



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

MAY 24 2016

Mr. Doug King
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Airgas Specialty Gases
600 Union Landing
Riverton, NJ 08077

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Mr. King:

This letter is in response to your petition dated March 31, 2016, in which you request approval to use an alternative procedure for the certification of National Institute of Standards and Technology (NIST)-traceable elemental mercury (Hg^0) cylinder gas standards because NIST-traceable research gas materials or standard reference materials are not yet available to allow use of the "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards"¹ (EPA Traceability Protocol) for certification of NIST-traceable mercury gas cylinders. More specifically, 40 CFR 63, Subpart UUUUU, the National Emission Standards for Hazardous Air Pollutants: Coal- and Oil-fired Electric Utility Steam Generating Units and 40 CFR 63, Subpart LLL, the National Emission Standards for Hazardous Air Pollutants from the Portland Cement Manufacturing Industry, by reference to Performance Specification 12A (40 CFR 60, Appendix B) and Procedure 5 (40 CFR 60, Appendix F), both require the use of NIST-traceable mercury gases for mercury monitoring system certifications and ongoing quality assurance. These rules further establish that NIST-traceable mercury gas cylinders must be certified according to the EPA Traceability Protocol¹ to yield what are referred to as 'protocol gases.'

The EPA Traceability Protocol requires that 'protocol gases' be certified traceable by an unbroken chain of comparisons -- each contributing to the overall measurement uncertainty -- back to a reference standard. For these purposes, currently acceptable reference standards include NIST standard reference materials (SRM), NIST-traceable reference materials (NTRM), NIST-certified reference materials (CRM), and NIST-certified research gas mixtures (RGM) or Van Swinden Laboratorium (VSL)² primary reference materials (VSL PRM) and VSL CRM (see Section 2.1.3 of the EPA Traceability Protocol). You correctly point out that there are currently no NIST or VSL reference compressed gas standards available to prepare Hg^0 protocol gases in

¹ EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, U.S. Environmental Protection Agency, Office of Research and Development, EPA/600/R-12/531, May 2012. Robert S. Wright, Air Pollution Prevention and Control Division, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, EPA/600/R-12/531, May 2012.

² The Van Swinden Laboratorium is the Swedish equivalent of the U.S. National Institute of Standards and Technology.

the concentration range necessary to support the measurements and monitoring required for the above-referenced EPA rules. However, NIST does possess the ability to certify individual points for Hg⁰ reference gas generators, which are currently accepted by the EPA to support EPA regulatory compliance programs.

To address the current lack of NIST or VSL mercury gas reference standards noted above, you are proposing to use, as an alternative to a NIST-certified RGM or other compressed gas reference standard, the gas output at individually certified set points from a 'Vendor Prime' elemental mercury gas generator³ that has been recently certified by NIST. In other words, you would substitute a NIST-certified Vendor Prime elemental mercury gas generator's individually certified points, including associated uncertainty, for a NIST-certified RGM cylinder gas in the Assay and Certification procedures when preparing your compressed gas standards, according to the EPA Traceability Protocol (Sections 2.2 and 2.3).

More specifically, you would establish the stability of and certify individual compressed gas standards using an unbroken chain of comparisons and the EPA Traceability Protocol based on the individually NIST-certified set points of your Vendor Prime mercury gas generator. These individually certified gases would be either Gas Manufacturer Intermediate Standards (GMIS) as allowed in the EPA Traceability Protocol or mercury compressed gas cylinders to be offered for sale. The certified NIST-traceable mercury compressed gas cylinder standards offered for sale would be identified as Gas Manufacturers Alternative Certified Standards (GMACS) and would be used by facilities and others to meet the requirements in 40 CFR 63, Subparts LLL and UUUUU and potentially the other subparts mentioned later in this letter.

In recognition of the critical need for elemental mercury calibration standards or 'protocol gases' to meet continuous emission monitoring requirements for mercury and the current lack of National or International reference materials to which a protocol gas may be made traceable, we are approving your proposed alternative to substitute a NIST-certified Vendor Prime elemental mercury gas generator for a RGM in the EPA Traceability Protocol¹ with the following required provisos:

- (1) The reference concentration (tag value) of each GMACS shall:
 - (a) Be based on an unbroken chain of comparisons; and
 - (b) Use instrumental analysis where the calibration of the instrument is referenced to the Vendor Prime elemental mercury gas generator NIST-certified values and instrumental assays for GMACS certification are performed in accordance with EPA Traceability Protocol¹ Section 2.2 or 2.3.

- (2) The Vendor Prime elemental mercury gas generator used must have been certified by NIST within the last 24 months.

³ "Interim Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators," July 01, 2009, see: <https://www3.epa.gov/ttn/emc/metals.html>.

- (3) Each GMACS elemental mercury gas cylinder shall be assessed and demonstrate acceptable stability; at a minimum, acceptable stability must be demonstrated by meeting the requirements for reactive gases in Section 2.1.5.2 of the EPA Traceability Protocol.¹
- (4) You must include the following items in the uncertainty budget supporting the certification of the GMACS Hg⁰ compressed gas standards:
 - (a) The Vendor Prime elemental mercury gas generator set point concentration uncertainty from the NIST certification;
 - (b) The instrument calibration curve error associated with assay of the candidate GMACS;
 - (c) Replicate measurement instrument error and precision; and
 - (d) The variability of the Vendor Prime elemental mercury gas generator set point output concentrations over time.
- (5) The combined, expanded uncertainty of the GMACS shall be calculated as the root sum square of the standard uncertainty budget items based on the gravimetric preparation and the instrumental assay using the coverage factor $k=2$.
- (6) The combined expanded uncertainty ($k=2$) of your vendor-certified standards must be less than 5.0 percent.
- (7) You must provide a certificate of analysis (COA) with each GMACS cylinder sold that contains the following information:
 - (a) Identification of the gas as a Gas Manufacturer Alternative Certified Standard according to this approved alternative (ALT-118) found at <http://www3.epa.gov/ttn/emc/approalt.html>;
 - (b) The certified concentration of the GMACS;
 - (c) The combined, expanded uncertainty ($k=2$) of the certified GMACS value calculated as the root sum square of the uncertainty budget items based on items in (3) above;
 - (d) A quantitative standard uncertainty breakdown of the components of each uncertainty budget (i.e., the Vendor Prime elemental mercury gas generator certified set point concentration uncertainty from the NIST-certification and the variability of the Vendor Prime elemental mercury gas generator set point output concentrations over time) sufficient to verify individual budget elements and to independently calculate the combined, expanded uncertainty. Since you will be performing the instrumental analyses and associated uncertainty calculations according to the EPA Traceability Protocol¹, you may report the instrumental analysis uncertainty as a single value and state that your analyses are performed in accordance with the EPA Traceability Protocol as an alternative to reporting the uncertainties of the individual instrumental analysis elements;

- (e) The intended life time (i.e., maximum storage life and expiration date) of the GMACS including the basis and associated data supporting acceptable stability; and
 - (f) Any other relevant comments or instructions (e.g., storage conditions, minimum pressures, recommended regulator, etc.).
- (8) This alternative test method approval will be reconsidered and may be withdrawn at a future date, pending availability and usability of NIST or VSL primary standards. Modification or intent to withdraw this alternative method approval will be announced via a Federal Register notice.

This alternative is applicable to Performance Specification 12A (all certification tests), Procedure 5 (quarterly audits) and 40 CFR 63, Subpart UUUUU, Appendix A, where NIST-traceable gases must be used to assess instrument performance and on-going data quality. Because we believe that this alternative is appropriate for broad application under 40 CFR 63, Subparts LLL and UUUUU, as well as 40 CFR 63, Subpart DDDDD, National Emission Standards for Hazardous Air Pollutants for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters and 40 CFR 60, Subparts CCCC and DDDD for Commercial and Industrial Solid Waste Incineration Units, we will announce it on the EPA's website at <http://www3.epa.gov/ttn/emc/approalt.html>.

If you have any questions regarding this approval or need further assistance, please contact Robin Segall at (919) 541-0893 or segall.robin@epa.gov.

Sincerely,



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