ORD Methods Development Support to OAQPS

Jeff Ryan
919 541-1437
Ryan.jeff@epa.gov

OAQPS Measurements Technology Workshop
January 27, 2015
Research Triangle Park, North Carolina

Office of Research and Development
National Risk Management Research Laboratory.

United States Environmental Protection Agency

Topics

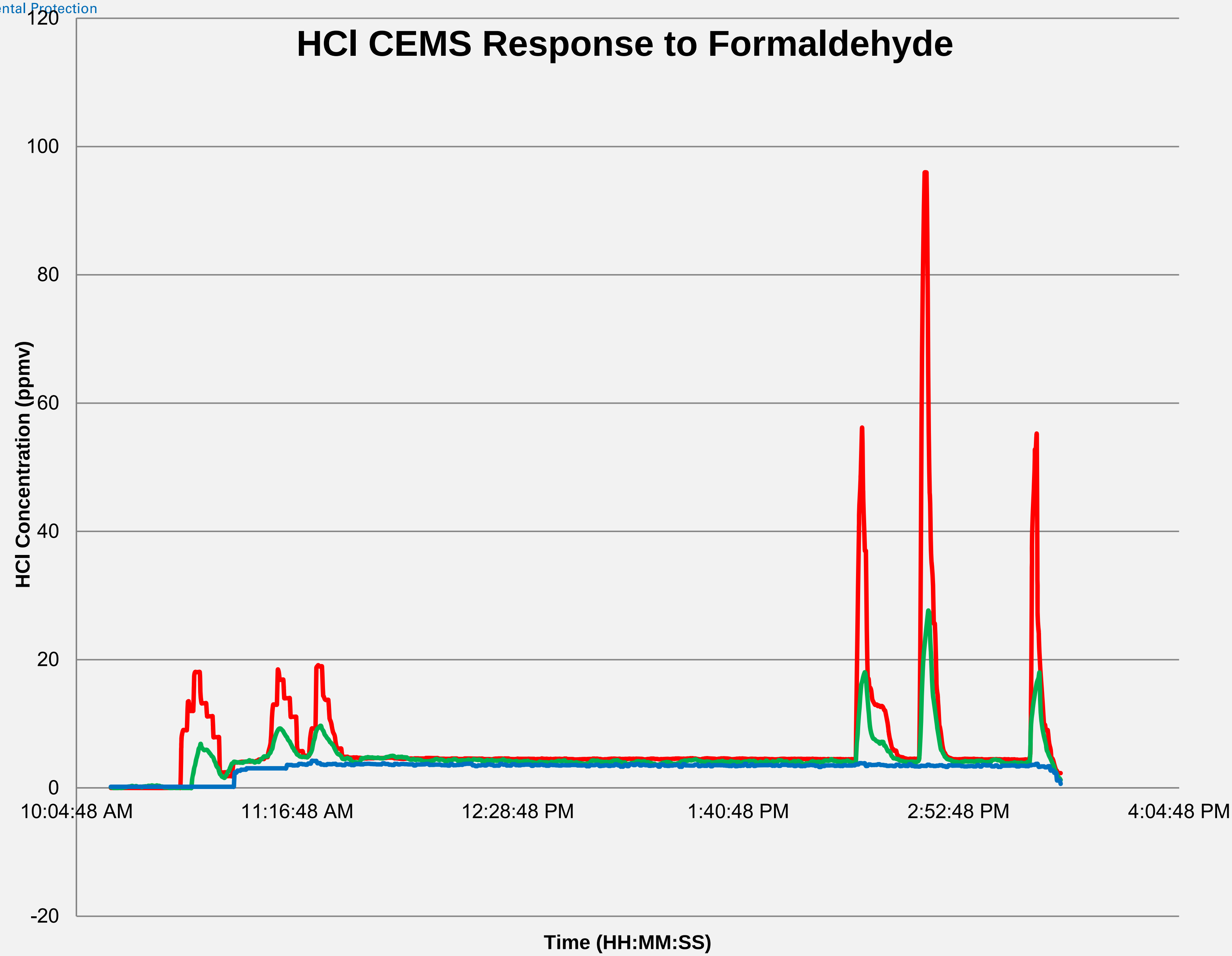
- Update on HCl measurements testing
- Update on HCl gas standards
- Update on Hg gas standards
- Performance-based measurements
- Bromine addition for Hg control
- Planned measurements research

EPA United States Environmental Protection Agency

PS-18 Elements and ORD Testing Focus

- **Interference Tests**
- **Limit of Detection (LOD) Tests**
- 7-Day Drift
- Linearity
- RATAs
- **Dynamic Spiking**
- **Reference Methods**

United States Environmental Protection Agency



EPA United States Environmental Protection Agency

LOD Testing

		Reference FTIR	HCl CEMS "A"	HCl CEMS "B"	HCl CEMS "C"
0.5 ppm Point	avg	0.61	0.57	0.78	0.70
	std	0.03	0.02	0.01	0.07
	LOD	**0.08**	**0.05**	**0.04**	**0.22**
2 ppm Point	avg	2.00	1.99	2.61	1.95
	std	0.04	0.01	0.04	0.05
	LOD	**0.12**	**0.04**	**0.12**	**0.16**
0.2 ppm Point	**avg**	**0.19**	**0.19**	**0.41**	**0.35**
	std	0.02	0.01	0.04	0.07
	LOD	**0.06**	**0.04**	**0.13**	**0.21**

Method 26A - How low can you go?

- Analytical

Cal Points ug/mL	Area Counts	Calculated ug/mL	Agreement %
0.20	6.81088	0.19	**-3.74%**
1.00	36.57592	1.03	**3.29%**
5.00	178.89946	5.05	**1.03%**
10.00	353.41158	9.98	**-0.21%**
15.00	529.28789	14.94	**-0.37%**

y = mx+b
m = 35.41747
b = -7.8701E-03
y = area
x = amount
MDL = 0.03 ug/mL

- In-stack Example

Target Conc. ug/ml	Dilution Factor	Functional Conc. ug/ml	Liquid Sample Volume mL	Total Sample Mass mg	Sample Rate cfm	Sample Time min	Total Sample Volume ft3	Total Sample Volume m3	Sample Conc mg/m3	**Sample Conc ppm**
0.20	1	0.2	275.0	0.06	0.75	30	22.5	0.637	0.086	**0.06**

Reference Method Agreement

Fuel/Coal Type	M26A ppmv (wet)	RD	FTIR ppmv (wet)	Absolute Difference ppmv	Relative Difference %
Natural gas	0.27	6.3%	0.19	0.08	33.6%
Natural gas	0.59	1.1%	0.59	0.00	0.1%
Natural gas	2.02	1.7%	1.98	0.04	2.1%
Bituminous	23.36	0.7%	24.37	1.01	4.2%
Bituminous	25.06	0.7%	25.87	0.81	3.2%
Bituminous	20.15	3.7%	25.71	5.56	24.3%
Bituminous	23.42	0.3%	26.46	3.04	12.2%
PRB	3.44	1.0%	3.82	0.38	10.4%
PRB	3.58	0.0%	3.99	0.41	10.9%
PRB	4.08	8.4%	4.25	0.18	4.3%
Lignite	2.03	9.4%	2.34	0.31	14.3%
Lignite	2.33	0.3%	2.52	0.20	8.2%
Bituminous	30.35	2.1%	33.14	2.79	8.8%
Bituminous	29.86	1.1%	32.30	2.45	7.9%
	Average	2.6%		Average	10.3%

HCl Gas Standard Testing

- Compressed Gases:
  - Have come a long way
    - Lower levels
    - Stable
  - Dilution for low levels

Gas Cylinders Stability

	3/26/2013		1/17/2014	
AirgasTag Value	FTIR Measured Value	Agreement	FTIR Measured Value	Agreement
ppm	ppm	%	ppm	%
1.843	1.846	0.2	1.892	2.7
4.600	4.525	-1.6	4.598	0.0
9.280	9.439	1.7	9.237	-0.5

Gas Cylinders with Gas Divider

Set Point Conc. (ppmv)	Theoretical Conc. (ppmv)	FTIR Measured Conc. (ppmv)	Relative Difference %	RSD (%)
0.5	0.45	0.44	-2.3%	8.5%
1	0.90	0.88	-2.0%	4.1%
2	2.25	2.25	0.2%	1.9%
5*	4.60	4.49	-2.4%	1.8%
10*	9.28	9.15	-1.4%	0.5%

* = Gas direct from cylinder

HCl Evaporative Generator

- Hovacal/Evaporative Generators:
  - Alternative to compressed gases
  - Testing to evaluate comparability
  - Testing to determine uncertainty of gases generated
  - Testing to inform Traceability Protocol

HovaCAL - Moisture Fixed at 8%

Set Point Conc. (ppmv)	Theoretical Conc. (ppmv)	FTIR Measured Conc. (ppmv)	Relative Difference %	RSD (%)
0.5	0.53	0.49	-7.9%	6.6%
1	1.02	1.02	-0.3%	4.3%
2	2.09	2.06	-1.6%	1.8%
5	5.31	5.37	1.2%	0.9%
9	9.00	8.79	-2.3%	1.0%

HCl Gas Standard Comparison

HCl Cylinders			Evaporative Generator		
Airgas Tag Value	FTIR Measured Value	Relative Difference	Theoretical Conc.	FTIR Measured Value	Relative Difference
ppm	ppm	%	ppm	ppm	%
-	-	-	1.02	1.02	-0.3
1.843	1.869	1.4	2.09	2.06	-1.6
4.600	4.562	-0.8	5.31	5.37	1.2
9.280	9.338	0.6	9.00	8.79	-2.3

NIST Status

- Established capabilities to provide traceability
  - Developed multiple working ref HCl gas cylinders (1, 8-14ppm)
    - Primary HCl standard = 400 ppm
  - NIST concentrations confirmed by VSL (within uncertainties)
  - Have characterized HCl RGMs from 2 gas vendors
    - HCl concentrations 8-12 ppm
    - Uncertainties ~1.5%, one year certification (for now)
  - Recognize the need to expand the range of concentrations
    - Targeting vendor supplied concentrations from 0.5 ppm to > 500 ppm

NIST Traceable HCl Reference Gases

NIST HCl Reference Gas Standards

HCl Concentration ppm	Uncertainty (k=2) ppm	Uncertainty (k=2) %
1.074	0.010	0.93
1.947	0.020	1.03
2.192	0.020	0.91
7.963	0.072	0.90
10.18	0.16	1.57
12.20	0.16	1.31

Airgas RGMs

HCl Concentration ppm	Uncertainty (k=2) ppm	Uncertainty (k=2) %
9.86	0.17	1.72
10.1	0.17	1.68
9.78	0.17	1.74
12.34	0.21	1.70
12.16	0.21	1.73

Gas Vendor Status

- Multiple gas vendors are now providing low level (<10 ppm) HCl gas standards
  - Targeting <1 ppm gases
- Based on NIST RGM uncertainties, out-the-door uncertainties for commercial HCl gases expected to be **well below 5%**
- Current commercial gases have agreed well with FTIR reference spectra and have been used to conduct field Calibration Error testing
- Evaluating HCl-specific regulators for improved performance
- Discussing guidance for cylinder use

United States Environmental Protection Agency

Commercial NIST Traceable HCl Gases

Airgas NIST Traceable Gases

Airgas Value	NIST Traceable Value	Estimated Uncertainty (k=2)	Relative Difference
ppm	ppm	%	%
0.539	0.540	1.87	-0.12%
1.440	1.425	2.29	1.02%
2.536	2.500	2.57	1.44%
4.519	4.480	2.19	0.87%
5.618	5.540	2.41	1.40%
9.273	9.070	1.77	2.24%

EPA Traceability Protocol for Qualification and Certification of Evaporative Hydrochloric Acid Gas Generators and Humidification of Gases from Cylinders

- Qualification Tests
  - Performed by manufacturer
  - Demonstrates the adequacy of each model, not each unit
  - Manufacturer's Disclosure defines for customer the range of conditions under which the model can operate reliably
- Certification
  - Unit-specific – serial number recorded on documentation
  - Performed by manufacturer, but may be repeated by customer or third-party if in-field recertification becomes necessary
  - Defines the relationship between reported concentrations and corresponding NIST-traceable concentrations.

Certification

- NIST-traceable reference devices/materials required
  - HCl source material – liquid or gaseous standard with traceable concentration
  - Gas flow(s) – independent traceable standard(s), with unexpired certification, covering the full range of gas flows required
  - Liquid flow(s) – usually performed by gravimetric means, using a balance calibrated with NIST-traceable weights
- Output Verification
  - Demonstrates that the actual HCl output concentration agrees with the calculated concentration from the NIST-traceable inputs
  - Comparison with NIST-traceable bottled gas
- Option for direct “naming” of evaporator output
  - Based on direct comparisons to NIST traceable compressed gases

United States Environmental Protection Agency

Summary …

- Testing to date has successfully supported proposal of PS-18
- 26A and FTIR RM measurements are comparable and capable of measuring at low stack HCl levels (<0.5ppm)
- Multiple, viable options exist to provide the NIST Traceable HCl calibration gases required by PS-18 and Procedure 6
  - HCl concentrations <1 ppm to >10 ppm (supporting span ranges of 5 and 10 ppm)
  - Uncertainties well less than 5%
- Draft HCl Traceability Protocol now available

Hg Gas Standards

- NIST status and capabilities
- Status of Hg^0 compressed gas standards
- Oxidized Hg
- Traceability Protocols going forward

The Vendor Prime certification process …

- Hg^0 generator certification is now a formal NIST "calibration service"
- NIST has 22 "reference gas" concentrations ranging from 0.2 – 292 µg/m^3
  - Vendor must specify the points they want
  - You don't have to match NIST's points
- Stated turnaround time is 3 months
- NIST provides a Certification Report

Hg^0 Compressed Gas Standards

- A recognized need for Hg^0 cylinders
- Why aren't Hg^0 cylinders being used?
  - Not allowed?
  - They aren't stable?
  - They still have the "creep" problem?
- What's needed for their use?

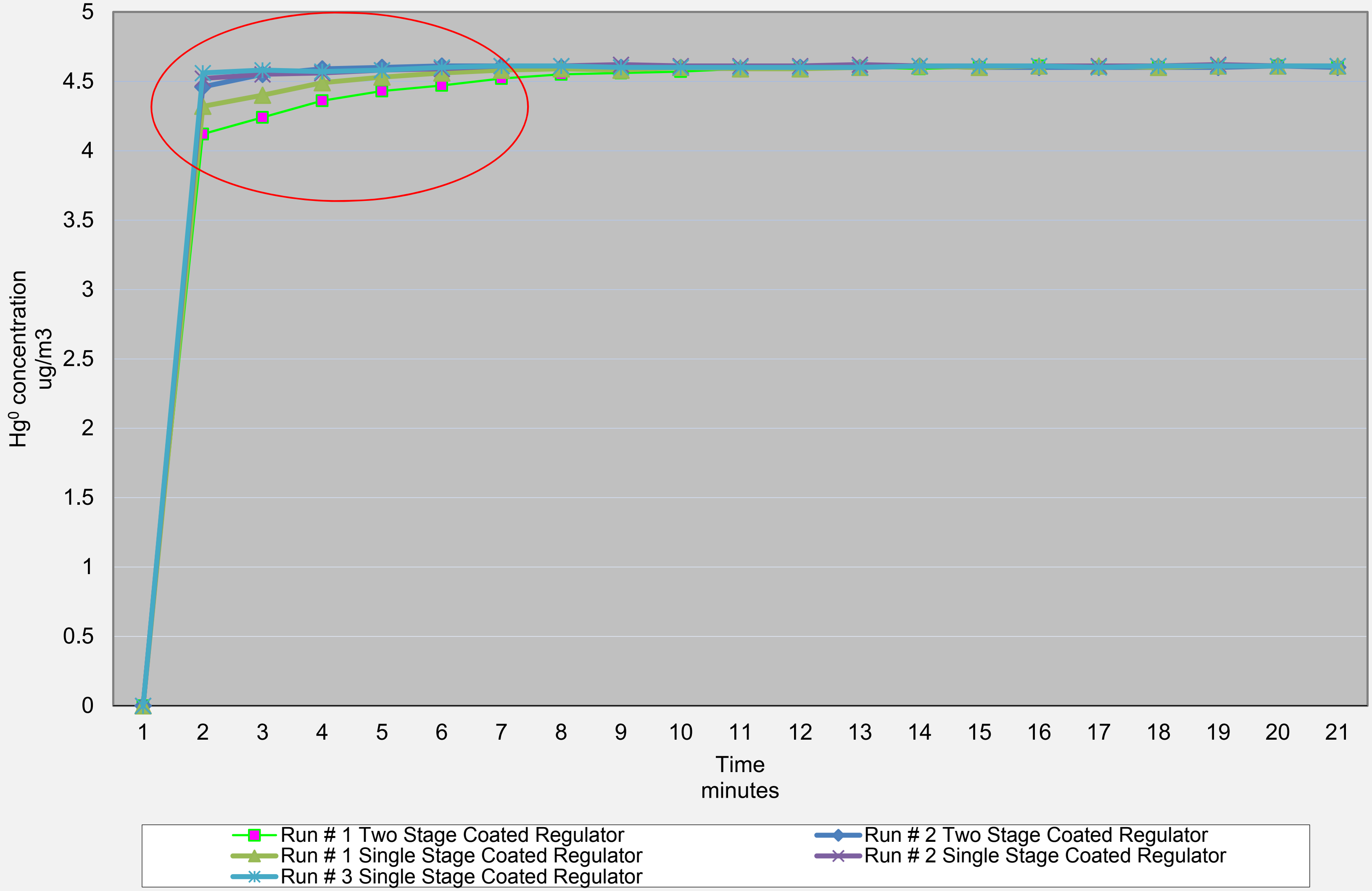
What the Rules Say About Hg^0 Compressed Gas Standards …

- PS12A, Section 7.1 says ….“The use of NIST traceable gases is required.” There is no reference to the Interim protocols.

- MATS, Appendix A, Section 3.2.1.2.1, says…..”Only NIST-certified or NIST-traceable calibration gas standards and reagents (as defined in 3.1.4 and 3.1.5) shall be used for the tests and procedures required under this subpart.”

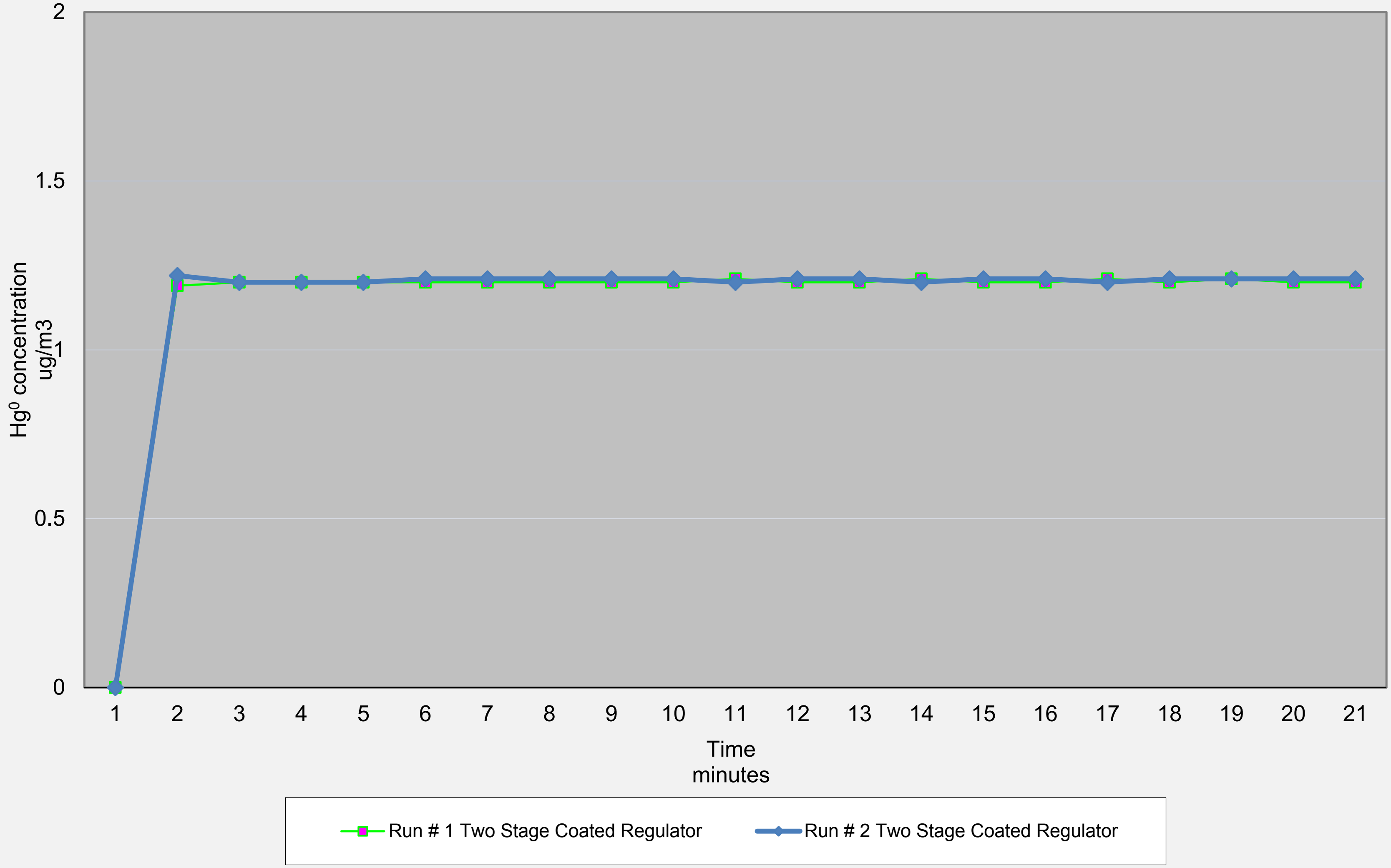
- MATS, Appendix A Section 3.1.4 says….”NIST-Traceable Elemental Hg Standards means either: compressed gas cylinders having known concentrations of elemental Hg, which have been prepared according to the *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards* – AKA “The 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.”

Hg^0 Cylinder "Creep"*



* Data courtesy Doug King/Airgas

Hg^0 Cylinder "Creep"*



* Data courtesy Doug King/Airgas

Hg^0 Compressed Gas Standards: Moving Forward …

- The door is open for use of Hg^0 compressed gas standards
- The most direct path …
  - Add Hg^0 to the "Green Book"
  - NIST needs to be willing to name RGMs (which they are)
  - Follow the procedures in the "Green Book"
- Indirect path …
  - Name cylinders from "vendor prime" generators
  - Follow the procedures in the "Green Book"
- Hg^0 compressed gas certified concentration target is ≤ 5% U

Oxidized Hg …

- EPA's goal is for oxidized Hg ($HgCl_2$) standards to be of the same quantitative quality as the Hg^0 gases (i.e., ≤ 5% U)
- The "discrepancy" issue for evaporative $HgCl_2$ generators has not gone away …
  - EPA and NIST are continuing to collaborate
  - Potential for international collaboration
- EPA is exploring the "naming" of evaporative $HgCl_2$ generator outlet concentrations as an option

Traceability Protocols …

- EPA has not identified a specific need to update either protocol at this time
- Updates are anticipated as more experience is gained and technical issues are encountered

United States Environmental Protection Agency

Future Plans …

- Include Hg^0 compressed gas standards in the next revision of the “Green Book”

- Continue to work on the oxidized Hg “discrepancy” issue

- Solicit feedback on Traceability Protocol implementation experiences

United States Environmental Protection Agency

Hg Gas Standard Summary

- Hg gases with Uncertainties ≤ 5% is the ultimate goal
- NIST is fully open for business
- Hg^0 compressed gas standards will be a viable option
  - Hg^0 concentrations <1 µg/m^3 expected
  - Uncertainties expected to be well below 5%
- EPA sees resolution of the $HgCl_2$ evaporative generator "discrepancy" as a priority issue
- Feedback on Traceability Protocols implementation welcomed

Performance-based Measurements

- Performance-Based Measurements (PBMs) offer multiple advantages over the standard, prescriptive methods
- PBMs can be applied to instrumental and chemical/manual methods, including specific components within a method
- PBMs are well suited for regulatory compliance measurements
- PBMs result in data of known and acceptable quality
- You should be rewarded for doing good work
- There should be an incentive for continued measurement improvement

United States Environmental Protection Agency

PBM Measurement Quality Elements

- PBMs are based on **Measurement Quality Objectives** (MQOs) that identify and define measurement quality requirements
  - Selective
  - Accurate
  - Precise
  - Sensitive
  - Representative
  - Assessed Vulnerabilities
  - "Incentivized"

MQO - Selectivity

- Correctly identify and measure pollutant of interest in the presence of expected physical and chemical interferences
- Available PBM approaches:
  - Spectral interference tests
  - Matrix interference tests
  - Matrix spiking tests
  - Matrix blanks
  - Comparison to other methods
  - Knowledge of technique and vulnerabilities critical

United States Environmental Protection Agency

MQO - Accurate

- Measurement within a known relation to the "true" value (or within a known tolerance of bias)
- Available PBM approaches:
  - Calibration
    - Control calibration tolerance
    - System vs. detector
    - Measurements must be in the calibrated range
  - Bias tests
    - Assess the overall measurement
    - Matrix spikes/standard addition
    - Dynamic spiking
  - Audit samples

MQO - Precision

- Assess random error
  - Repeatability – agreement when measuring the same thing under the same conditions
  - Reproducibility – agreement when measuring the same thing under varied conditions
- Available PBM approaches:
  - Replicate measurements
  - Matrix spikes/matrix spike duplicates
  - Measurement RSD
  - Paired Trains

MQO - Sensitivity

- Low enough to meet needs, but above definable detection limits and within quantitative requirements
- Available PBM approaches:
  - Determine MDLs
  - Determine LODs
  - Minimum measurement a function of sufficient distance from MDL/LOD and within calibrated range
  - Empirical confirmation in matrix
    - e. g., matrix/dynamic spikes at low levels

EPA United States Environmental Protection Agency

MQO – Vulnerability Assessment

- Those failure scenarios or extremes that may be encountered and how to assess them – the “what ifs?”
- Examples include
  - Breakthrough determinations
  - Sampling system reactivity and losses
  - Effect of temperature and pressure on spectra
  - Chemical form(s) from source considered?
  - Sample preservation and stability
  - “Ruggedness” testing?

United States Environmental Protection Agency

MQO – “Incentivize”

- Creating incentives or drivers within the method that promote advancements in the measurement, technology, equipment that result in improved data quality and benefits to user
- Hard to define
- Examples
  - Not allowing blank corrections with Method 30B
    - Created incentive to minimize blank levels
  - MDL used in compliance emission calcs for NDs
    - Incentive to lower MDLs
  - Opportunity for reduced costs

Examples of MQO Approach

- Manual Method (with analytical)
  - Specifies representative sample collection
  - Choice of sampling media may be performance-based
  - Any sample prep and analytical approach that can meet performance criteria can be used
  - Key performance criteria
    - MDL determination
    - Laboratory recovery study for sample prep/analytical bias
    - Calibration tolerance and quantitation range
    - Paired sample agreement for precision
    - Presampling spike recovery for overall bias assessment
    - Relies on liquid and/or gaseous standards

United States Environmental Protection Agency

Examples of MQO Approach

- Instrumental Method
  - Specifies representative sample collection
  - Any instrument that can meet performance criteria can be used
  - Key performance criteria
    - Interference Test
    - LOD Tests
    - Measurement Error Test (through system)
    - Dynamic spiking for overall bias assessment
    - Daily Drift check
    - Relies on gaseous standards

Bromine Addition for Hg Control

- Bromine, added directly to coal, is one of the available Hg control options for electric utilities
- The levels used result in excess HBr/Br_2 present in the gas stream
- Potential impact on Hg and M26A measurements?
- Where does the bromine go?

United States Environmental Protection Agency

Planned Measurements Research

- Bromine related measurement issues
  - Potential impact on M26A measurements
  - Ability to measure bromine species
  - Potential impact on Hg measurements (collaboration with EPRI)
- Evaluate FTIR for additional pollutants of interest (e.g., HF, HBr, HCN, formaldehyde, etc)
- Support potential Method 320/PS-15 revisions
- Evaluate ambient methods with dynamic dilution (e.g., SUMMA cans for organics, cavity ring-down analyzers for HF, formaldehyde, etc)
- Continued PBMs testing
  - Comprehensive characterization of dynamic spiking tool
  - Continued investigation of interference and LOD approaches

United States Environmental Protection Agency

Questions …