



## ● Mercury Freedom CEMS

**CEMTEK User Group Meeting/Training  
September 28, 2016**

# Mercury Freedom™ System Overview

Model 82i Probe Controller

Model 80i Mercury Analyzer

Model 81i Mercury Calibrator

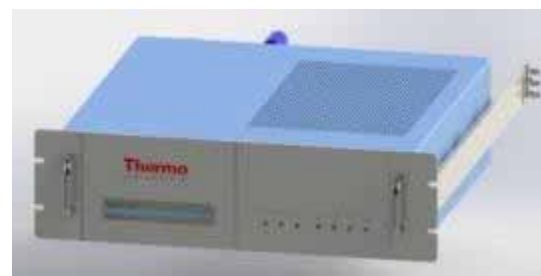
Zero air supply  
Optional Nitrogen Generator



Model 83i  
Inertial Probe

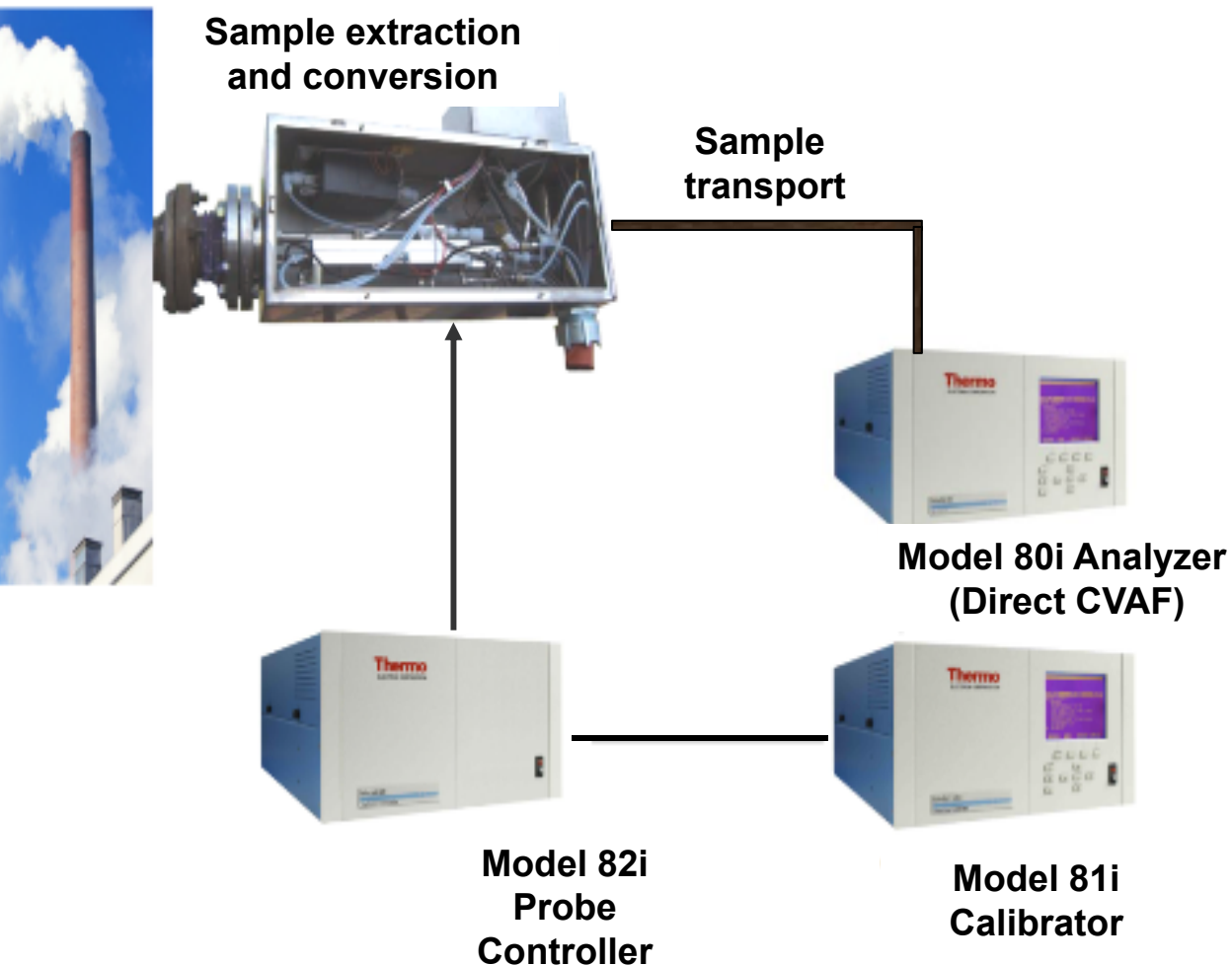


M&C  
SP2006HgT  
Probe



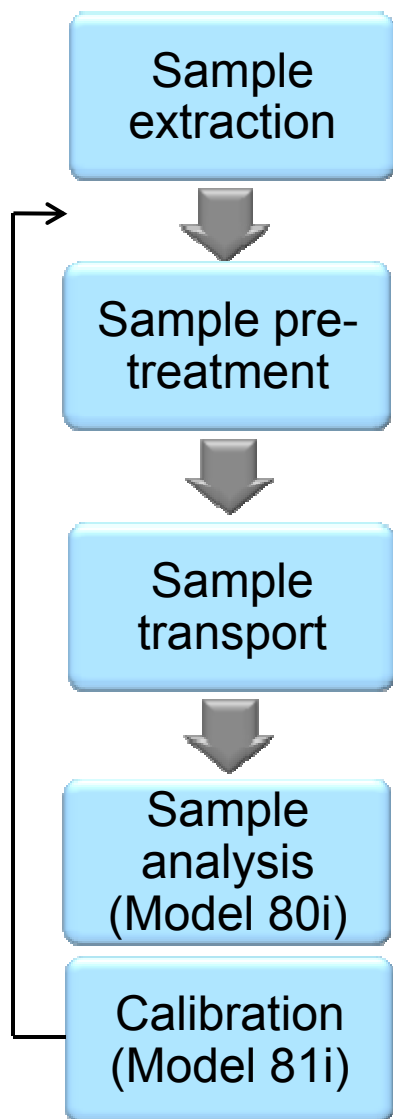
Optional Model 84i Permeation oven

# Mercury Freedom<sup>®</sup> CEM System Overview



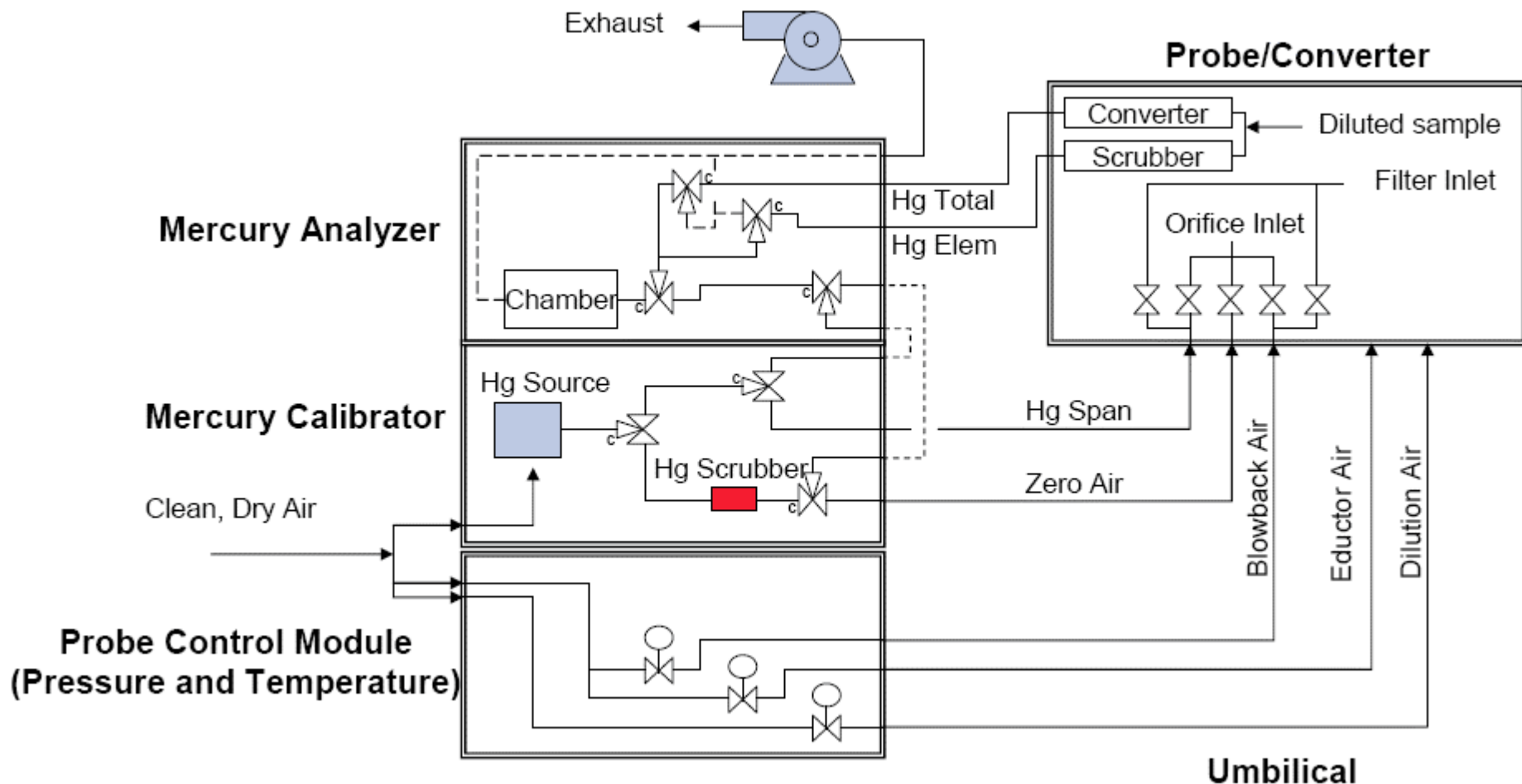
- Dilution based measurement
- Conversion at the Stack
- Direct Measurement CVAF
- Sample Line 158F (70C)
- Real-time monitoring
- iSeries platform

# Combining Performance with Ease of Use

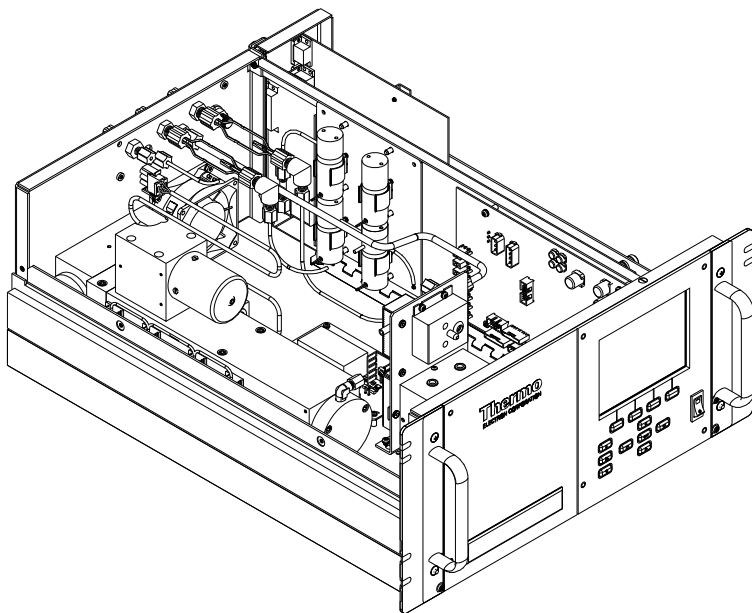


- Probe with high flow inertial filter is proven to work in high dust applications. Standard dilution probe for other applications
- Dry conversion at stack avoids potential loss or chemistry changes of oxidized Mercury in the sample line
- Dry conversion requires no wet chemistry or water supply. Allows transport at a low temperature!
- Direct measurement CVAF ensures linearity over broad range and avoids interferences with SO<sub>2</sub>
- High bench sensitivity eliminates need for expensive carrier gas and gold trap replacements
- Real-time monitoring with 10 second response time over entire range is ideal for process control
- *i*-Series platform offers modular design, enhanced interface capabilities with seamless integration into plant data flow

# Block diagram of the Mercury Freedom System



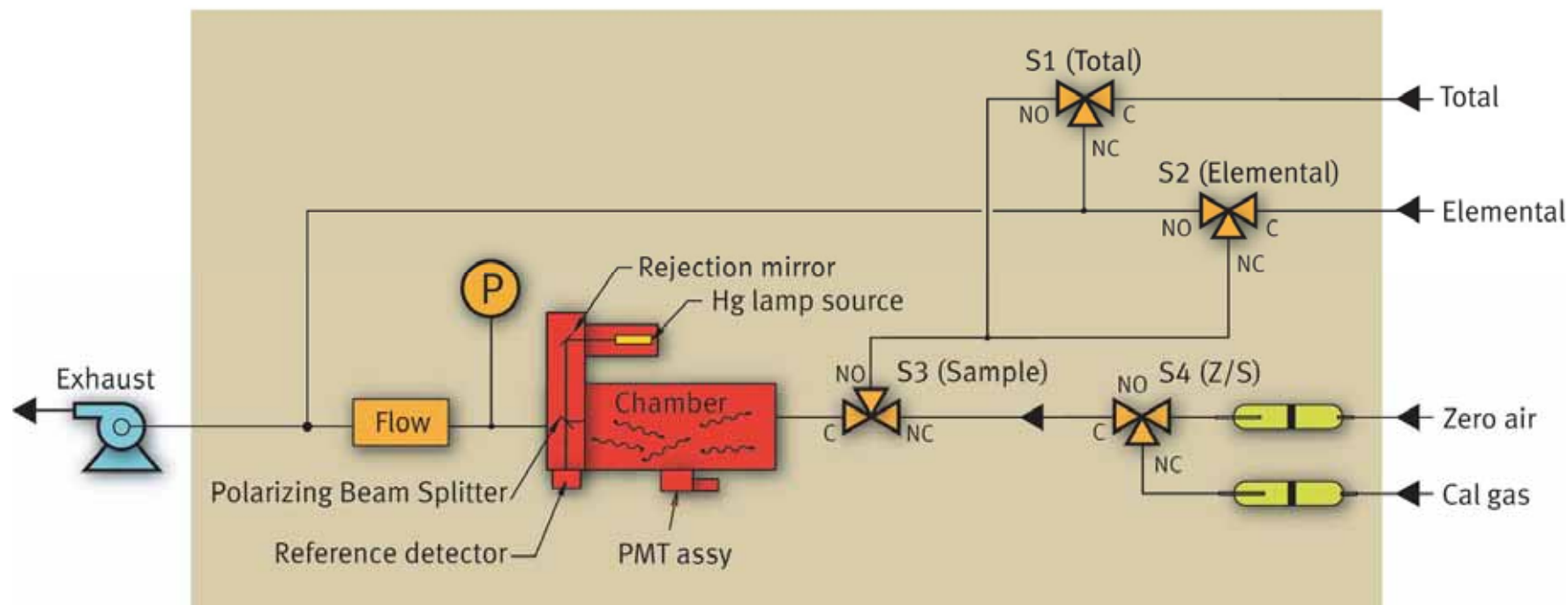
# Model 80i Hg Analyzer



- Direct Measurement CVAF
  - Continuous measurement
  - No additional gases required
- Diluted Sample
  - Lower moisture, less reactive
- Speciation
  - Measures either  $\text{Hg}^{\text{T}}$  or  $\text{Hg}^0$
- Analyzer Detection Limit:  $\sim 1 \text{ ng/m}^3$
- No cross interference with  $\text{SO}_2$

# Model 80i Hg Analyzer Flow Scheme

Model 80i Hg Analyzer



# Hg Fluorescence

$$I_f(M, p) = C * (p / (1 + \phi_M * p))$$

where  $I_f(M, p)$  = Fluorescence intensity of Mercury in mixing gas M at pressure p  
 $C$  = Constant depending on the mixing ratio  
 $p$  = Sample pressure  
 $\phi_M$  = Quenching coefficient for mixing gas M

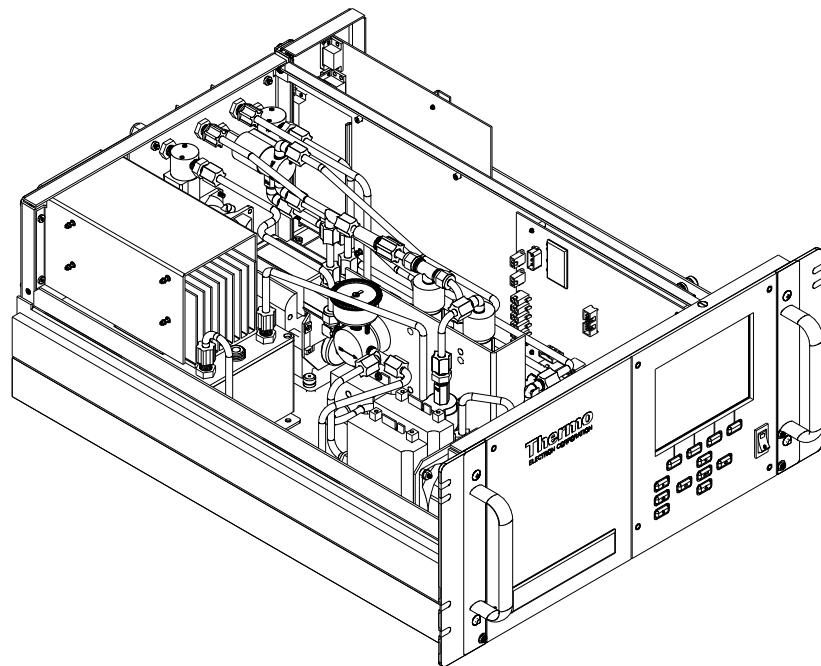
$$I_f(M, p) / I_f(M_{\text{Ref}}, 1 \text{ atm}) = (p * (1 + \phi_{M\text{Ref}})) / (1 + \phi_M * p)$$

where  $M_{\text{Ref}}$  = Reference mixing gas

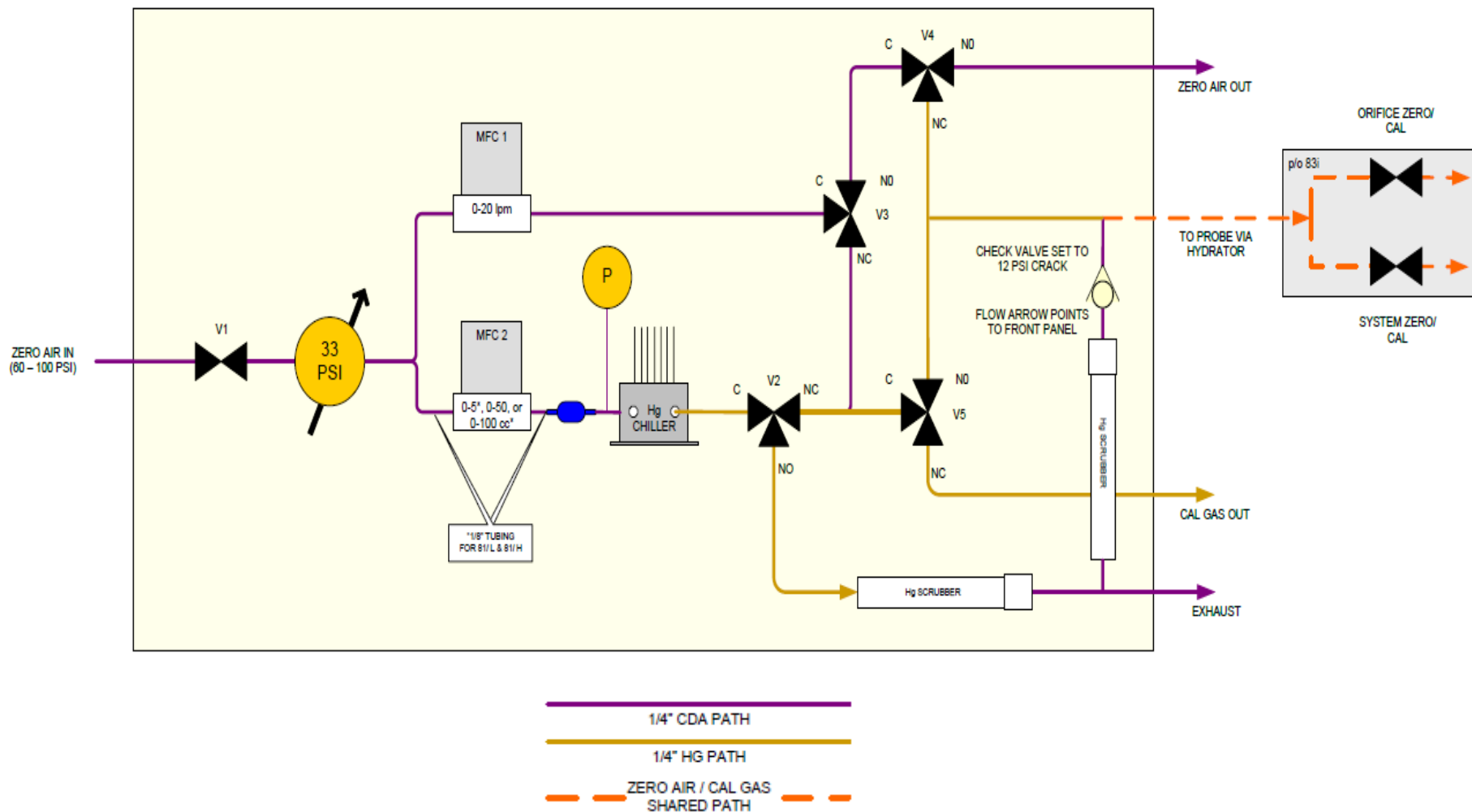


# Model 81*i* Hg Calibrator

- Used to calibrate directly to analyzer and probe
- Check dilution ratio
- Uses Peltier Cooler/vapor pressure control and mass flow controller
  - 1.5  $\mu\text{g}/\text{m}^3$  to 50  $\mu\text{g}/\text{m}^3$



# Hardware Overview: 81i Flow Diagram



# Standard and High Level Calibrators

- Standard Level Calibrator – 81i “Standard”
  - Ranges: 5, 10, 20, 30, 40, 50  $\mu\text{g}/\text{m}^3$ 
    - Output: 1-50  $\mu\text{g}/\text{m}^3$  (depending on range)
    - Hg Source Control: 6°C
- High Level Calibrator – 81iH
  - Ranges: 20, 30, 50, 300  $\mu\text{g}/\text{m}^3$
  - Output: 4-300  $\mu\text{g}/\text{m}^3$  (depending on range)
  - Hg Source Control: 8-18°C
  - Temperature changes with every Range Change



**Table C-3.** Write Coils for 81i

Coil Number	Action Triggered	Coil Group	Used Exclusively In
100	Invalid		
101	INSTRUMENT ZERO MODE	Zero Span Mode	
102	INSTRUMENT CAL MODE	Zero Span Mode	
103	ORIFICE ZERO MODE	Zero Span Mode	
104	ORIFICE CAL MODE	Zero Span Mode	
105	SYSTEM ZERO MODE	Zero Span Mode	
106	SYSTEM CAL MODE	Zero Span Mode	
107	STANDBY		
108	AOUTS TO ZERO	Analog Out Test	I/O Expansion Board Option
109	HG SPAN BIT 1	Span Level	
110	HG SPAN BIT 2	Span Level	
111	HG SPAN BIT 3	Span Level	
112	AOUTS TO FS	Analog Out Test	I/O Expansion Board Option
113	EXT ALARM 1		
114	EXT ALARM 2		
115	EXT ALARM 3		
116	RANGE 20	81i-H Range	81i-H
117	RANGE 30	81i-H Range	81i-H
118	RANGE 50	81i-H Range	81i-H
119	RANGE 300	81i-H Range	81i-H

- High Level Calibrator – 81iH
  - Ranges: 20, 30, 50, 300  $\mu\text{g}/\text{m}^3$
  - Output: 4-300  $\mu\text{g}/\text{m}^3$  (depending on range)
  - Hg Source Control: 8-18°C
  - Temperature changes with every Range Change

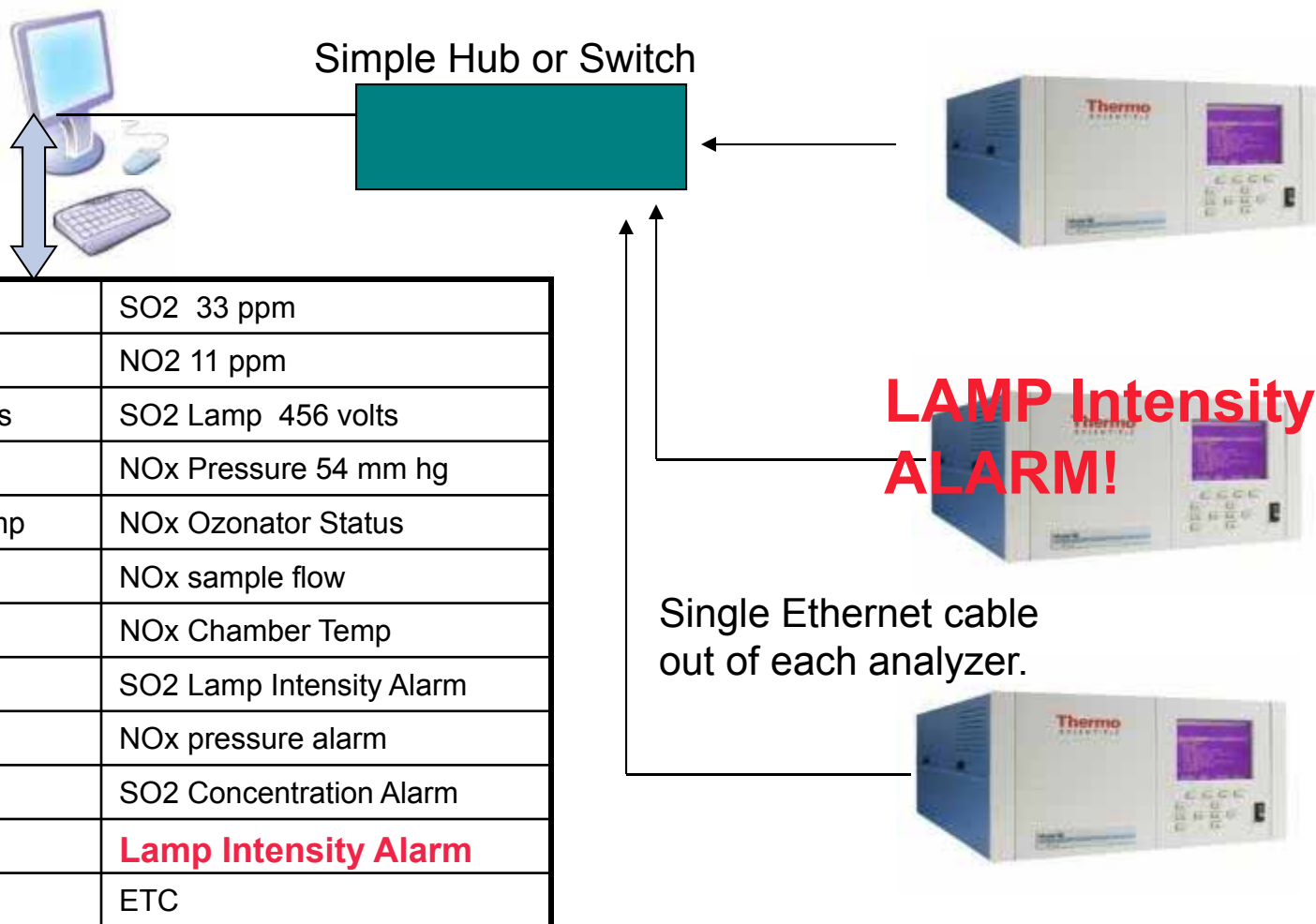
MODBUS COILS for 'Above Span'



## Model 83i Hg Probe



# Example: The modern method, using Ethernet



*Hundreds of pieces of information can be logged.*

# Some “nuts and bolts”. Imagine a 3-tabbed spreadsheet.

Example Read Register Table  
from 42i NOx analyzer

Register Number	Variable
1 & 2	NO
3 & 4	NO2
5 & 6	NOx
35 & 36	INTERNAL TEMPERATURE
37 & 38	CHAMBER TEMPERATURE
39 & 40	COOLER TEMPERATURE
41 & 42	NO2 CONVERTER TEMP
49 & 50	CHAMBER PRESSURE
51 & 52	SAMPLE FLOW
53 & 54	PMT VOLTS

Example Read Coil table is shown with an  
excerpt from the list for the 42i NOx analyzer:

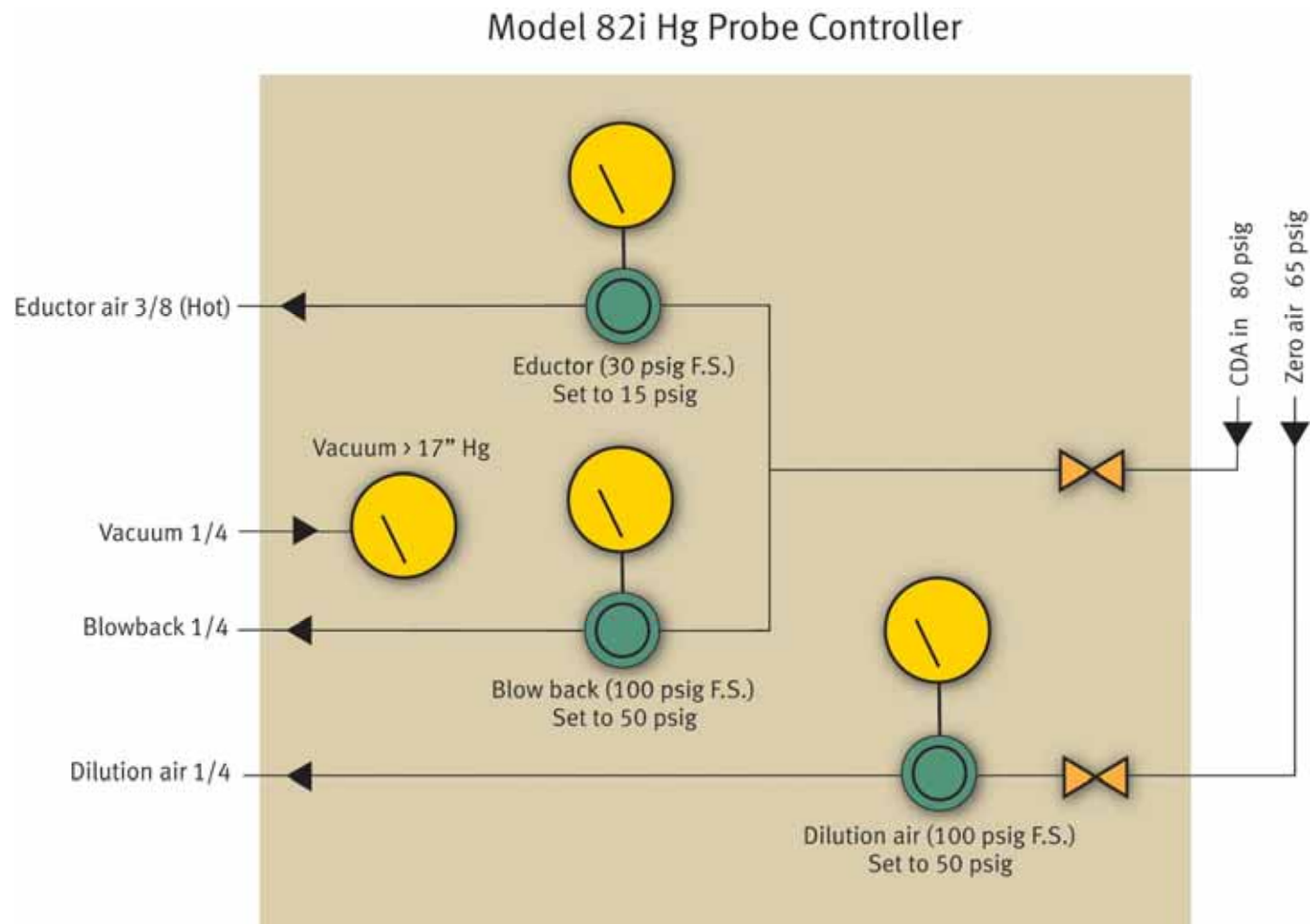
Coil Number	Status
1	AUTORANGE (NOx)
2	LOCAL/REMOTE
3	SERVICE
4	UNITS
5	ZERO MODE
6	SPAN MODE
7	NO MODE
8	NOx MODE
11	GEN ALARM
12	NO CONC MAX ALARM
22	INT TEMP ALARM
23	CHAMB TEMP ALARM
24	COOLER TEMP ALARM

Example Write Coil table  
is shown for 42i NOx analyzer:

Coil	Action Triggered
101	ZERO MODE
102	SPAN MODE
103	NO MODE
104	NOX MODE
107	SET BACKGROUND
108	CAL TO LO SPAN

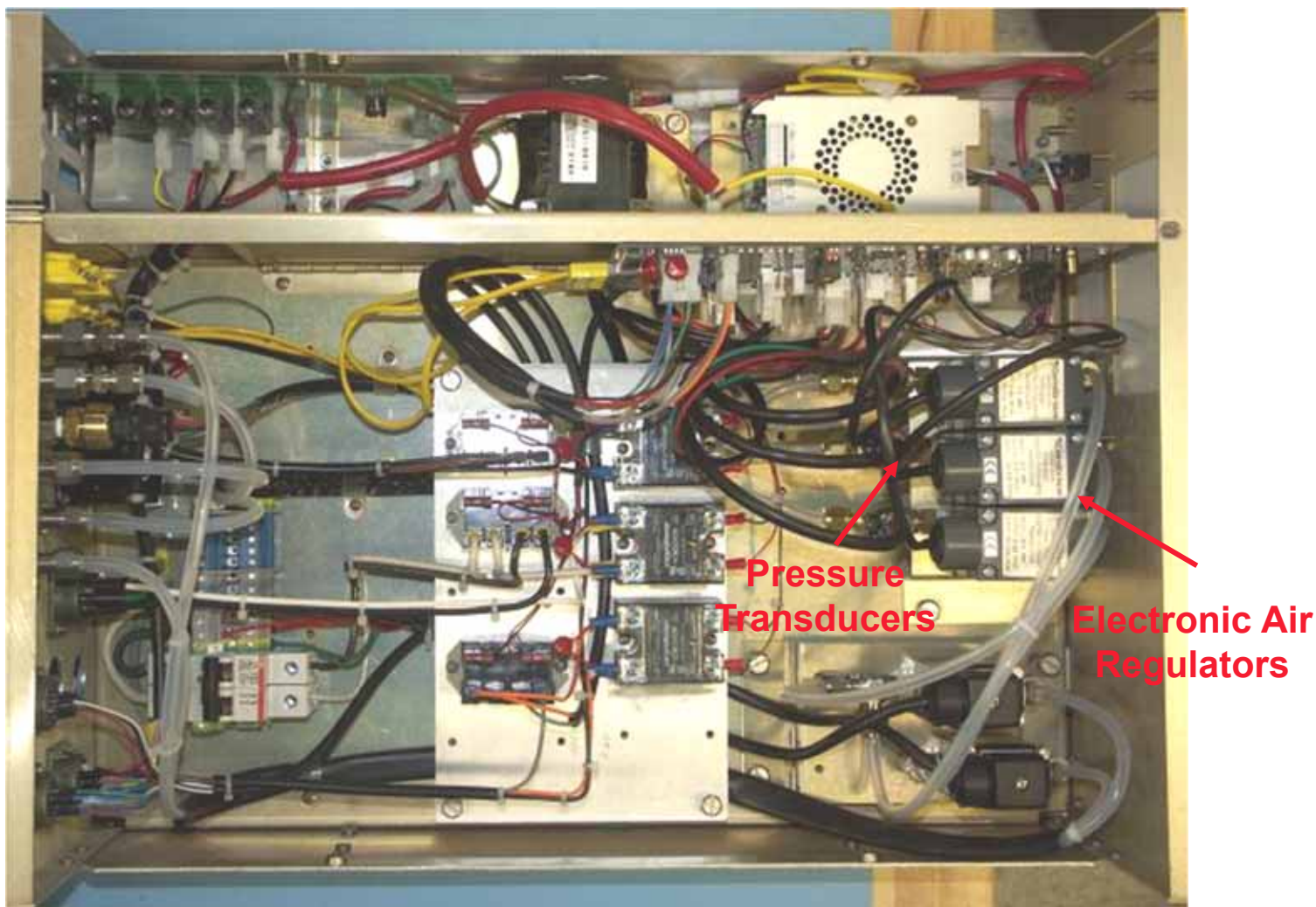


# Model 82i Probe Controller Flow Scheme



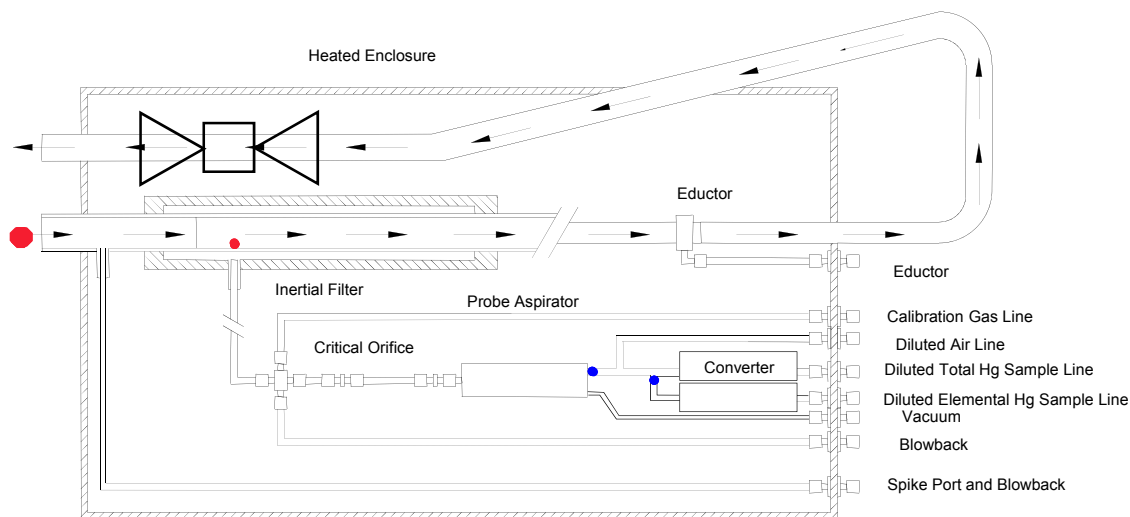


# Model 82i – Probe Controller



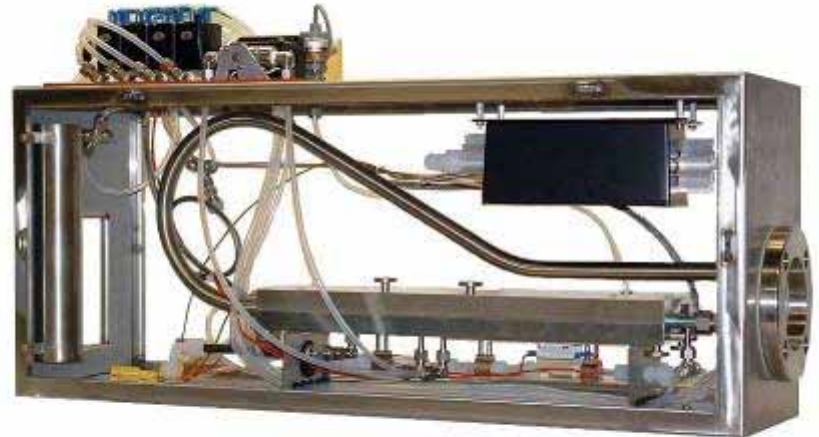
# Model 83*i* inertial probes

- Material: Silica Coated Stainless Steel
- Design Flow Rate (lpm): 10 – 50 (Standard)
- Ideal for Carbon Injection Systems
- Heated Filter/Inlet Stinger/Outlet Stinger Blowback

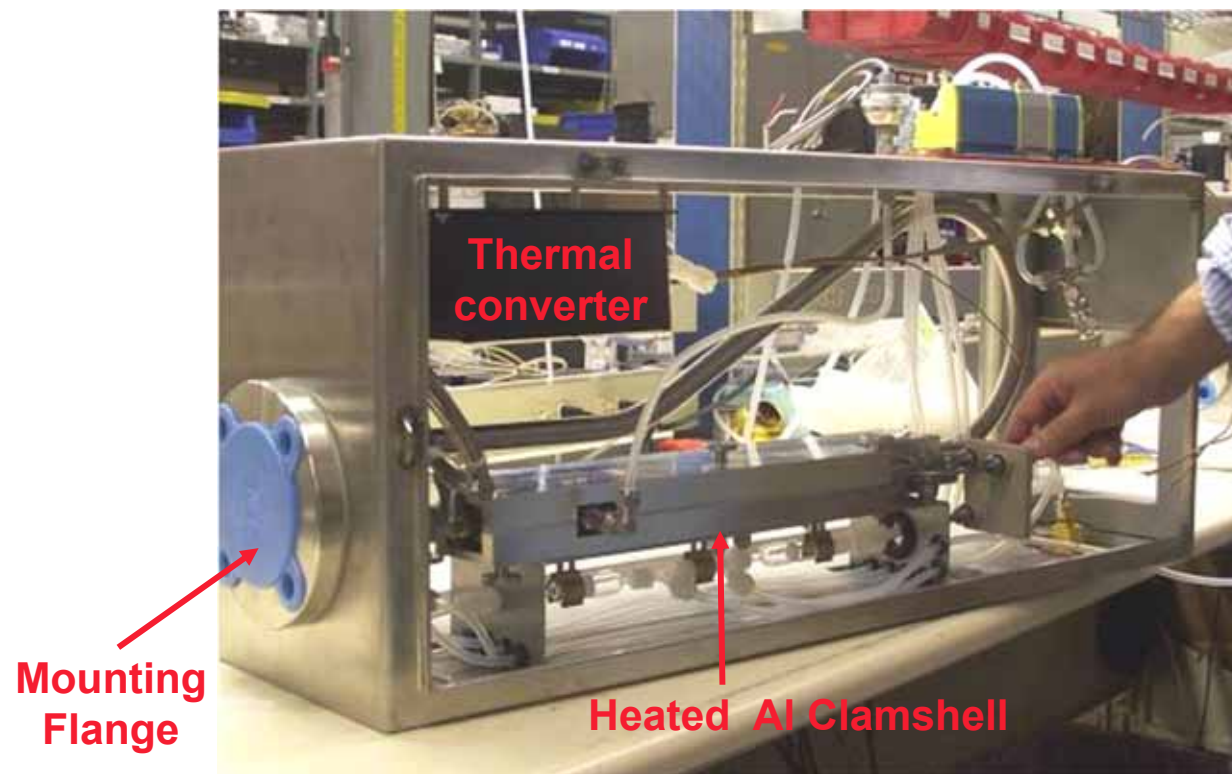


# Model 83*i* Probe/Converter

- Designed for serviceability
- Integrated Converter
- Integrated Oxidizer
- Dilution Module

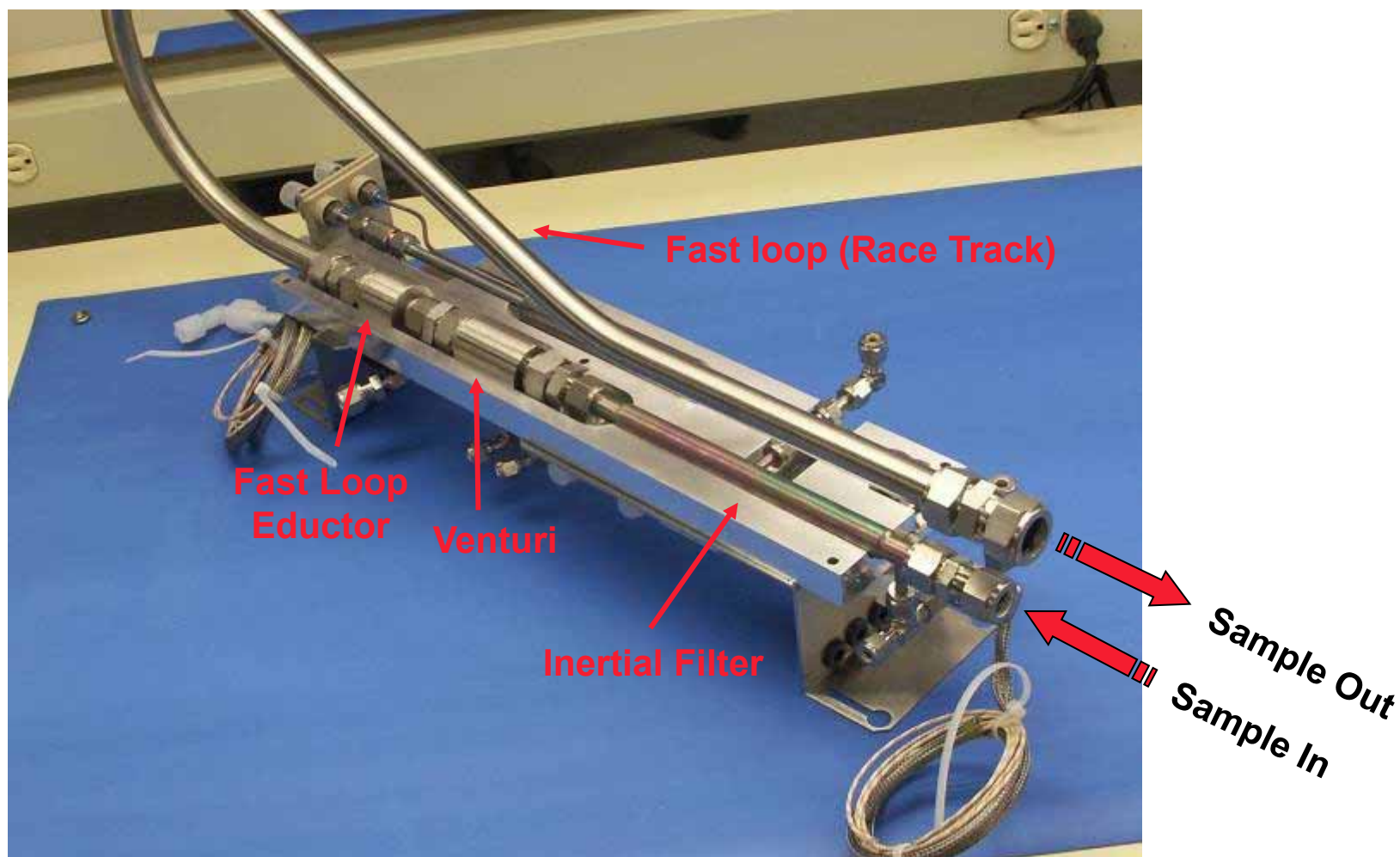


# Converter/Inertial Filter Probe



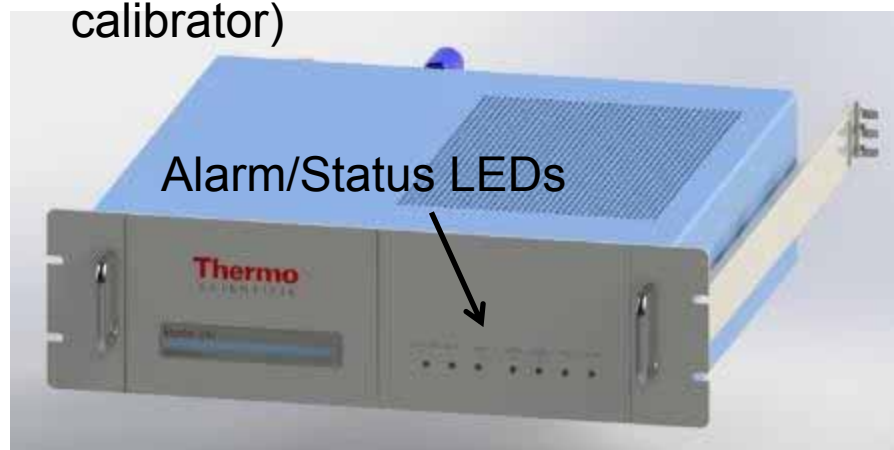
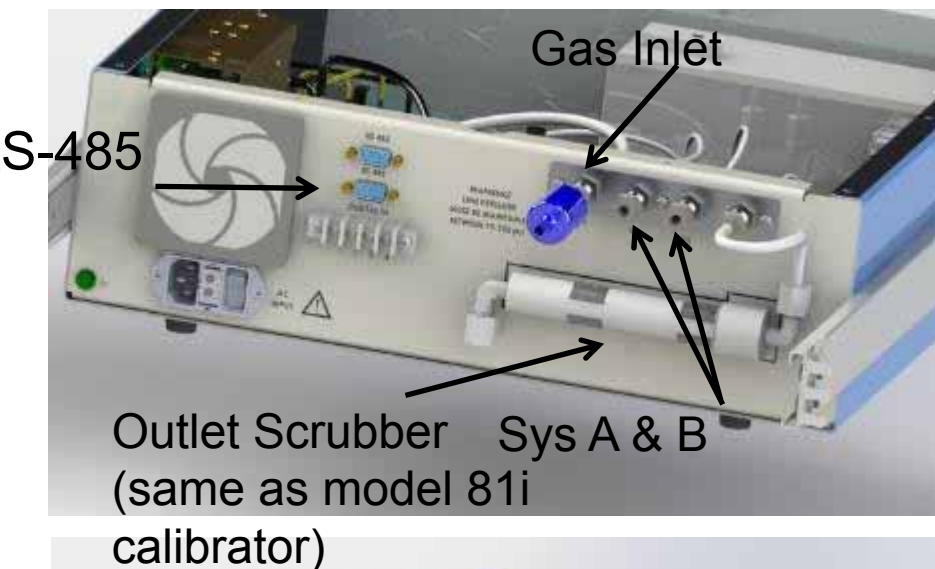


# Fast Loop Inertial Filter



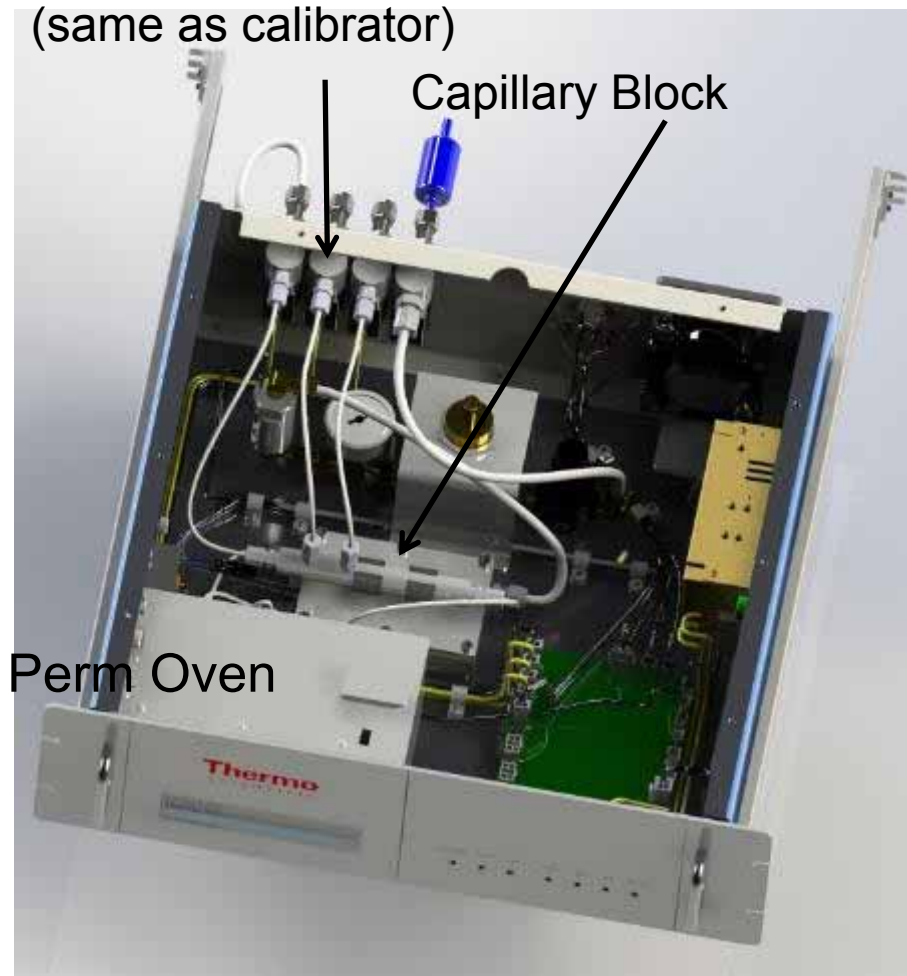


# Optional permeation source Model 84i



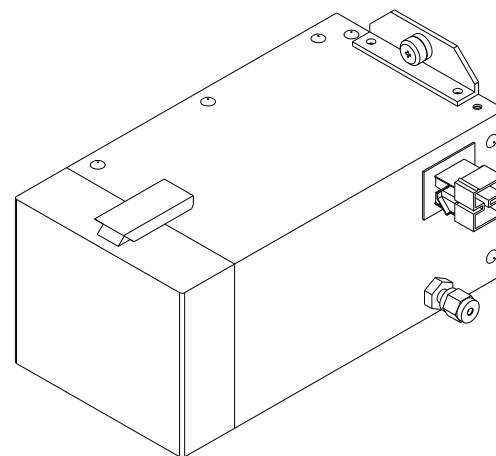
## Valves

(same as calibrator)



# Optional permeation source Model 84i

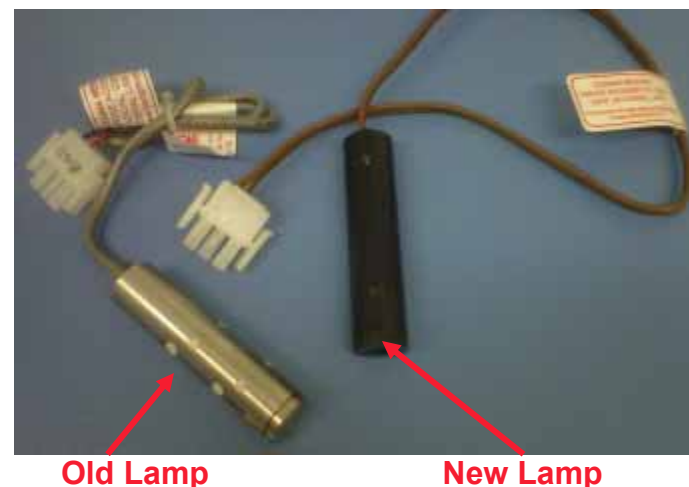
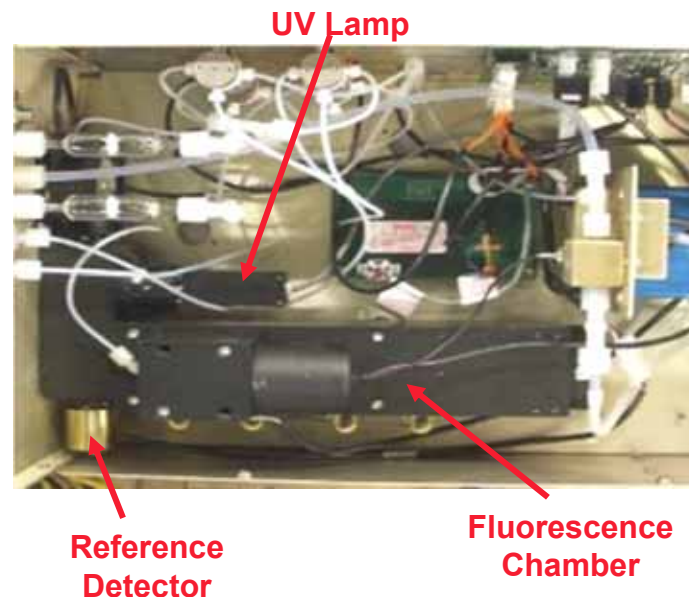
- The permeation oven supplies a reliable and consistent mercury concentration.
- It contains a permeation tube, permeation oven heater, oven thermistor and a gas thermistor.
- Thermistors are  $10\text{ K}\Omega$  @  $25^\circ\text{C}$
- When held at a constant temperature ( $100^\circ\text{C}$  for the Model 84i) the permeation tube outgases mercury at a constant rate. This gas is transported to the Model 80i Mercury Analyzer.
- A fixed and continuous flow rate and tight control of the permeation oven temperature assures a repeatable and stable mercury concentration.





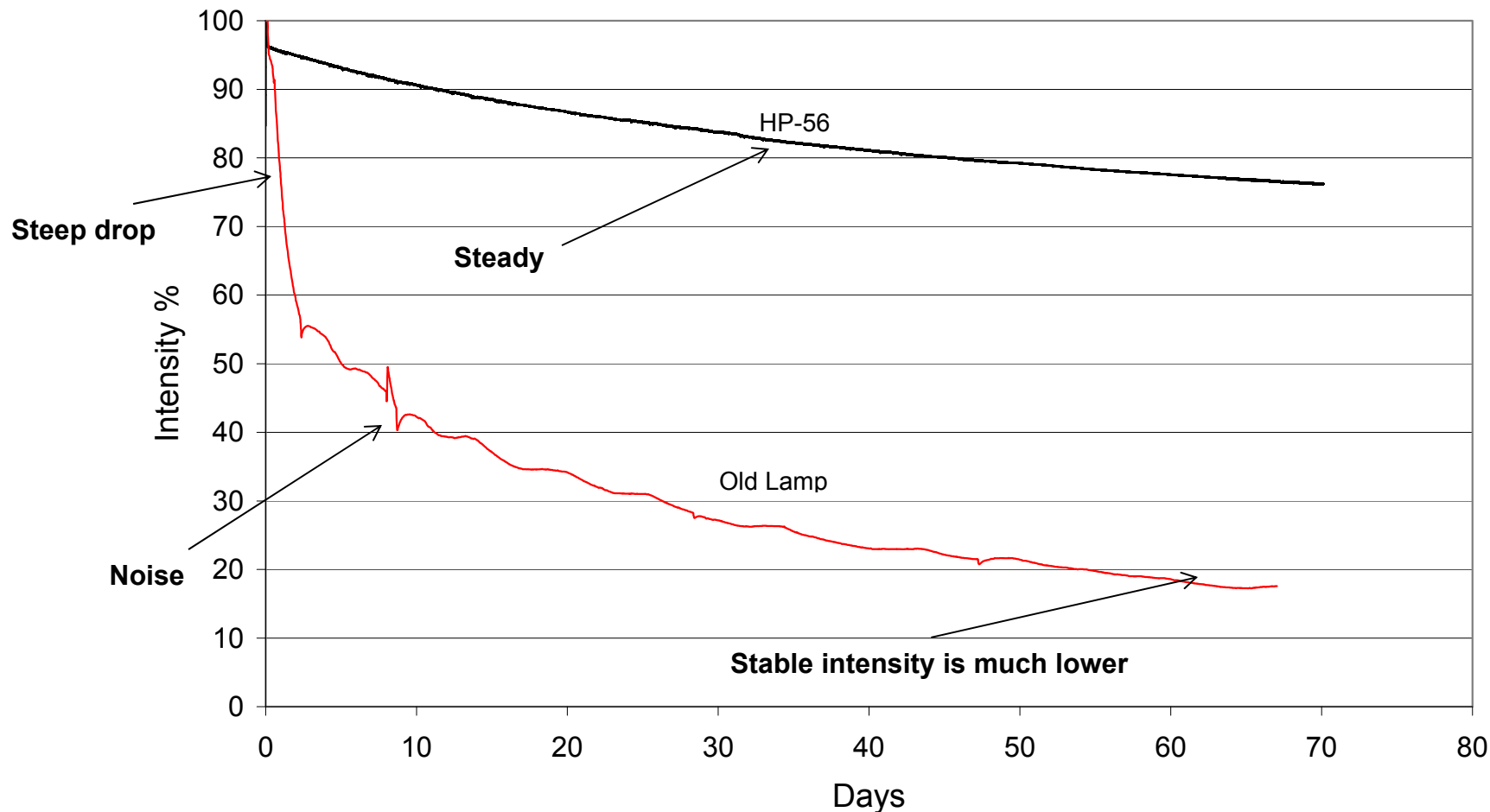
# New and improved Hg lamp (HP-56)

- Lamp performance affects analyzer sensitivity and stability
- Old lamps experienced:
  - Degradation of intensity
  - Start-up spike and noise
- New lamp design has:
  - Shorter stabilization time
  - Improved stability
  - Comparable signal-to-noise output
  - Longer life (18 months)
- New lamp is a drop-in replacement for the old lamp (with firmware update)



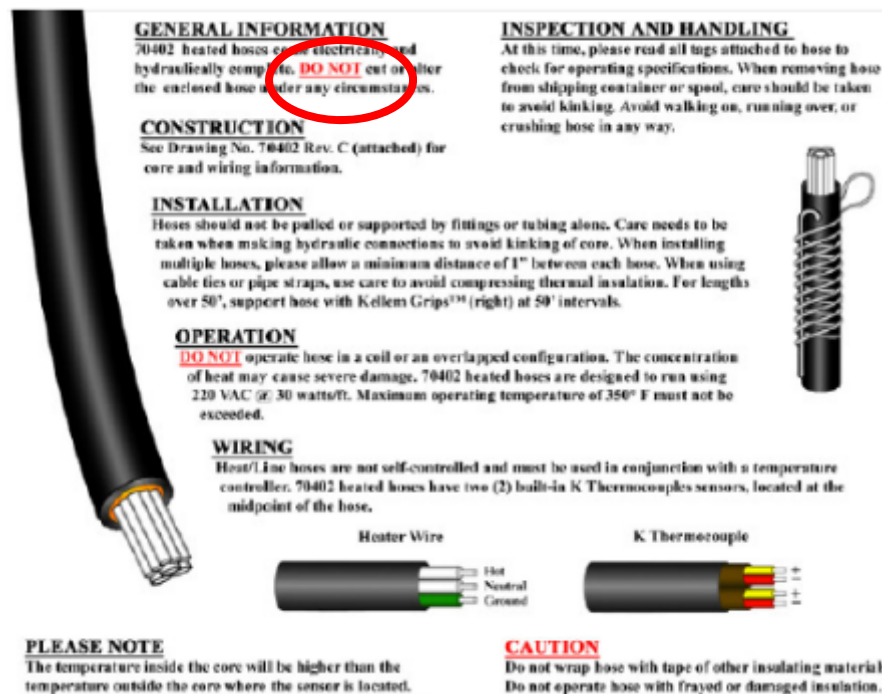
# New lamp drift is < 0.5% per day

New HP-56 Lamp Vs Older Style Lamp  
Data from actual customer units



# Reduced sample line temperatures

- Sample lines are expensive, difficult to install and contribute to risk
- After extensive testing, we lowered the temperature from **120°C to 70°C**



***Lower temperature increases reliability and reduces cost***

# Benefits of lower sample line temperatures

- **Longer sample line life and reliability**
- **Lower capital cost for sample lines**
- **Less power consumption is a direct savings**
  - Example: 500 ft. line with 30 watts/foot heating can be reduced to 15 watts/foot. At \$0.06 per kWh, Savings = **\$3,931 per year**
- **Increased safety:**
  - Heating circuit can be designed such that it will be impossible for a runaway condition that will damage line
- **Easier installation with smaller diameter sample lines**

# QC Checks using a Hg Permeation Source

**In order to comply with the 2009 Interim Elemental Mercury Gas Traceability Protocol, a Quarterly Audit is required:**

Option A: Field Reference Generator

Option B: Permeation Tube

Option C: Sorbent Tube

Option D: Cylinder Gas



Interim Elemental Mercury Gas Traceability Protocol -- July 01, 2009

Interim EPA Traceability Protocol for  
Qualification and Certification of Elemental Mercury Gas Generators

**7.0 QUALITY ASSURANCE**

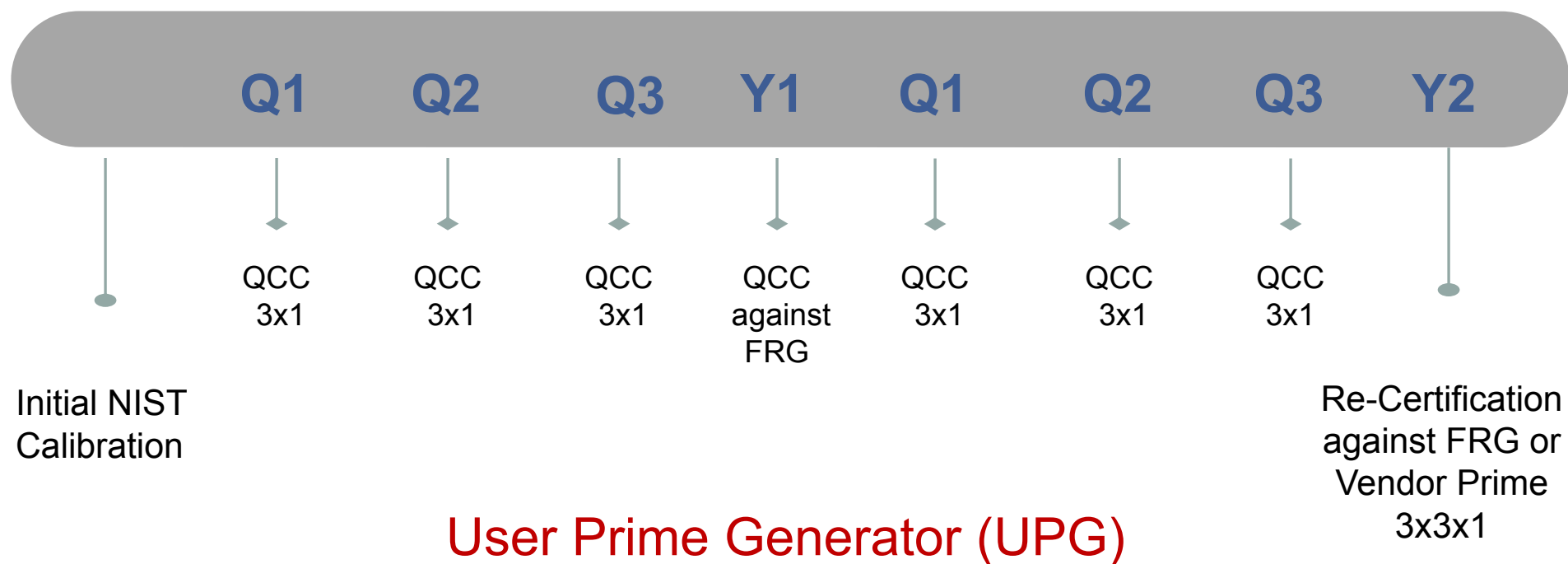
# QC Requirements per approach

Option	Approach	Frequency	What is involved	Pass/Fail Criteria
A	Field Reference Generator	Quarterly	Need a FRG Manual or automated	Avg of 3 replicates (bracketing) within $\pm 5.0\%$ or $\pm 0.5 \mu\text{g}/\text{m}^3$
B	Permeation Tube	Monthly or weekly	Automated via DAS	Avg of 1 to 3 pairs must be within $\pm 5.0\%$ of the base ratio (perm/gen)
C	Sorbent Tube	Quarterly	Manual Method	Avg of 3 replicates within $\pm 5.0\%$ of the certified concentration, or difference no greater than $0.5 \mu\text{g}/\text{m}^3$
D	Cylinder Gas	Quarterly	Automated Via DAS	average output conc. is within $\pm 5.0\%$ or $\pm 0.5 \mu\text{g}/\text{m}^3$ of the certified Hg conc

***At least two options are manually intensive***

# User Prime 81i QA Requirements

**Recertification of a User Prime generator** – Comparison against Vendor Prime or Certified Field Reference Generator using 3x3x1. Required annually or up to eight(8) quarters\*.



# 81i Calibrator

- **NIST Certified Ranges for 81i**

- 0 -10 ug/m<sup>3</sup>                      Set Points 2.7, 5.7, 8.1
- 0 - 5 ug/m<sup>3</sup>                      Set Points 1.2, 2.7, 4.7
- **0 - 1 ug/m<sup>3</sup>**                      **Set Points 0.2, 0.5, 1.0**

- **Certification and Upgrade Options**

- Service Depot - Franklin, MA
- On-Site Program

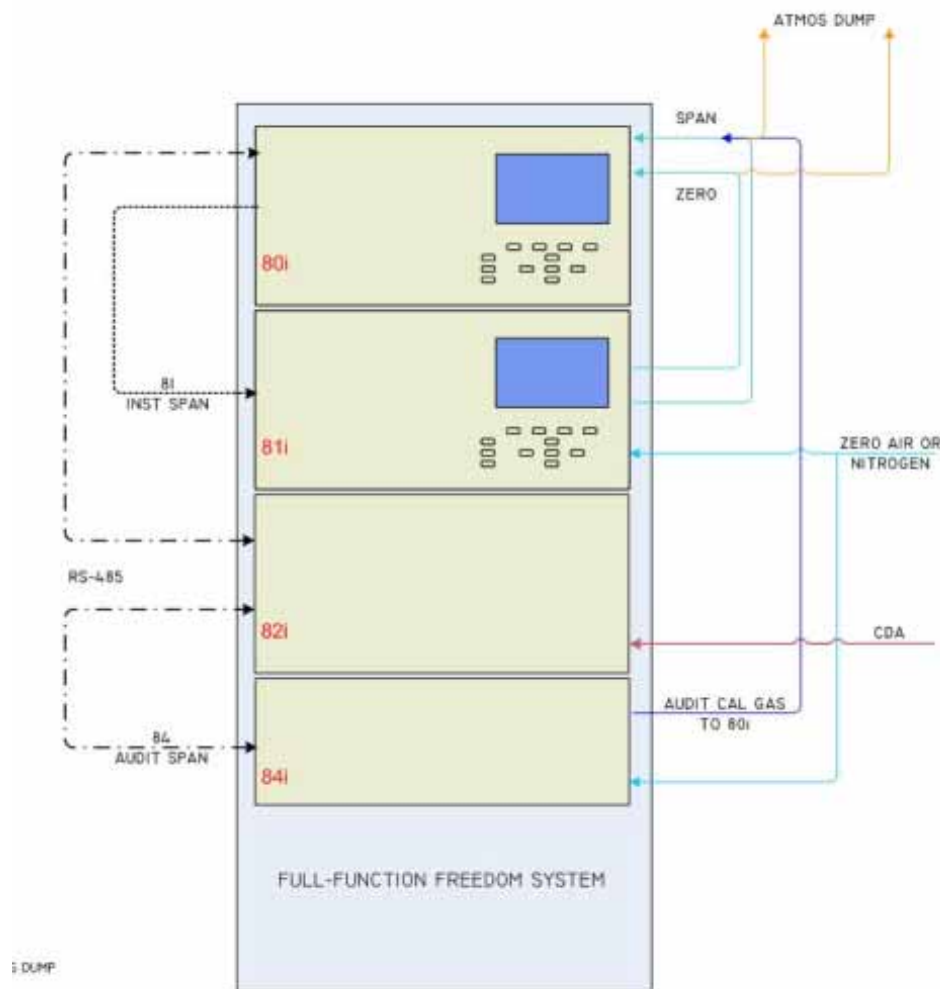
- **Capacity**

- Doubling our Equipment
- Cross Training Technician



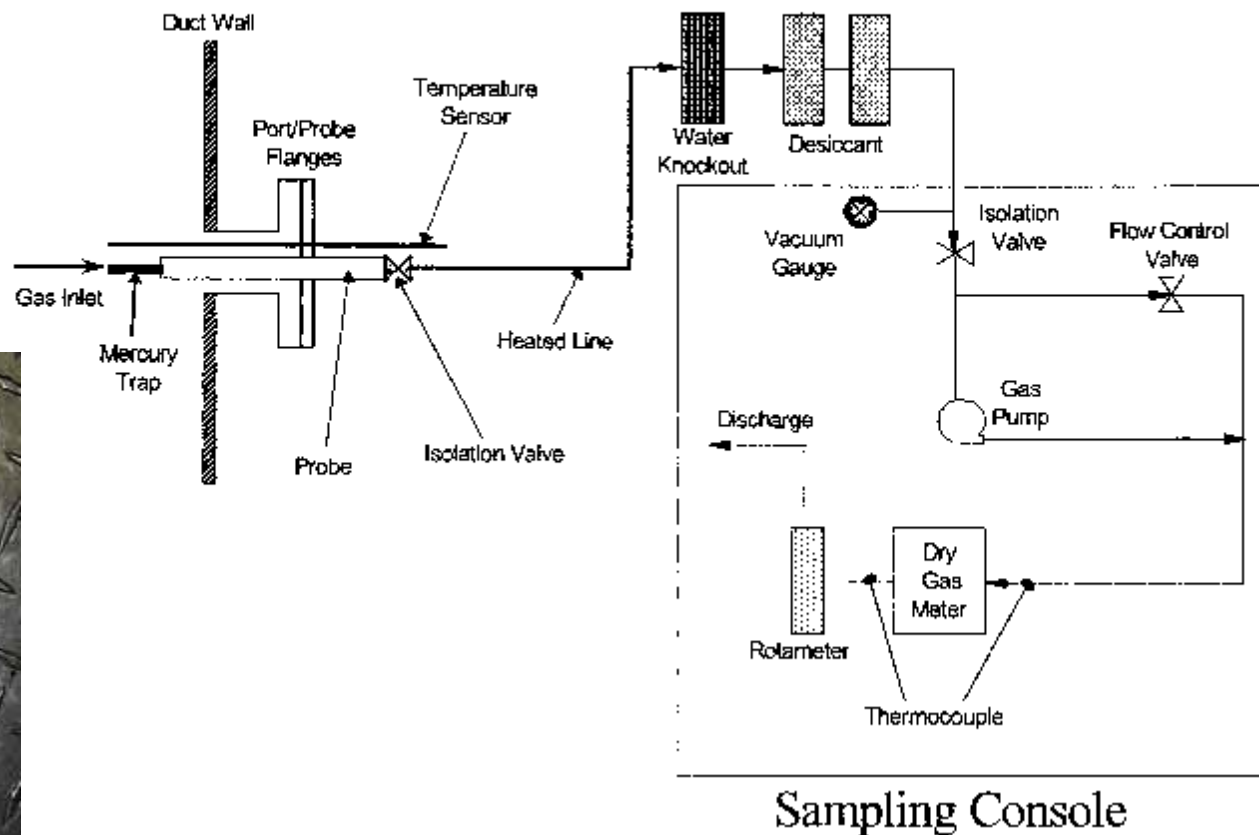
# QC Checks using a Permeation Source

- Thermo Fisher is developing a mercury permeation source that integrates into existing and new mercury CEMS in order to meet the requirements of Section 7
- Done at the instrument, **NOT** through the system, to check the precision of the NIST traceable mercury generator



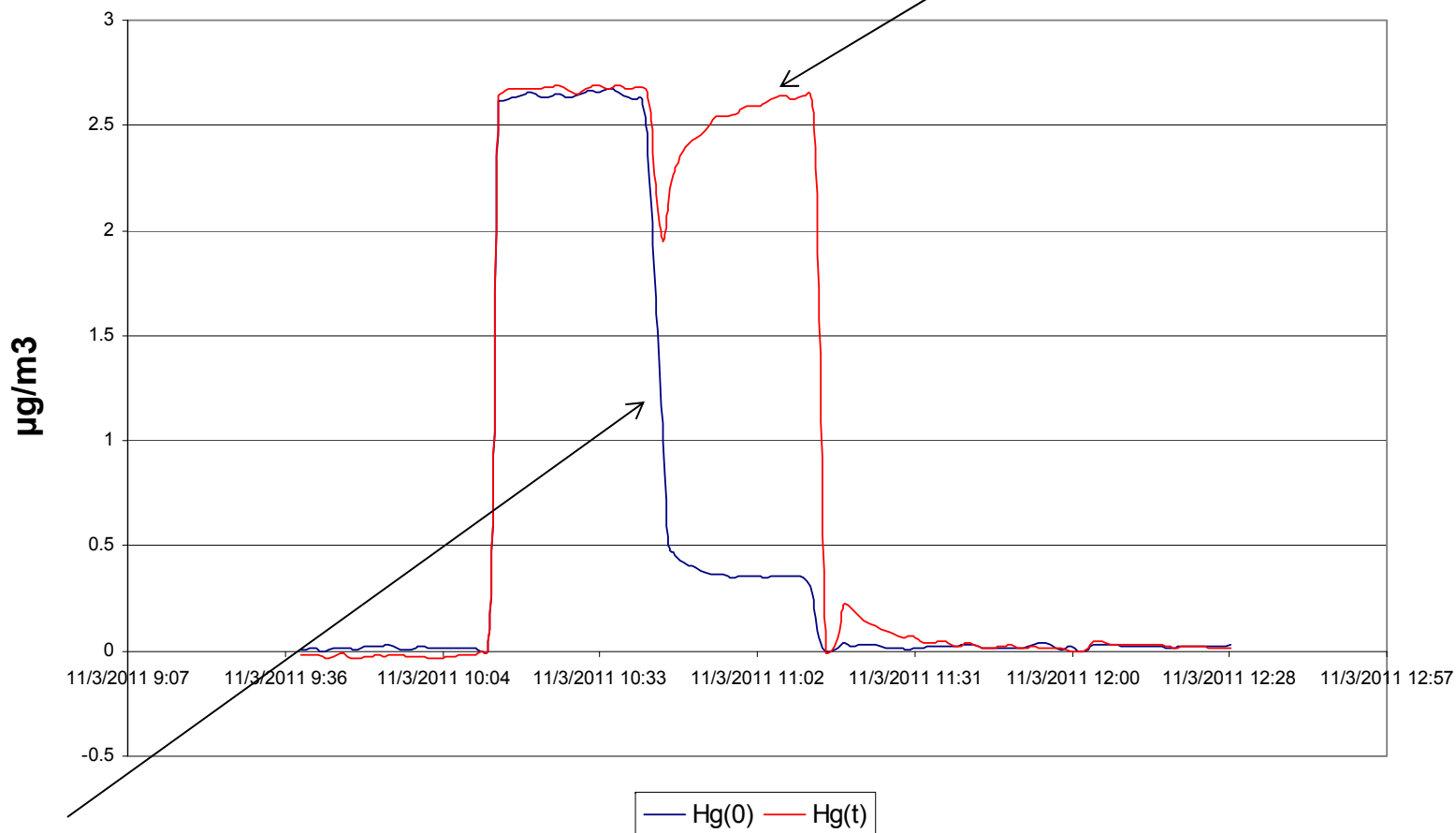
# Appendix K Sorbent Trap Hg Monitor

Figure K-1. Typical Sorbent Trap Monitoring System



# System Integrity Test

2. Conversion must be  $>90\%$  or  $0.8 \mu\text{g}/\text{m}^3$  (adjusting for the flow of  $\text{Cl}_2$ )



1. Oxidation must be  $>50\%$

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# **PREVENTATIVE MAINTENANCE**

# Mercury CEMS usually require more maintenance than other CEMS

## *Preventative Maintenance Schedule for Mercury Freedom System™*

Note: This document is a guideline only, many items are site specific

	Monthly	Quarterly	Semi-Annually	Annually
<b>Model 80</b>				
Clean outside of case	X			
Visual Inspection and cleaning	X			
Critical orifice inspection (qty 2)	X			
Fan filter inspection	X			
Lamp voltage/frequency check	X			
Leak Test				X
Replace analyzer lamp				X
Daily analyzer worksheet				
<b>Model 81</b>				
Cleaning outside of case	X			
Chiller fins inspection and cleaning	X			
Fan filter inspection and cleaning	X			
Leak test				X
Replace scrubbers				X
Daily calibrator worksheet				
<b>Model 82</b>				
None				
<b>Model 83</b>				
Hg converter core replacement			X	
15 micron filter				X
Hg scrubber (elemental channel)			X	
Thermocouple converter				X
Preventative maintenance kit				X
Clean inertial filter with brush		X		
Clean out inlet and outlet stingers		X		

# Maintaining the Model 83i GC Extraction Probe

Refer to the Model 83i GC Extraction Probe Instruction Manual, 105190-00, Preventative Maintenance and Servicing chapter.

Description	Replacement Interval
Filter Element, CR Coated	Annual
Orifice, SS, CR Coated, #7	As needed
Heater, Firerod, 240 V, 375 W	Annual
Thermocouple, 1/8"	Annual
Eductor Assembly	As needed
Filter, SS, CR Coated, 15 Micron	Annual
Filter, SS, 15 Micron	Annual
Core Assembly, Mercury Converter	6-12 months or as needed
Heater, Converter, 120 V, 250 W	Annual
Thermocouple, Converter	Annual
Solenoid Valve, 115 V	As needed
Heater Coil, 5 FT, 240 V, 600 W	Annual



The recommended replacement interval is site specific, therefore, the following provides only guidelines.

# System Preventive Maintenance Schedule

Task	Approximate Task Time	Semi-			
		Monthly	Quarterly	Annually	Annually
Cleaning Sample Lines (Total / Elem.)	4 Hours				X
Check Indicating Silica Gel on Dryer	30 Minutes	X			
Replace Dryrite™	30 Minutes			X	
Replace Carbon	30 Minutes			X	
Replace Purafil™	30 Minutes			X	
Replace Air Clean-up Filters	15 Minutes			X	
Replace Transport Pump	15 Minutes	As Required			
PMT & Dilution Factor Adjustments	3 Hours		X		

**PMT & Dilution Factors Adjustment should be done prior to all linearity test and RATA's.**

# Critical Parts Recommend On Hand

- 80i Analyzer
  - UV Lamp
  - Reference Detector
  - Solenoids
  - 250 mL/min Glass Orifices
- 81i Calibrator
  - Hg Scrubbers
  - Solenoids
- 82i Probe Controller
  - 3 - 27 psi Pressure Regulator / Transducer
  - 2 - 60 psi Pressure Regulator / Transducer
  - Solid State Relay (25A and 50A)
  - Relay / Switch



# Critical Parts Recommend On Hand

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- Oxidizer Heater
- Oxidizer Thermocouple
- 15 Micron Filter
- Orifice Pressure Transducer
- 250 mL/min Stainless Orifice for Chlorine Tank
- O-rings
  - Probe Filter Area
  - Dilution Module
  - Bypass Eductor
- 1/2" Graphite Ferrule
- 1/4" Graphite Ferrule

# Critical Parts Recommend On Hand

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- Other miscellaneous items
  - DX / BX/ CI Filters
  - Drierite
  - Purafil
  - Charcoal
  - Regulator Filters
  - N2 (Instrument Air) Filter
  - Teflon Tubing
    - 1/8", 1/4", 3/8"
  - Welsh Vacuum Pump

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# NITROGEN GENERATOR

# Nitrogen Generator Benefits

- Reduces system MDL from 0.04 mg/m<sup>3</sup> to 0.008 mg/m<sup>3</sup>
- Raises sensitivity by five orders of magnitude
- Recommended for installations with total stack Hg concentrations below 3.0 mg/m<sup>3</sup>
- Can be easily retrofitted into existing system



# Low Concentration Hg Measurements

## Zero Air

Total Hg concentrations  $> 2 \mu\text{g}/\text{m}^3$

- Standard dilution system
- Zero Air
- $1 \text{ ng}/\text{m}^3$  analyzer MDL
- 40:1 system dilution
  - CEMS MDL  $\sim 0.04 \mu\text{g}/\text{m}^3$

## Nitrogen Generator

Total Hg concentrations  $< 2 \mu\text{g}/\text{m}^3$

- Nitrogen dilution system
- Zero Air feed to Nitrogen generator
- $0.2 \text{ ng}/\text{m}^3$  analyzer MDL
- 40:1 system dilution
  - CEMS MDL  $\sim 0.008 \mu\text{g}/\text{m}^3$

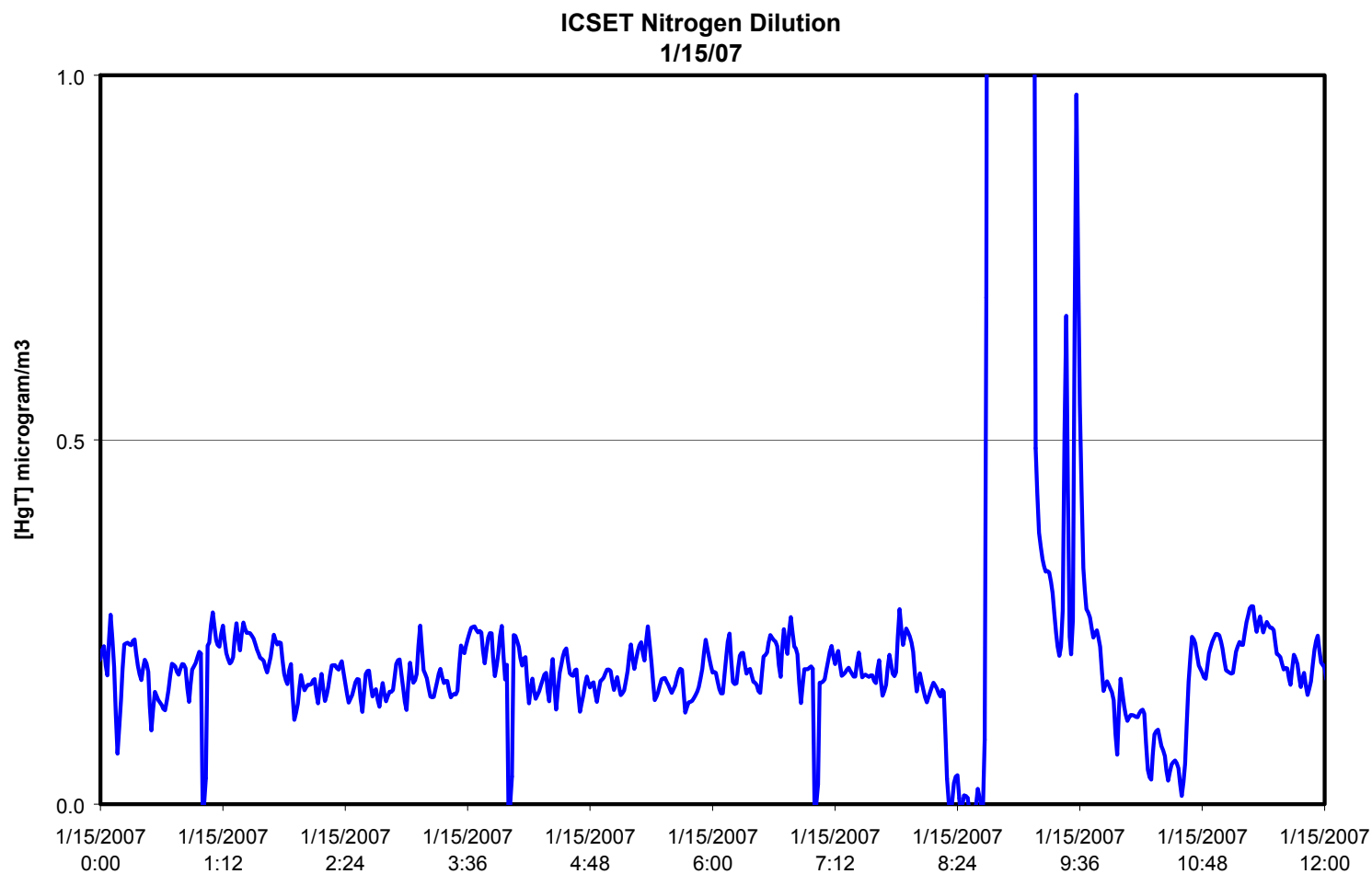


# Nitrogen Generator Purity Chart

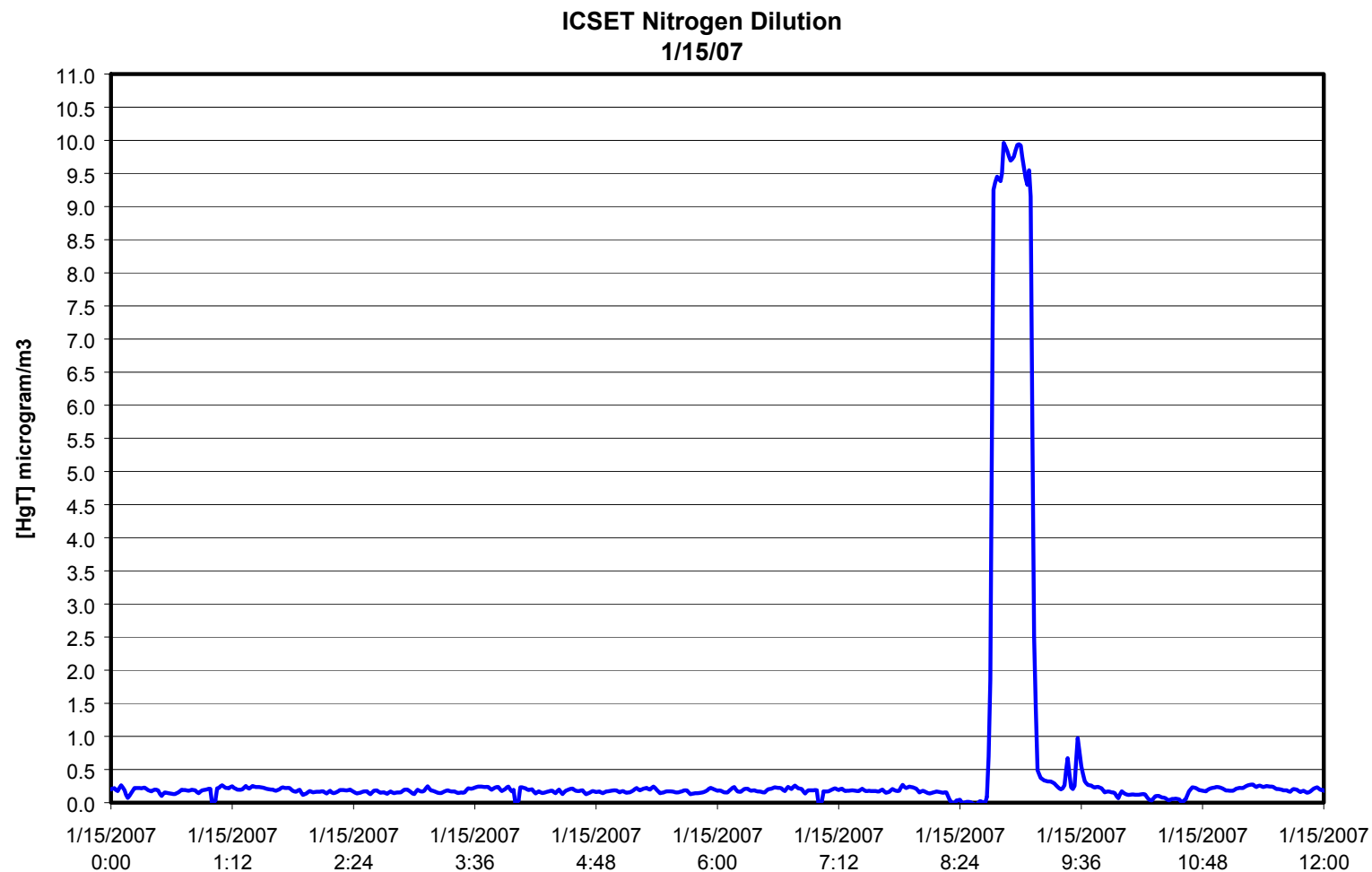
Minimum nitrogen production capacity in Nm3/hr*							Air consumption in Nm3/hr at minimum capacity						
Nitrogen purity %	99.5	99	98	97	96	95	Nitrogen purity %	99.5	99	98	97	96	95
4 bar(g)	0.76	1.13	1.69	2.23	2.76	3.36	4 bar(g)	5.79	6.21	6.95	7.57	8.02	8.72
5 bar(g)	0.95	1.41	2.12	2.78	3.46	4.19	5 bar(g)	7.24	7.77	8.69	9.46	10.0	10.9
6 bar(g)	1.19	1.77	2.67	3.35	4.37	5.27	6 bar(g)	8.94	9.56	10.7	11.4	12.7	13.7
7 bar(g)	1.39	2.07	3.11	3.91	5.09	6.15	7 bar(g)	10.4	11.2	12.5	13.3	14.8	16.0
8 bar(g)	1.59	2.36	3.56	4.46	5.82	7.03	8 bar(g)	11.9	12.7	14.2	15.2	16.9	18.3
9 bar(g)	1.75	2.63	4.03	5.30	6.60	8.00	9 bar(g)	13.3	14.5	16.1	18.0	19.1	20.8
10 bar(g)	1.99	2.95	4.45	5.58	7.28	8.79	10 bar(g)	15.1	16.2	17.8	19.0	21.1	22.9
11 bar(g)	2.08	3.14	4.80	6.22	7.93	9.62	11 bar(g)	17.3	18.5	20.2	21.2	23.8	25.0
12 bar(g)	2.17	3.33	5.16	6.87	8.58	10.4	12 bar(g)	18.0	19.6	21.7	23.4	25.7	27.2

**Higher pressure and volume = higher purity**

# ICSET Nitrogen Dilution Testing



# ICSET Nitrogen Dilution Testing





# Thirsty for more information?

- Questions?

Jeremy Whorton

27 Forge Park, Franklin, MA

508-269-9965

[Jeremy.whorton@thermofisher.com](mailto:Jeremy.whorton@thermofisher.com)

