

ALT-114 and ALT-118

Alternative Approaches to NIST-Traceable Reference Gases

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Overview

- Background
- Applicability
- Approach
- Some examples
- Reference gases of the future?
- **Green Book** updates?



Background

- NIST-traceable “Protocol” gases are often required for regulatory compliance applications
- These gases are prepared according to the **Green Book**
(EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards)
- Rely on NIST-traceable reference materials (RMs)
 - NTRMs, RGMs, other accepted RMs, etc
- Availability of RMs dependent on NIST capabilities
- Unavailability of necessary RMs limits EPA programs
- Approved Alternative methods can provide quality options

Applicability – Hg⁰

- PS-12A/Procedure 5 and Appendix A to 40 CFR Part 63, Subpart UUUUU require the use of NIST-traceable elemental Hg (Hg⁰) gas standards for Hg emissions monitoring
- Affected facilities under:
 - MATS Rule
 - Portland Cement MACT
- Not all Hg CEMS have NIST-traceable Hg⁰ generators
- Hg⁰ cylinders are a viable and *necessary* option
- ALT-118 developed based on formal request ...

What is ALT-118?

- Broadly applicable alternative test method approval issued under § 63.7(f) on 5/24/2016
- Provisions allow OAQPS to approve alternatives or changes to testing requirements under 40 CFR Part 63
 - If determined adequate for EPA Administrator's determination of compliance
- Broadly applicable alternative test method approval:
 - Multiple source categories
 - All gas vendors meeting requirements



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

MAY 24 2016

Mr. Doug King
Manager, Technology & Analytical Processes
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 Protocol 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.

ALT-118 Approach

- Based on naming Hg⁰ cylinders from NIST-traceable, Vendor Prime Hg⁰ gas generator as alternative to NIST Research Gas Mixture (RGM)
 - Vendor Prime Hg⁰ generator must be certified within last 24 months
- Can name either Gas Manufacturer Intermediate Standards (GMIS) or the commercial Hg⁰ cylinders Gas Manufacturer Alternative Certified Standards (GMACS) directly
- Instrumental analysis basically follows the **Green Book**
 - Stability determined as a “reactive gas”
- Uncertainty (U) budget must include:
 - Individual Hg⁰ set point certification U
 - Calibration curve
 - Replicate measurements
 - Hg⁰ generator set point variability

ALT-118 Approach (cont.)

- Both **Green Book** and ALT-118 require:
 - Documentation of uncertainty budget
 - Certificate of Analysis
- ALT-118 specific Certificates of Analysis are required
 - Identifies gases as GMACS
 - States the certified concentration, uncertainty ($U = \leq 5\%$), expiration date
 - Quantitatively reports all associated uncertainty components so that reported uncertainty can be independently confirmed



CERTIFICATE OF ANALYSIS

Grade of Product: GMACS

Part Number:	X02NI99T15W1234	Customer PO Number:	
Cylinder Number:	CC502000	Reference Number:	82-124755777-1
Laboratory:	ASG – Riverton, NJ	Cylinder Volume:	135 CF
Cylinder Pressure:	1890psig	Certificate Date:	December 15, 2016
Valve Outlet:	CGA 660	Expiration Date:	December 15, 2017

Certification performed in accordance with USEPA Alt-118 dated 5/24/16, entitled "Alternative Method for Preparation of NIST Traceable Elemental Mercury Gas Standards in Compressed Gas Cylinders". Processes used in the determination of the composition and uncertainty of this cylinder are through the use of the ALT-118 procedure. Measurement uncertainty and stability evaluation is per the EPA Traceability Protocol (May, 2012). There are no significant impurities which affect the use of this calibration mixture. All concentrations are on a microgram per cubic meter ($\mu\text{g}/\text{M}^3$) basis. Do not use this cylinder below 100 psig, i.e. 1 Mega Pascal

ANALYTICAL RESULTS: GAS MANUFACTURERS ALTERNATIVE CERTIFIED STANDARD

Component	Requested Concentration	Actual Concentration	Total Relative Uncertainty	Assay Dates
Mercury	9 $\mu\text{g}/\text{M}^3$	8.86 $\mu\text{g}/\text{M}^3$	+/- 3.1%	10/4/16, 12/15/16
Nitrogen	Balance	Balance		

CALIBRATION SYSTEM

Instrument Make/Model	Serial #/Lot ID	NIST Certification Report	NIST Report Date
Thermo 81i Calibrator	0730625309	646.03-16-008	10/9/15

ANALYTICAL EQUIPMENT

Instrument/Make/Model	Principal	Last Multipoint Calibration
Thermo 80i	UV Fluorescence	December 14, 2016

Components of Uncertainty: coverage factor K=2

Thermo 81i Certification Uncertainty:	11.00 $\mu\text{g}/\text{M}^3$ +/- 0.174 $\mu\text{g}/\text{M}^3$ absolute, +/- 1.35% relative
Multipoint Calibration Curve Uncertainty:	+/- 0.2 $\mu\text{g}/\text{M}^3$ absolute, +/- 1.0% relative
Measurement Precision:	+/- 0.22 $\mu\text{g}/\text{M}^3$ absolute, +/- 2.4% relative
Calculated Thermo 81i Generator Drift:	+/- 0.2 $\mu\text{g}/\text{M}^3$ absolute, +/- 1.0% relative

QA Approved, Title

Applicability - HCl

- Promulgated Performance Specification 18 (PS-18) and Procedure 6 for HCl CEMS in July 2015
- Affected facilities choosing to use PS-18/Procedure 6 for HCl monitoring under:
 - MATS Rule
 - Portland Cement MACT
- PS-18/Procedure 6 require NIST-traceable “Protocol” HCl gases
- HCl Protocol gases were not sufficiently available as compliance dates approached
- An interim solution was needed to address absence of HCl standards
- ALT-114 developed based on formal request ...

What is ALT-114?

- Broadly applicable alternative test method approval issued under § 63.7(f) on 2/22/2016
- Provisions allow OAQPS to approve alternatives or changes to testing requirements under 40 CFR Part 63
 - If determined adequate for EPA Administrator's determination of compliance
- Broadly applicable alternative test method approval:
 - Multiple source categories
 - All gas vendors meeting requirements



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 22 2016

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Chief Technical Officer
Air Liquide America Specialty Gases, LLC
6141 Easton Road
Plumsteadville, PA 18949

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, 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.

ALT-114 Approach

- A Performance-based approach
- Based on independent verification of gravimetrically prepared Gas Manufacturer Primary Standards (GMPS)
 - Fundamentally independent approach based on wet chemistry, or
 - Comparison to National or International RMs (allows for dilution)
 - Agreement must be within 4%
 - Certified value may be based on gravimetric or independent analysis, or average of both
- GMPS used to instrumentally confirm the gravimetrically prepared Gas Manufacturer Alternative Certified Standards (GMACS)
 - Instrumental analysis follows the **Green Book** from this point
 - Instrumental analysis must agree with gravimetric value within 4%
 - Certified value based on the average of gravimetric and instrumental analysis

ALT-114 Approach (cont.)

- Confirmation of GMACS gravimetric value is key to approach
 - This confirmation also serves to confirm stability
- Both **Green Book** and ALT-114 require:
 - Documentation of uncertainty budget
 - Certificate of Analysis
- ALT-114 specific Certificates of Analysis are required
 - Identifies gases as GMACS
 - States the certified concentration, uncertainty ($U = \leq 5\%$), expiration date
 - Quantitatively reports all associated uncertainty components so that reported uncertainty can be independently confirmed

CERTIFICATE OF ACCURACY: HCl GMACS (Gas Manufacturer Alternative Certified Standard)

ASSAY LABORATORY	Customer Information	
AIR LIQUIDE AMERICA SPECIALTY GASES LLC Exploratory Products Group 6141 Easton Road Plumsteadville, PA 18949	Sales Order#: 2198185 Item No.: A0921633 P.O. No.: X704782X Folio #: 8 ppmHCl; 5 ppm SF6	ABC CEMENT COMPANY Kiln #1 123 Clinker Street Concrete, CT 01357

PRODUCT INFORMATION	CERTIFIED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
COMPOSITION			
Hydrogen Chloride	7.98 PPM	0.27 PPM	3.50 %
Sulfur Hexafluoride	5.02 PPM	0.03 PPM	0.63 %
Nitrogen	Bal		

Cylinder Number: **CC481165**
Cylinder Type: **30L Aluminum**
Cylinder Pressure: **1920 PSIG**
Mixture Dew Point: **N / A**

Certification Date: **21-Mar-16**
Prior Certification Date: **None**
Expiration Date: **22-Mar-17**
Lot No.: **403-339834**

CERTIFICATION DATA	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
GravStat™ Blending Process			
COMPOSITION			
Hydrogen Chloride	7.987 PPM	0.032 PPM	0.403 %
Sulfur Hexafluoride	5.022 PPM	0.032 PPM	0.634 %

Confirming Analysis	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
COMPOSITION			
Hydrogen Chloride	7.98 PPM	0.27 PPM	3.34 %

INSTRUMENT MODEL / ANALYTICAL PRINCIPLE
Tiger Optics HALO HCl Cavity Ring Down Spectrometer

Reference Standard(s)	Cylinder Number:	GMPS ND50602	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)	EXPIRES:
COMPOSITION						
Hydrogen Chloride			10.02 PPM	0.32 PPM	3.22 %	17-Mar-17

Calibration Curve Data:	Curve Order	Correlation	Slope	Intercept
	1st Order -	0.999892	0.000998	0.027432
	10 Points, Incl zero			

INTERLOCK STATISTICS	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
GravStat Result	7.987 PPM	0.032 PPM	0.403 %
Analysis Result	7.98 PPM	0.27 PPM	3.34 %
Interlock Result	7.98 PPM	0.27 PPM	3.50 %

COMMENTS / SPECIAL INSTRUCTIONS

1. This GMACS was certified according to the EPA approved alternative (Alt-114) found at <http://www3.epa.gov/ttn/emc/approalt.html>.
2. Do not use this standard if pressure is less than 200 psig.
3. Do not use or store this product at or below the stated dew point.

APPROVED BY:

S. Hausman

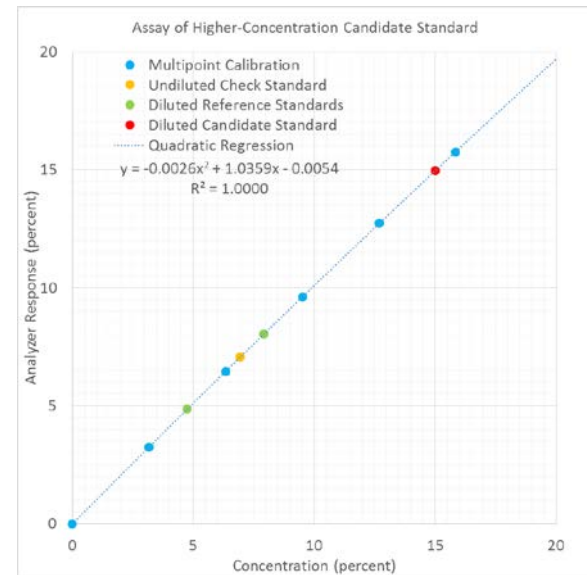


Future of ALT-114 and ALT-118

- Our ultimate goal remains NIST traceability fully implemented by the **Green Book** process (i.e., Protocol gases)
- Thus we may withdraw ALT-114 and ALT-118 once NIST-traceable HCl and Hg⁰ reference materials, inclusive of the full range of necessary concentrations, are widely available ...
- However, the procedure set forth in ALT-114 will serve as a template for *rapid* development of new reference gases to support the advancement of additional HAPS measurement and monitoring (e.g., HF, HCN, NH₃, formaldehyde, etc)

Green Book Revisions ...

- Bob Wright now working on **Green Book** revisions
- Mostly minor changes (e.g., updates to Tables 2-2, 2-3, etc)
- Of significance, dilution approach for high level Protocol gases
 - Procedure for diluting Protocol candidate to level comparable to available RGMs/NTRMs
 - Expands working ranges of Protocol gases



- Link to **Green Book** questions:

www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards

Questions ...



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What the Rules Say About Hg⁰ Compressed Gas Standards ...

- **PS12A**, Section 7.1 says“The use of NIST traceable gases is required.” There is no reference to the Interim protocols.
- **Procedure 5**, Section 5.1.2 (CGA) says ... “Use elemental Hg and oxidized Hg (mercuric chloride, HgCl₂) audit gases that are National Institute of Standards and Technology (NIST)-certified or NIST-traceable following an EPA Traceability Protocol
- **MATS, Appendix A**, Section 3.2.1.2.1, *now* says.....”Only NIST-certified or NIST-traceable calibration gas standards and reagents (as defined in 3.1.4 and 3.1.5), *and including, but not limited to, Hg gas generators, Hg gas cylinders*, shall be used for the tests and procedures required under this subpart.”
- **MATS, Appendix A Section 3.1.4** says....”NIST-Traceable Elemental Hg Standards means either: *compressed gas cylinders* having known concentrations of elemental Hg, which have been prepared according to the *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards* – AKA “The Green Book”; or calibration gases having known concentrations of elemental Hg produced by a generator that meets the performance requirements of the ‘*EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators*’ or an interim version of that protocol.”