Sampling and Analysis of Ultra-Trace Hg

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Commonly Used Units for Trace and Ultra Trace Components

Name of concentration unit	*Part per thousand*	*Part per million*	*Part per billion*	*Part per trillion*	*Part per quadrillion*	*Part per quintillion*	*Part per sextillion*
Volume/volume concentration	vpth (ppth v/v)	vpm (ppm v/v)	vpb (ppb v/v)	vpt (ppt v/v)	vpq (ppq v/v)	vpq_{ui} (ppq_{ui} v/v)	vps (pps v/v)
Mass-mass concentration	ppth	ppm	ppb	ppt	ppq	ppq_{ui}	pps
Percentage (%)	10^{-1}	10^{-4}	10^{-7}	10^{-10}	10^{-13}	10^{-16}	10^{-19}
Amount of analyte in 1 g sample	1 milligram (1 mg)	1 microgram (1 µg)	1 nanogram (1 ng)	1 picogram (1 pg)	1 femtogram (1 fg)	1 attogram (1 ag)	1 zeptogram (1 zg)

Concentration of major ions in rainwater.

Concentration of Hg in rainwater and ambient air.

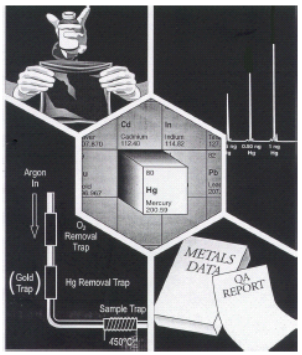
Namieśnik, 2002.

Analytical Methods and Detection Levels

EPA
United States Environmental Protection Agency

Method 1631, Revision E:
Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002



Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-5

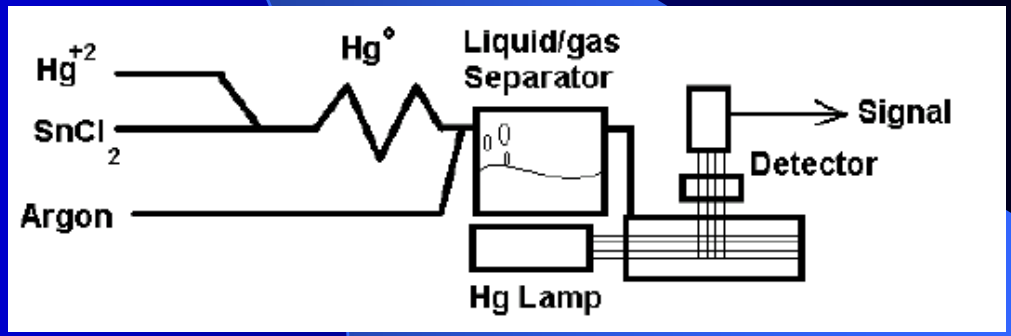
SAMPLING AND ANALYSIS FOR VAPOR AND PARTICLE PHASE MERCURY IN AMBIENT AIR UTILIZING COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY (CVAFS)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

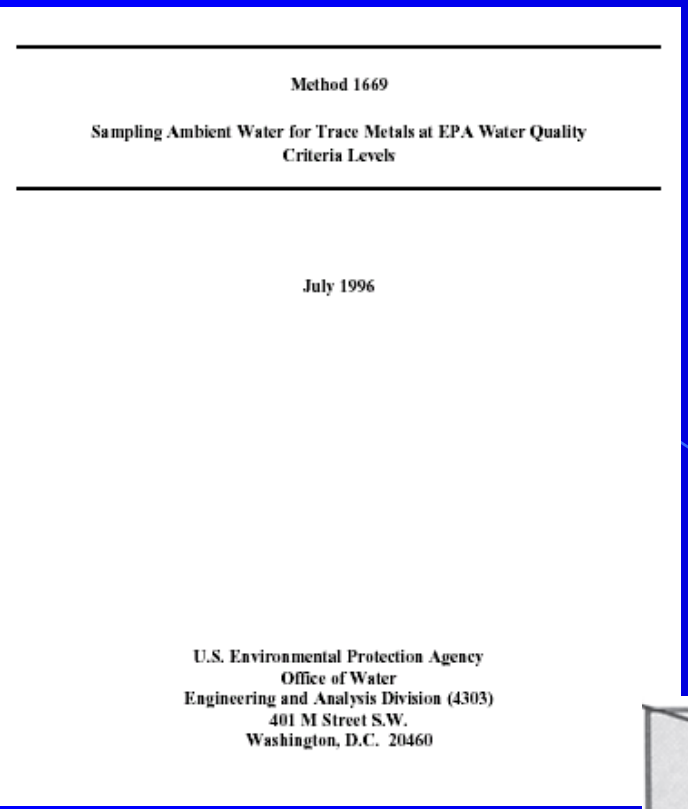
June 1999

Method Source	Method Number	Media Name	Instrumentation	Detection level
EPA-NERL	245.1	WATER	CVAA	0.2 ug/L
EPA-NERL	245.2	WATER	CVAA	0.2 ug/L
EPA-OSW	7470A	VARIOUS	CVAA	0.2 ug/L
USGS	I-2462	WATER	CVAA	0.1 ug/L
USGS	I-1462	WATER	CVAA	0.5 ug/L
USGS	I-5462	OTHER	CVAA	0.5 ug/L
USGS	I-7462	WATER	CVAA	0.5 ug/L
USGS	I-3462	WATER	CVAA	0.5 ug/L
NOAA_NST	131.01	ANIMAL TISSUE	CVAA	0.012 ug/L
NOAA_NST	131	SOIL/SEDIMENT	CVAA	0.012 ug/L
EPA-EAD	1631	WATER	CVAFS	0.0002 ug/L
EPA-OSW	6010 C	VARIOUS	ICP-AES	17 ug/L
EPA-NERL	200.7	WATER	ICP-AES	7 ug/L
EPA-NERL	200.8	WATER	ICP-MS	0.2 ug/L
ASTM	D6502	WATER	XRF	1 ug/L

CVAFS:



Cleanness Classes of Laboratory Air



Method 1669

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

July 1996

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

For Hg sampling and analysis, a class 100 clean room is required. This means that no more than 100 particles (diameter $\geqq 0.5\mu m$) per cubic foot of air in the clean room.

Acid clean of sampling devices to prevent contamination.

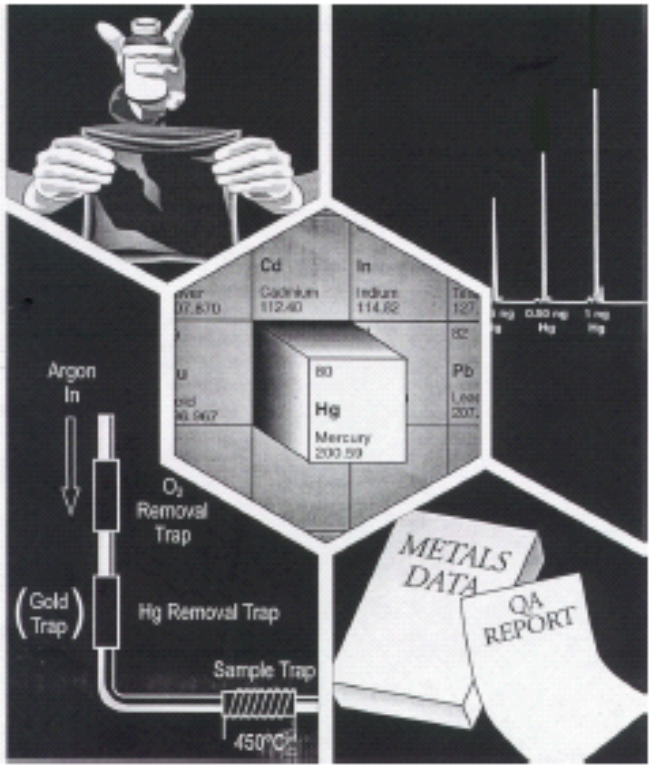
Class of air cleanness \ Particle diameter	0.1	0.2	0.3	0.5	1.0	5.0
1	35	7	3	1	-	-
10	350	75	30	10	-	-
100	-	750	300	100	-	-
1,000	-	-	-	1,000	-	7
10,000	-	-	-	10,000	-	70
100,000	-	-	-	100,000	-	700

EPA Method 1631 Rev. E

EPA
United States
Environmental Protection
Agency

Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002

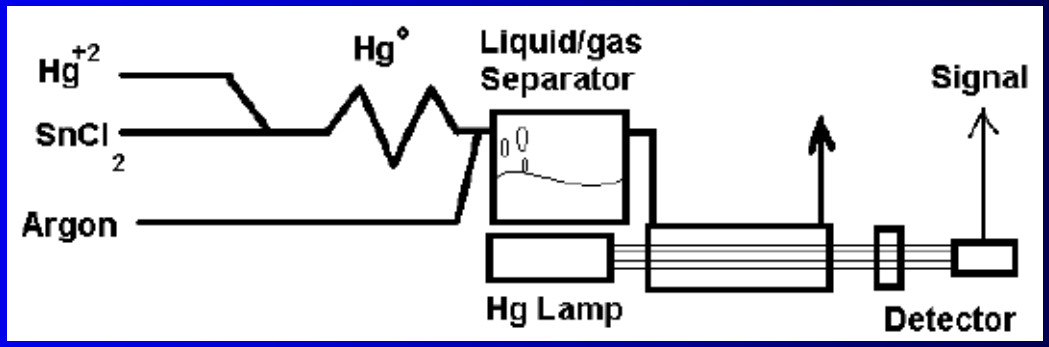


Techniques for Determination of Ultra-Trace Level Hg

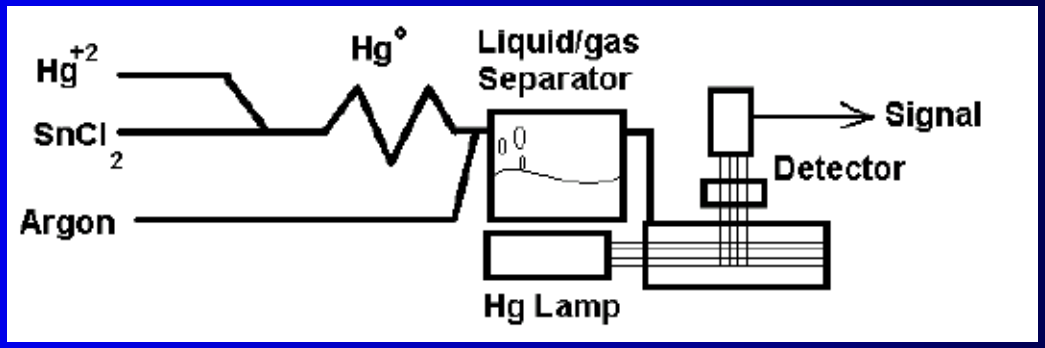
- Cold Vapor Atomic Absorption Spectrometry
  - CVAAS (Method 245.1)
- Cold Vapor Atomic Fluorescence Spectrometry
  - CVAFS (Method 245.7 & 1631 revision E)

Techniques for Determination of Ultra-Trace Level Hg

- CVAAS:



- CVAFS:



Flexibility in EPA Method 1631

- Method 1631 is Performance Based:
  - Changes that do not compromise method performance are allowed
  - Changes to improve performance or reduce measurement cost are allowed
- Examples of allowable changes:
  - Single-trap amalgamation
  - Use of CVAAS if less sensitivity is acceptable

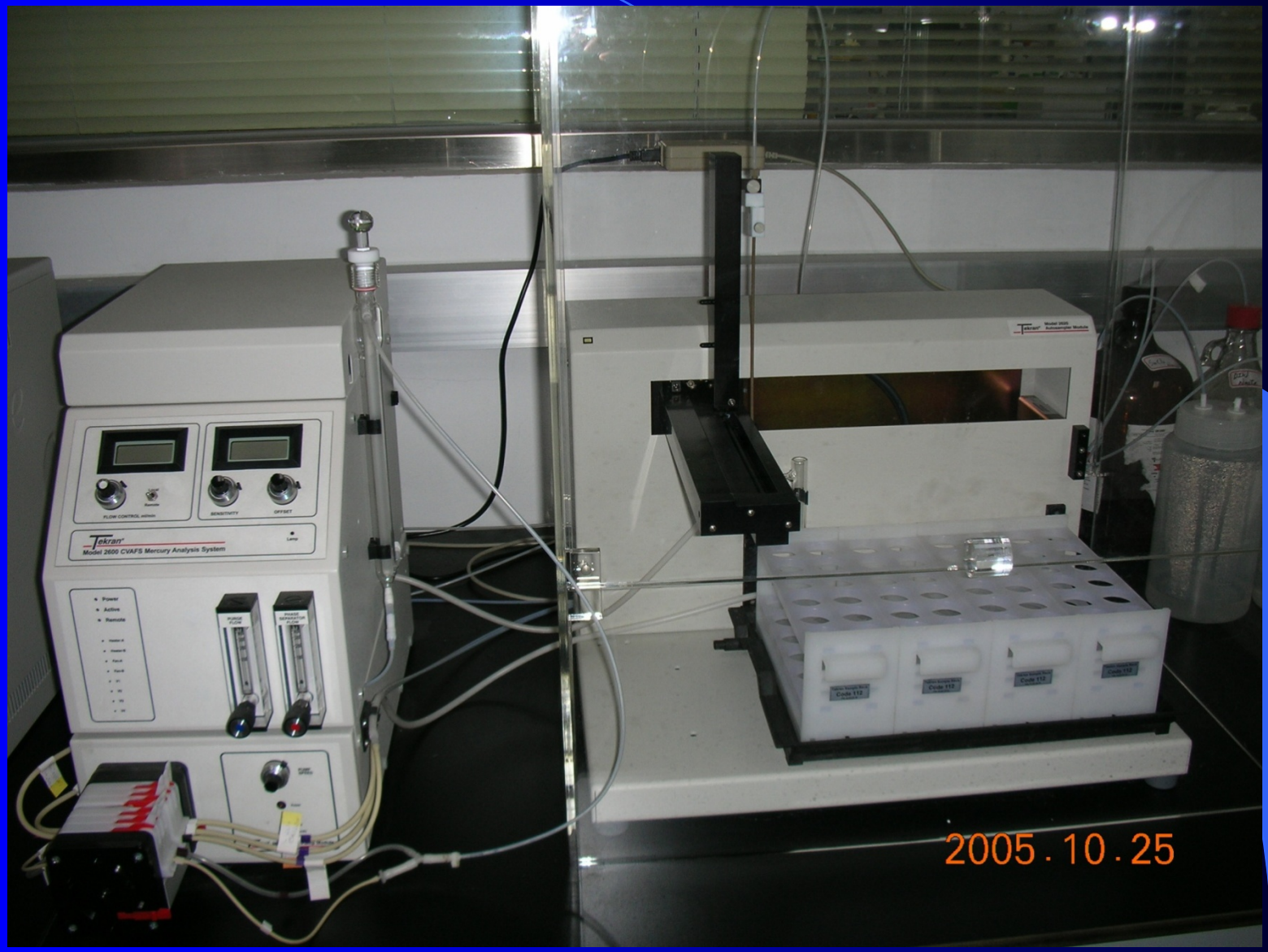
EPA Method 1631 Summary

- Reporting Detection Limit: 0.5 ng/L
- BrCl Oxidizer/Preservative
- $NH_2OH \cdot HCl$ pre-reduction for free BrCl
- $SnCl_2$ reduction of Hg^{2+} to Hg^0
- Purge Hg^0 from water with Ar or N_2
- Trap Hg^0 on gold-coated quartz sand
- Thermally desorb Hg^0 into Ar stream
- Dual Amalgamation
- CVAFS

Clean Lab and Ultra-Trace Hg Analysis

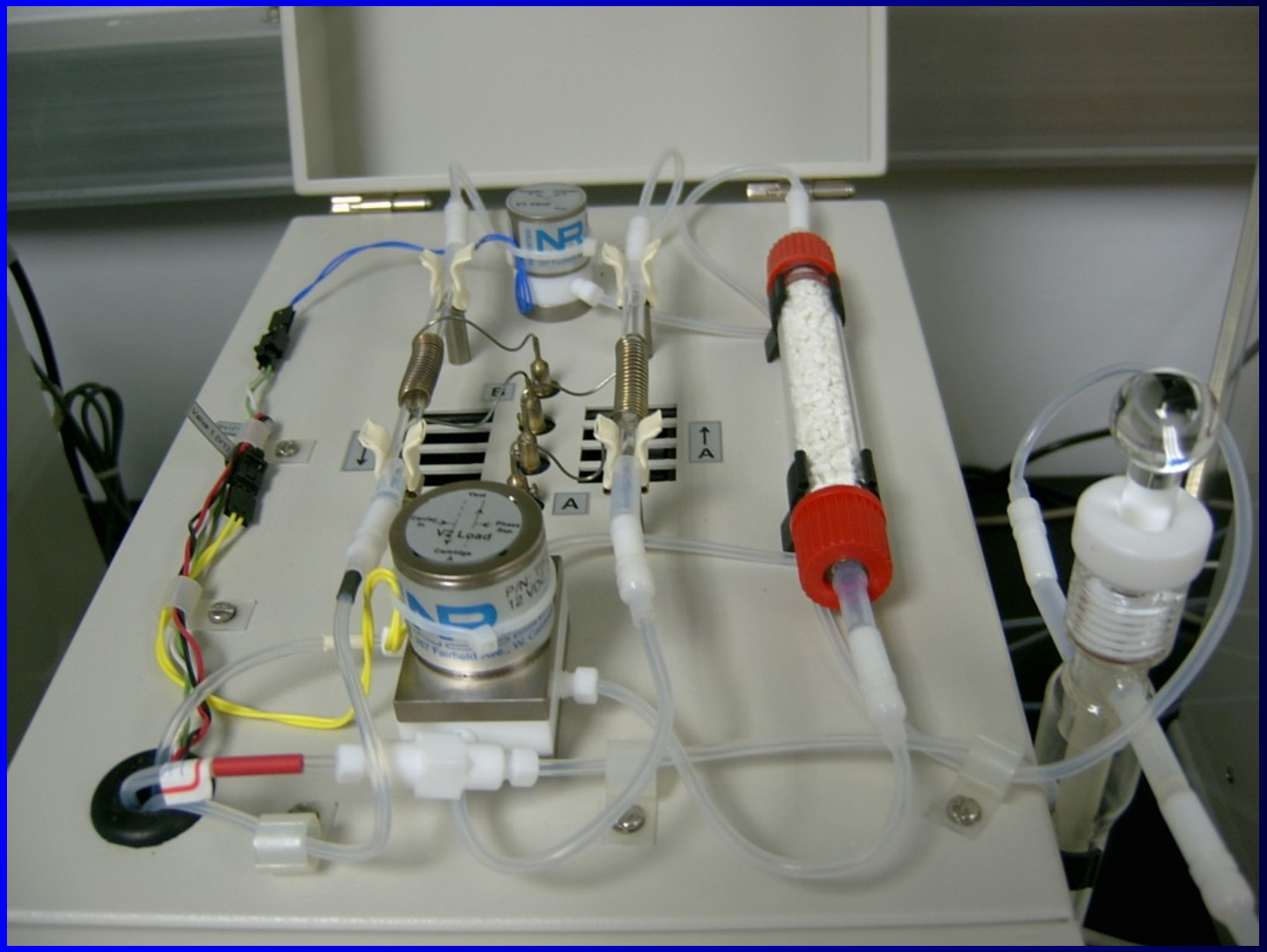
- 2007: Established an ultra-trace level Hg lab at NCU (class 100 clean room and acid-clean protocol)
- 2008: Established a Taiwan wet Hg deposition monitoring network with 12 sampling sites

Tekran Series 2600 CVAFS



Tekran Series 2600 CVAFS

Tekran Series 2600 CVAFS



EPA Method IO-5

Compendium of Methods
for the Determination of
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in Ambient Air

Compendium Method IO-5

SAMPLING AND ANALYSIS FOR VAPOR AND PARTICLE PHASE MERCURY IN AMBIENT AIR UTILIZING COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY (CVAFS)

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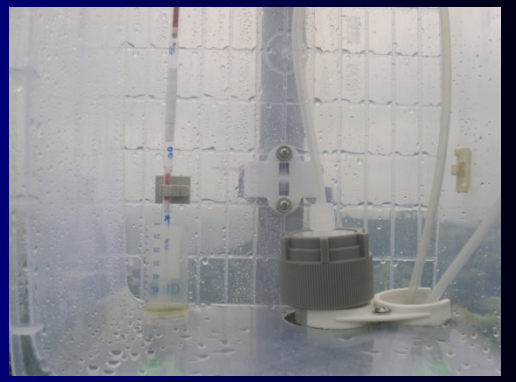
Cincinnati, OH 45268

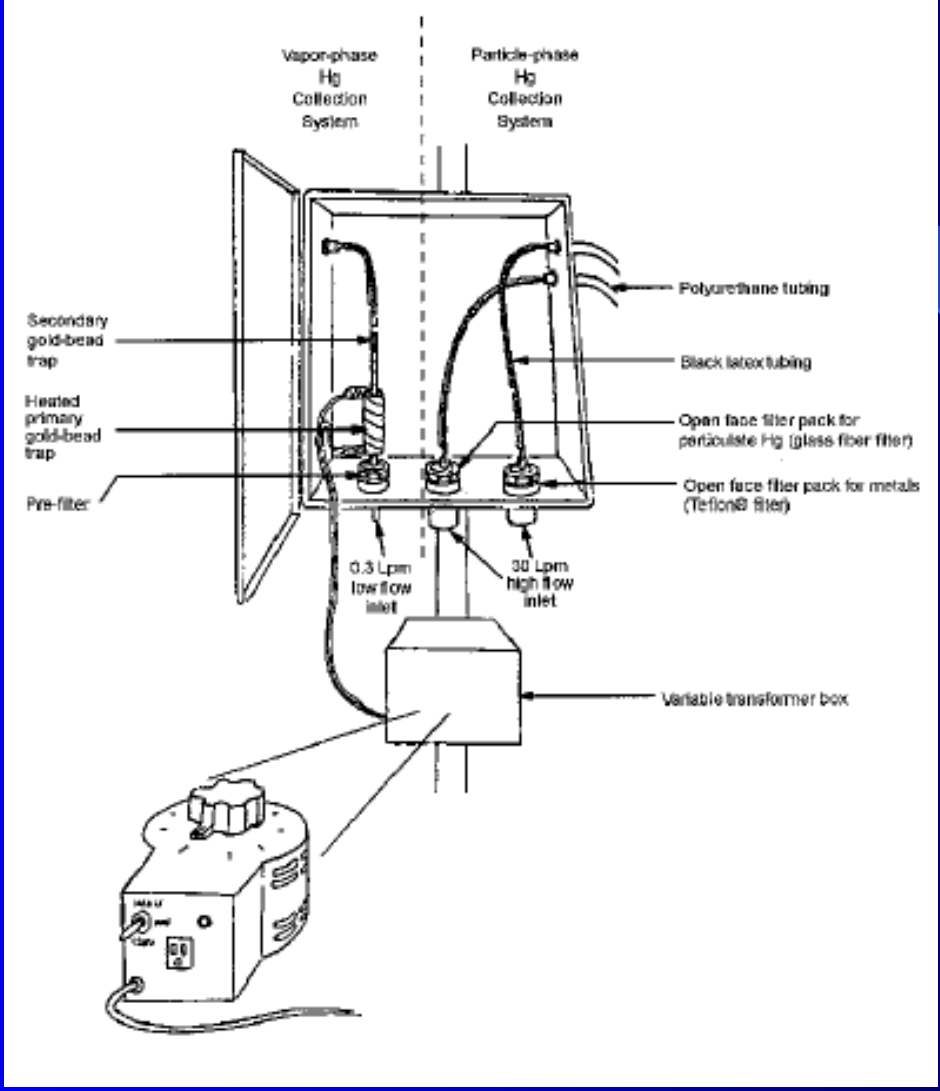
June 1999

EPA Method IO-5 Summary

- Vapor-phase Hg is collected using gold traps. Air is pulled through the sampling system using a vacuum pump at a nominal flow rate of 0.3 Lpm.
- Particle-phase Hg is collected using a glass-fiber filter in an open-faced Teflon filter pack. Air is pulled through the sampling system using a vacuum pump at a nominal flow rate of 30 Lpm.
- Both are determined by dual-amalgamation CVAFS.



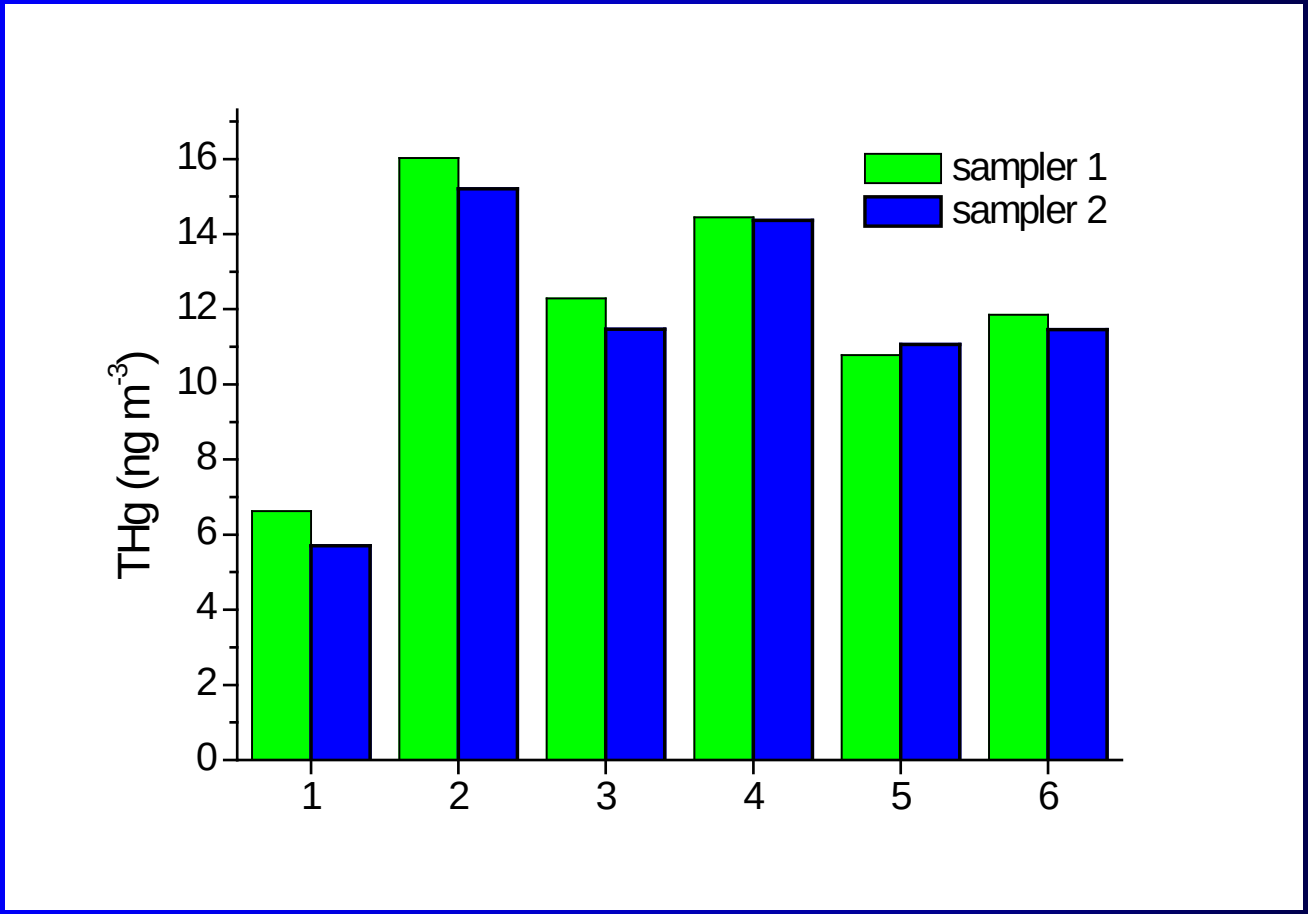
Ambient Sampling System for Collection of Vapor and Particle Phase Mercury



EPA Method IO-5 Summary

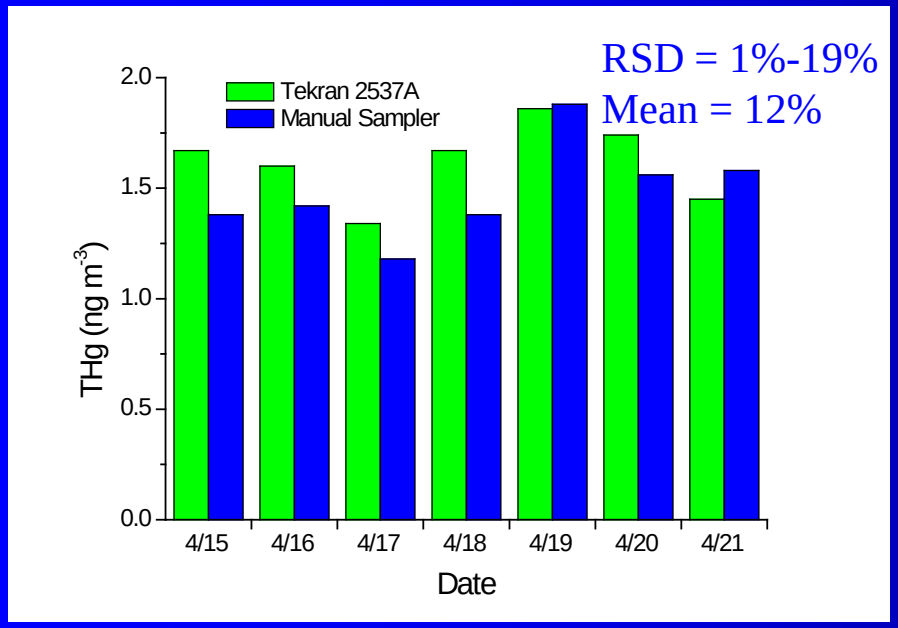
- The amount of vapor-phase Hg collected on the gold trap is determined directly by CVAFS.
- Determination of particle-phase Hg requires digestion of the glass-fiber filters prior to CVAFS analysis.
- Detection Limits:
  - 30 pg/m^3 for particulate Hg
  - 45 pg/m^3 for vapor-phase Hg

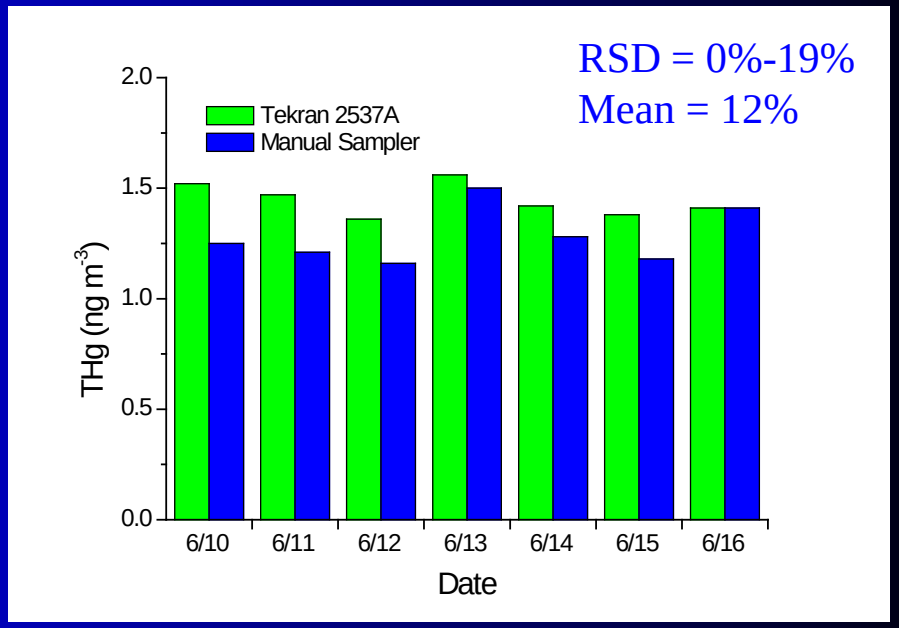
Manual Sampling System Parallel Test

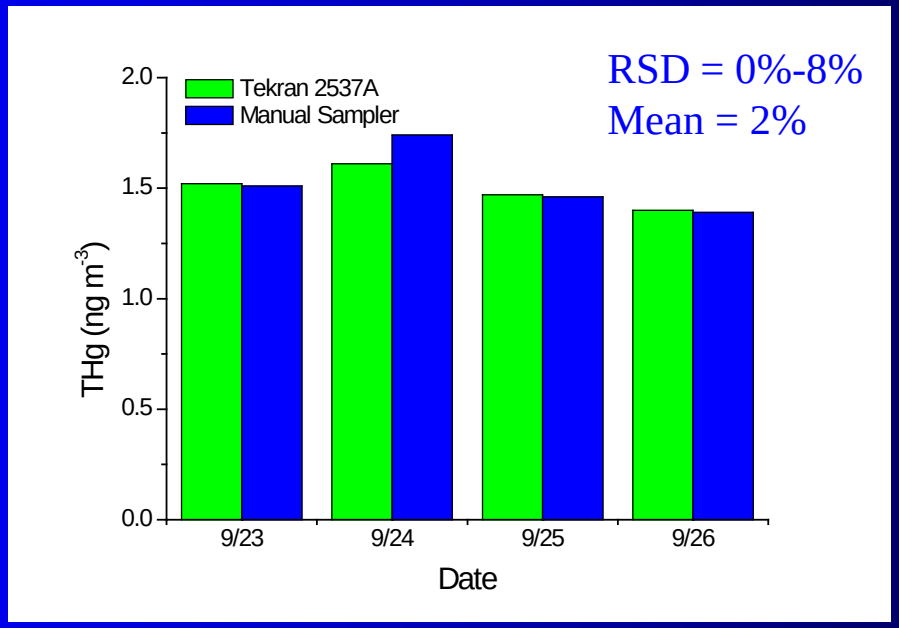


- RSD ranged between 2.6 and 15.9% with a mean of 4.8%.

Manual vs. Automated System at LABS







Method 1669

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EPA Method 1669 (In General)

- Performance Based
- Training & Practice & Communication
- Attention to Cleaning
- Requires Two People: Clean Hand/Dirty Hand
- Non-Metal Containers and Clean Gloves
- Audits

EPA Method 1669 (Field Sampling)

- Field Blank & Duplicates
- Face Upwind & Upstream
- Surface Samples: Grab Samples Preferred
- Subsurface Samples: Pumping if Required
- Field (or Near-Field) Filtration
- Preservation – Uncontaminated
- Documentation

EPA Method 1669

- Site Selection:
  - Representative & Homogeneous
  - Located Away from Metals (eg. Bridges)
  - Less Polluted Sites First

EPA Method 1669

- Avoid Contamination Sources:
  - Carryover
  - Separate Highly Contaminated Sources
  - Indirect Sources
  - Airborne Particulates/Dust
  - Bridges
  - Open Containers

EPA Method 1669

- Avoid Contamination:
  - Minimize Exposure
  - Wear Gloves
  - Use Metal-Free Apparatus
  - Pre-Cleaning & Bagging
  - Protective Clothing
  - Reagent Grade Water and Preservatives
  - Clean Room (or Laminar Flow Hood)

Table 2. Mercury Contamination Sources

Reagents	Equipment	Environment	Analyst
reagent water	sample bottle	laboratory air	gloves
hydrochloric acid	hoses and tubes	particulates	laboratory coat
potassium bromide	gas-supply line	bench top	dental work
potassium bromate	autosampler vial	ventilation hood	
stannous chloride	gas–liquid separator		
hydroxylamine hydrochloric acid	pipet tips		
argon			

EPA Method 1669

- Apparatus and Materials:
  - Pre-Cleaning: Water & Reagents
  - Storage-Protection-Documentation
  - Sample Bottles: Teflon
  - Sampling Device & Technique
  - Coolers
  - Tubing

EPA Method 1669

- Quality Assurance:
  - Performance Based Method
  - Equipment Blanks
  - Field Blanks
  - Field Replicates
  - Less Polluted Sites First