

Overview of Sampling and Analysis of Ultra-Trace Hg

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Trace and Ultra Trace

Table 1. Classification of analytical methods and techniques by analyte concentration in a sample.

<i>General name of analyte</i>	<i>Analyte concentration</i>	<i>Common term for analytical procedure</i>	<i>Examples</i>
Sub-microtrace component	< 1 ppt ($< 10^{-8}\%$)	TRACE ANALYSIS	Determination of dioxins in samples of various matrices
Ultra-microtrace component	< 1 ppb ($< 10^{-6}\%$)		Determination of trihalomethanes in drinking water and human urine. Determination of volatile organic compounds in indoor air
Microtrace component	< 1 ppm ($< 10^{-4}\%$)		Determination of carbon monoxide in ambient air
Trace component	< 100 ppm ($< 0.01\%$)		Determination of methane in ambient air
Secondary component (admixture)	< 1%	SEMI-MICROANALYSIS	Determination of carbon dioxide in ambient air
Primary component	1-100%	MACROANALYSIS	Determination of oxygen in waste gases. Determination of oxygen in flue gases.

Commonly Used Units for Trace and Ultra Trace Components

<i>Name of concentration unit</i>	<i>Part per thousand</i>	<i>Part per million</i>	<i>Part per billion</i>	<i>Part per trillion</i>	<i>Part per quadrillion</i>	<i>Part per quintillion</i>	<i>Part per sextillion</i>
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)	vp _s (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.

Mercury is a natural element existing everywhere in the environment.

It is extremely important to avoid contamination during sampling, storage, treatment, and analysis.

*EPA Method 1669 、 1631 、
IO-5*

EPA Method 1669

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**

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)

Cleanness Classes of Laboratory Air

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

<i>Particle diameter</i> <i>Class of air cleanness</i>	<i>0.1</i>	<i>0.2</i>	<i>0.3</i>	<i>0.5</i>	<i>1.0</i>	<i>5.0</i>
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

Acid clean of sampling devices to prevent contamination.

EPA Method 1669

Table 2. Mercury Contamination Sources

Reagents

reagent water
hydrochloric acid
potassium bromide
potassium bromate
stannous chloride
hydroxylamine hydrochloric acid
argon

Equipment

sample bottle
hoses and tubes
gas-supply line
autosampler vial
gas-liquid separator
pipet tips

Environment

laboratory air
particulates
bench top
ventilation hood

Analyst

gloves
laboratory coat
dental work

EPA Method 1669

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

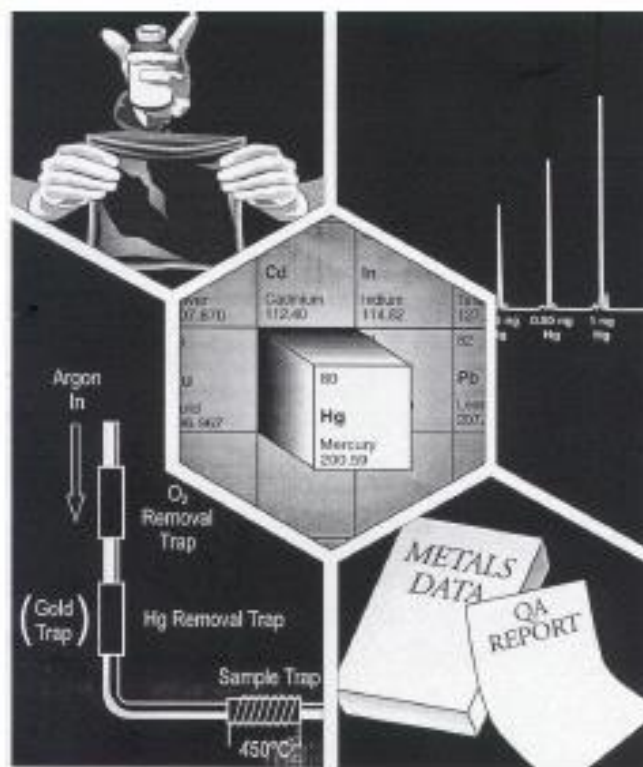
EPA Method 1669

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

EPA Method 1631 Rev. E

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

August 2002



Common Analytical Methods for Metals

- ◆ Flame Atomic Absorption spectroscopy (FAAS)
- ◆ Graphite Furnace Atomic Absorption spectroscopy (GFAAS)
- ◆ Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- ◆ Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
- ◆ Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)



Analytical Methods and Detection Levels

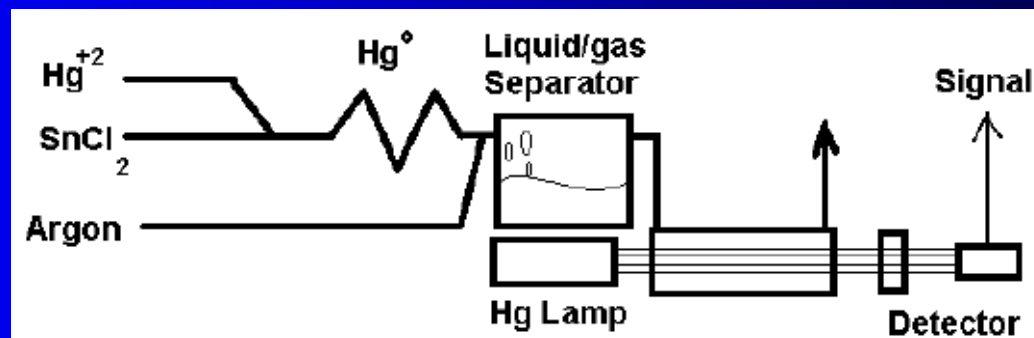
Method Source	Method Number	Media Name	Instrumentation	Detection level
EPA-NERL	245.1	WATER	CVAA	0.2 ug/L
EPA-NERL	245.2	WATER	CVAA	0.2 ug/L
EPA-OSW	7470A	VARIOUS	CVAA	0.2 ug/L
USGS	I-2462	WATER	CVAA	0.1 ug/L
USGS	I-1462	WATER	CVAA	0.5 ug/L
USGS	I-5462	OTHER	CVAA	0.5 ug/L
USGS	I-7462	WATER	CVAA	0.5 ug/L
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

Techniques for Determination of Ultra-Trace Level Hg

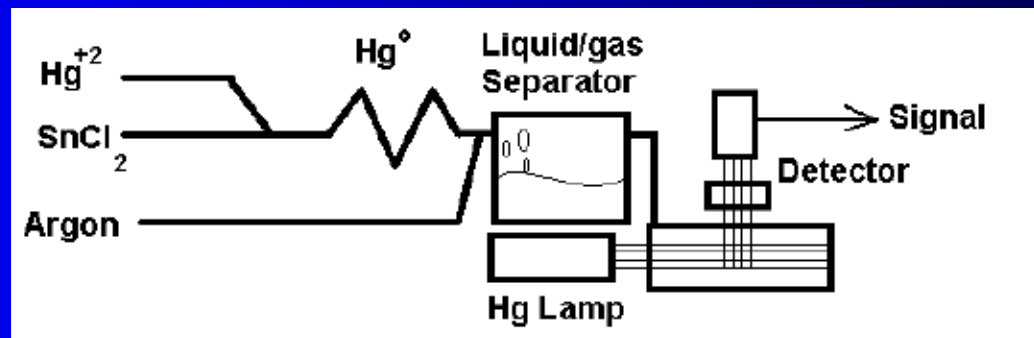
- Cold Vapor Atomic Absorption Spectrometry
 - CVAAS (Method 245.1)
- Cold Vapor Atomic Fluorescence Spectrometry
 - CVAFS (Method 245.7 & 1631 revision E)

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

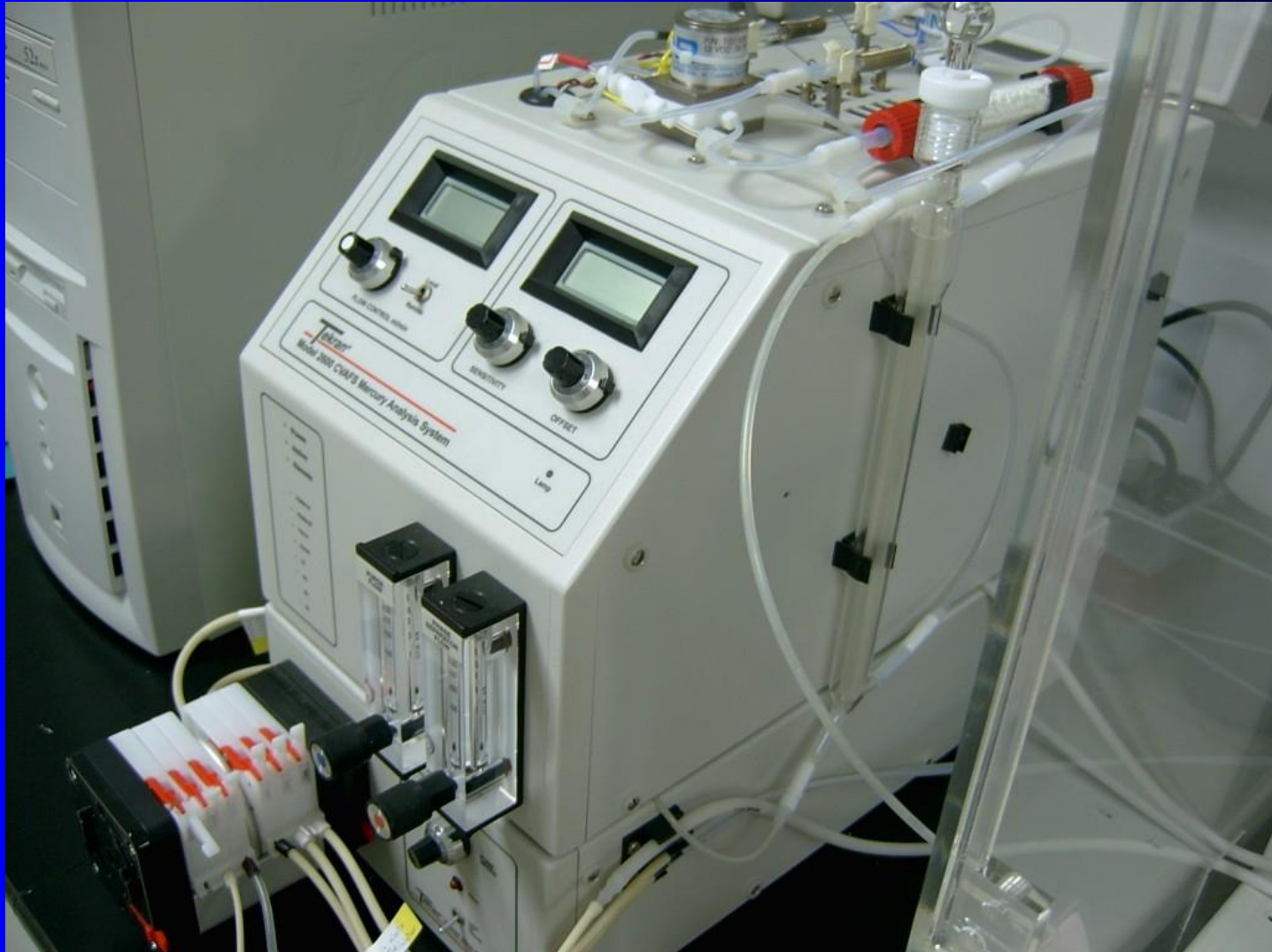
EPA Method 1631 Summary

- Reporting Detection Limit: 0.5 ng/L
- BrCl Oxidizer/Preservative
- $\text{NH}_2\text{OH}\cdot\text{HCl}$ 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

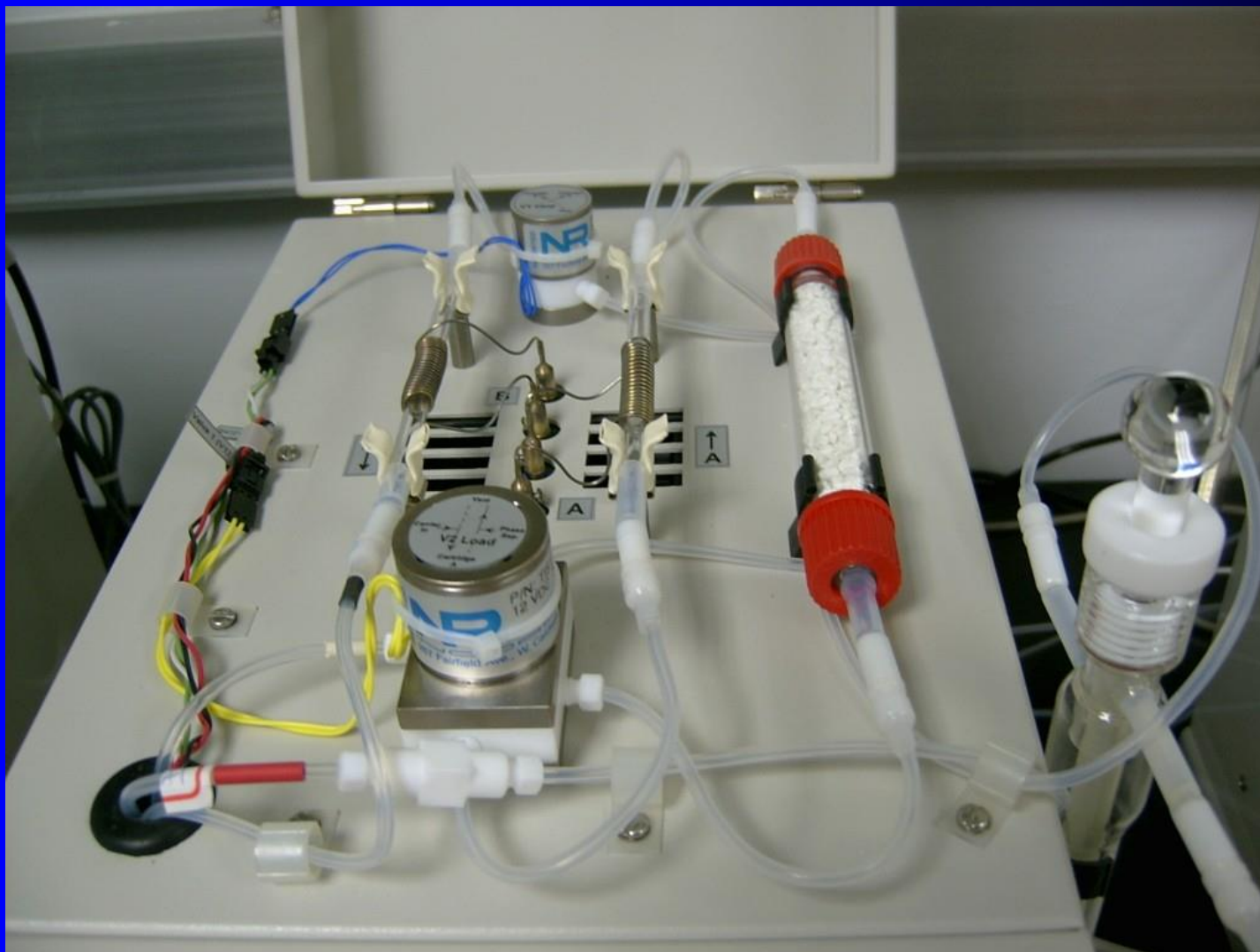
Tekran Series 2600 CVAFS



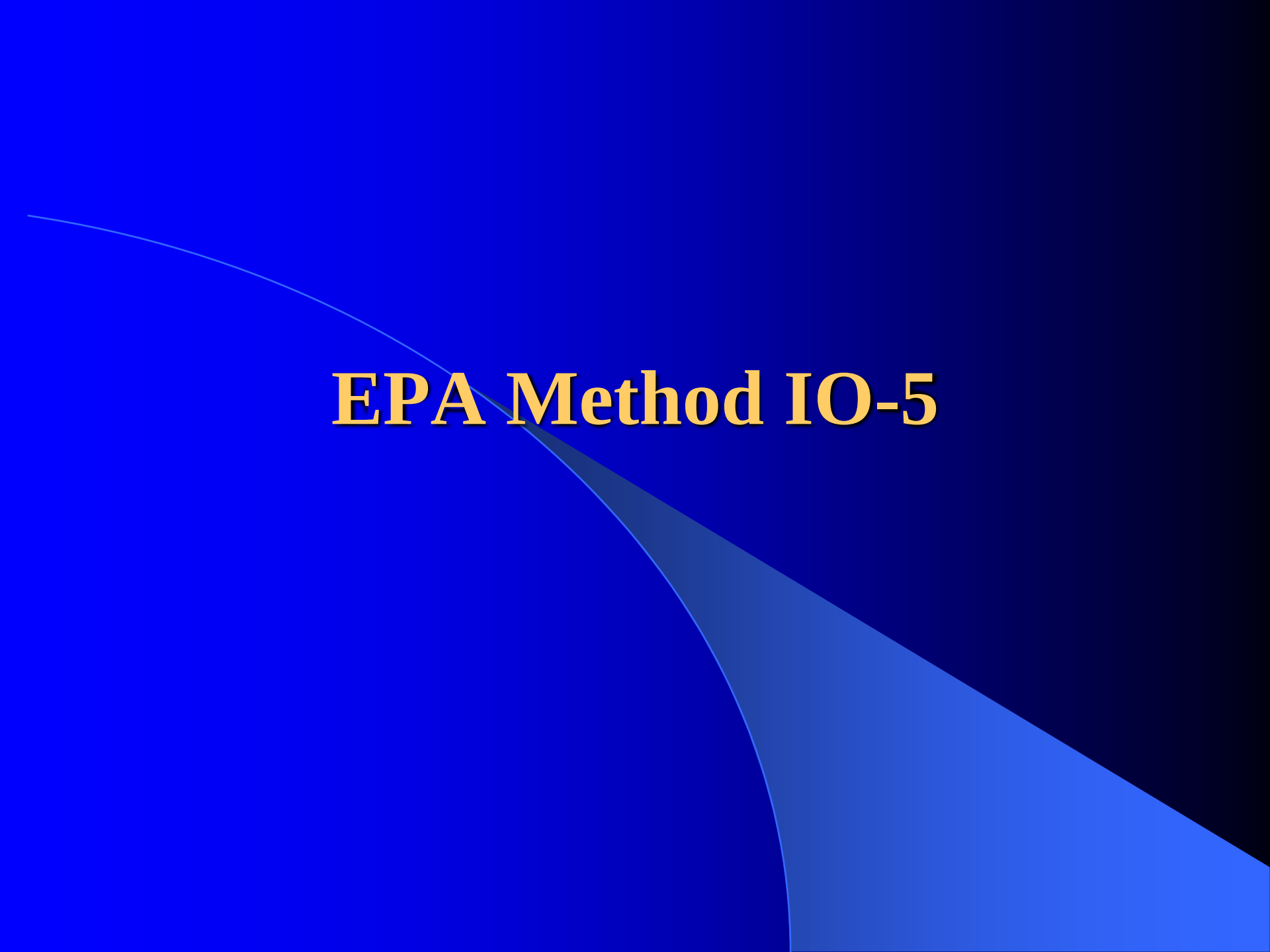
Tekran Series 2600 CVAFS



Tekran Series 2600 CVAFS



EPA Method 10-5

The background is a solid blue gradient. A thin, light blue curved line starts from the left edge, arcs downwards and to the right, and then curves back towards the bottom left. A larger, semi-transparent blue shape, resembling a quarter-circle or a large sector, is positioned in the lower right quadrant, partially overlapping the main blue background.

**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

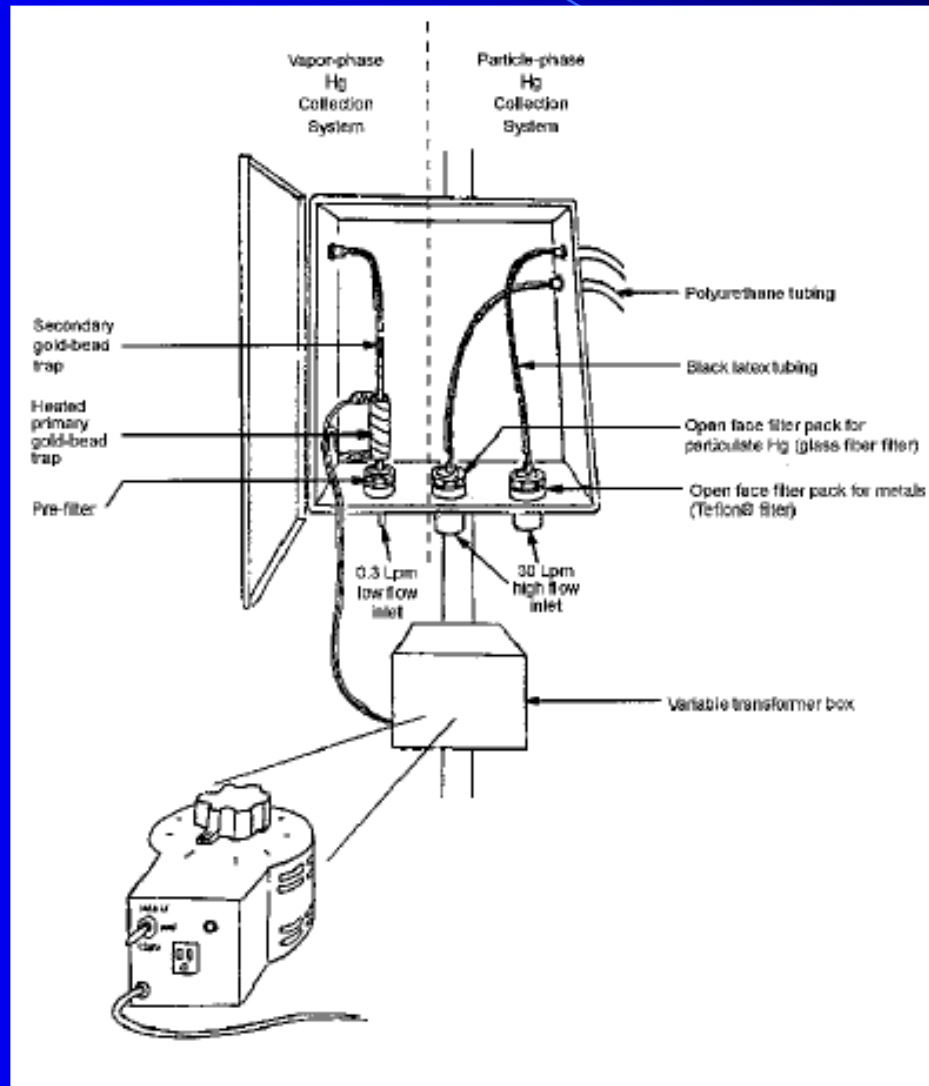
June 1999

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.



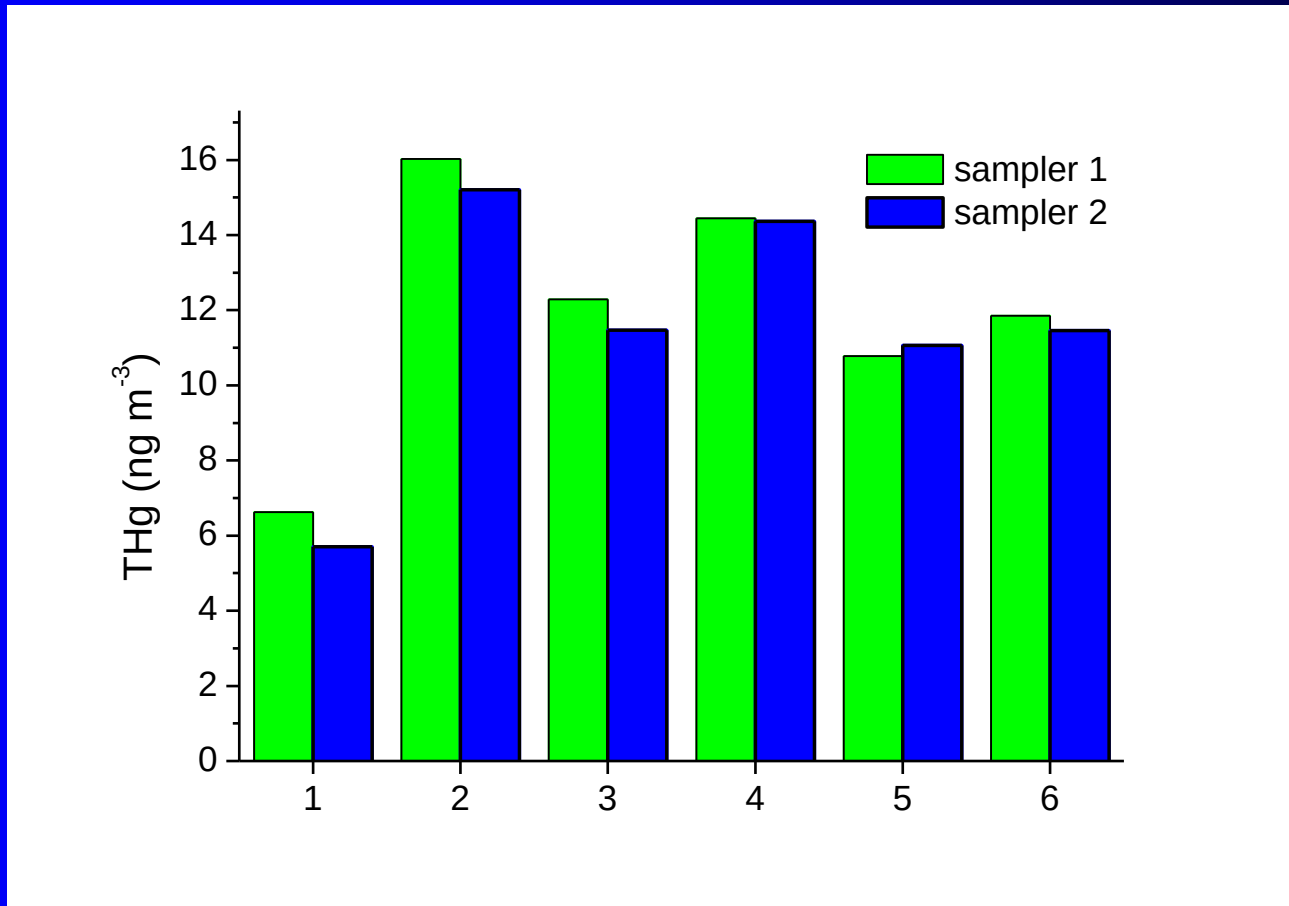
Ambient Sampling System for Collection of Vapor and Particle Phase Mercury



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/m³ for particulate Hg
 - 45 pg/m³ for vapor-phase Hg

Manual Sampling System Parallel Test



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

Atmospheric Hg Monitoring at LABS

- Automated Sampling:
 - Since April 13, 2006
 - Tekran 2537A/1130/1135 Speciation System
 - Speciation of atmospheric Hg: GEM/RGM/ PHg
 - Flow rate = 10 L min⁻¹
 - Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)

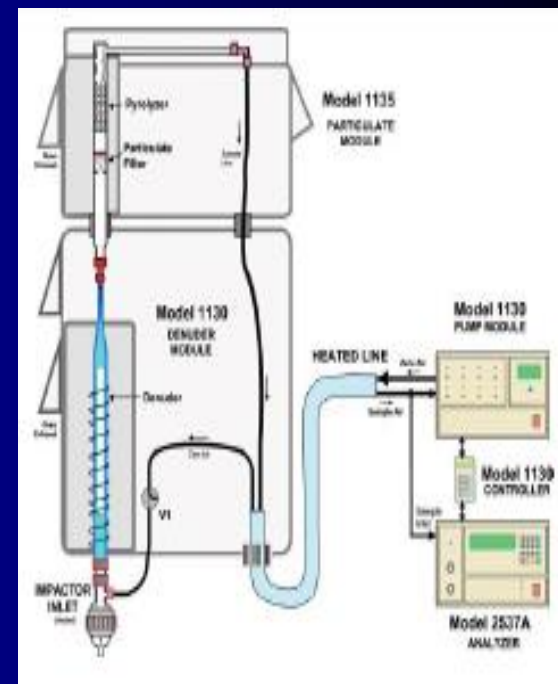


Tekran
2537A

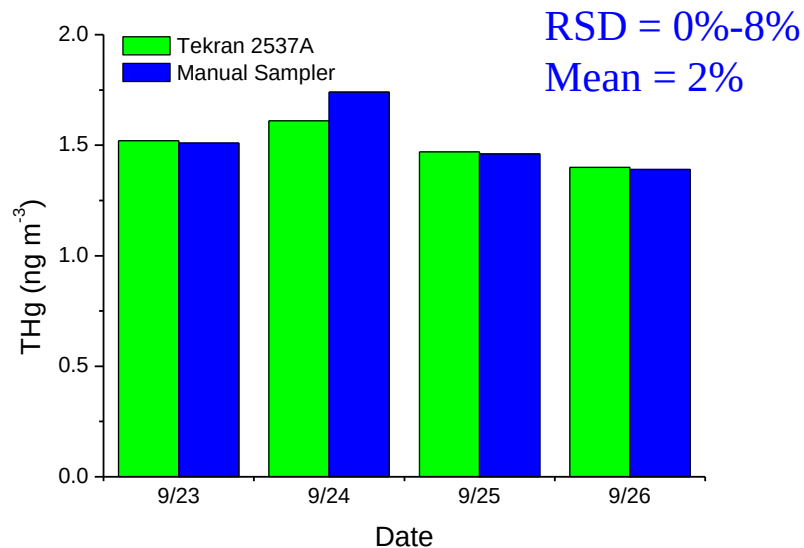
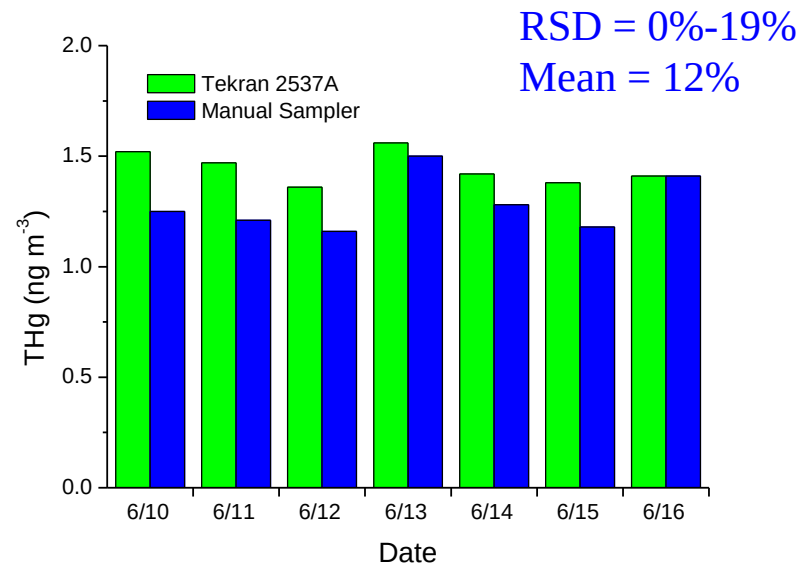
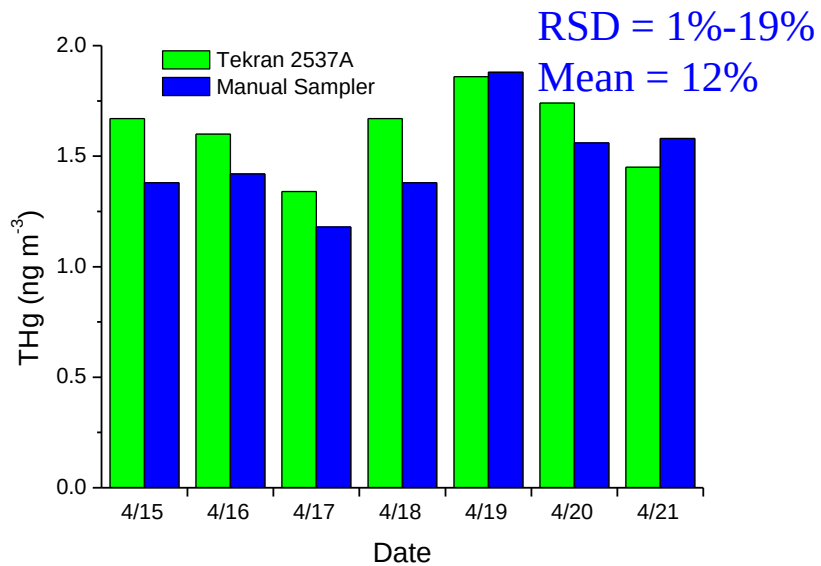
Tekran 1130 pump unit



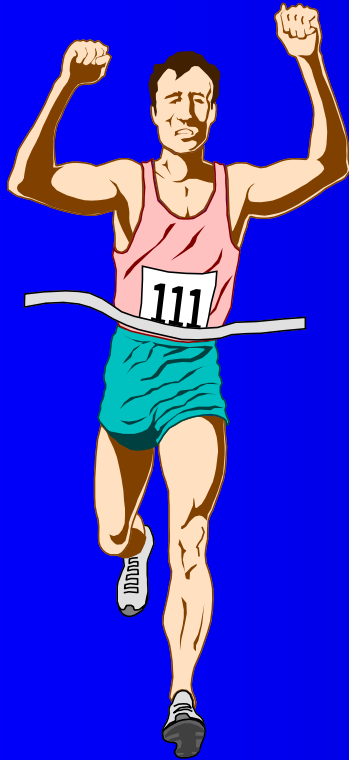
Tekran
1135
Tekran
1130



Manual vs. Automated System at LABS in 2008



THANK you!



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