Overview of Sampling and Analysis of Ultra-Trace Hg

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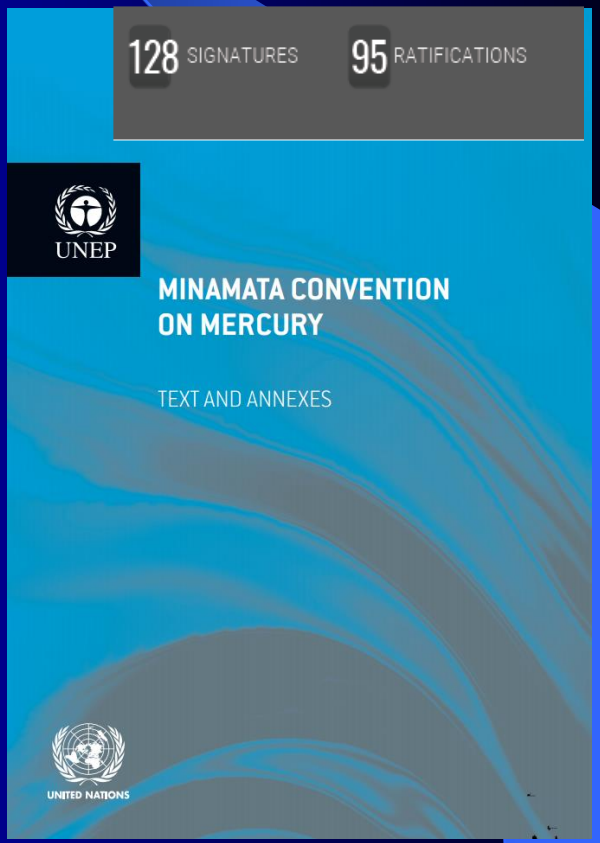
Minamata Disease and Hg Pollution

- Minamata disease, a neurological disease caused by severe Hg poisoning due to consumption of contaminated fish, was first discovered in Minamata, Japan in **1956**.
- Hg-containing industrial wastewater discharge was the major Hg source to the fish in Minamata Bay.

(Time, 2010)

Minamata Convention on Mercury

- The Minamata Convention on Mercury was opened for signature by governments at a Diplomatic Conference on October 9-11, 2013 in Japan.
- Minamata Convention on Mercury entered into force on August 16, 2017.



Global Hg Pollution

GLOBAL REPORT

MERCURY IN WOMEN OF CHILD-BEARING AGE IN 25 COUNTRIES

bri
Biodiversity Research Institute
Innovative wildlife science

IPEN
a toxics-free future

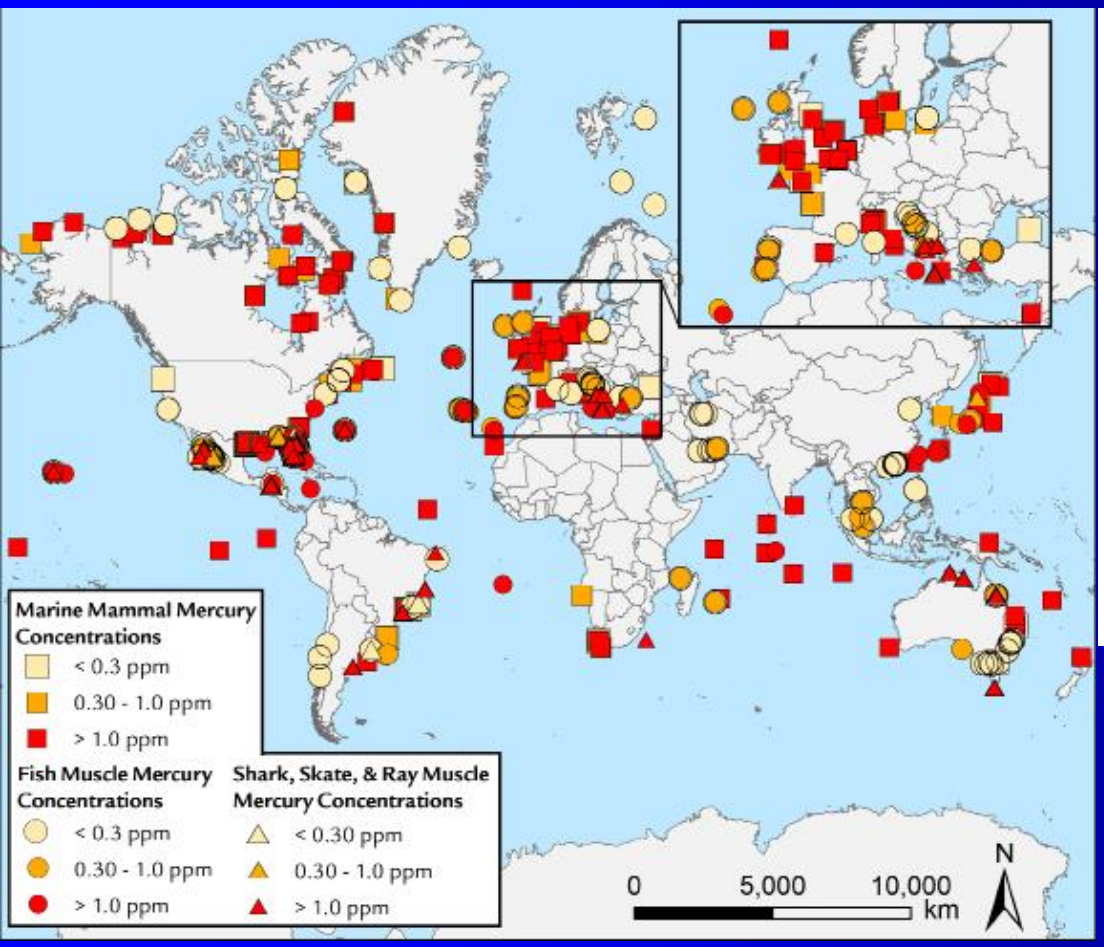
KEY FINDINGS

- 1044 women of child-bearing age from 25 countries participated in the study. 42% of them had mercury levels greater than 1 ppm – the level that approximately corresponds to the US EPA reference dose.* 55% of the women had mercury levels greater than 0.58 ppm mercury, a more recent, science-based threshold based on data indicating harmful effects at lower levels of exposure. Mercury is a health threat to women and the developing fetus.
- Women of the Pacific Islands have elevated mercury levels, likely due to a fish-rich diet. Distant air emissions of mercury from coal-fired power plants, cement kilns and other industries contaminate ocean fish that serve as a primary protein source for Pacific Islanders.
- Artisanal small-scale gold mining results in high mercury body burdens in women from Indonesia, Kenya, and Myanmar. Two likely mercury exposure sources are burning mercury amalgam and eating contaminated fish.
- Industrial mercury emissions contaminate local fish and elevate mercury levels in Thai women living nearby.
- Indigenous women in Alaska have mercury levels of concern due to their subsistence diet of sea mammals and fish. Consumption of seals may be a key source of mercury exposure.
- Women from locations in Albania, Chile, Nepal, Nigeria, Kazakhstan, and Ukraine have mercury levels of concern due to localised pollution of water-ways and suspected fish contamination.
- Women using mercury to gold plate statues in Nepal have elevated mercury levels.

* This is the daily exposure that US EPA considers "likely to be without an appreciable risk of deleterious effects during a lifetime."

Global Hg Pollution

- Fish consumption is the major exposure route of Hg to many people worldwide.
- Hg concentrations in fish are elevated globally.

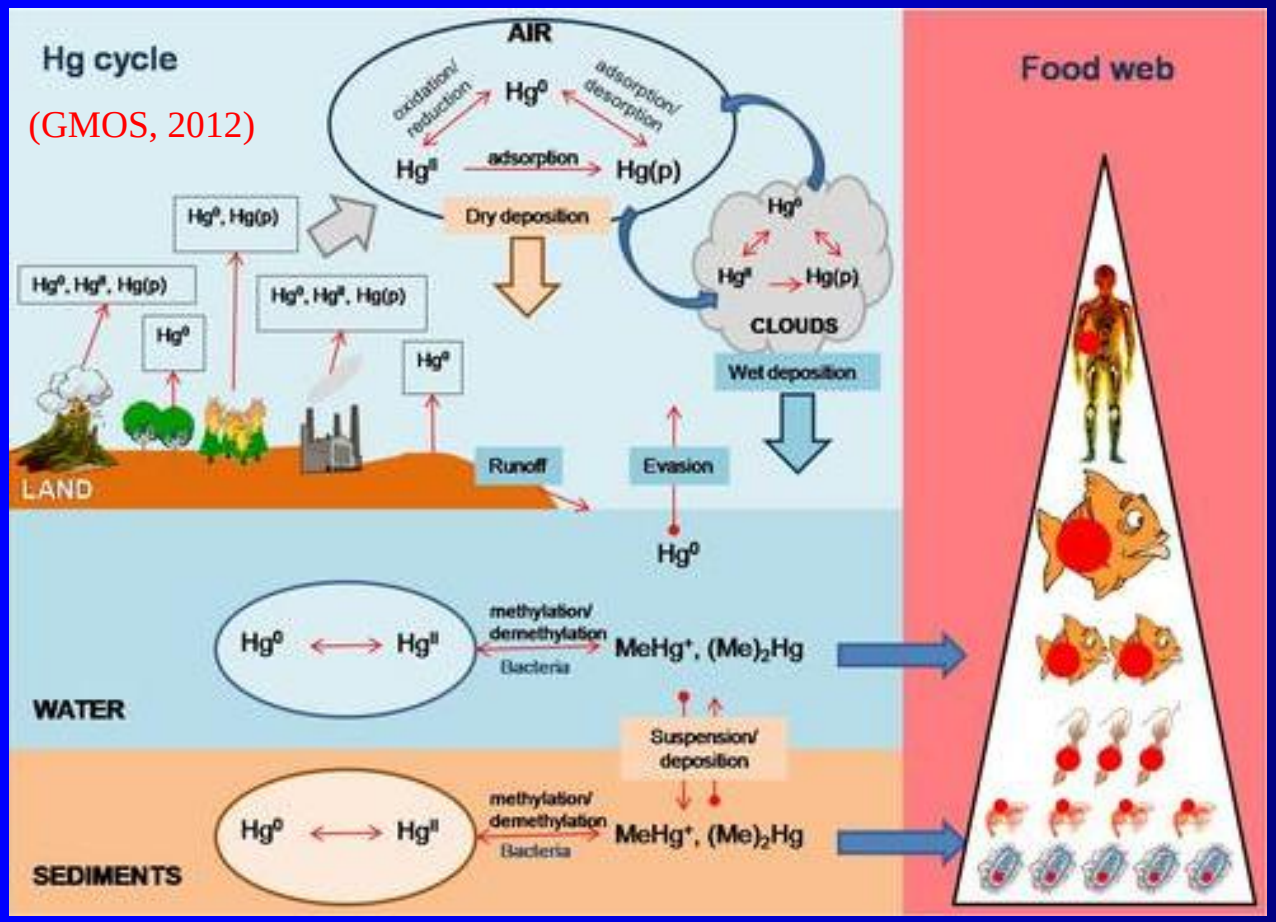


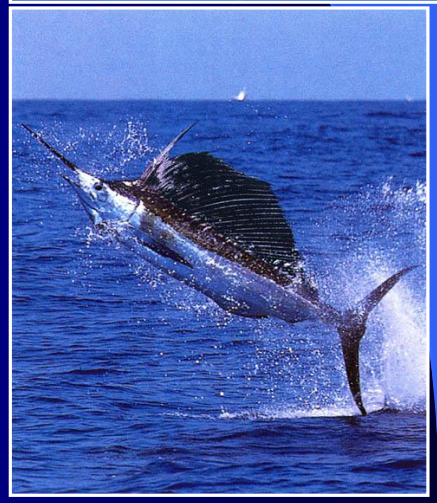
Nation	Standards
International Food Standards (Codex Alimentarius)	Fish: less than 0.5 mg/kg of methyl mercury Carnivorous fish (shark, swordfish, and tuna): less than 1 mg/kg of methyl mercury
US	Fish: less than 1 mg/kg of methyl mercury
EU	Fish: less than 0.5 mg/kg of total mercury Carnivorous fish including shark: less than 1 mg/kg of total mercury
Japan	Seafood (excluding abyssal fish and tuna): less than 0.4 mg/kg of total mercury, less than 0.3 mg/kg of methyl mercury
Australia and New Zealand	Fish: less than 0.5 mg/kg of total mercury Carnivorous fish including shark: less than 1 mg/kg of total mercury
Korea	Seafood (excluding abyssal fish and tuna): less than 0.5 mg/kg of total mercury

(Evers et al., 2012)

Global Hg Pollution

- Atmospheric deposition is the major source of Hg to many aquatic ecosystems.
- Once deposits from atmosphere, inorganic Hg can get methylated by bacteria to form MeHg then bioaccumulates through food chain, resulting in higher concentrations in large long-lived predatory fish.





Mercury is a natural element existing everywhere in the environment.

(Theodore Gray, The Elements)

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

Mercury Detection – the Challenges

- Total Hg in rainwater = 10 ng/L
  - Equals 10 parts per trillion (ppt)

- GEM = 1.7 ng/m^3
  - Equals 0.2 parts per trillion (pptv)
  - 5 x 10^6 molec/cm^3

- GOM and PBM = 10 pg/m^3
  - Equals 1.1 parts per quadrillion (ppqv)
  - 2.7 x 10^4 molec/cm^3

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.

Mercury Detection – the Challenges

- ***Sensitivity***
  - Mercury is present in the low pptv to ppqv range
- ***Selectivity***
  - Potential interferents are present at ***1000's of times*** higher concentration than mercury
    - O_3
    - SO_2
    - NO_X
    - HCl

Sampling and Analysis of Ultra-Trace Hg

- EPA Method 1669
- EPA Method 1631 Rev. E
- EPA Method 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)

- Attention to Cleaning
- Non-Metal Containers and Clean Gloves
- Requires Two People: Clean Hand/Dirty Hand
- Training & Practice & Communication
- Performance Based
- 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 100/1000 clean room is required. This means that no more than 100/1000 particles (diameter $\geqq 0.5\mu m$) per cubic foot of air in the clean room.

Particle diameter / Class of air cleanness	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

Acid clean of sampling devices to prevent contamination.

EPA Method 1669

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

EPA Method 1631 Rev. E

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）

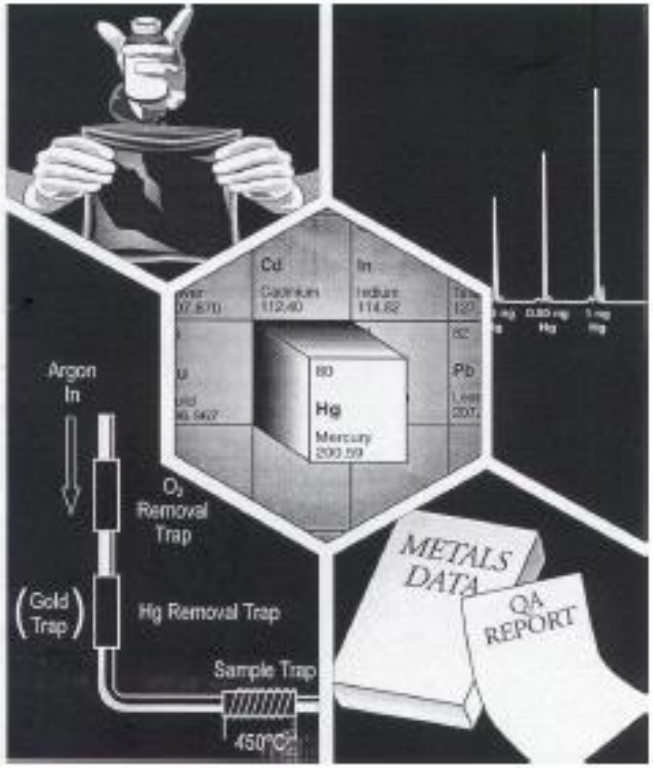
Analytical Methods and Detection Levels

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

EPA
United States
Environmental Protection
Agency

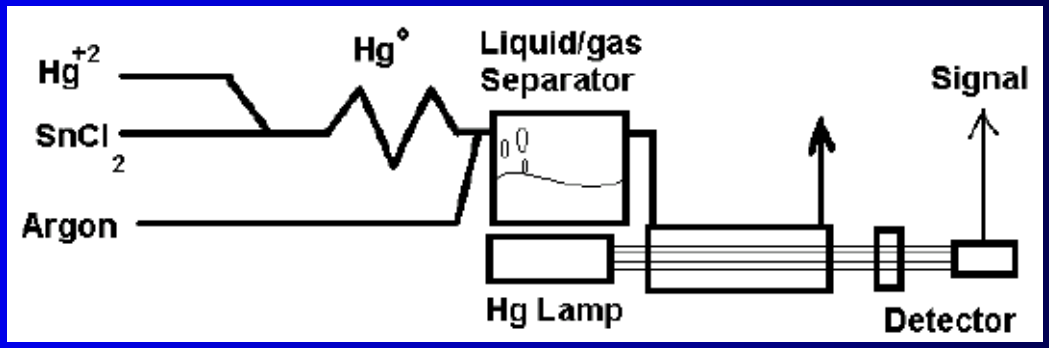
Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002

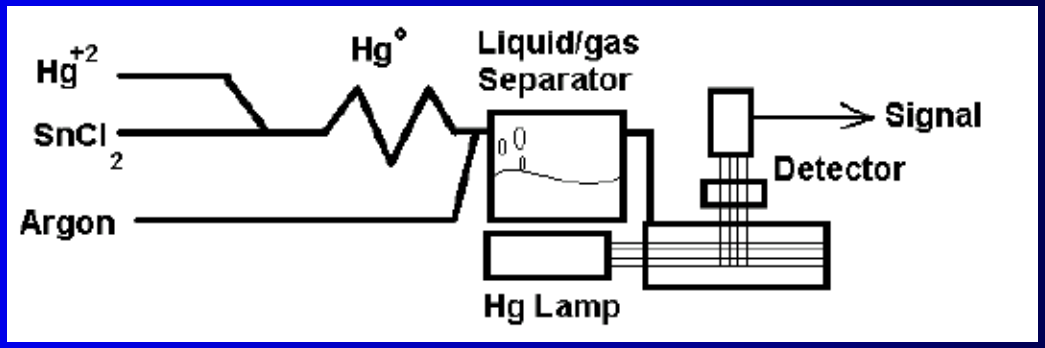


Techniques for Determination of Ultra-Trace Level Hg

- CVAAS:



- CVAFS:



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

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

Tekran Series 2600 CVAFS

EPA Method IO-5

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

Compendium Method IO-5

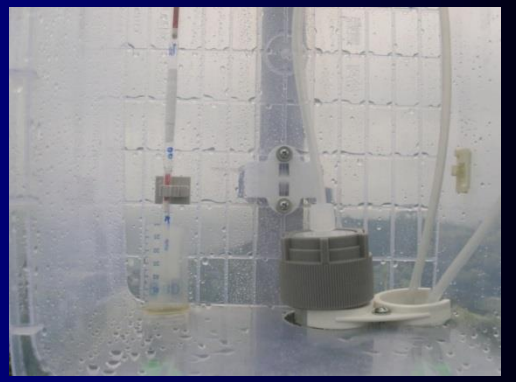
SAMPLING AND ANALYSIS FOR VAPOR AND PARTICLE PHASE MERCURY IN AMBIENT AIR UTILIZING COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY (CVAFS)

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

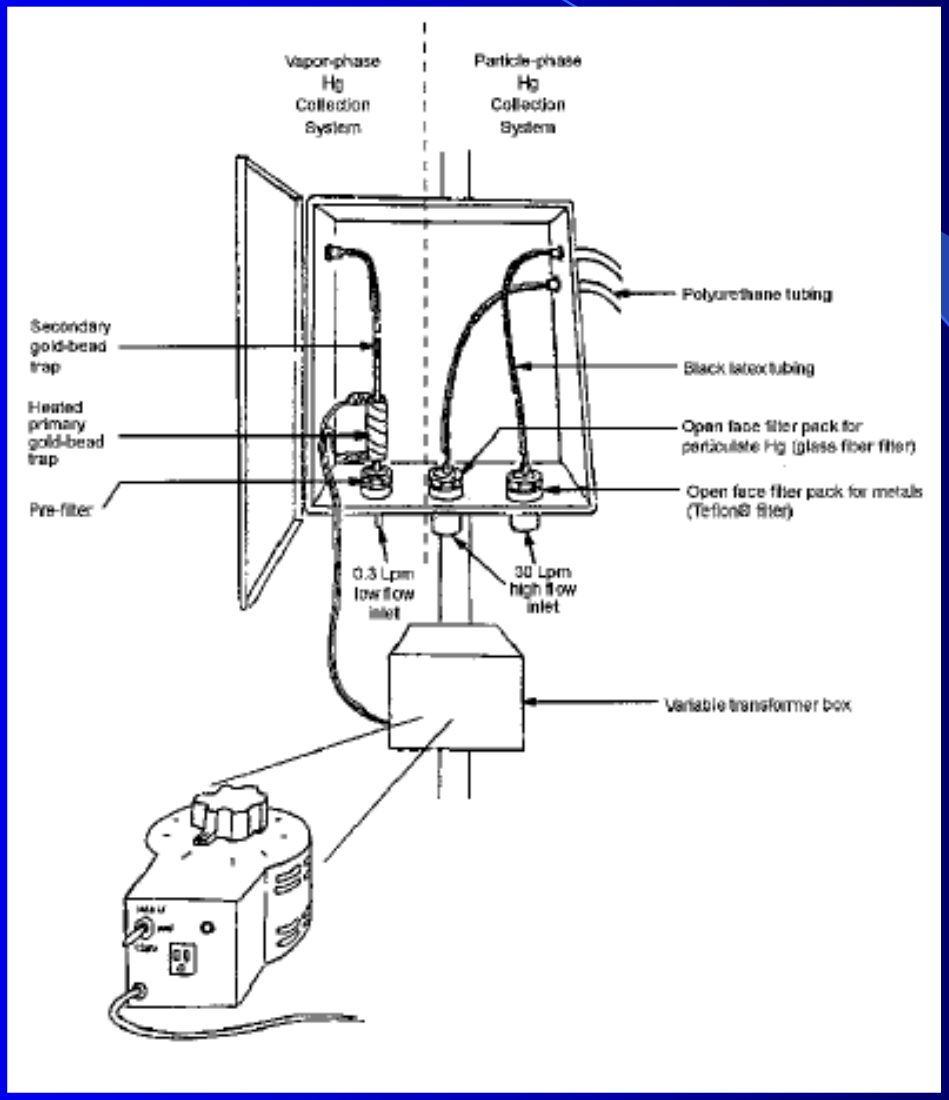
June 1999

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/m^3 for particulate Hg
  - 45 pg/m^3 for vapor-phase Hg

THANK YOU!

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