Strategies to Optimize the Determination of Mercury in Water by Cold Vapor Atomic Absorption & Fluorescence

David Pfeil
06 August 2014

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Where to Start?

- Is the analysis regulated?
  - Who regulates the analysis?
  - Are there specific methods that must be followed?
  - Which types of waters are included?
  - What concentration ranges are significant?
  - Which technologies are permitted or required?

Regulatory Agencies/ USA

- **USEPA/ Office of Water**
  - **Office of Ground Water and Drinking Water**
    - oversees implementation of the Safe Drinking Water Act.
  - **Office of Wastewater Management**
    - oversees a range of programs contributing to the well-being of the nation's waters and watersheds and supports the Federal Water Pollution Control Act, commonly known as the Clean Water Act
  - **Office of Wetlands, Oceans and Watersheds**
    - protects US marine and fresh water ecosystems, including watersheds, coastal ecosystems and wetlands. We regulate and monitor ocean dumping, manage dredged materials, and reduce marine debris. We protect water quality and habitats in 28 estuaries around the nation.
  - **Office of Science & Technology**
    - responsible for developing sound, scientifically defensible standards, criteria, advisories, guidelines and limitations under the Clean Water Act and the Safe Drinking Water Act.

Time to Decide

Drinking Water

- Legal driver: SDWA
- Technique: CVAAS
- Methods: 245.1 & 200.8

Wastewater Management

- Legal driver: CWA
- Technique: CVAFS & CVAAS
- Methods: 1631E,245.7, & 245.1

Let’s Start with Drinking Water

Analytical Methods and Laboratory Certification

Drinking Water

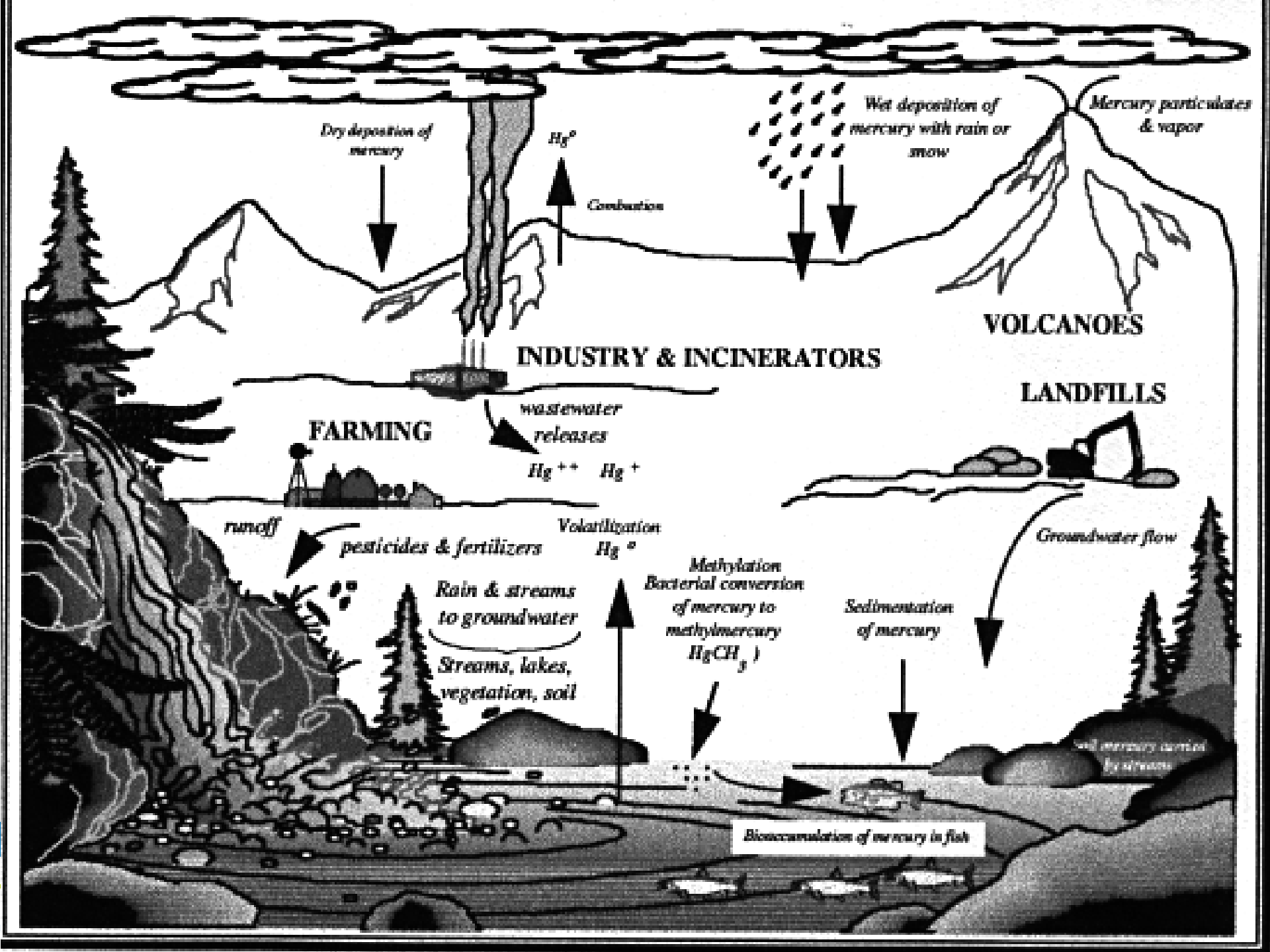
- Public water systems require periodic monitoring for the presence of specific contaminants, including mercury.

- Approved analytical methods must be used to meet federal monitoring requirements and to demonstrate compliance with drinking water regulations.

- Laboratories that analyze these compliance samples must be certified by EPA or the State.

Inorganic Mercury

- Maximum Contaminant Level (MCL) = 2 parts per billion (ppb)
- Maximum Contaminant Level Goal (MCLG) = 2 ppb
- Sources of Contamination
  Erosion of natural deposits; discharge from refineries and factories; runoff from landfills; runoff from croplands
- EPA regulates mercury in drinking water to protect public health. Mercury may cause health problems if present in public or private water supplies in amounts greater than the drinking water standard set by EPA.


Dry deposition of mercury
Hg°
Combustion
Wet deposition of mercury with rain or snow
Mercury particulates & vapor
VOLCANOES
INDUSTRY & INCINERATORS
LANDFILLS
FARMING
wastewater releases
Hg ++ Hg +
runoff
pesticides & fertilizers
Volatilization Hg °
Groundwater flow
Methylation Bacterial conversion of mercury to methylmercury HgCH3)
Rain & streams to groundwater
Streams, lakes, vegetation, soil
Sedimentation of mercury
Bioaccumulation of mercury in fish

40 CFR 141 National Primary Drinking Water Regulations

- §141.1 Applicability.
  - This part establishes primary drinking water regulations pursuant to section 1412 of the Public Health Service Act, as amended by the Safe Drinking Water Act (Pub. L. 93-523); and related regulations applicable to public water systems.

Contaminant	Methodology[13]	EPA	ASTM[3]	SM[4] (18th, 19th ed.)	SM[4] (20th ed.)	SM Online[22]	Other
16. Mercury	Manual, Cold Vapor	245.1[2]	D3223-97, 02	3112 B		3112 B-99	
	Automated, Cold Vapor	245.2[1]					
	ICP-Mass Spectrometry	200.8[2]					

Only two approved choices: CVAAS & ICP-MS

Method 245.1

Summary of Method

- A known portion of a water sample is transferred to a BOD bottle, equivalent ground glass stoppered flask or other suitable closed container.
- It is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for two hours at 95°C.
- Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

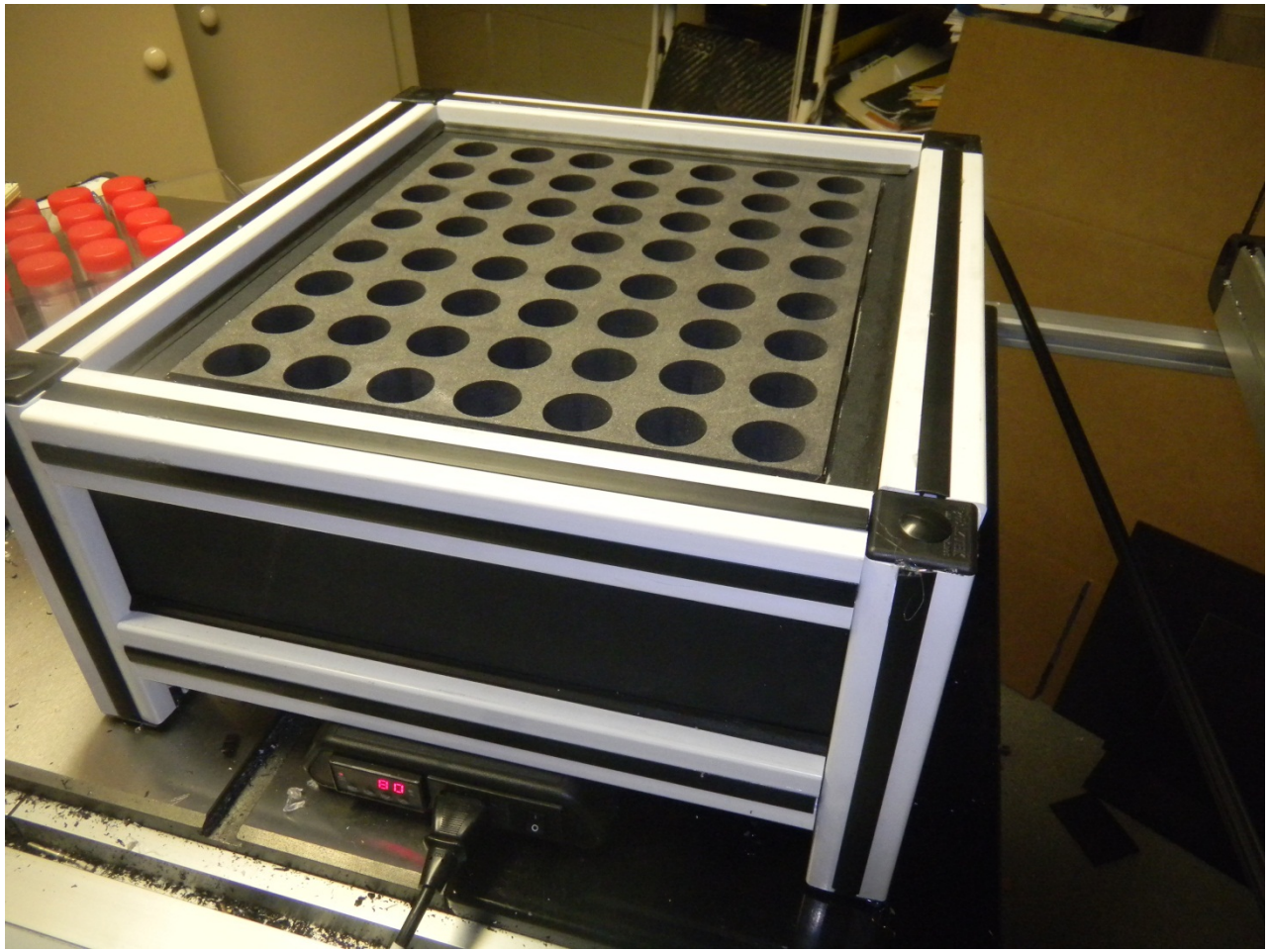
245.1

Sample Digestion Procedure

To 100mL of water (sample)

- Add 5mL H_2SO_4
- Add 2.5mL HNO
- Add 15mL $KMnO_4$ solution (5%)
- Shake & add more KMnO4 until purple color persists >15min
- Add 8mL $K_2S_2O_8$ solution
- Mix, cap and heat at 95ºC for two hours
- Cool to room temperature
- Add 6mL NaCl-$(NH_2OH)\cdot H_2SO_4$ solution to remove excess permanganate

Automated Hot Blocks



245.1
Analysis

Method 245.1 is a manual method although it practice it is almost always automated.

Three manual configurations are provided in the method:

1. Employs a valve to recirculate the carrier gas
2. Is a flow-through system with liquid scrubber
3. Is the same flow-through system with a carbon scrubber

Most labs replace the B.O.D. bottle with a gas/liquid separator and use a pump to introduce sample & reductant.

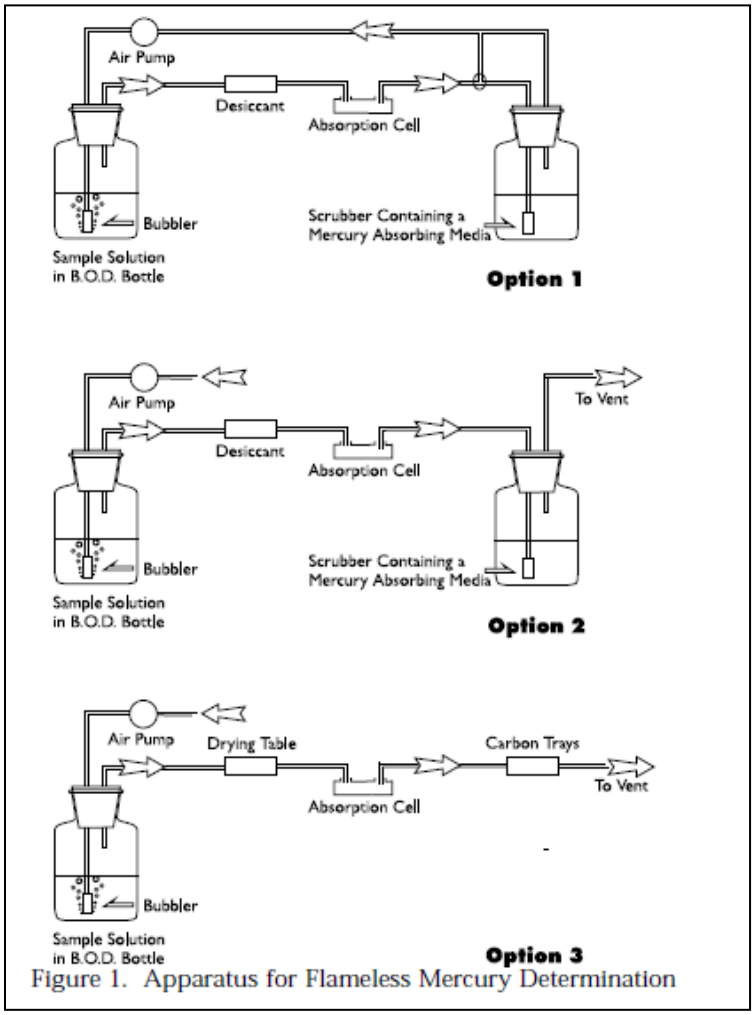
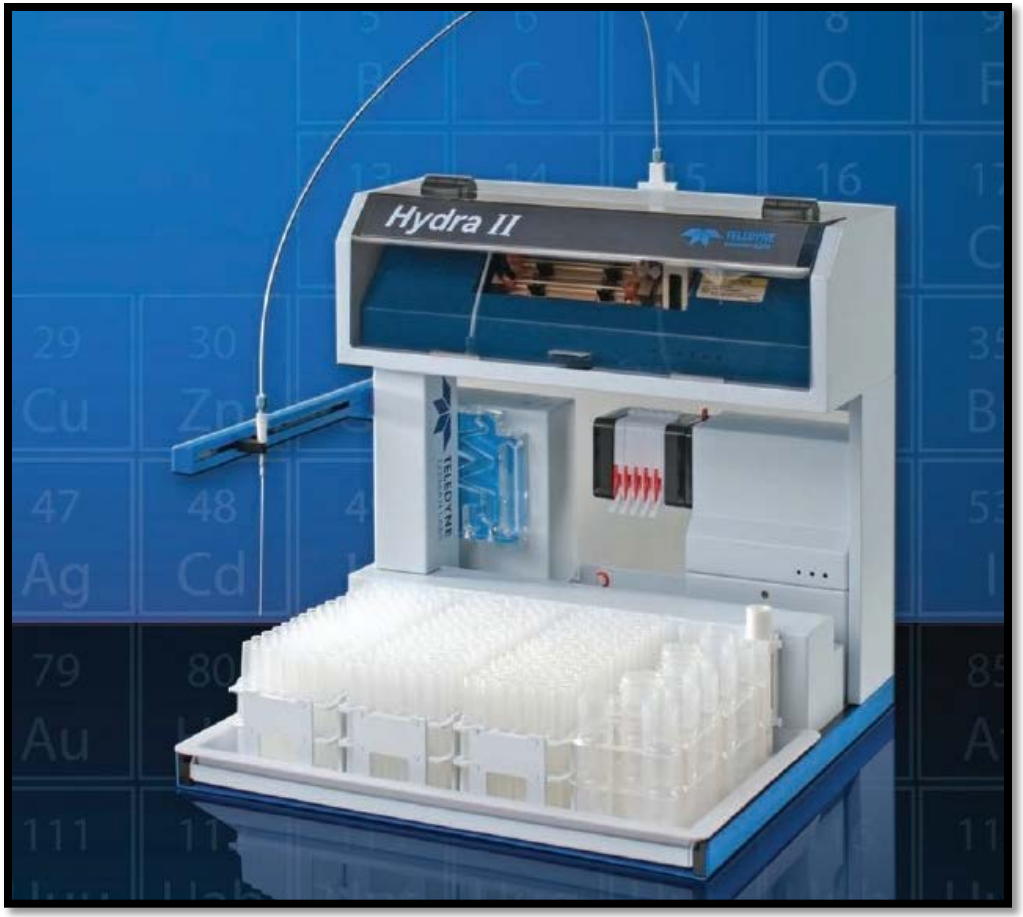


Figure 1. Apparatus for Flameless Mercury Determination

Automated Cold Vapor Atomic Absorption (CVAA)

- *Hydra II*$_{AA}$ Mercury Analyzer for the Determination of Mercury in Drinking Water by CVAA



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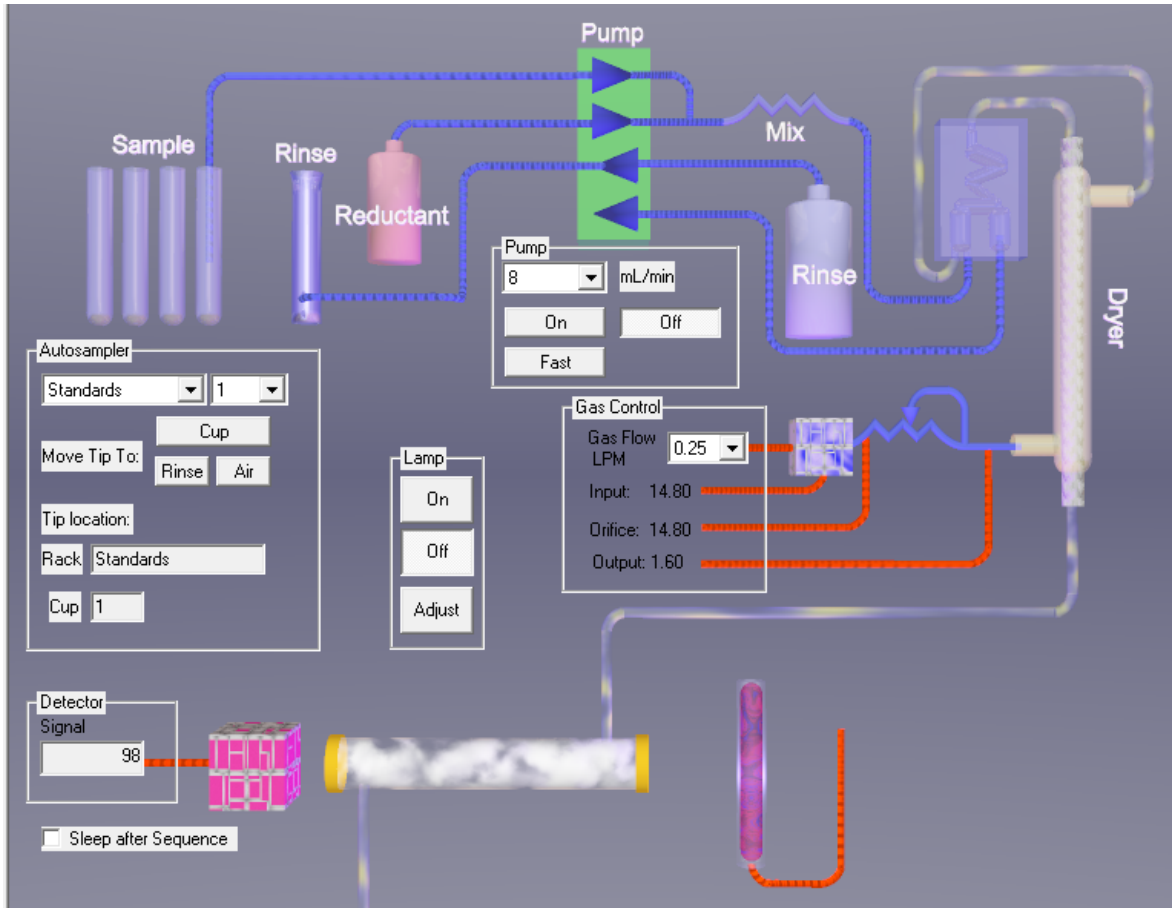
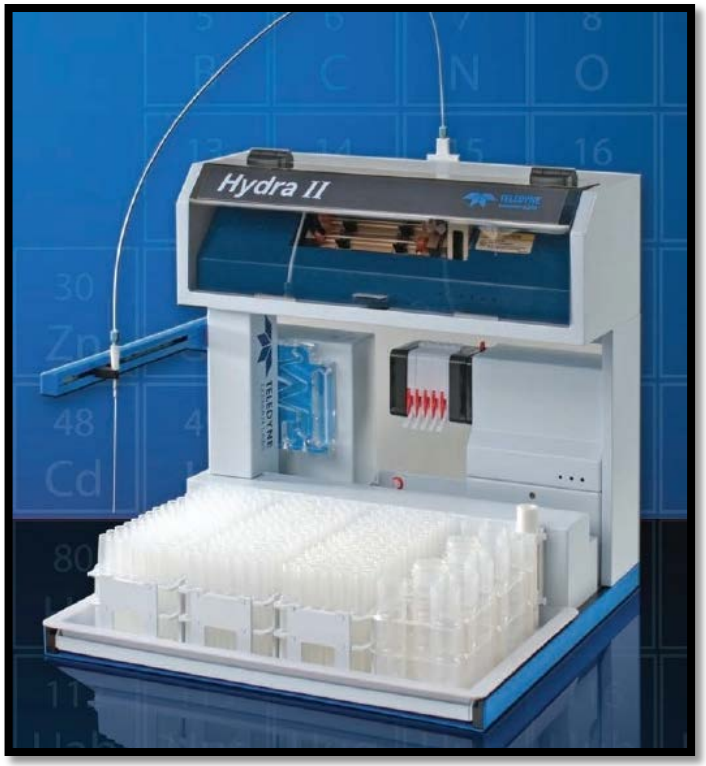
The Hydra II$_{AA}$ Automated Analyzer

- Standards, samples and rinse are mixed with stannous chloride and enter a gas/liquid separator.
- Gas bubbles through the liquid and carries mercury vapor through a dryer to an absorption cell while liquid is pumped to waste.



Benefits Provided with Hydra II$_{AA}$

- It's Fast
  - Results in as little as 1 minute per sample
- It's Sensitive
  - Detection limits are about 1 ppt (ng/L)
- It's Robust
  - The sipper filter eliminates particulates
  - The gas/liquid separator destroys bubbles
- It's Unique Over-range Protection
  - Quick recovery from contaminated samples
  - No costly downtime
- It's High Capacity Autosampler
  - Up to 270 samples
  - Large reservoirs for recurring QCs
  - Intelligent decision making



Short Analysis Cycle

- High sensitivity and high throughput
- Qualify for contracts with low report limit requirements that other systems are unable to meet.

Conditions:
Pump 10 mL/min
Gas 0.20 LPM
Rinse 25 secs.
Uptake 40 secs.
Integ. 3x2 secs

Total time 71 secs
Detection limit 1.1 ppt

About 1 minute/sample at best detection limit with 3 repeats

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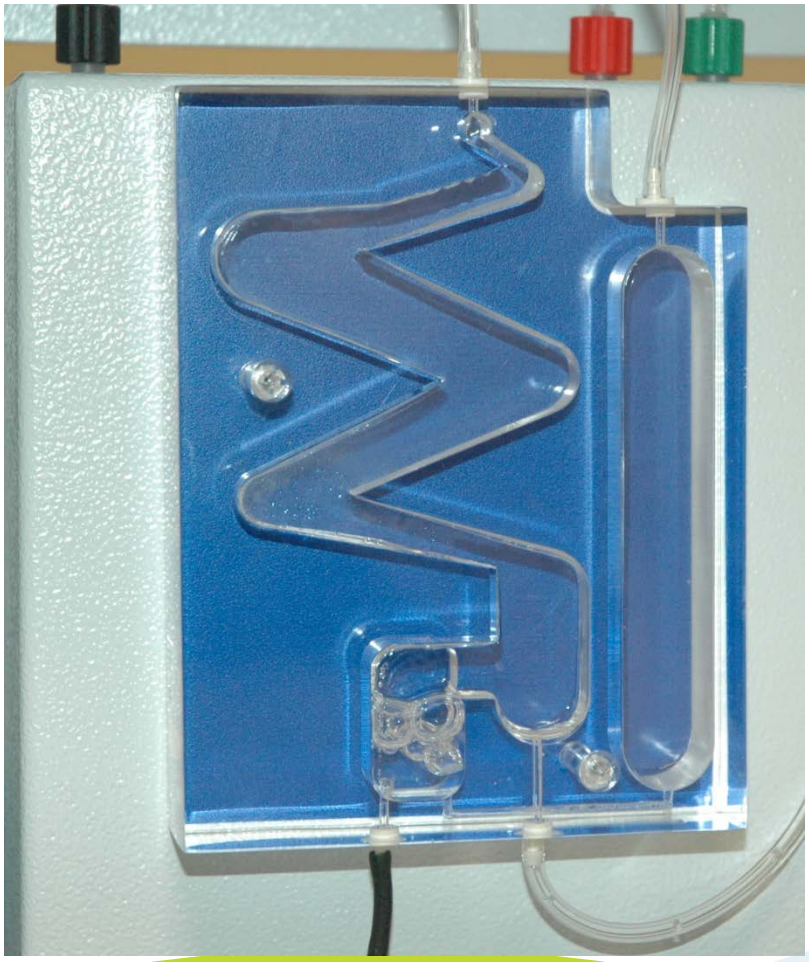
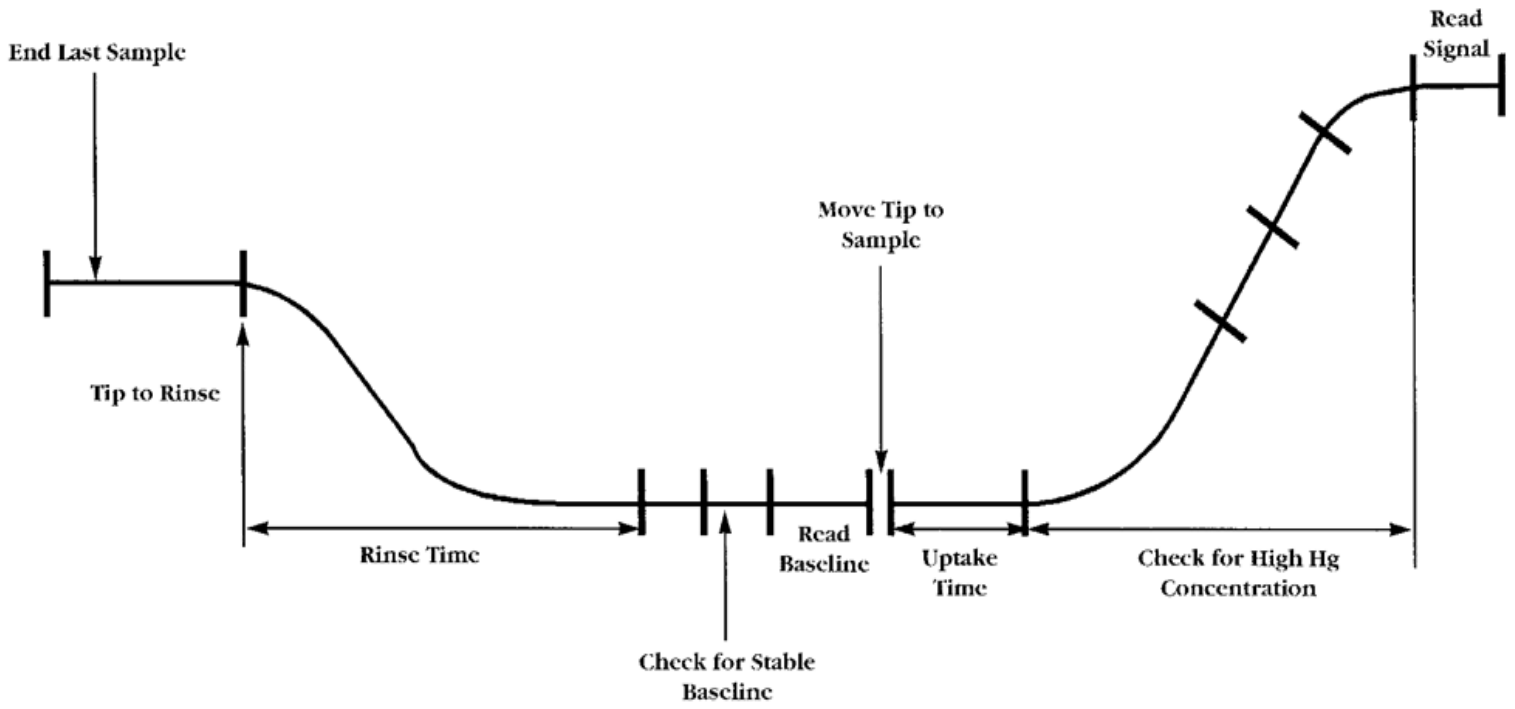
Process Tough Samples

- Foamy samples
  - Serpentine path breaks up bubbles
- Particulates & precipitate
  - Filter tip probe rejects solids
  - No narrow restrictions to clog
- Difficult to reduce
  - Long reaction time
  - Vigorous gas shearing action



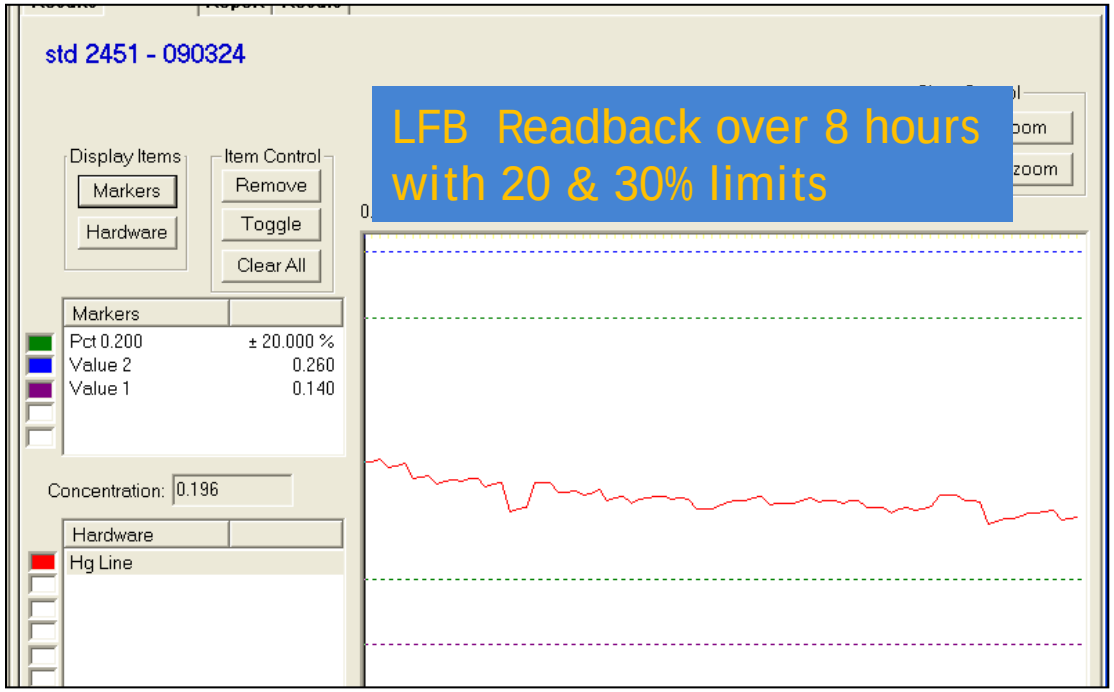
Baseline Correction and Over-Range Protection



- Integrates at the same time interval for consistency from sample to sample
- Verifies baseline between each sample

Stability

- Calibration Precision for Method 245.1
  - 0.2ppb repeated every 10 samples for 270 samples



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Let’s Look at Wastewater

Approved Methods

Wastewater

- Approved General-Purpose Methods
  - The analytical methods promulgated under the authority of Section 304(h) of the Clean Water Act are sometimes referred to as the "304(h)" or "Part 136" methods.
  - The methods measure chemical and biological pollutants in media, such as wastewater, ambient water, sediment, and biosolids (sewage sludge).
  - These various CWA methods are tested in a variety of labs and matrices. In addition to Part 136 methods, some approved methods are published or incorporated by reference at 40 CFR Parts 401-503, approved industry-specific methods.

Mercury Methods on the Approved List and Quantitation Limits

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology[58]	EPA[52]	Standard methods	ASTM	USGS/AOAC/Other
35. Mercury—Total,[4] mg/L	Cold vapor, Manual	245.1, Rev. 3.0 (1994)	3112 B-2009	D3223-02(07)	977.22,[3] I-3462-85.[2]
	Cold vapor, Automated	245.2 (Issued 1974)[1]			
	Cold vapor atomic fluorescence spectrometry (CVAFS)	245.7 Rev. 2.0 (2005)[17]			I-4464-01.[71]
	Purge and Trap CVAFS	1631E[43]			

Method	Quantitation Limit
245.1 and 245.2	>200ng/L
245.7	5ng/L
1631E	0.5ng/L

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Method 245.7 Approval

OFFICE OF WATER

signed: August 23, 2007

MEMORANDUM

SUBJECT: Analytical Methods for Mercury in National Pollutant Discharge Elimination System (NPDES) Permits

FROM: James A. Hanlon, Director
Office of Wastewater Management

TO: Water Division Directors, Regions 1 – 10

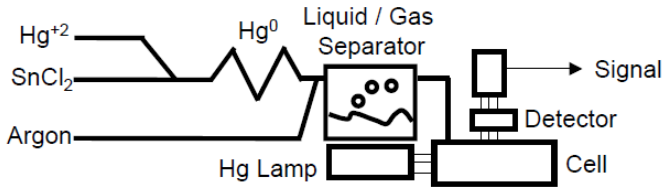
The purpose of this memorandum is to inform you of EPA's March 12, 2007, approval of Method 245.7 for measurement of mercury and modified versions of approved analytical methods for mercury as well as the impact of their approval on the NPDES permitting process. While several different methods are currently approved under 40 CFR Part 136 for the analysis of mercury, some of these methods have much greater sensitivities and lower quantitation levels than others. This memorandum clarifies and explains that, in light of existing regulatory requirements for NPDES permitting,[1] only the most sensitive methods such as Methods 1631E and 245.7 are appropriate in most instances for use in deciding whether to set a permit limitation for mercury and for sampling and analysis of mercury pursuant to the monitoring requirements within a permit.

Similarities in the Fluorescence Methods

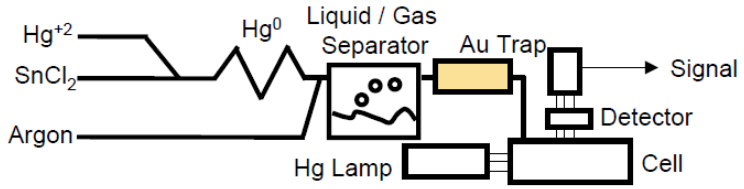
- Same Clean Hands/Dirty Hands sampling procedure
- Similar preservation requirements
- Similar digestion reagents
- Same Calibration Algorithm
- Similar analytical instrumentation
  - The difference is use of a gold amalgamator in 1631E only

Mercury Analyzers

Method 245.7 : Leeman Labs, Hydra AF



Method 1631 : Leeman Labs, Hydra AF Gold



As implemented on Leeman Labs Inc. (Hudson, N.H.) Hydra mercury systems.

Mercury - Water Quality Criteria

Criterion	NTR (ng/L)	Great Lakes (ng/L)
Freshwater Acute	2400	1440
Freshwater Chronic	12	770
Marine Acute	2100	-
Marine Chronic	25	-
Human Health	140	1.8
Wildlife	-	1.3

Circled values require CVAFS
Values in red require Method 1631.

POTW Monitoring Strategy

This DRAFT is being circulated for comment. Comments are due no later than June 15, 2005. Please send comments to the email address or physical address shown below.

DRAFT

May 9, 2005

POTW MERCURY CONTROL STRATEGY

Addendum to the Region 8 Strategy for the Development of Local Limits
U.S. EPA Region 8, Industrial Pretreatment Program

The POTW should carefully evaluate whether a MDL of <0.2 ug/L is adequate. More POTWs are realizing that they must use Method 1631 (currently approved under 40 CFR Part 136) or Method 245.7 (expected to be approved) for mercury analyses. Failure to use these more sensitive methods may result in significant re-sampling requirements to obtain a definitive value for mercury.

Draft Document – EPA Region 8 cam Industrial Pretreatment Program 4/28/05

Mercury Methods and Source Characterization [8] [16] [17] [19] [20] [21]

Source	Typical Concentration	Method Options
POTW wastewater influent	21 - 500 ng/L	1631 (dilution) 1631 modified (245.7)
POTW wastewater effluent	1 – 51 ng/L	1631
POTW sludge or biosolids	0.2 – 30 mg/Kg (dry weight) – Generally on the lower end	SW846: 7471B
POTW Collection System	50 - 1000 ng/L	1631 (dilution) 1631 modified (245.7) 1631 modified (CVAAS) 245.1 (optimized & dedicated instrument)
Industrial Effluent - SIUs	138 ng/L	1631 1631 modified (245.7) 1631 modified (CVAAS)
Commercial Effluent	489 ng/L	1631 modified (245.7) 1631 modified (CVAAS) 1631 (dilution) 245.1
Residential	38 ng/L	1631 1631 modified (245.7) 1631 modified (CVAAS)
Trucked and Hauled Waste	3057 ng/L	1631 (dilution) 1631 modified (245.7) 1631 modified (CVAAS) 245.1 (optimized & dedicated instrument)
Surface Water	0.2 - 10 ng/L	1631
Dental office discharge (without separator treatment and no dilution by sanitary wastewater)	episodic discharges ranging to > 5,000,000 ng/L	245.1 1631 modified (CVAAS) 1631 modified (245.7)

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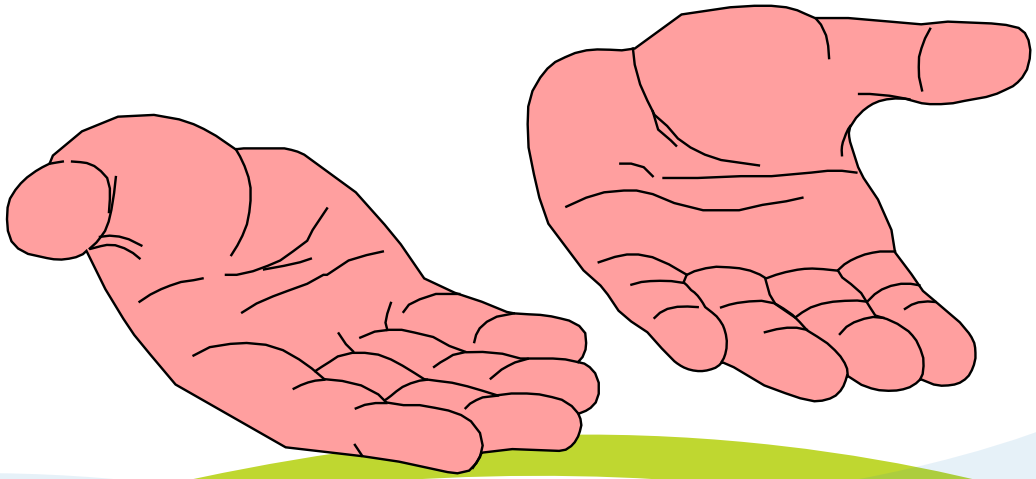
1669 Summary

- **Fluoropolymer or borosilicate glass bottle**
- **Double bagged bottle**
- ***Dirty Hands***
  - **operation of machinery, sampler preparation, outside bag handling**
- ***Clean Hands***
  - **inside bag handling**
  - **sample bottle**
  - **sample transfer**



Controlling Contamination

You will need to plan any place that samples will be prepared and an analyzer used to conduct Method 1631E.

- Method 245.1 Detection limit = 200 ppt
- Method 1631E Highest standard = 100 ppt
  Detection limit = 0.2 ppt
- Method 245.7 Detection limit = 2.0 ppt

Is a Class 100 Clean Room necessary?

Probably Not; But Contamination Sources Must Be Controlled

Reagents

Water

HCl

KBr

$KBr0_3$

$SnCl_2$

NH_2OH HCl

Ar

Analyst

gloves

lab coat

dental work

Environment

air - vapor/particulates

thermometer, manometer, barometer

bench top

ventilation hood

Equipment

sample bottle

hoses & tubes

gas supply line

autosampler vial

gas/liquid separator

pipette tips

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Mercury Enclosure

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Sparging Process

- Teflon tube extension
- Gas flow: ~5 LPM
- Time: >30 min

Water Sources

Source	Counts
Default de-ionized water	49,105
Filtered de-ionized water	6,300
Tap water	20,951

Waters run as samples with sparged reductant and rinse solutions.

The filter used to clean the de-ionized water at the spigot was a Barnstead International Ultrapure filter (part number D8911). They are available from Thermo Fisher Scientific amongst others and cost about $40.00 each.

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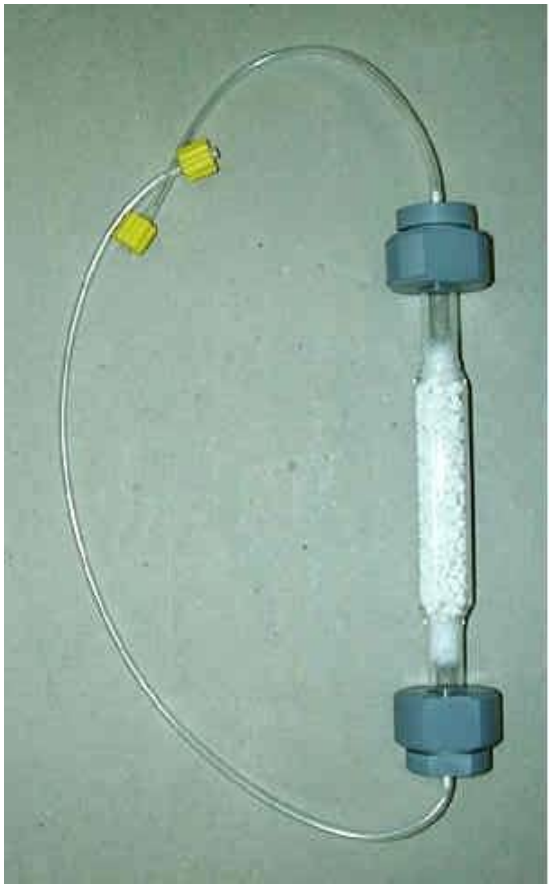
2-Stage Drying
The Soda Lime Dryer

- Contains:
  - Calcium oxide
  - Sodium hydroxide (5-20%)
  - Water (6-18%)
- Demonstrated superior liquid phase removal



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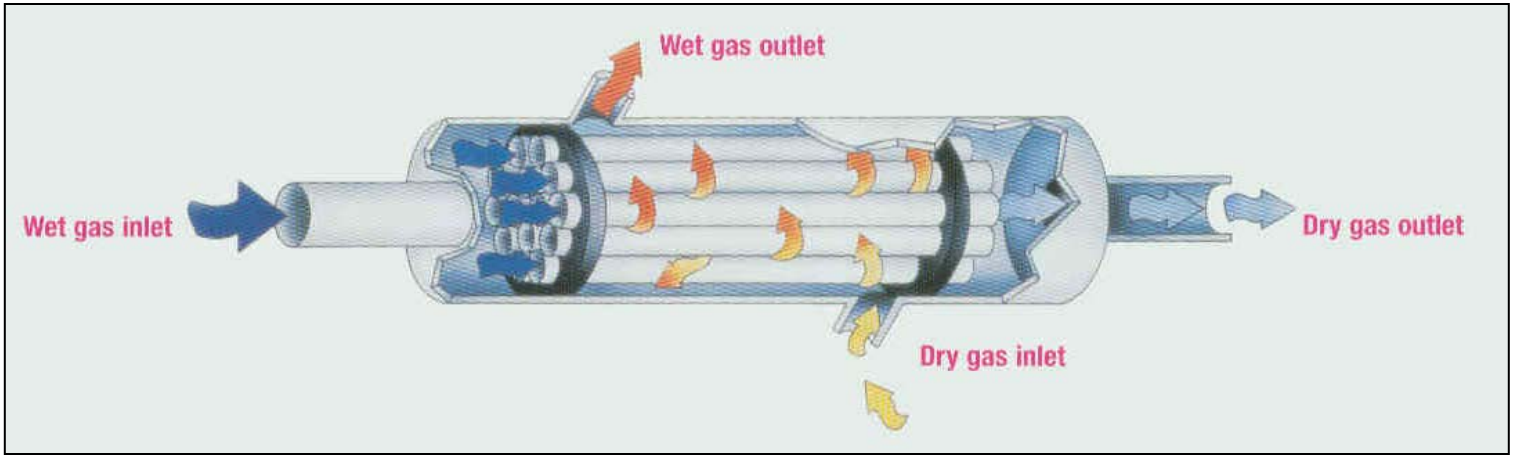
2-Stage Drying
Nafion Dryers

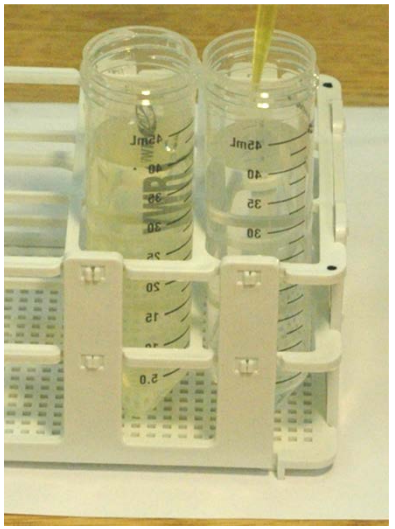
Counter-current gas flow design



Available in various lengths, materials, and shapes

1631 Summary

- BrCl Oxidizer / Preservative
- $NH_2OH \cdot HCl$ prereduction for free Br & Cl
- $SnCl_2$ reduction of Hg^{2+} to Hg^0
- Purge Hg^0 from water with Ar or N_2
- Trap Hg^0 on Au coated sand
- Thermally desorb Hg^0 into Ar stream
- Cold vapor atomic fluorescence spectrometry



Calibration Factor Algorithm

Conc ng/L	Peak area	Blk subtracted area	Cal Factor	Calc conc ng/L	%R	QC check
0	28266	avg blk		0.20		<0.5
0	28901	28584		0.21		<0.5
0.5	110243	81660	163319	0.59	118%	100+/-25%
1	167870	139287	139287	1.01	101%	
2	287869	259286	129643	1.88	94%	
5	663325	634742	126948	4.60	92%	
10	1389643	1361060	136106	9.86	99%	
20	2685733	2657150	132857	19.25	96%	
		avg CF	138027			
		%RSD	10%			<15%

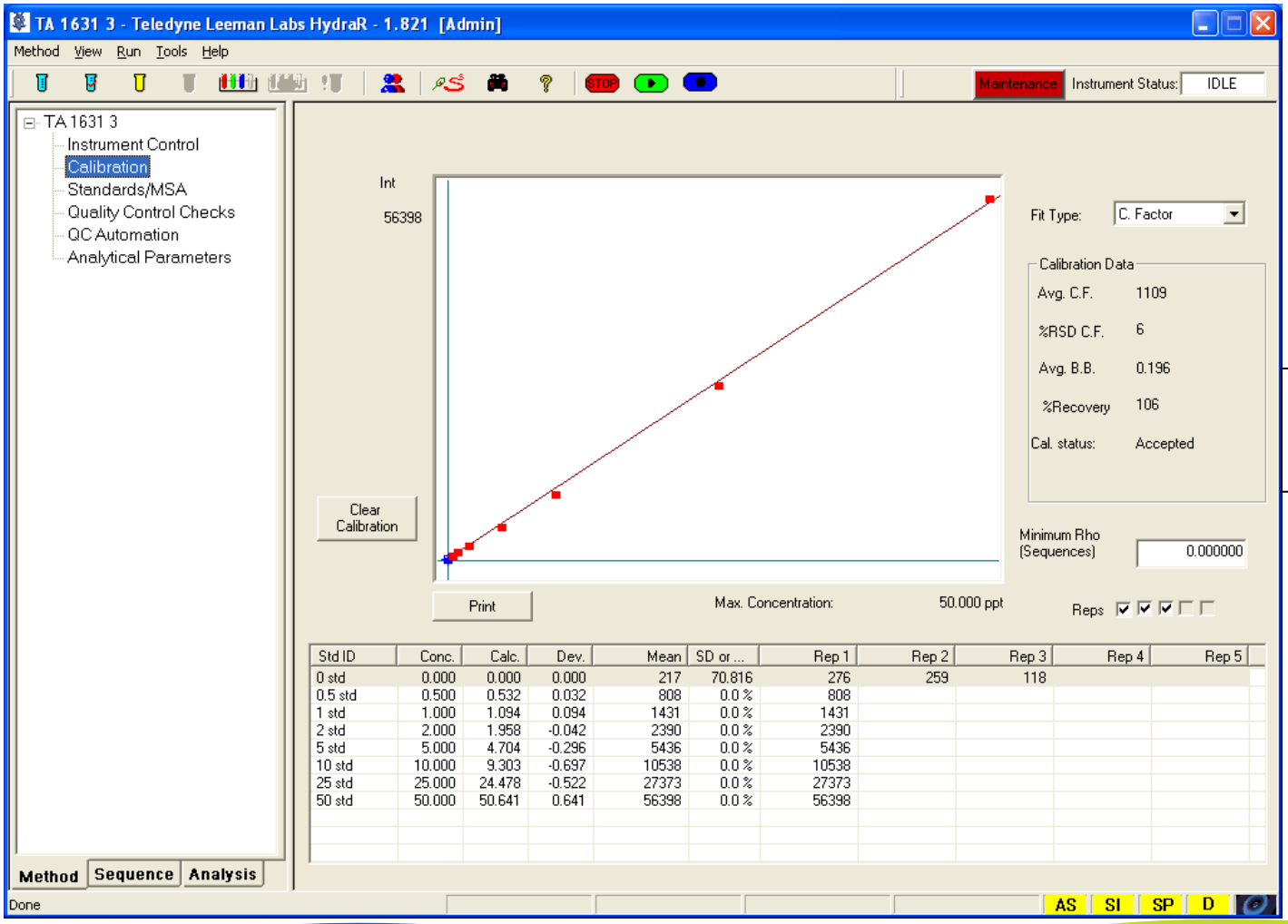
Calibration Checks

System blank

0.5ppt %Rec.

CF %RSD

Calibration Factor



Acceptance Criteria

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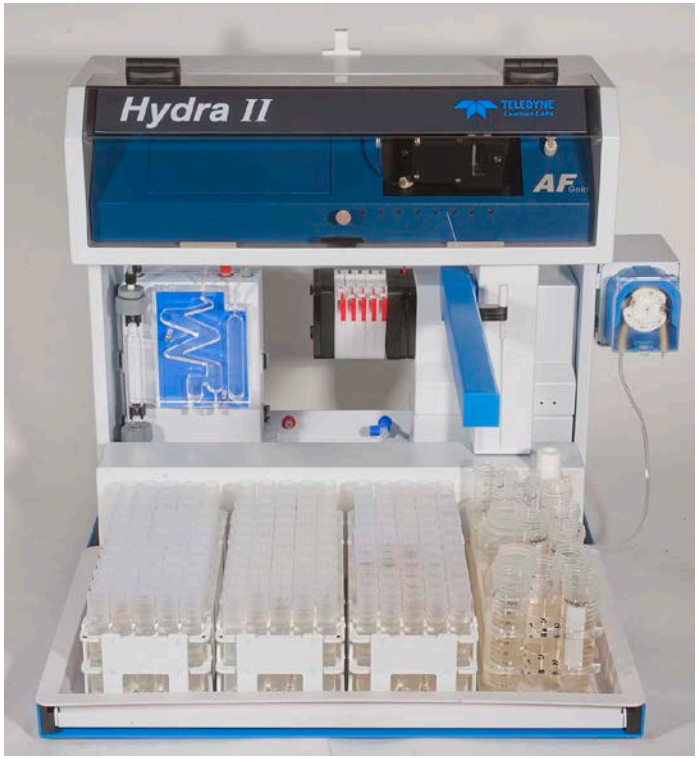
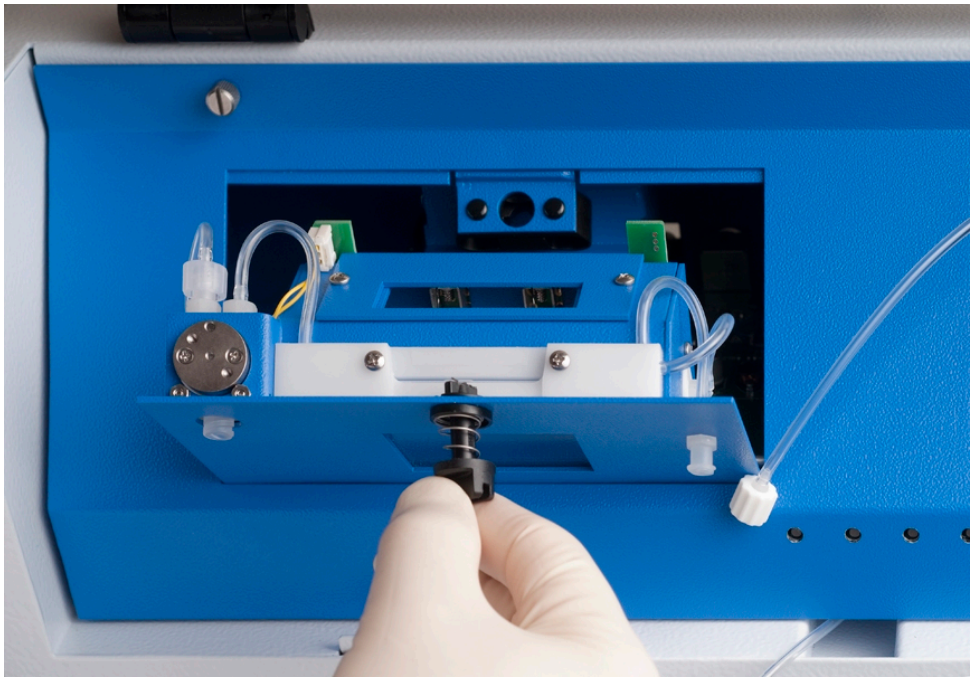
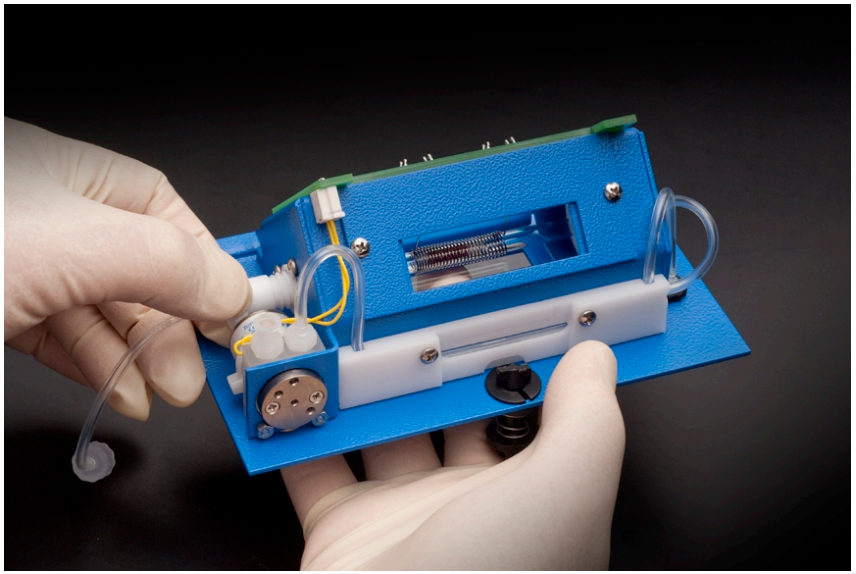
The Hydra II AF and the Hydra II AFGold



Easy Access Gold Trap

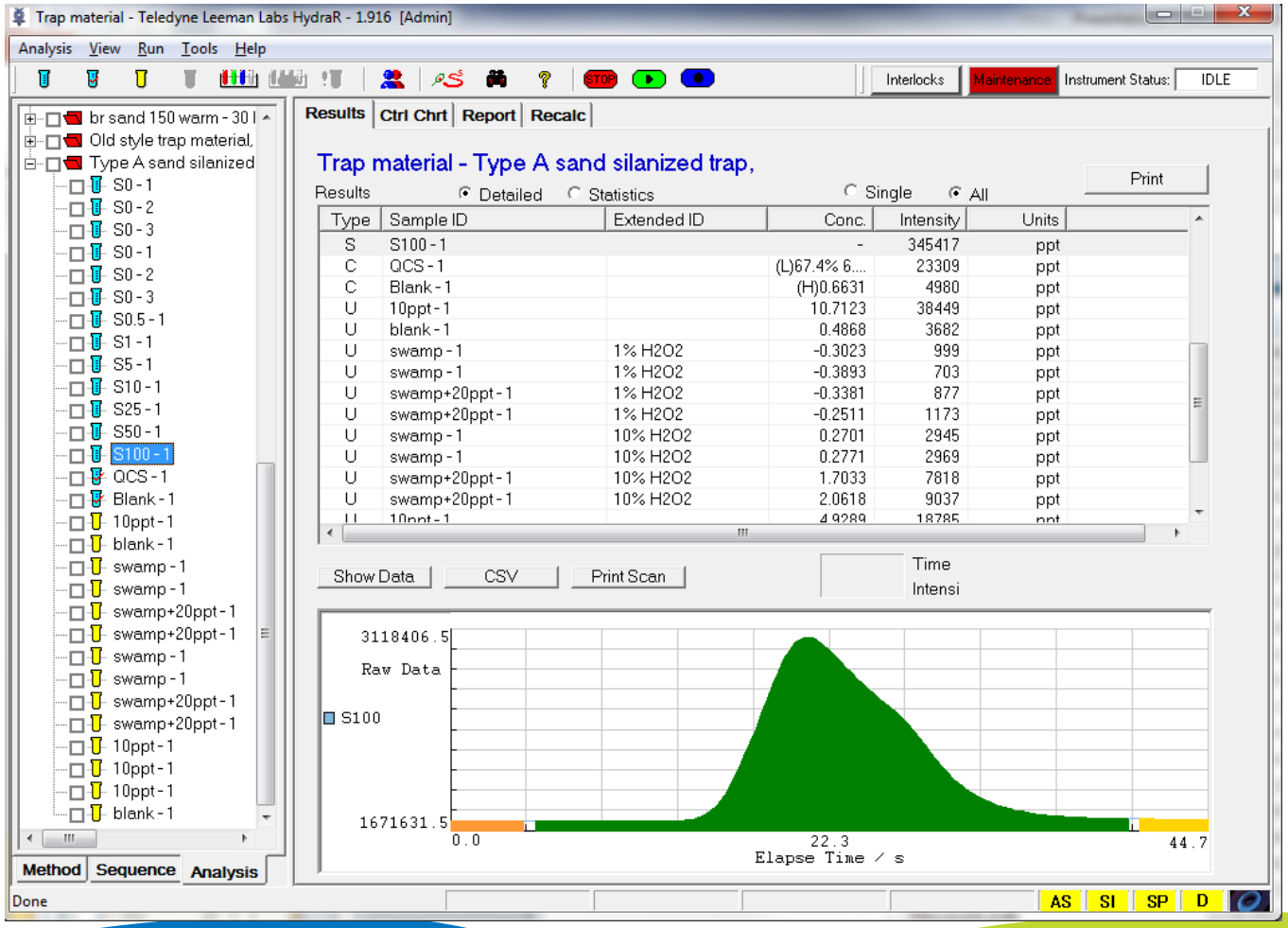


Quarter turn opens compartment



Trap assembly lifts off for access to gold trap

Typical Signals AF Gold



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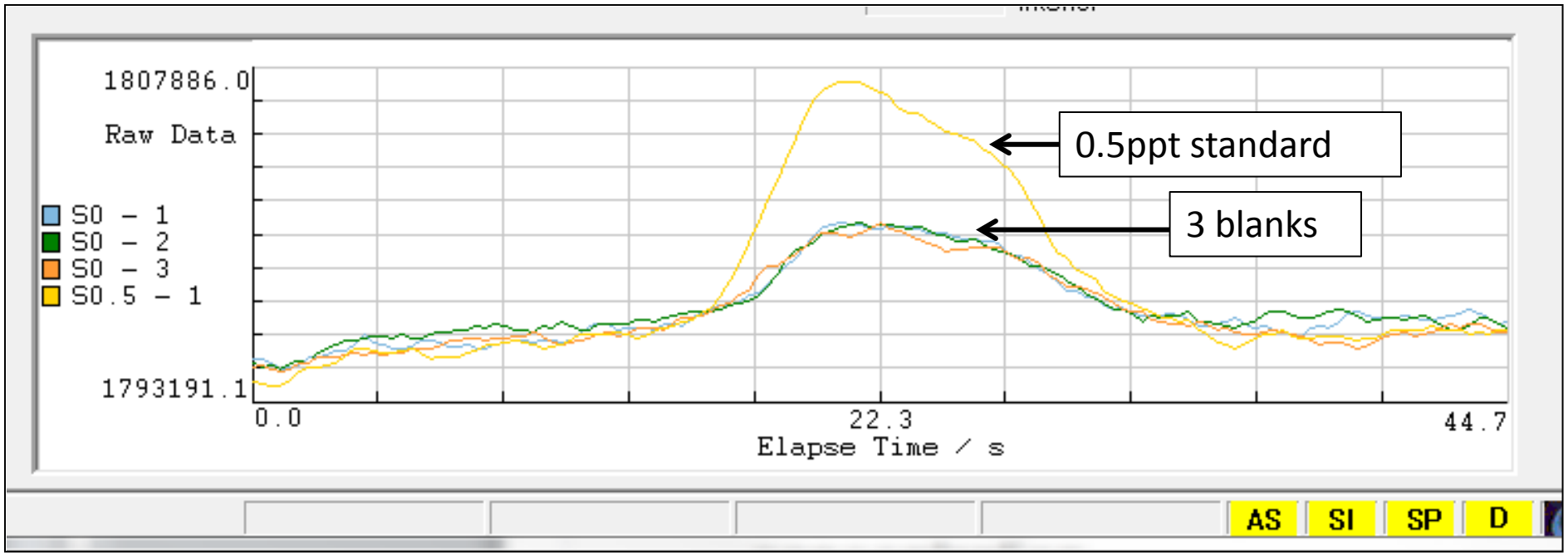
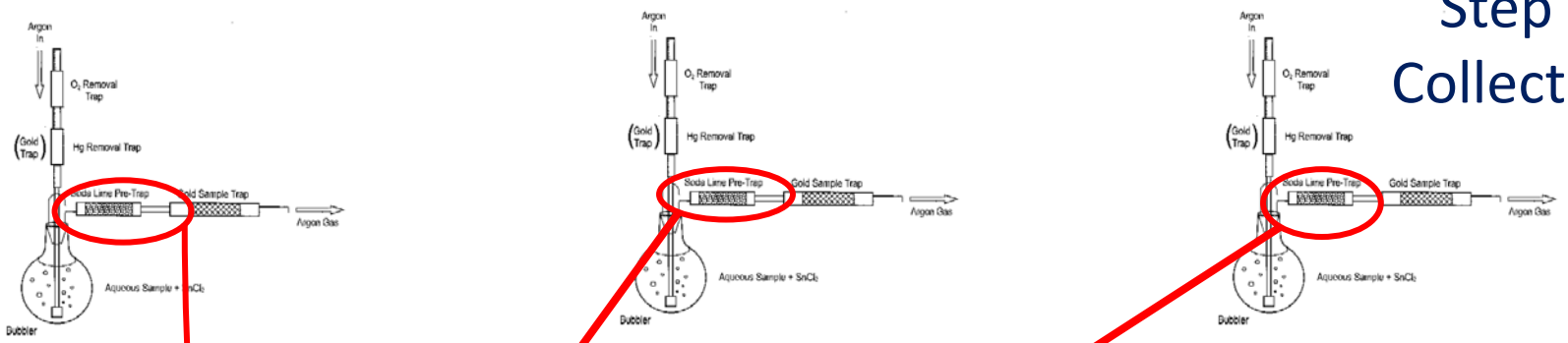
Sensitivity & Precision



Blanks apparent concentrations are less than 0.5ppt and show good reproducibility.

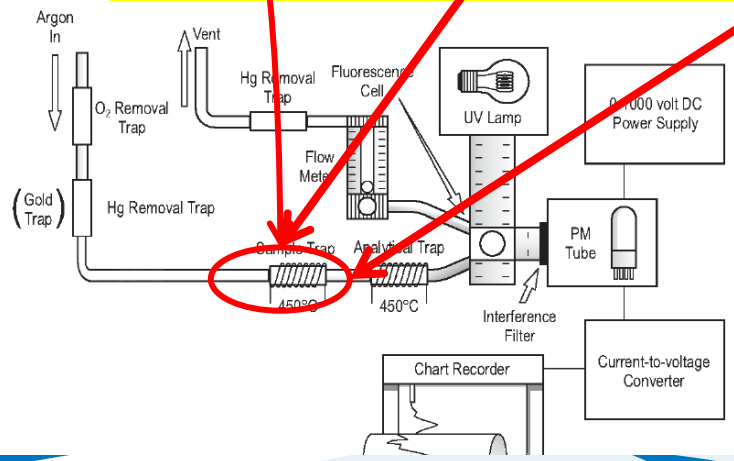
One or Two Traps?



Step 1
Collection

Sample 1 Sample 2 Sample 3

Multiple collection stations used different traps



Step 2
Analysis

USEPA Method 1631B

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117-00106 1631 Compliance Assistance

- 117-00106 On-Site Technical Assistance for Method 1631 Certification
- Two days of on-site training and evaluation by a qualified analytical chemist wherein we will demonstrate the operation and assist your laboratory personnel in the subtleties of meeting the requirements of EPA Method 1631. Includes site evaluation and recommendations.
- A specialist will co-ordinate the visit with the arrival of a pretested kit containing calibration standards and reagents in glass containers so that on-site exposure is minimized. A set of pre-cleaned glass bottles and standard cups will also be provided, as well as a tool for purging reagents.

Benefits of the Hydra II AFGold

- **Complies with Method 1631E**
  - Tough QC requirements have no flexibility
- **Speed**
  - 3-5 min/sample with amalgamation
  - 1-2 min/sample without amalgamation
- **Service Options**
  - Fast, low-cost modular replacements
  - On-site service option
- **Compliance Assistance**
  - On-site technical support available
    - Part #117-00106 @$4870.00
- **Pre-screening**
  - High concentration samples can wreak havoc on others
- Adaptive Technology
  - Convert to CVAAS

Instrumentation for EPA Water Methods

Method	Technique	Configuration	Water Type
245.1 & 245.2	CVAAS	Hydra II_{AA}	All >200ppt
245.7	CVAFS	Hydra II_{AF}	Wastewaters >5ppt
1631E	CVAFS/amalgam	Hydra II_{AFGold}	All Wastewaters

Hydra II_{AA}

Hydra II_{AF}

Hydra II_{AFGold}

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Combination Systems

- Hydra II AA
  - Add AF transition kit PN 125-00173-1
  - Add AFGold transition kit PN 125-00173-2

Questions?