QRAG's minimum and maximum limits as determined by the manufacturer. Minimum of 12 data points

4.0 Performance Criteria and Calculations

4.1 What performance criteria must my QRAG meet?

Your QRAG must meet the following performance criteria to be certified as a quantitative reference aerosol generator. You must demonstrate that your QRAG meets these criteria on an annual basis at a minimum.

4.1.1 NIST-Traceability

You must ensure that the generated aerosol concentration of the QRAG is process traceable to NIST or equivalent. This process traceability is established by confirming the traceability of the QRAG's parameters[1,2]. You must obtain documentation demonstrating that the QRAG's key components have NIST-traceable or equivalent certification and that the certification is current. But changes, bumps needs to be validated before use. Dan is concerned that in this early stages of use, there is significant room for developing leaks and other problems between when it was last certified and when it might be used. He feels for a while we need to demonstrate that it is working prior to its use. This isn't too much of a problem if we use the XFM to certify it prior to use. E. G. install the QRAG and start generating an aerosol. Then collect a XFM sample or series of samples and fedx them back to the lab for analysis.

4.1.2 Stability Criteria

You must determine the percent relative standard deviation (PRSD) of the analyte concentration in the QRAG aerosol over a 12-hour tests period. The PRSD must be less than 5% (see also Section 4.2.3). Specify minimum # of measurements need instructions on how to do the tests and how many data points do we need.

4.1.3 Linearity Criteria

You must demonstrate that a linear relationship exists between the QRAG generated aerosol analyte concentration and the reference method measured concentration. This relationship must meet the following criteria (see also Section 4.2.4):

- The correlation coefficient (*r)* must be greater than 0.95.
- The slope must be equal to 1.00 ± 0.15%.
- The intercept must be less than $1/10^{th}$ the applicable compliance or other regulated concentration. Dan was somewhat confused with this section and how it related to bias, etc.

4.2 What calculations and data analyses are required?

4.2.1 Arithmetic Mean

Calculate the arithmetic mean of a data set as follows.

$$\bar{x} = \frac{1}{n}\sum x_i$$ **Equation 1**

Where:

$\bar{x}$	=	Arithmetic mean
n	=	Number of data points
x_i	=	Value of each data point

4.2.2 Standard Deviation

$$SD = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$ **Equation 2**

Where:

SD	=	Standard deviation
$\bar{x}$	=	Arithmetic mean
n	=	Number of data points
x_i	=	Value of each data point

4.2.3 Stability

To measure the stability of your QRAG, you must conduct a 12-hour test run using a reference or other EPA approved method to measure the analyte concentration in the emitted aerosol. You must take a minimum of 6 measurements during this time period. Calculate the PRSD using the following equation:

$$PRSD = \left(\frac{SD}{\bar{x}}\right) * 100\%$$ **Equation 3**

Where:

$PRSD$	=	Percent relative standard deviation
SD	=	Standard deviation
$\bar{x}$	=	Arithmetic mean

4.2.4 Linearity

To determine the linearity of your QRAG, you must measure the concentration of its aerosol emissions with the reference or other EPA approved method over the applicable concentration range (Section 3.3). You must test the QRAG at the

following aerosol concentrations at a minimum: one concentration must be at or above the upper end of the concentration range, two concentrations must be between this concentration and a blank, and one test must be a blank. You must calculate the QRAG's generated aerosol concentration using equations defined by the manufacturer. You must determine the slope, correlation coefficient, and the intercept using a least squares linear regression of the aerosol concentration as measured by the reference or other EPA approved method and the QRAG reference aerosol analyte concentration. The relationship must be in the form of a straight line as follows:

$$y = b_1 x + b_0 \qquad \textbf{Equation 4}$$

Where:

y	=	reference method measured aerosol concentrations
x	=	predicted generated aerosol concentrations
b_0	=	y intercept
b_1	=	slope

To calculate the slope, b_1:

$$b_1 = \frac{\sum (x_i - \bar{x})(y_1 - \bar{y})}{\sum (x_i - \bar{x})^2} \qquad \textbf{Equation 5}$$

Where:

x_i	=	value of the ith data point for data set x
$\bar{x}$	=	average of the values in data set x
y_i	=	value of the ith data point for set of data y
$\bar{y}$	=	average of the values in data set y

To calculate the intercept, b_0:

$$b_0 = \bar{y} - b_1 \bar{x} \qquad \textbf{Equation 6}$$

In addition to determining the slope and intercept of the linear relationship, you must calculate the correlation coefficient, r, according to the following equation:

$$r = \frac{\sum (x_i - \bar{x})(y_1 - \bar{y})}{\sqrt{\sum (x_i - \bar{x}) \sum (y_1 - \bar{y})}} \qquad \textbf{Equation 7}$$

4.2.5 Uncertainty

It is also recommended that you report the uncertainty of the QRAG's generated aerosol concentration. This uncertainty should be determined using standard propagation of error techniques[3] relevant to the parameters used to calculate aerosol analyte concentration. The uncertainty values for the parameters are those listed as certified uncertainties by the manufacturers of the key components and/or NIST or equivalent. This procedure should be consistent with those used by NIST[4,5,6]. How is this used? Is it confusing? A distinction needs to be made between propagated uncertainty, measured error and how each is used and for example type of illustrations. Do we need a sample calculation or a discussion of how this uncertainty is calculated? Should we make the analogy with the uncertainty associated with a cal gas?

5.0 Other Requirements and Information

5.1 What quality control and assurance procedures are required by PS-XX?

You must ensure that the QRAG components are NIST-traceable after installation and before using the generated reference aerosol in a compliance or other regulated application. You must obtain valid NIST certifications for all key components and standards as well as document all equipment calibrations with NIST standards. You must also ensure that the QRAG is functioning according the manufacturer's specifications prior to aerosol generation

5.2 What standardization procedures must I use?

The QRAG generated aerosol analyte concentration is based on parameters such as solution concentration, gas flow, rate of solution mass loss, and rate of vapor loss. You must document and demonstrate that each of the parameters affecting the final concentration of aerosol emissions is process traceable to a NIST standard and certification of the standard is current.

5.3 What pollution prevention procedures must I follow?

The excess aerosol generated by the QRAG should be trapped in a filter and disposed of according to appropriate regulations. Unused hazardous supplies should also be disposed of according to regulation.

5.4 What waste management procedures are required by PS-XX?

Any hazardous materials used should be handled according to their Material Safety Data Sheets.

5.5 What references apply to PS-XX?

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4. Scace, G.E. and J.T. Hodges. Uncertainty of the NIST Low Frost-Point Humidity Generator. Gaithersburg, MD: National Institute of Standards and Technology; 2004.

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6. Taylor, B.N. and C.E. Kuyatt. Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. Gaithersburg, MD: National Institute of Standards and Technology [NIST]; 1994. Available from: NIST, Gaithersburg, MD; TN 1297.