UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Dr. Miller:

This letter is in response to your letter dated October 1, 2015, to Steffan Johnson requesting approval for users of EPA Protocol gases to use alternative HCl gas standards in instances where EPA Protocol gases are not available due to lack of appropriate national or international reference materials to which the protocol gases must be analytically and statistically traceable. We identify 40 CFR part 63, Subpart LLL, National Emission Standards for Hazardous Air Pollutants From the Portland Cement Manufacturing Industry; 40 CFR part 63, Subpart UUUUU, National Emission Standards for Hazardous Air pollutants: Coal- and Oil-fired Electric Utility Steam Generating Units; 40 CFR part 63, Subpart DDDDD, National Emission Standards for Hazardous Air Pollutants for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters; and requirements proposed in 40 CFR part 60, Subpart CCCC and DDDD, Commercial and Industrial Solid Waste Incineration Units, as the current relevant requirements where your request would apply.

All of the referenced regulatory subparts require or allow use of HCl continuous emission monitoring systems (HCl-CEMS) according to the EPA's Performance Specification 18 for HCl continuous monitoring (40 CFR part 60, Appendix B) and the associated quality assurance provisions in Procedure 6 (40 CFR part 60, Appendix F). Performance Specification 18 and Procedure 6 require HCl calibration gases prepared in accordance with the "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards"[1] to yield what are referred to as 'protocol gases.' Protocol gases are certified traceable by an unbroken chain of comparisons ultimately to National or International gaseous reference materials such as National Institute of Standards and Technology (NIST) standard reference materials (SRM), NIST-traceable reference materials (NTRM), certified reference materials (CRM), and research gas

[1] EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, U.S. Environmental Protection Agency, Ooffice 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.

mixtures (RGM) or Van Swinden Laboratorium (VSL)[2] primary reference materials (VSL PRM) and VSL CRM. You point out that there are currently no NIST or VSL reference standards for the calibration gases needed to prepare HCl protocol gases in the concentration range required for the referenced EPA rules.

To address the absence of NIST or International reference materials, you propose, as an alternative, to produce gravimetrically-prepared gas standards that you will independently verify and use to certify the measured concentration of HCl gas cylinder standards that you offer for resale to meet the requirements in the referenced subparts. Once verified, these primary standards you prepare would become Gas Manufacturer Primary Standards (GMPS) and would substitute for the NIST or VSL reference gas materials (e.g., NTRMs, SRMs, RGMs), and the remainder of the unbroken chain of comparisons would follow the EPA Traceability Protocol[1].

You propose to analyze your gravimetrically-prepared GMPS with a classical chemical sampling and analysis approach and requirements similar to EPA Method 26A. You indicated that the calibration for the classic chemical analysis would be done using NIST-traceable liquid calibration standards. You contend that this analytical approach used to measure the gravimetrically-prepared standard concentration essentially duplicates the methodology that NIST would follow to prepare traceable HCl cylinder gas standards.

The relative agreement between the gravimetrically-prepared standard value and the classically analyzed value is the basis for verifying the concentration of cylinder. Once verified, it would become your GMPS. Once you have prepared your GMPS, you propose to use this reference standard to calibrate an instrument (e.g., Fourier Transform Infrared (FTIR), Cavity Ring Down Spectroscopy (CRDS), gas filter correlation (GFC)) that will be used to verify the gravimetric concentration of HCl cylinder gas standards, which are your Gas Manufacturers Alternative Certified Standards (GMACS) produced for commercial sale.

In recognition of the critical need for HCl calibration gases that are currently not available as National or International reference materials to which a protocol gas may be made traceable, we are approving your proposed alternative with the following required provisos:

1) The reference concentration of each GMPS:
    a. Shall be based on gravimetric preparation with independent verification.
        i. The independent verification must be experimentally based on wet chemical sampling and analysis. To constitute verification, the concentration calculated from the gravimetric preparation process must agree within 4.0 percent of the independently measured concentration.
        ii. Alternatively, the independent verification may be based on comparison to a NIST or VSL NTRM, SRM or RGM or GMIS traceable to the National or International gaseous reference gases. A single comparison to a serially diluted candidate GMPS may be used to verify not only the individual

[2] The VanSwinden Laboratorium is the Swedish equivalent of the U.S. National Institute of Standards and Technology

candidate GMPS, but also the parent candidate GMPS from which it is derived. The results of analysis of the two standards must agree within 4.0 percent.

b. When using a GMPS to qualify GMACS, the verified GMPS reference concentration may be based on the gravimetric value, the independently verified value, or the average of the two; however, each gas vendor may use only one of these three options.

2) The scale used to generate gravimetric reference standards must be independently calibrated at the target masses with ASTM E617-13 Class 1 weights on no less than a yearly basis. At a minimum, you must also check the calibration before each weighing with a weight in the appropriate range that meets ASTM E617-13 Class 1 requirements.

3) The reference concentration (tag value) of each GMACS shall:
   a. Be based on gravimetric preparation with instrumental analysis verification.
   b. Be verified by instrumental analysis where the calibration of the verifying instrument is referenced to the GMPS.
      i. Instrumental analyses for verification shall be performed in accordance with EPA Traceability Protocol Section 2.2 or 2.3.
   c. Carry a certified concentration which is the average of the gravimetrically determined concentration and the instrumental analysis concentration.

4) Each GMACS HCl gas cylinder shall be assessed and demonstrate acceptable stability and:
   a. The gravimetric concentration and the final instrumental analysis verification concentration must be within 4.0 percent (RPD).
   b. Alternatively, acceptable stability may be demonstrated by meeting the requirements for reactive gases in Section 2.1.5.2 of the EPA Traceability Protocol.[1]

5) You must include the following uncertainty budget items in the documentation certifying GMACS HCl gas standards preparation and analysis:
   a. Gravimetric Preparation:
      i. The purity of the HCl reagent and the balance gas;
      ii. The measured accuracy of the (electronic) balance including consideration the uncertainty of the calibration weights, the calibration uncertainty and its linearity;
      iii. The repeatability of the balance readings including errors caused by the location of the cylinder on the balance;
      iv. Balance Buoyancy effects;
      v. Effects of moisture adsorption and dust on the outer surface of the cylinder;
      vi. Errors due to loss of material during transfer into the cylinder; and
      vii. Dilutions used to prepare target concentrations, including propagated uncertainties through controlled periodic validations.
   b. Wet Chemistry Analysis
      i. The error in volumetric sampling of the HCl gas;
      ii. The error in replicate sampling;
      iii. The uncertainty of the reference analytical solution and propagated uncertainties through serial dilutions;

iv. The calibration curve error; and
v. The error in replicate analyses.

c. Instrumental Analysis
i. The Reference Standard uncertainty;
ii. The instrument calibration curve error; and
iii. Replicate measurement instrument error and precision.

6) 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 analysis, inclusive of the GMPS(s) using the coverage factor k=2.

7) The combined expanded uncertainty (k=2) of your vendor-certified standards must be less than 5.0 percent.

8) 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-114) 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 GMACS reference value calculated as the root sum square of the uncertainty budget items based on items in 5) above.
d. A quantitative standard uncertainty breakdown of components of each uncertainty budget (i.e., gravimetric, GMPS verification, instrumental analysis) sufficient to verify individual budget elements and to independently calculate the combined, expanded uncertainty. If you are performing the instrumental analyses and associated uncertainty calculations according to the EPA Traceability Protocol[1], 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.
f. Any other relevant comments or instructions (e.g., storage conditions, minimum pressures, recommended regulator, etc.).

9) 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 18 (all certification tests), Procedure 6 (quarterly audits) and Procedure 1 (40 CFR part 60, Appendix F; quarterly audits) where NIST-traceable gases must be used to assess instrument performance and on-going data quality. Allowance for use of other gases either in the referenced Performance Specification, QA Procedures, or Subparts still apply including the use of vendor-certified gases for daily calibrations under Procedure 6. Because we believe that this alternative is appropriate for broad application under 40 CFR part 63, Subparts LLL, UUUUU, DDDDD, and 40 CFR part 60

Subpart CCCC and DDDD, 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 either Ray Merrill at (919) 541-5225 or *Merrill.raymond@epa.gov* or Robin Segall at (919) 541-0893 or *Segall.robin@epa.gov*.

Sincerely,

Steffan Johnson, Group Leader
Measurement Technology Group

cc.
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