Low Level Mercury Workshop
Jacksonville, Florida

Satisfying Certification Requirements of EPA Method 1631: One Experience in Certification

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Denise D. Stalvey, Oxford Analytical
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What's coming in this presentation?

- How mercury criteria got so low
- Method 1631 Background
- Instrumentation
- One experience in state certification
- Contributions from other labs

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Where Are We?

- **1987 Clean Water Act**
  - States must implement water quality-based control strategies to ensure water quality is attained
  - Water quality controls reflect *water quality standards* designated by each state
    - Designated use(s) of water body or segment
    - WQC necessary to protect designated use(s)
    - Anti-degradation policy
- **1987 Great Lakes Initiative**
  - Joint EPA and Environment Canada agreement
  - Calls for virtual elimination of mercury while providing incentives and options for cost-effective implementation that consider mercury sources
- **National Toxics Rule**
  - Established numeric WQC for toxic pollutants
  - Brought non-compliant States into compliance with 1987 amendments to CWA Section 303(c)(2)(B)

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 below approved methodology contract required detection limit.

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EPA Method1631

- Developed by Nicholas Bloom at Frontier Geoscience labs
- Currently released in revision E
  - **Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry**
    August 2002.
  - **Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury (40 CFR part 136)**
  - **Method 1669: Sampling Ambient Water for Trace Metals at EPA**
    Water Quality Criteria Levels
    July 1996

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1631 Summary

- BrCl Oxidizer / Preservative
- NH_2OH 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 spectrometer

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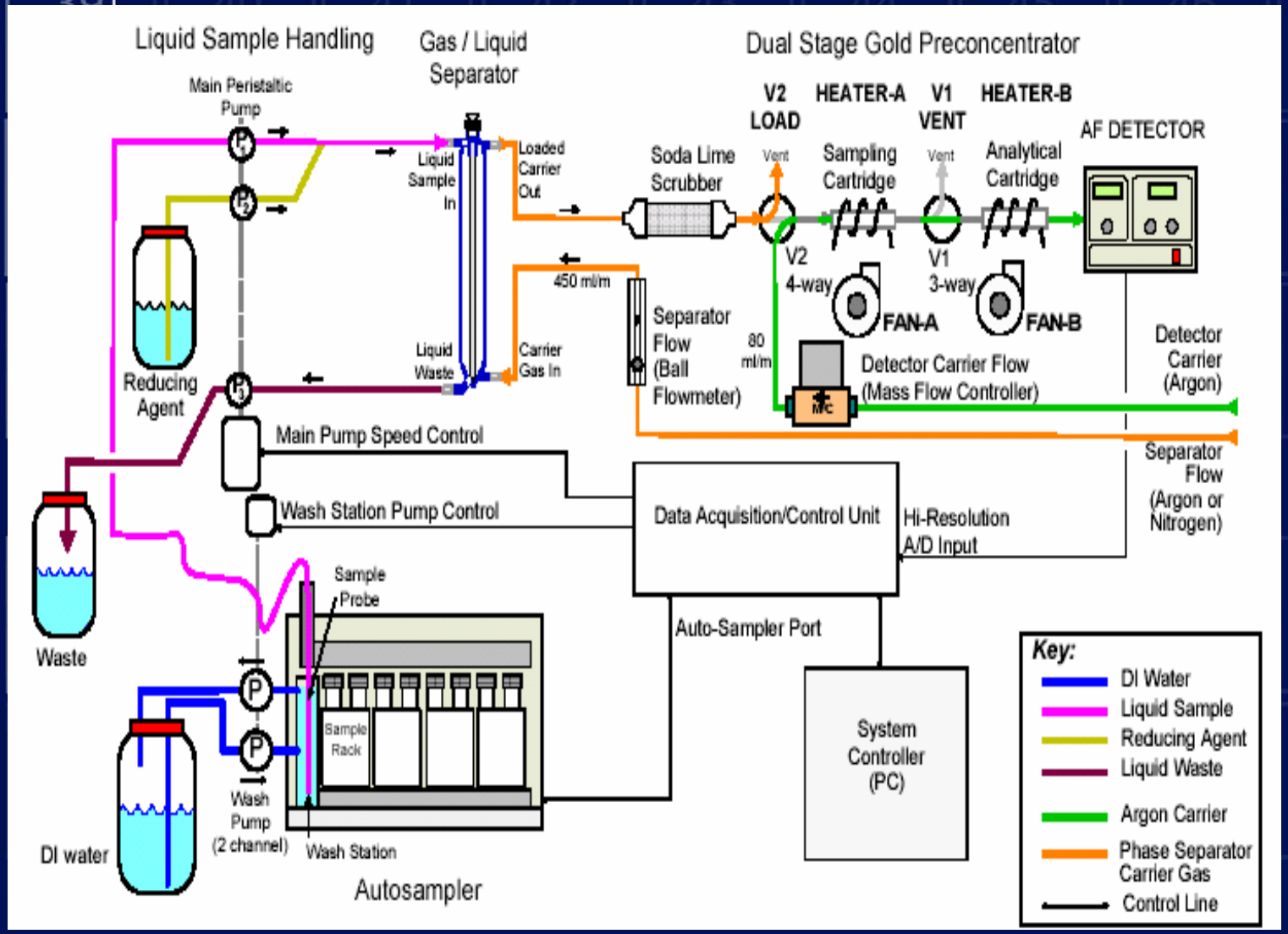
1631E Flow Injection Schematic



Hydra AF *gold plus*
Automated Fluorescence Hg Analyzer

Designed to meet the demands of EPA Methods 1631 and 245.7

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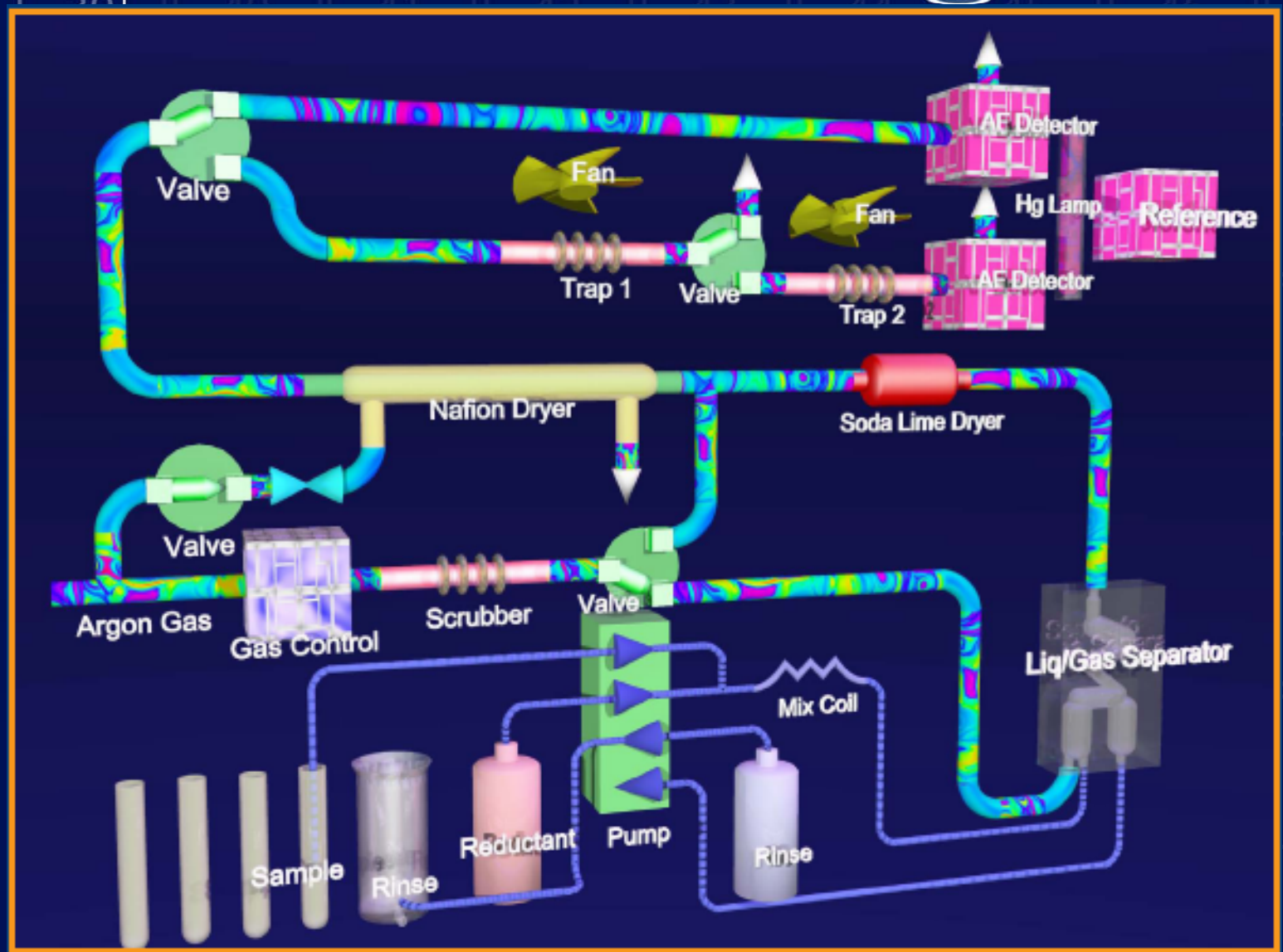
Schematic for Hydra AF Gold*plus*



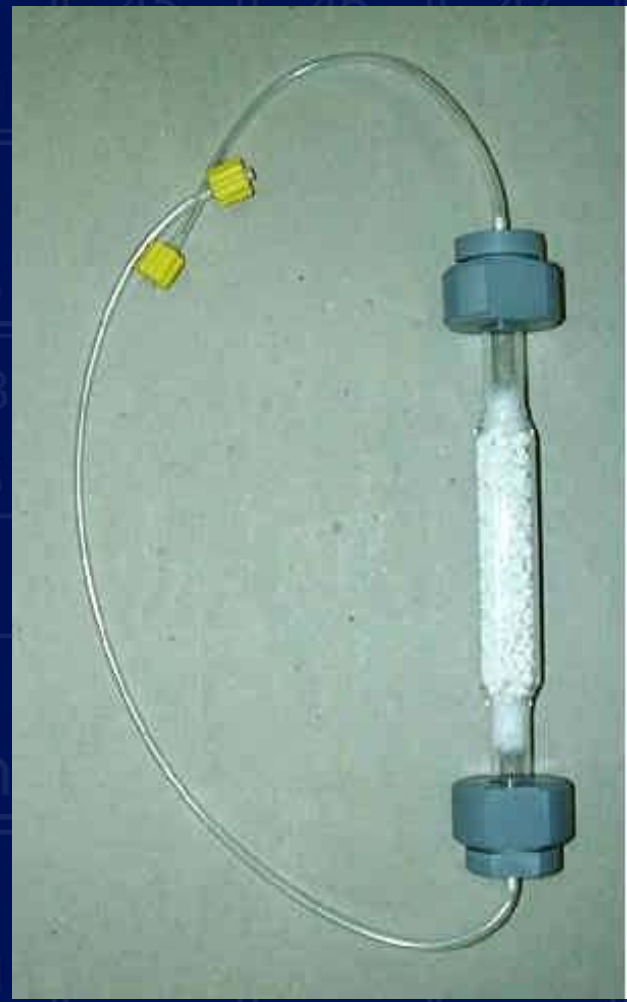
2-stage Drying

2 Detectors

Prescreen capability

Soda Lime Dryer

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



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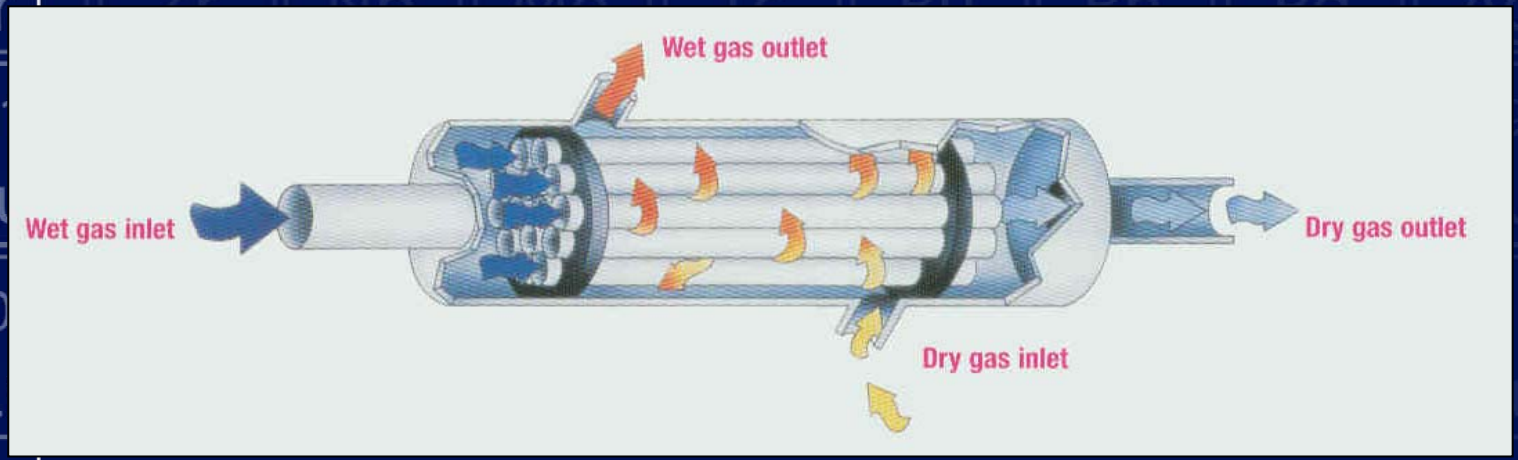
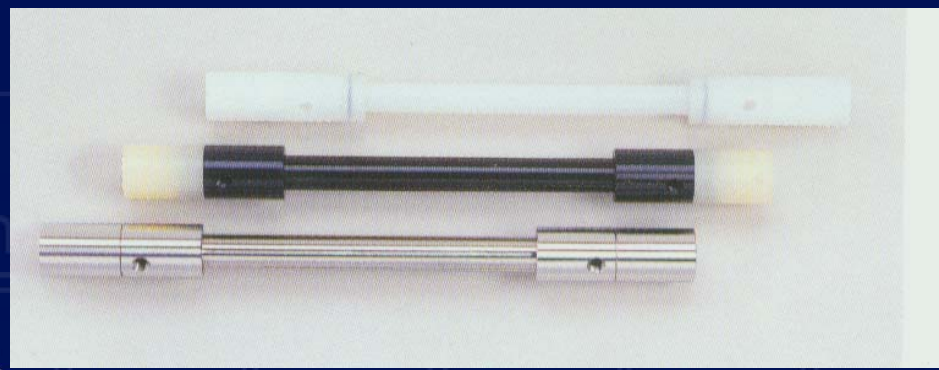
Nafion Dryers

Counter-current gas flow design



Available in various lengths, materials, and shapes



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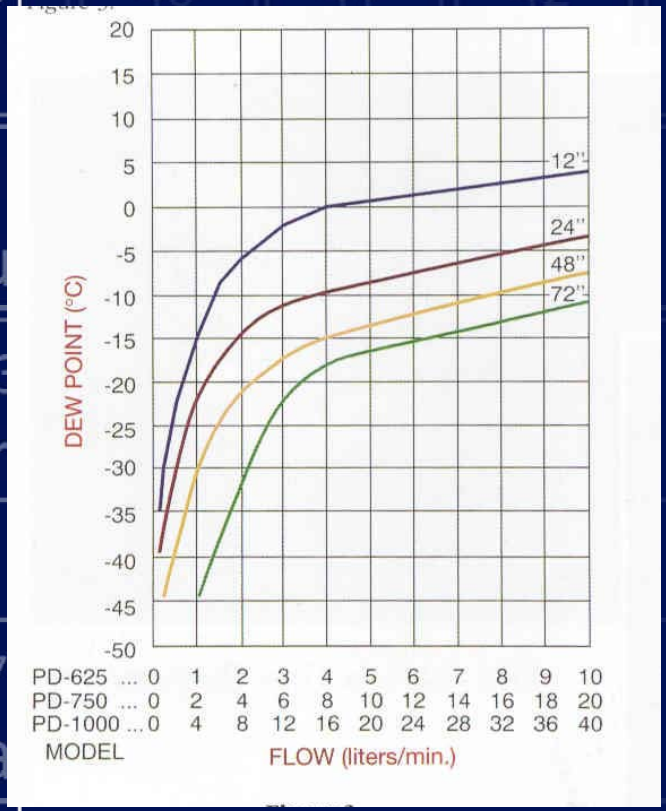
Nafion™ Performance



- No moving parts
- No required maintenance
- Dew points as low as -45°C (75ppm H_2O)

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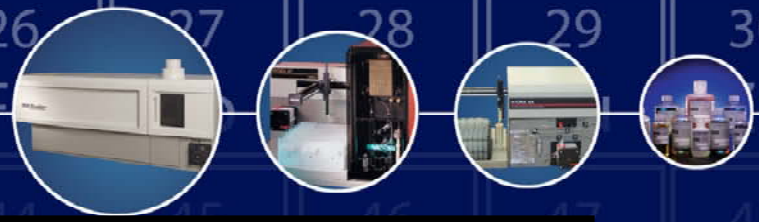
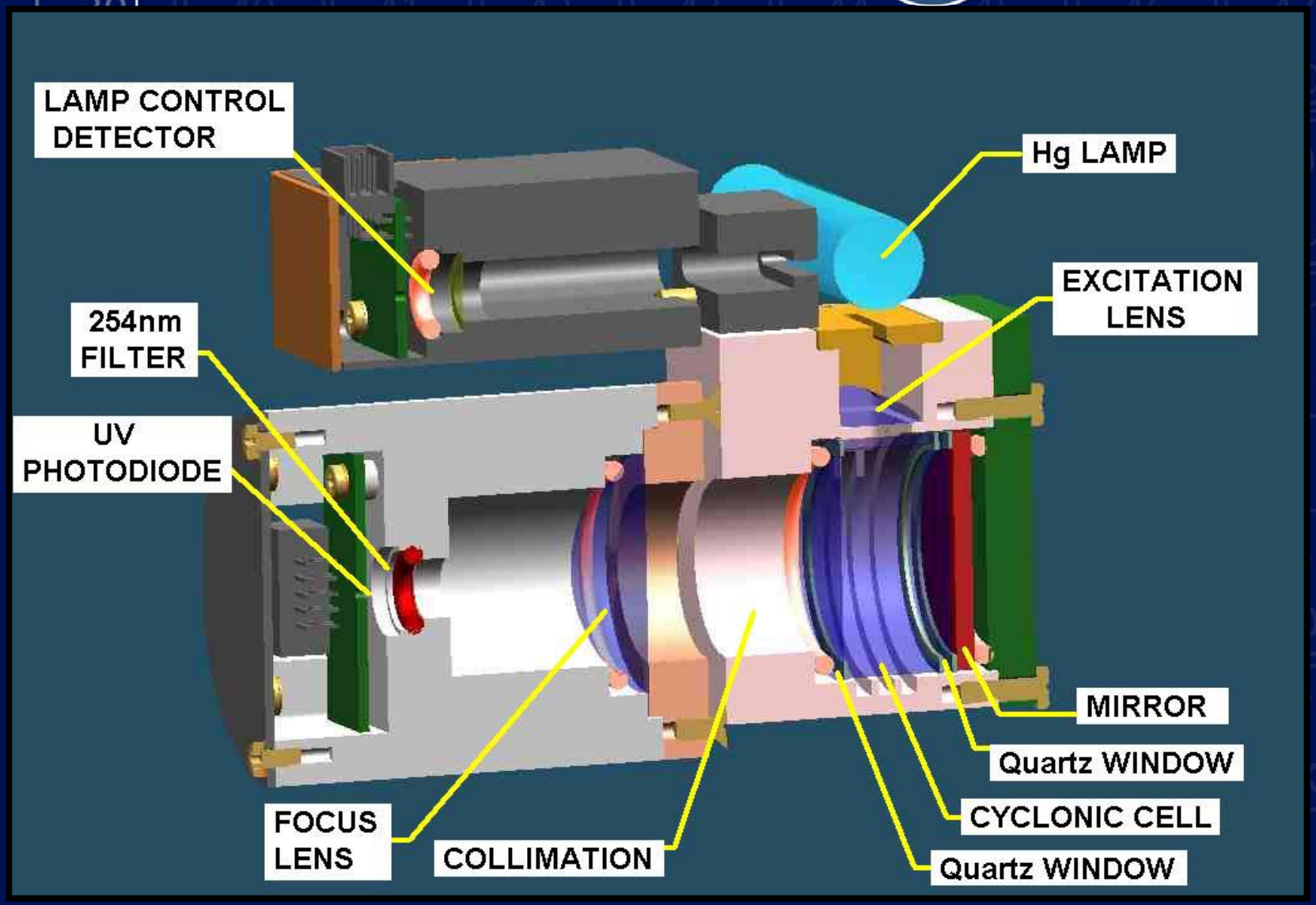
Fluorescence Detector Design





One Experience in State Certification

- **Oxford Lab**
  - Wilmington, NC
  - **NC State announced that effective Sept 1, 2003, determination using 1631 for all permits where effluent concentration is less than 0.2ppb.**
  - **Oxford Lab management decided to offer method 1631 and wanted to be certified by North Carolina before the method ruling was implemented.**
    - **Literature search**
    - **Facilities modification**
    - **Instrument & accessories purchase**

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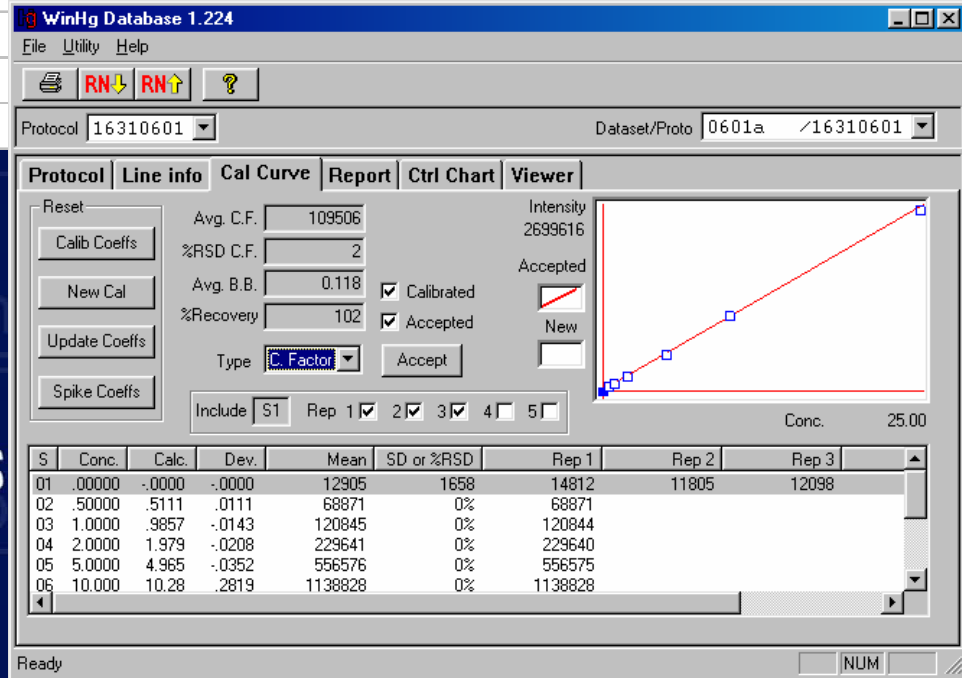
1631 Calibration

Conc ng/L	Peak area	Blk subtracted area	Cal Factor	Calc conc ng/L	%R	QC check
0	28266	avg blk		0.20		Pass
0	28901	28584		0.21		Pass
0.5	110243	81660	163319	0.59	118%	Pass
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%			Pass

Common failures?

- System blank
- CF %RSD.
- 0.5ppt %Rec.

Usually caused by contamination!



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Not So Blank Blanks

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
- autosampler vial
- hoses & tubes
- gas/liquid separator
- gas supply line
- pipet tips

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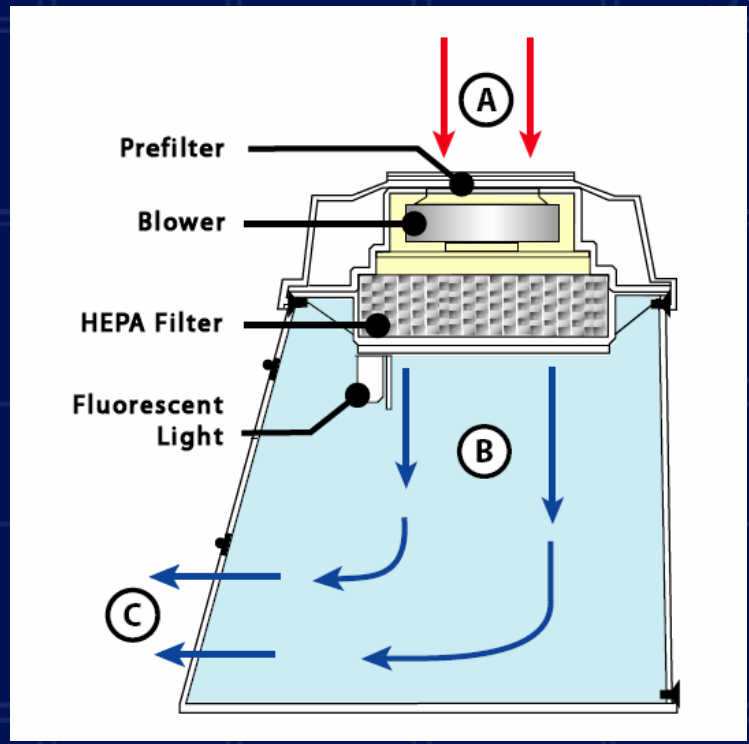
System Enclosures

AirClean System's 600 Series



Oxford Labs bought two hoods

-One for sample and reagent preparation

-One for analyzer

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Attractive Features of
AirClean System 600

- Variable blower control
- Automatic face velocity controller
- Two sash opening levels (8 & 16”)
- All polypropylene construction
- High efficiency HEPA filter for particulates.
- Qualifies as a class 100 clean bench

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Other Lab Facility Changes

- Freshly painted walls (S-Doped)
- Limited Access
- Sticky pad at doorway
- Air brought in from outside
- Installed local de-ionized water supply

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Laboratory Reagents

- H_2O, De-ionized water system provided by Eagle Water, Durham, NC. with additional Barnstead International Ultrapure filter added (D8911).
- HCl, sub-boiled distilled HCl (O2SI, 060100-03-1L) used for 1% HCl and BrCl solution.
- HCl, EM Omnitrace (VWR, EM-HX0607-2) used for 2% rinse.
- $SnCl_2$, J.T. Baker (VWR,JT3980-1)
- Hydroxylamine hydrochloride, J. T. Baker (VWR, JT2196-01)
- BrCl solution, (O2SI, 160073-0).

Rinse solution and reductants purified by sparging.

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Sparging Process

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

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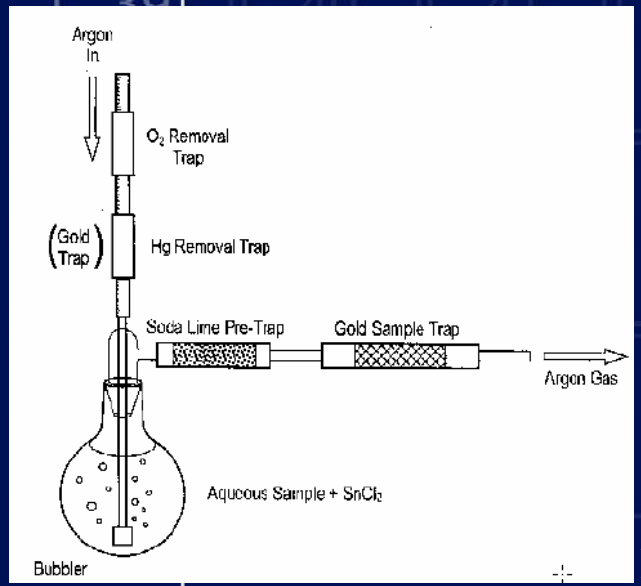
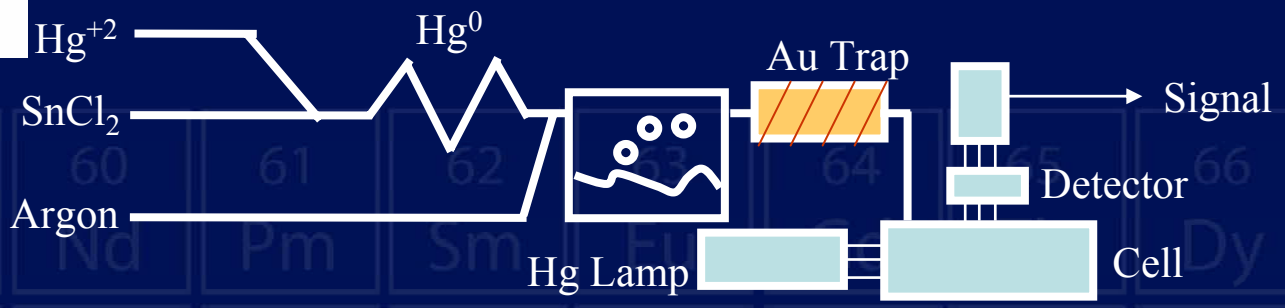
System vs. Bubbler Blanks



- **Clean all three input reagent streams**
  - Sparge $SnCl_2$ solution
  - Sparge rinse solution
  - Run rinse as sample



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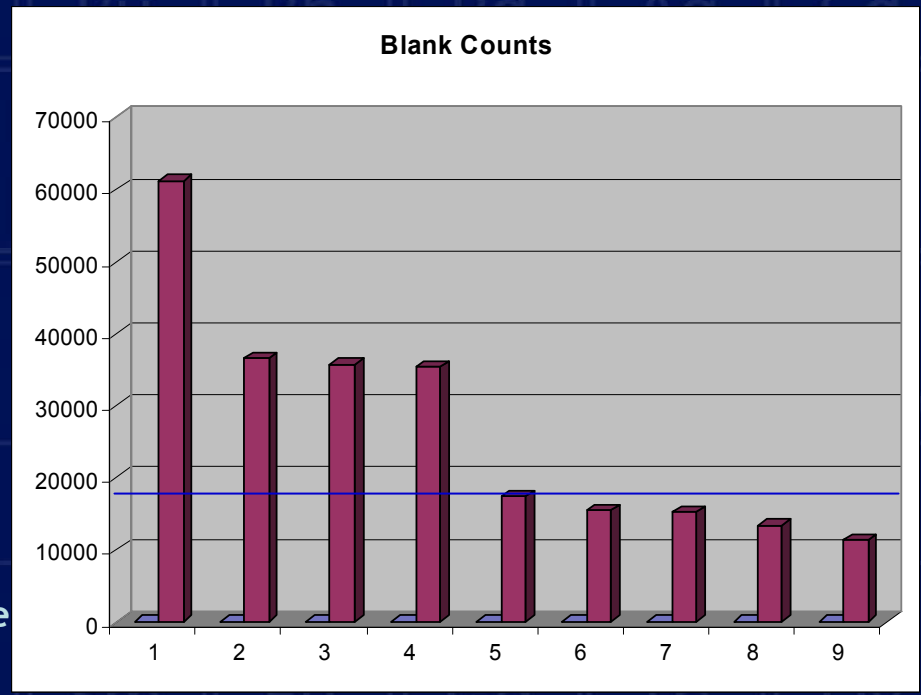
Effect of Acid Source
@ 240 sec. uptake

	Rinse	Sample	Reduct
1	Production	Production	Still #7
2	OmniTrace	OmniTrace	Still #7
3	OmniTrace	Ultrex	Still #7
4	Ultrex	Ultrex	Still #7
5	Ultrex	Ultrex	Ultrex
6	Ultrex	Ultrex	Ultrex
7	OmniTrace	OmniTrace	Ultrex
8	OmniTrace	OmnitTrace	OmniTrace
9	Omni/ultrex mix	Omni	Sparged Ultrex



Blue line represents 0.5 ppt signal

Typically blank counts must be <15,000 counts to pass system blank

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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.

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BrCl

- BrCl solution added to samples and standards at 5mL/L.
- Check mercury content by multiple additions

Volume Multiple	Counts
1	10,140
2	12,667
4	14,180

About 1000 counts/volume added

New solution prepared and counts rose to:
43,451; 23,897; 43062 most likely due to contaminated glassware

Second solution prepared and 3 blanks returned counts of 11,067; 11207; 10,752.

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Not So Blank Blanks

Reagents

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- $KBr0_3$
- $SnCl_2$
- NH_2OH HCl
- Ar

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air - vapor/particulates

thermometer, manometer, barometer

bench top

ventilation hood

Equipment

sample bottle	autosampler vial
hoses & tubes	gas/liquid separator
gas supply line	pipet tips

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Reagent Containers

1% HCl Solution

Container Type	Counts
Teflon	5206 2353 2588
Fluorinated LPE	17901 19388

1% HCl solutions run as samples with sparged reductant and rinse solutions.

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Sample Glassware

Technical Background

ENVIRONMENTAL SAMPLING SUPPLY

Certification/ Quality Control

Automation

Preparation & Cleaning Procedures

Operational Advantages

- ESS CONTAINER CLASS DEFINITIONS -

UC CLASS
UnCertified™ containers with Teflon®-lined* closures attached.

PC CLASS
PreCleaned Certified™ containers with Teflon®-lined* closures attached. Certification is provided with each case.

QC CLASS
Quality Certified™ precleaned containers with Teflon®-lined* closures attached are analyzed by independent, certified laboratories. Analytical test results are provided with each case of QC Class containers, which are excellent for use in litigation applications.

* Not all HDPE/LDPE products are available with Teflon®-lined closures.

Home | Technical Background | Company Background | Products | Contact ESS | What's New

ESS. We Sell Experience With Every Container.

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Sample Containers

Method 1631 Section 6.1.2.4 and Method 245.7 Section 6.1.1.4 state:

> "As an alternative to cleaning by the laboratory, bottles may be purchased from a commercial supplier and each lot certified to be clean. Bottles from the lot must be tested as bottle blanks …and demonstrated to be free of mercury at the ML of this method."

We have used pre-cleaned, quality-certified 16 ounce glass bottles from Environmental Sampling Supply* and found not appreciable mercury (Method 1631)

- Each bottle individually double bagged
- Teflon-lined screw caps
- Clear Boston round, narrow mouth design
- PN 0500-0100-LP

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ESS
9601 San Leandro St.
Oakland, CA
800-233-8425

Autosampler Cups

- **Polypropylene acceptable for analysis only**
  - Short residence time in cup
  - Glass and Teflon™ cups also permitted

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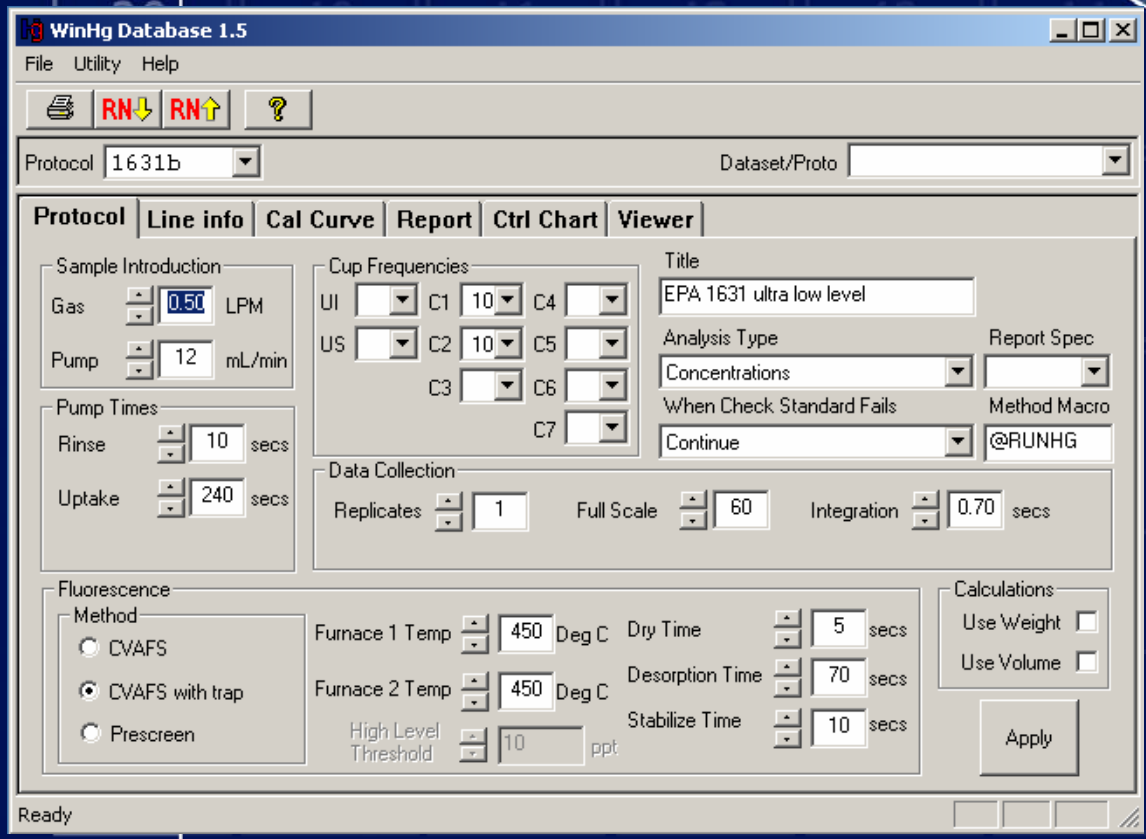
Optimized Analysis Conditions



Gas Flow: 0.50 LPM
Pump Speed: 12 mL/min.
Rinse Time: 10 secs
Uptake Time: 240 secs.

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Ready to Begin?

- EPA QC Requirements
  - Bubbler or system blank (0.25, 0.5ppt)
  - Calibration Factor precision (RSD <15%)
  - Low standard recovery (75-125%)
  - Initial Precision & Recovery (IPR) (79-121%)
  - On-going Precision & Recovery (OPR) (77-123%)
  - Method Detection Limit (0.2 ppt)
  - Matrix Spikes (71-125% recovery)
  - Relative Percent Difference (24%)

- State requirements; in this case NC
  - 3 blanks
  - Calibration curve
  - Initial Precision & Recovery check (IPR)
  - QCS
  - 7 x 1ppt for detection limit
  - Method blank
  - 4 OPR checks
  - Sample
  - Sample spike
  - Sample spike duplicate
  - Method blank
  - OPR

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Does not include a variety of blanks

State requirements, NC

- 3 blanks
- Calibration curve
- Method Blank
- Initial Precision & Recovery check (IPR)
- QCS
- 7 x 1 ppt for detection limit
- Method blank
- 4 OPR checks
- Sample
- Sample spike
- Sample spike duplicate
- Method blank
- OPR

Seq.	Content	Counts	Avg.
1	Blank	13,438	14,968
2	Blank	17,029	
3	Blank	14,439	
5	1	50,822	
6	5	172,712	
7	10	331,330	
8	15	425,569	
9	30	973,459	

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%RSD C.F. 9
Avg. Blank 0.473
%Rec. 113

Requirements, cont.

3 blanks
Calibration curve
Method Blank
Initial Precision & Recovery check (IPR)
QCS
7 x 1 ppt for detection limit
Method blank
4 OPR checks
Sample
Sample spike
Sample spike duplicate
Method blank
OPR

Seq	Content	Conc. (ppt)
10	Blank	0.254
11	IPR	4.82
12	QCS (10)	8.51
13	1	1.17
14	1	1.15
15	1	1.05
16	1	1.02
17	1	0.977
18	1	1.03
19	1	1.06

Std. Dev.
0.07 ppt

Avg. Recovery
106.5%

MDL
0.2 ppt

Rec./MDL (<10)
4.8

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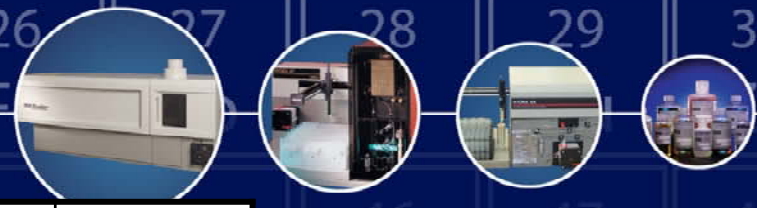
Requirements, cont.



- 3 blanks
- Calibration curve
- Method Blank
- Initial Precision & Recovery check (IPR)
- QCS
- 7 x 1 ppt for detection limit
- Method blank
- 4 OPR checks
- Sample
- Sample spike
- Sample spike duplicate
- Method blank
- OPR

Seq	Content	Conc. (ppt)
20	Blank	-0.1
21	OPR	5.35
22	OPR	5.25
23	OPR	5.43
24	OPR	5.39
25	Sample	1.11
26	Samp spk	13.7
27	Samp spk	14.0
28	Blank	0.17
29	OPR	4.90

OPR:
sd = 0.077
Avg. = 5.35
%Rec. = 107

Matrix Spike (12.5ppt)
Avg. Rec. = 102%
RPD = 2.17%

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Results submitted to state by 10:00AM. Certification confirmed by 2:00PM same day, Aug. 27, 2003.

1631 Certification in NC

- **Minimum of 6 labs certified for method 1631.**
  - NC State now requires determination using 1631 for all permits where effluent concentration is less than 0.2ppb.
- **Oxford Lab has improved its reagent clean-up procedures and routinely achieves system blanks under 0.25 ppt.**
- **There are 3 instrument manufacturers providing systems claiming to meet method 1631 requirements: Leeman Labs, PSAnalytical, & Tekran.**
- **Reagents for EPA method 1631 are available from several sources including Leeman Labs & O2SI.**

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What We Learned at Oxford Labs

- Clean before use all reagents that can be cleaned.
- Test all reagents before use.
- Segregate glassware used for method 1631
- Glass containers can remain clean for months.
  - At least for 1% acid
- Don't recycle soda lime.

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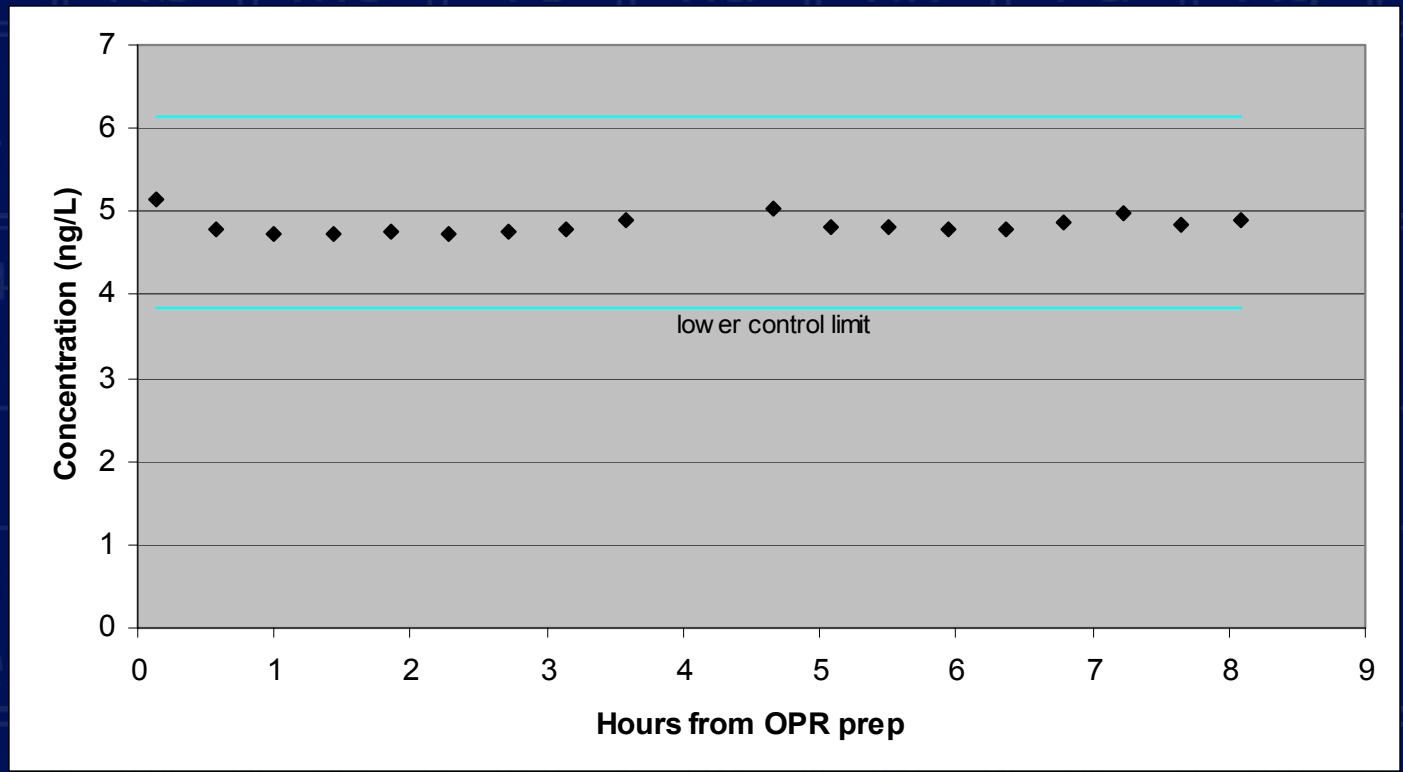
Contributions from Other Labs

5 ppt standard read back over eight hours



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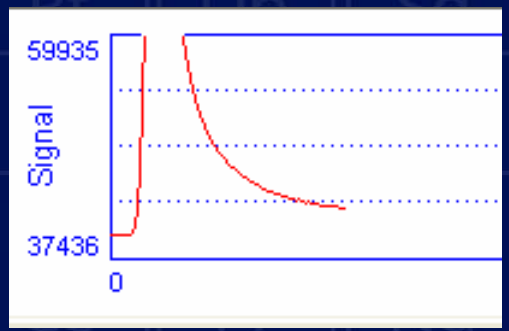
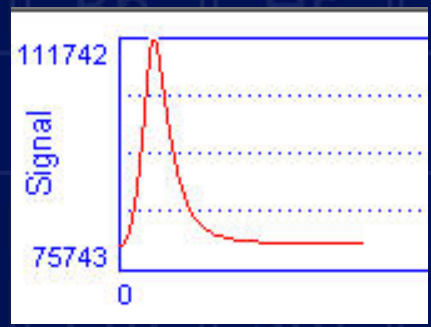
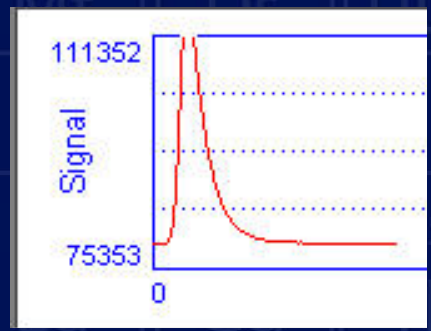
Courtesy of Dr.Mark Bruce, Severn Trent Labs

Other Stumbling Blocks

- **Gold Traps**
  - Signal must return to baseline
  - Delay in appearance time required to establish baseline







Excessive memory **Premature appearance** **Good**

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Contaminated Laboratory Air

- **Often misinterpreted as an instrument problem.**
  - Sometimes fresh blanks are acceptable.
  - Occasional blank signals equal 2 ppt.
  - Poor fit for standards
    - High standards always appeared low
  - Response for a single solution increases with time & handling.

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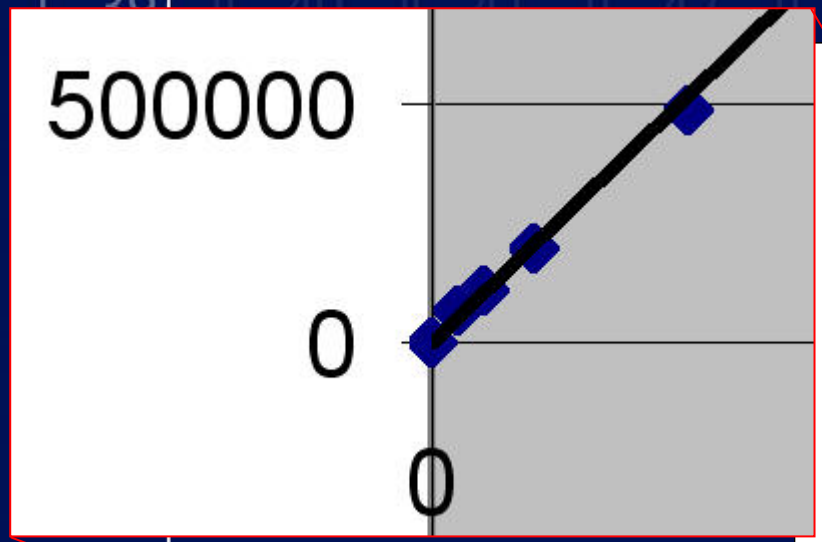
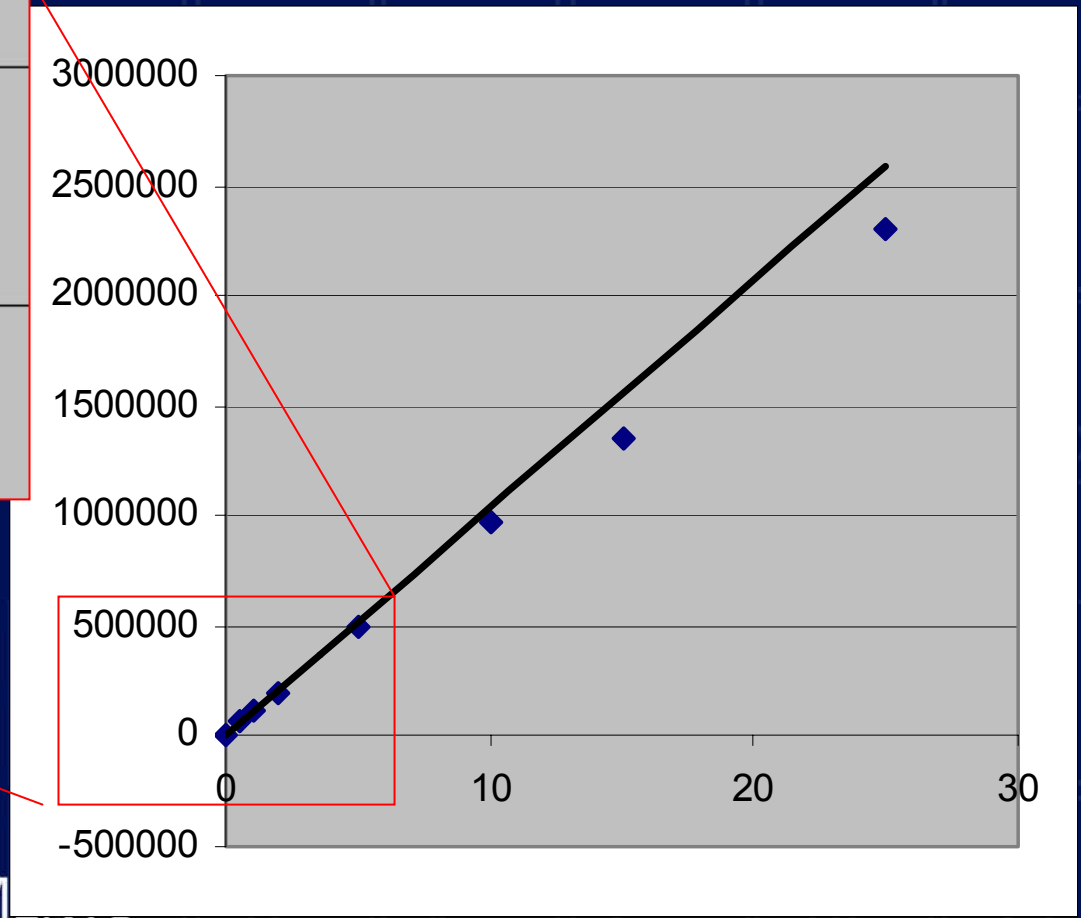
Calibration with Contaminated Air Using Calibration Factor





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Contaminated Laboratory Air (cont.)

Standards Preparation (w/w dilution)

1. Made two Liters of 5% BrCl blank (diluent)
2. Made 1 ppm Hg intermediate stock from 100 ppm Hg
3. Made 10 ppb intermediate stock from 1 ppm Hg
4. Made 100 ppt intermediate standard from 10 ppb
5. Made 20 ppt working standard from 100 ppt Hg
6. Made 15 ppt standard from 100 ppt Hg
7. Made 10 ppt standard from 100 ppt Hg
8. Made 5 ppt standard from 100 ppt Hg
9. Made 1 ppt standard from 20 ppt working standard
10. Made 0.5 ppt standard from 20 ppt working standard

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Blank/diluent opened a minimum of 10 times.

Contaminated Laboratory Air (cont.)

- **Environment**
  - Preparation done outside laminar flow hood
  - Room filled with sample containers & metal racks
  - Air vent directly above balance
- **Counts for BrCl solution before standards preparation**
  - <20,000
- **Counts for BrCl solution after standards preparation**
  - >60,000
- **Temporary solution: balance moved outside building & standard preparation done externally.**

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