EPA's Hg Gas Traceability Approach for Source Emissions Measurement and Monitoring




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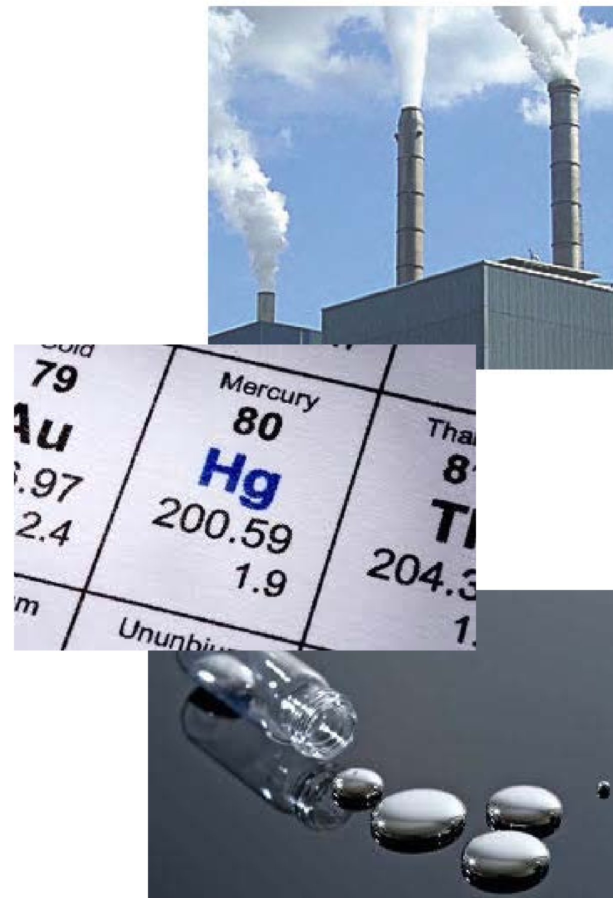
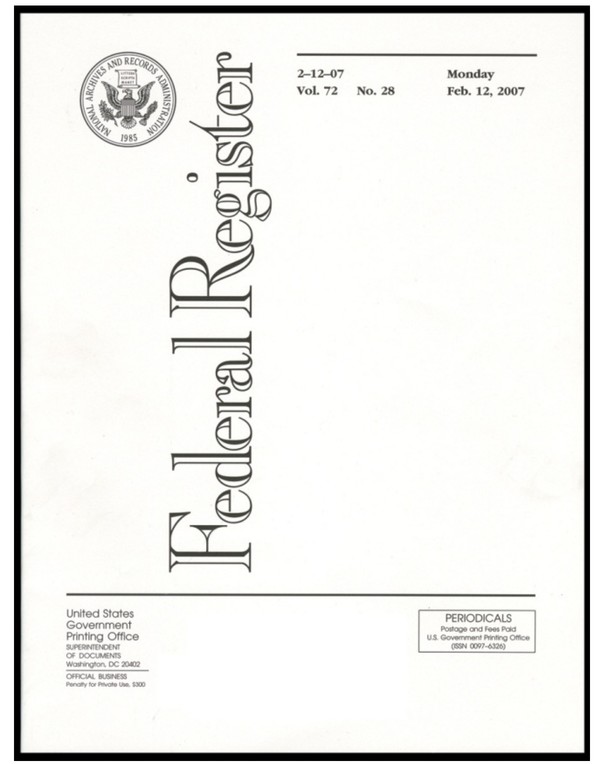
Overview

- US EPA Hg emissions regulations
- Hg emissions measurement requirements and approaches
- Hg Reference Standards and Traceability
- Need for International consensus Hg Gas Standards?
- Summary messages



US Regulations with Mercury Emissions Measurement and Monitoring Requirements

- Mercury Air Toxics Standards (MATS) for power plant boilers
- Portland Cement MACT
- Industrial Boiler MACT
- Commercial & Industrial Incinerator MACT
- Sewage Sludge Incinerator MACT



Mercury Emissions Measurement Quality

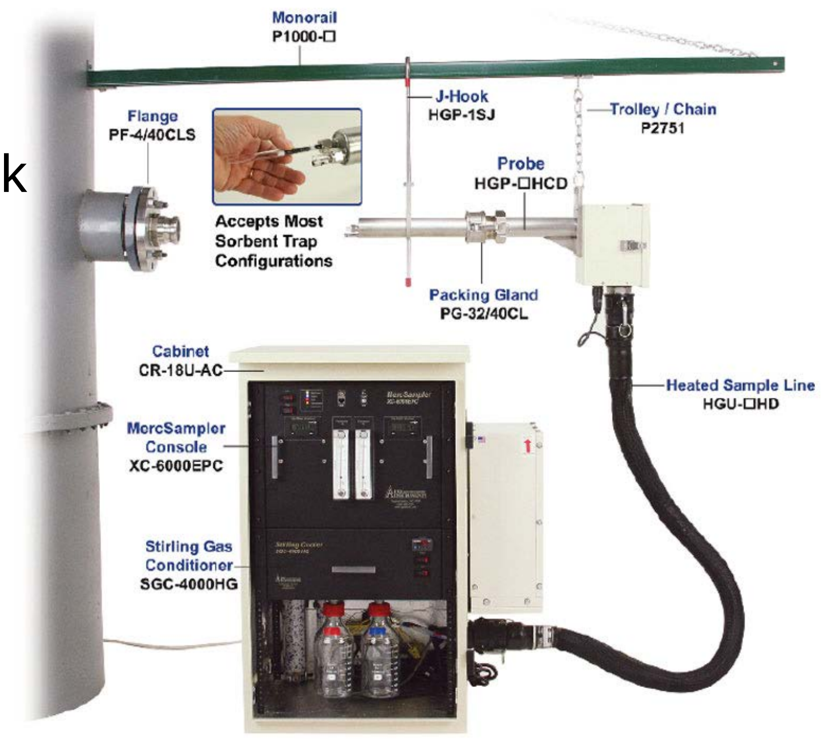
- EPA regulations specify the use of National Institute of Standards and Technology (NIST) traceable reference materials to ensure the quality of Hg emissions measurements
  - Liquid standards
  - Gaseous elemental mercury (Hg^0)
  - Gaseous oxidized mercury ($HgCl_2$)
- EPA defines NIST traceability requirements
- **These standards provide a common and consistent quantitative basis for mercury emissions reporting**

EPA Hg Measurement Options

- Two primary mercury emissions measurement options for stationary sources:
  - **Continuous Emissions Monitoring Systems (CEMS)**
  - Sorbent trap systems
- All methods require NIST traceable reference materials

Method 30B/PS 12B

- Performance-based
  - Amenable to new sorbents, equipment, and analytical technologies
- Principle
  - Gas sampled through paired, in-stack 2-section sorbent traps
  - Analysis by any system meeting performance criteria
  - Liquid Hg standards used for calibration
  - Gaseous Hg^0 used for trap spiking



Mercury CEMS Background

- Hg CEMS measure total gaseous Hg
  - Elemental (Hg^0)
  - Oxidized (Hg^{2+}); typically converted to elemental Hg for measurement
- Use of NIST-traceable elemental and oxidized Hg gas standards required for emissions measurement QA/QC

Hg CEMS QA/QC

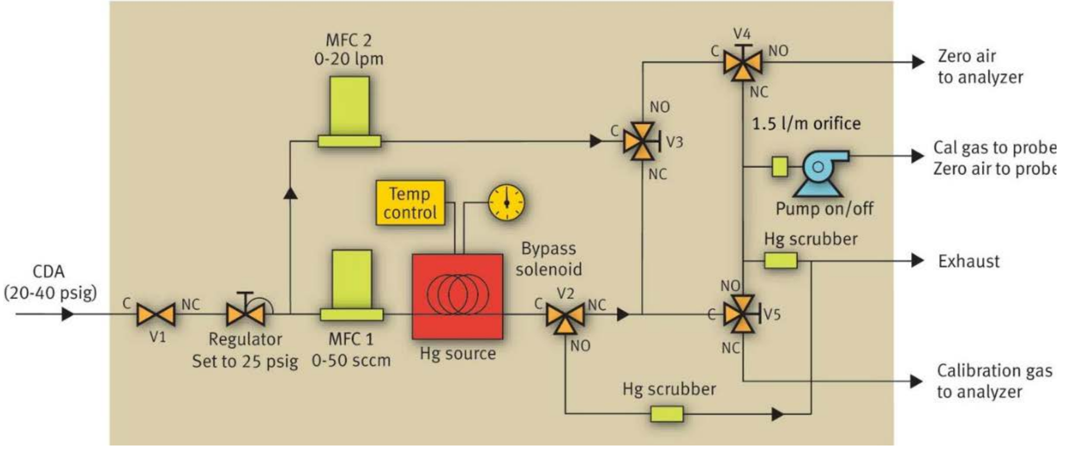
- QA/QC Requirements for initial Hg CEMS certification
  - 7-day drift test – with Hg^0 *or* $HgCl_2$
  - Measurement error test (at 3 levels) – with Hg^0 *and* $HgCl_2$
  - Relative accuracy test (RATA) compared against a reference test method (typically 30B)
- QA/QC Requirements for continued Hg CEMS operation
  - Daily drift check with Hg^0 *or* $HgCl_2$
  - Weekly System Integrity Check with $HgCl_2$
  - Quarterly Measurement Error test – with Hg^0 *and* $HgCl_2$
  - Annual RATA

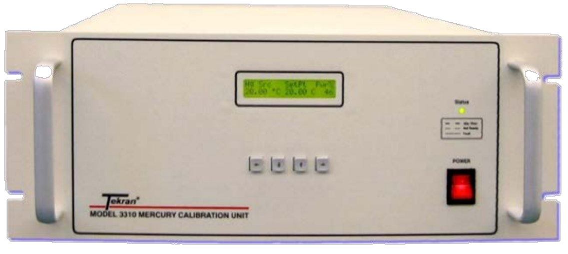
Gases for Calibration and QA/QC

- For the most part, CEMS vendors are using Hg^0 and $HgCl_2$ mercury gas generators to provide reference gas standards for their instruments
- Hg^0 compressed gas cylinders emerging as a viable option
- Working range of Hg gas concentrations: 0.2 – 350 µg/m^3

Elemental (Hg^0) Gas Generators

Produce known concentrations of Hg^0 gas by passing a controlled gas stream though the headspace of a temperature controlled reservoir of Hg and then blending with a dilution gas stream





Oxidized ($HgCl_2$) Gas Generators

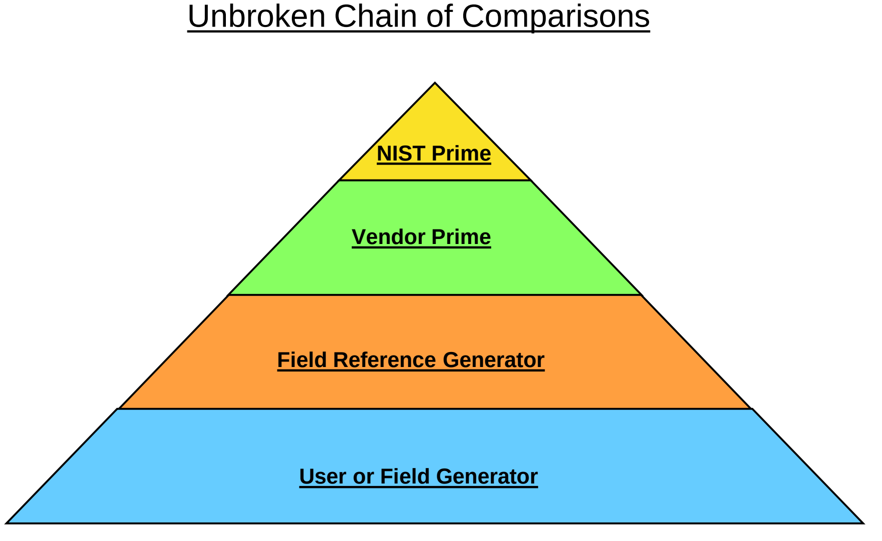
- Two types currently in use:
  - Evaporative $HgCl_2$ generator, which produces gas by vaporization of known concentration of a $HgCl_2$ solution and quantitatively mixes with a diluent gas
  - Device that converts output from an elemental Hg generator to $HgCl_2$ by reacting with Cl_2

EPA Gas Standard NIST Traceability

- EPA establishes what constitutes "*NIST Traceability*"
- EPA defines NIST traceability of gas standards as an *"unbroken chain of comparisons"* to a primary NIST standard
- Gas standards are traceable to a measured, not theoretical, concentration
- Not so easy for Hg …
- EPA has published traceability protocols used to establish NIST traceability of both elemental and oxidized mercury gas standards
- **Lack of method for direct measurement of $HgCl_2$ precluded 'unbroken chain of comparisons' for certification of oxidized Hg gas generators**

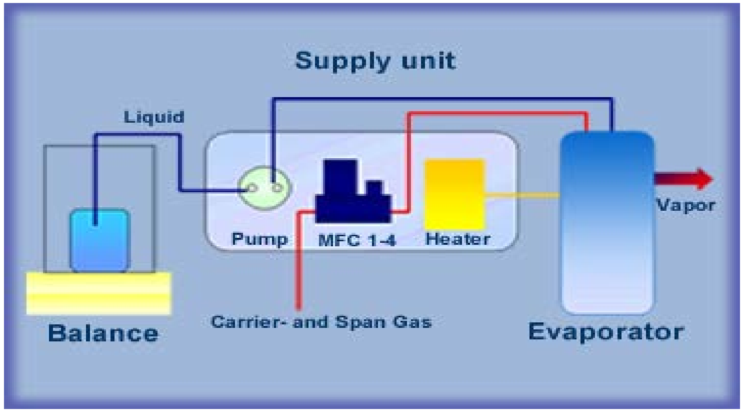
Traceability for Hg^0 Generators

- NIST certifies '***NIST Prime***' generators which are used to certify '***Vendor Primes***' generators that a manufacturer uses to certify '***Field Reference or User***' generators contained in the Hg CEMS
- Calculations provided to determine combined, expanded uncertainty of the generated concentrations
- **Uncertainty of User Generators must be ≤ 5%**



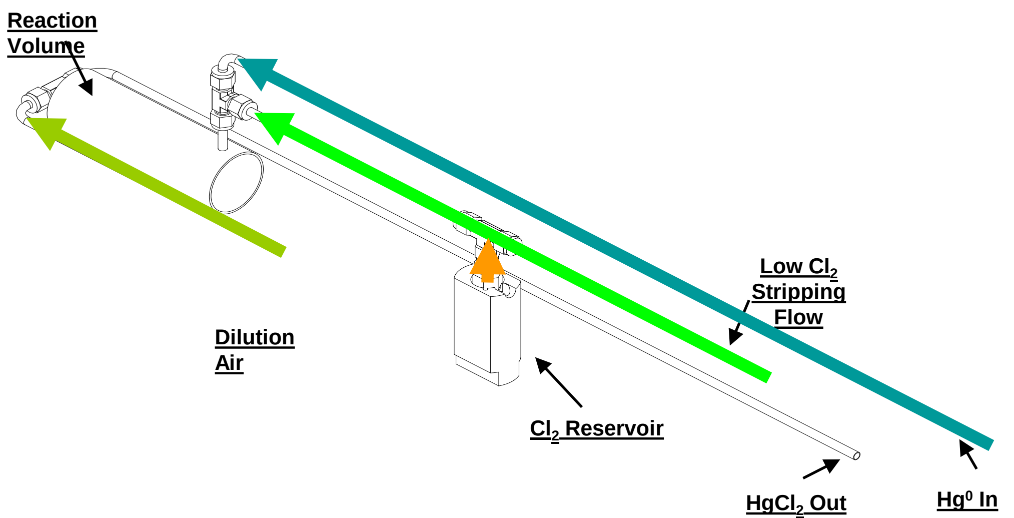
Traceability for Evaporative $HgCl_2$ Generators

- Based on traceability and uncertainty of the following components:
  - Working solution concentration
  - Liquid feed rates
  - Carrier gas flow rate
- Calculations provided to determine combined, expanded uncertainty of the generated concentrations
- **No direct measurement or verification**
- Resulting Uncertainty ≤ 10%
- **"Correction Factor" to allow agreement with Hg^0**



Traceability for Generators That Convert Hg^0 to $HgCl_2$

- Combined uncertainty of the $HgCl_2$ standard is based on the uncertainty of the elemental Hg generator, the water vapor dilution (where applicable), and the chlorine dilution
- Calculations provided to determine combined, expanded uncertainty of the generated concentrations
- **No direct measurement or verification**
- Resulting Uncertainty ≤ 10%



Elemental vs. Oxidized Hg: The Discrepancy

$$Hg^0 \neq HgCl_2!$$

- Recognized, but not understood, 7-10% discrepancy between Hg^0 and evaporative $HgCl_2$ gas standards
  - *Many have tried … Many have failed …*
- Confounded by the lack of a reliable $HgCl_2$ measurement technique
- The "discrepancy" issue for evaporative $HgCl_2$ generators won't go away …
  - EPA and NIST are continuing to collaborate to resolve the issue
- EPA and NIST are exploring the "naming" of evaporative $HgCl_2$ generator outlet concentrations as an option
- EPA's need is for $HgCl_2$ standards to be of the same quantitative quality as the Hg^0 gases! (i.e., ≤ 5% U)

Need for International Consensus Hg Standards

- Emerging need for the International use of Hg gas standards as International use of Hg CEMS expands:
  - U.S. companies now selling Hg CEMS worldwide
  - Global Mercury Partnership of Minamata Convention supporting development of Hg measurement/monitoring capabilities
  - EPA Hg Methods promoted by UNEP and being adopted internationally
- Need for International Hg measurements to be comparable
- Practical options for providing traceable Hg gas standards needed
- International Consensus Hg Gas Standards seems logical

Summary …

- Hg^0 and $HgCl_2$ gases of the same quality is EPA's absolute need
  - Uncertainties ≤ 5%
  - Based on measured, not theoretical, output
- EPA sees resolution of the $HgCl_2$ evaporative generator "discrepancy" as a critical issue
  - EPA and NIST will continue to tackle the problem, but welcome help
- A sound, direct $HgCl_2$ measurement approach is also critical
- Expanding International use of Hg CEMS warrants consideration of establishing International Consensus Hg Gas Standards

Questions …

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