

# $\text{Hg}^0$ and $\text{HgCl}_2$ Reference Gas Standards: NIST Traceability and Comparability (And EPA ALT Methods for Hg and HCl )

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# Overview

- NIST/EPA  $\text{HgCl}_2$  evaporative generator research
- ALT-118 for  $\text{Hg}^0$  cylinders
- ALT-114 for  $\text{HCl}$  cylinders



# Background

- Early Hg CEM demonstration studies found that elemental ( $\text{Hg}^0$ ) and evaporative  $\text{HgCl}_2$  generators do not agree
  - ~7-10% differences have been observed
- The Oxidized Hg Traceability Protocol allows a “correction factor” to force agreement
- Evaporative  $\text{HgCl}_2$  reference gases are not of the same quality as  $\text{Hg}^0$  reference gas standards
- MATS Rule now prohibits use of  $\text{HgCl}_2$  gases for daily checks:

“5.1.2.1 Calibration error tests of the Hg CEMS are required daily, except during unit outages. Use a NIST-traceable elemental Hg gas standard for these calibrations. If your Hg CEMS lacks an integrated elemental Hg gas generator, you may continue to use NIST-traceable oxidized Hg gases for the 7-day calibration error test (or the daily calibration error check) until such time as NIST-traceable compressed elemental Hg gas standards, at appropriate concentration levels, are available from gas vendors.”



# Background

- NIST Standard Reference Material (SRM) 3133 is *the* common denominator Hg reference material
  - SRM 3133 traceable solution used to analyze NIST prime certification sorbent traps
  - SRM 3133 traceable  $\text{HgCl}_2$  feed solution used for evaporative generators
  - SRM 3133 traceable calibration solution used for Method 30B trap analysis
- *In theory,  $\text{Hg}^0$  and  $\text{HgCl}_2$  evaporative generators should agree at identical concentrations as both tied to SRM 3133*
- *In theory, Method 30B trap analyses should agree with NIST trap analyses as both analyses tied to SRM 3133*
- NIST and EPA collaborating to investigate these theories



# Objectives

- *Revisit the  $\text{Hg}^0$  generator –  $\text{HgCl}_2$  evaporative generator discrepancy issue*
- Accurately measure the output from NIST-certified  $\text{Hg}^0$  and evaporative  $\text{HgCl}_2$  generators using two fundamentally-different analytical techniques
- Quantitatively determine the difference(s), if any
- Quantitatively compare NIST's sorbent trap analytical approach with the Method 30B sorbent trap analytical approach
  - Do they agree?
  - How well?



# Approach

- Use sorbent traps to measure the outputs from a NIST-certified  $\text{Hg}^0$  generator and a Hovacal and a Tekran 3315  $\text{HgCl}_2$  evaporative generator
- Sorbent trap sampling followed by Method 30B thermal analysis *and* NIST isotope dilution – inductively coupled plasma mass spectrometry (ID-ICPMS) analysis



# Approach

- Tekran 3310  $\text{Hg}^0$  generator (Vendor Prime)
  - Target at least 3 different  $\text{Hg}^0$  concentrations (and therefore vary  $\text{Hg}^0$  generator operating conditions)
    - $\sim 5 \mu\text{g}/\text{m}^3$
    - $\sim 1 \mu\text{g}/\text{m}^3$
    - $\sim 20 \mu\text{g}/\text{m}^3$
- Hovacal and Tekran 3315  $\text{HgCl}_2$  evaporative generators
  - Run using SRM 3177 ( $\text{HgCl}_2$ ) solution
  - Moisture at multiple concentrations (vary solution feed rate)
    - $\leq 5\%$
    - $\sim 10\%$
    - $\sim 20\%$



# Approach

- Generator Sampling:
  - Ohio Lumex 6mm traps (low iodated carbon)
  - System suitable for wet and dry sampling
  - High accuracy total volume sampling (Alicat MFM)
  - Target a fixed Hg sample mass (e.g., 100 ng)





# Approach

- Sorbent Trap Analyses:
  - Thermal desorption analyses with the Ohio Lumex sorbent trap analysis system
    - SRM 3133 analytical solutions for quantitation
    - Characterization of analytical precision
      - Liquid solution injection volume
      - $\text{Hg}^0$  gaseous spike (solution through  $\text{SnCl}_2$ )
  - NIST with microwave acid digestion/ID-ICPMS analysis
    - Same procedure used to certify NIST Primes
    - Isotopically-labelled Hg solutions traceable to SRM 3133



# Summary

- We're going to get to the bottom of the  $\text{Hg}^0$  vs.  $\text{HgCl}_2$  generator discrepancy ...
- We'll be able to compare NIST's analytical approach to the Method 30B analytical approach so widely used
  - Both are anchored to NIST SRM 3133
- Potentially opens the door for options to improve or finalize NIST traceability protocol for  $\text{HgCl}_2$  evaporative generators
- NIST traceable  $\text{HgCl}_2$  reference gases of the same functional quality as NIST traceable  $\text{Hg}^0$  reference gases remains the ultimate goal



# Background – ALT Methods

- 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 – Hg<sup>0</sup>

- PS-12A/Procedure 5 and Appendix A to 40 CFR Part 63, Subpart UUUUU require the use of NIST-traceable elemental Hg (Hg<sup>0</sup>) gas standards for Hg emissions monitoring
- Affected facilities under:
  - MATS Rule
  - Portland Cement MACT
- Not all Hg CEMS have NIST-traceable Hg<sup>0</sup> generators
- Hg<sup>0</sup> cylinders are a viable and *necessary* option
- ALT-118 developed based on a 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 ( $\text{Hg}^0$ ) 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"<sup>1</sup> (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)<sup>2</sup> 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  $\text{Hg}^0$  protocol gases in

<sup>1</sup> 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.

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

# ALT-118 Approach

- Based on naming Hg<sup>0</sup> cylinders from NIST-traceable, Vendor Prime Hg<sup>0</sup> gas generator as alternative to NIST Research Gas Mixture (RGM)
  - Vendor Prime Hg<sup>0</sup> generator must be certified within last 24 months
- Can name either Gas Manufacturer Intermediate Standards (GMIS) or the commercial Hg<sup>0</sup> 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 Hg<sup>0</sup> set point certification U
  - Calibration curve
  - Replicate measurements
  - Hg<sup>0</sup> 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"<sup>1</sup> 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

<sup>1</sup> 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			
COMPOSITION	CERTIFIED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
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			
GravStat™ Blending Process			
COMPOSITION	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
Hydrogen Chloride	7.987 PPM	0.032 PPM	0.403 %
Sulfur Hexafluoride	5.022 PPM	0.032 PPM	0.634 %

Confirming Analysis			
COMPOSITION	MEASURED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel)
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: <b>GMPS ND50602</b>			
COMPOSITION	CERTIFIED CONCENTRATION	UNCERTAINTY (Abs)	UNCERTAINTY (Rel) EXPIRES:
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:

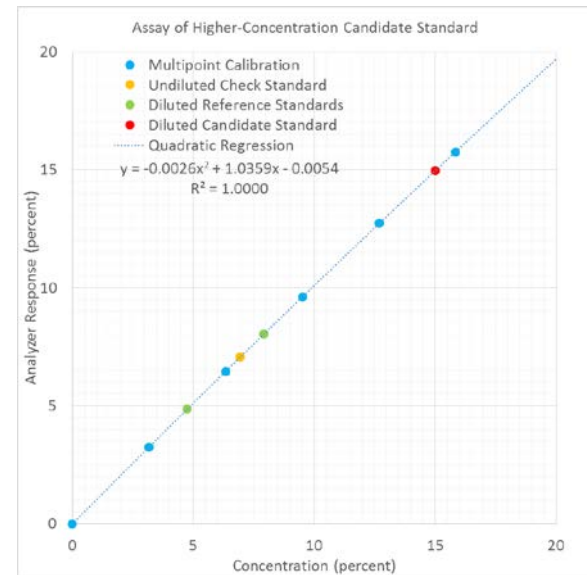
*S. Hausman*

# 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 Hg<sup>0</sup> 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, NH<sub>3</sub>, formaldehyde, etc)

# Green Book Revisions ...

- EPA 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](http://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards)

# Questions ...



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# What the Rules Say About Hg<sup>0</sup> 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, HgCl<sub>2</sub>) 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.”