

CERTIFICATION & ONGOING NIST REQUIREMENTS FOR HG CALIBRATION GAS GENERATORS

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Types Hg Gas Generators

- ▣ Elemental (Hg^0) Hg Calibration Gas
 - Head-space Hg Gas Generator
 - Calibration Gas Cylinder
 - Permeation Source
- ▣ Oxidized (Hg^{2+}) Hg Calibration Gas
 - Evaporative Generators
 - Conversion Generators

NIST Traceability

- ▣ EGU MATS Rule Requires NIST Standards
 - Section 3.2.1.2.1 of Appendix A of Subpart UUUUU
- ▣ Interim EPA Traceability Protocols
 - Elemental Hg Protocol
 - ▣ Issued July 2009
 - Oxidized Hg Protocol
 - ▣ Issued July 2009
- ▣ Developed via a collaboration between Hg Vendors, EPA, EPRI, Hg CEMS Users and NIST.

NIST Traceability

- ▣ Elemental Mercury (Hg^0) Interim Protocol
 - Detailed initial certification criteria
 - Ongoing QA procedures
- ▣ Oxidized Mercury (Hg^{2+}) Interim Protocol
 - Uses Hg^0 as Anchor
 - Passing System Integrity Check
- ▣ Protocols designed such that Hg CEMS are based on elemental Hg calibration gas.

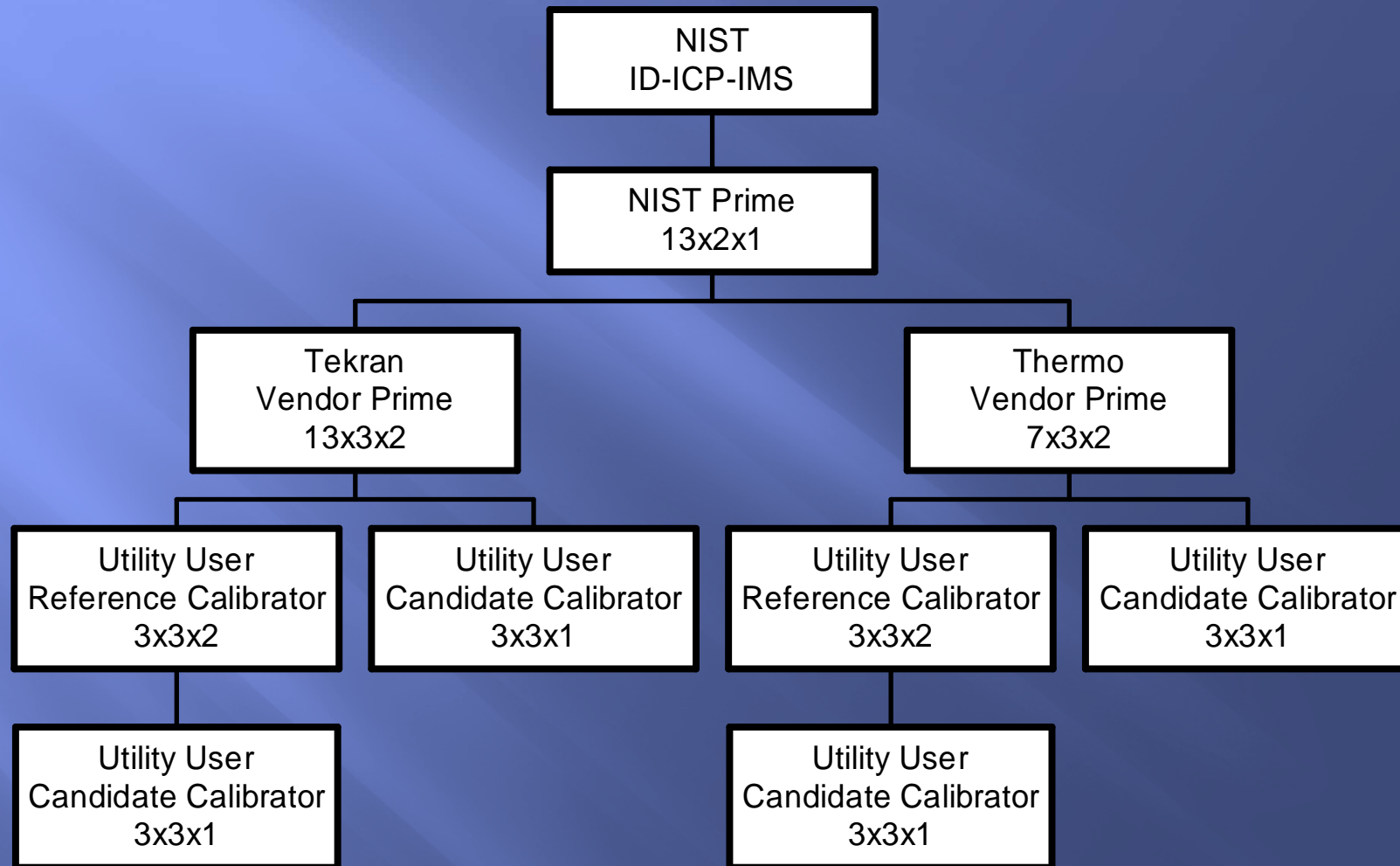
NIST Traceability

- ▣ EPA issued “Final” Interim Protocols in July 2009.
 - *ONLY applicable to spans > 5ug/m³*
 - *MATS Rule limit is ~1.2 ug/m³*
- ▣ Initial Steps for Hg⁰ Gas Generator
 - Manufacturer qualification test
 - Provides basic operating specifications for the elemental calibrator
- ▣ Bracketing test (i.e., the calibrator installed in your Hg CEMS compared against a Vendor Prime or Reference Calibrator.)

Bracketing Test

- ▣ “Bracketing” is the term used to describe the procedure used to determine the output of a Hg⁰ Gas Generator at certain setpoints.
- ▣ Comparison versus a “Reference” Device
 - NIST Prime
 - Vendor Prime
 - Reference Generator
- ▣ Source Hg⁰ Gas Generator (aka, User Prime) is only NIST certified at the setpoints used during the bracketing test

NIST Traceability



NIST Traceability

▣ NIST Prime

- Tekran Model 3310 that has been certified using NIST's ID-ICP-MS
- Maintained by NIST in Gaithersburg, MD.

▣ Vendor Primes

- Maintained by the Hg CEMS Vendors
- Periodically returned to NIST to verify outputs
 - ▣ Every 2 years
- Conduct inter-lab comparisons of multiple Vendor Primes to identify issues.

NIST Traceability

▣ Reference Generator

- Certified by comparing output to a Vendor Prime
- Requires a minimum 3x3x2 matrix
 - ▣ 3 – Sample concentrations
 - ▣ 3 – Comparisons at each sample concentration
 - ▣ 2 – Number of Repetitions
- Can be used to certify User Primes in the field

▣ User Prime

- Hg⁰ Gas Generator used to perform daily and quarterly calibration checks
- Certified by comparing output to a Vendor Prime or Reference Generator
- 3x3x1 Matrix

NIST Traceability

- ▣ Calibrator Certification using Bracketing Procedure
 - Calibrator will be certified at 3 output concentrations
 - ▣ Low, Mid and High
- ▣ Interim Protocol Requires
 - ▣ Periodic checks
 - ▣ Recertification at all 3-levels every 24-months
- ▣ Types of Periodic Checks
 - ▣ Single-level comparison vs. Reference Calibrator
 - ▣ Hg Gas Cylinder
 - ▣ Permeation Source
 - ▣ Sorbent Tubes

Ongoing QA/QC Requirements

- ▣ User Prime Quarterly Checks
 - Comparison at a single-level against either a:
 - ▣ Reference Generator
 - ▣ Certified Hg Cylinder
 - ▣ A 3x1x1 bracket comparison
 - Collect sorbent-traps at a single-level
 - ▣ Minimum of 3 paired-sorbent traps
 - ▣ Collect a minimum of 15 liters
 - ▣ Collect a target mass of 100 nanograms (ng)

Ongoing QA/QC Requirements

- ▣ User Prime Monthly Checks
 - Comparison against a permeation source
 - ▣ Establish initial ratio of User Prime and Permeation source as soon as possible after User Prime certification
 - ▣ Determine response ratio on a monthly basis
 - Interim Protocol recommends weekly basis.
 - ▣ Tekran Hg CEMS has a model-specific procedure that is incorporated into the software.
 - ▣ Thermo working to develop permeation module
- ▣ Specification of $\pm 5.0\%$ from reference value
 - For all ongoing checks.

Oxidized Hg Gas Generators

- ▣ Two-types of Oxidized Hg Gas Generators
 - Evaporative Generators
 - ▣ Uses a NIST-traceable liquid solution of HgCl_2 as the Hg^{2+} source.
 - ▣ Nebulizes the liquid & mixes with air to form calibration gas
 - ▣ *~7 to 9% bias between the Evaporative Oxidized and Elemental outputs.*
 - ▣ Manufacturer must supply the proper correction factor for the evaporative generator.

Oxidized Hg Gas Generators

- ▣ Two-types of Oxidized Hg Gas Generators
 - Elemental Conversion Hg^{2+} Gas Generators
 - ▣ Use Elemental Hg source to react with Chlorine to form HgCl_2
 - ▣ Must demonstrate at least 50% conversion from $\text{Hg}^0 \rightarrow \text{Hg}^{2+}$

NIST Certification of Hg²⁺ Gas Generators

- ▣ Note: The oxidized protocol does not establish true NIST traceability. NIST cannot measure Hg²⁺ directly.
 - Only establishes NIST traceability of key components of the calibrator.
 - ▣ Mass flow meter, pumps, HgCl₂ solution
- ▣ Oxidized Gas Generators were not intended to be the primary calibration device.
 - Intent of protocols was for all measurements to be based on NIST-traceable elemental Hg gas generators.
 - ▣ In essence, no adjustment of Hg CEMS response based on oxidized calibration gas.

NIST Certification of Hg²⁺ Gas Generators

- ▣ Interim Oxidized Protocol
 - Details how to calculate uncertainty of the Hg²⁺ Gas Generators
 - Provides minimal ongoing QA/QC requirements
 - No “bracket” tests associated with Hg²⁺ Gas Generators
 - Must have some source of NIST certified elemental calibration gas to meet ongoing QA/QC requirements

Ongoing QA/QC for of Hg^{2+} Gas Generators

- ▣ Evaporative Oxidized Generators
 - Pass a calibration error test using a zero and “certified” elemental upscale calibration gases.
 - Conduct and pass a system integrity check.
 - Monthly basis

Ongoing QA/QC for of Hg^{2+} Gas Generators

- ▣ Elemental Conversion Oxidized Generators
 - Operate in speciated mode (i.e., Hg^0 , Hg^{2+} & HgT)
 - Pass a calibration error test using a zero and “certified” elemental upscale calibration gases.
 - Meet system integrity criteria using HgT reading
 - Over 50% of HgT should be measured as Hg^{2+}
 - Monthly basis

Ongoing QA/QC for of Hg^{2+} Gas Generators

- ▣ Performance is based on response versus a “certified” (i.e., a NIST traceable) elemental Hg calibration source
 - Certified elemental Hg gas generator
 - Certified elemental Hg gas cylinder
- ▣ For a Hg CEMS that uses Hg^{2+} Gas Generator as the daily calibration device:
 - Source will still need a certified Hg^0 Gas Source to verify operation of Hg^{2+} Gas Generator.

Hg Calibration Gas Cylinders

- ▣ Hg Calibration Gas Cylinders
 - 6-month certifications
 - Expensive relative to traditional SO₂/NO_x cylinders
 - Requires regulators that have been conditioned to minimize Hg loss
 - Concentration ranges 1-60 µg/scm
 - Balance in either air or N₂
 - ▣ For Thermo Hg Freedom Systems w/out N₂ system must get with balance in air.
 - ▣ Not viable option for Thermo Hg Freedom Systems w/ N₂ systems.