U.S. EPA APTI
Compliance Test and Source Test Observation
On-Site Changes to FRMs

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On-site Request for Changes to FRMs

- The U.S. EPA has established administrative procedures in place to allow deviations to Federal Reference Methods (FRMs) in the field. When a stack tester requests the use of an alternative method or modification of an existing FRM, an EPA Agency response is expected within a reasonable time.
- EPA developed a logical approach for approval called the "bias concept".

Bias Concept

- When the bias (from prior knowledge or comparative data) is determined to be insignificant or against (deterrent) the initiating party or the party who bears the burden of proof, the alternative or modified method is acceptable for enforcement or compliance testing. For most sources, this equates to agency—negative bias; industry—positive bias.

Changes to On-site FRMs

- Minor Changes
  - Does not affect the stringency of the emission limitation or standard(i.e., no emission limit or standard relaxation);
  - Has no national significance (e.g., the change will not affect the applicable regulation's implementation for other sources in the affected category); and
  - The minor change to the methodology produces test results equal to or greater than what would be produced utilizing the specified reference method.

Example of Minor Changes

- Examples of Minor Changes
  - Selecting alternative sample traverse points to avoid interference from an obstruction in the stack;
  - Adding one or more moisture collection impingers to a sampling train configuration for high moisture;
  - Extending the sampling time to increase sensitivity of a sampling test method or a low concentration emission level source; and
  - Accepting emission results for a test run conducted with a lower than specified filter temperature (e.g., less than 250 F).

Changes to On-site FRMs

- Major Changes
  - The requested change in the testing or monitoring method or procedure should provide a determination of compliance status at the same or higher stringency as the method or procedure specified in the applicable methodology;

Major Changes

- The requested change in the testing or monitoring method should include compelling reasons which prompted the change; That is, a request for any change should address significant deficiencies in applying the prescribed procedure or provide the meaningful improvements achieved over the existing procedure or method.

Major Changes

- Compelling Reasons
  - Overcoming significant interferences or biases (e.g., addition of an HCI-filled impinger to remove an SO_2 gas sample);
  - Allowing for new technology for improving method accuracy, lower cost procedures, or increased applicability (e.g., use of specially-treated canisters in lieu of Tedlar bag or solid adsorbent tube sampling); and
  - Allowing for alternative measurement locations for hybrid processes subject to multiple regulations.

Requesting Party Responsibility

- Responsible For:
  - Assuring that the techniques or alternatives are in fact applicable and are properly executed;
  - Including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction and the degree of detail should be similar to the detail contained in the reference methods); and
  - Providing any rationale or supporting data necessary to show the validity of the alternative in the particular application.

Example of Guidelines
(See Resource CD, Session 1)

FRM	Options	Responsible Party	Affects on Emissions
1	Circular Stack: Use of Particulate Traverse Not In Plane of Bend	Tester	Equal or Lower Emissions
2	Use of Standard Pitot Tube Rather than Type-S	Tester	Equal Values (Observe Possible Plugging)
3	Leak Check of Orsat Analyzer	Tester	Inaccurate O_2 and CO_2 Measurements
4	Use of Flexible Tubes Between Impingers	Tester	None
5	Nozzle Design Other Than Button-hook or Elbow	Administrator	None or Less

Compliance Test and Source Test Observation

Stack Testing Special Topics:

Compliance Test and Source Test Observation

Stack Testing Special Topics:

- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

Typical Sources With High Moisture Content In Stack

- Lime Hydrators
- Evaporators
- Coke Oven Quench Towers
- Ammonia Nitrate Prilling Facilities
- Steam Generators

The Problem

- High moisture in stack gas causes pitot tube to plug, thus poor Δp readings (i.e., velocity measurements)

- Problems with maintaining isokinetic sampling rate (i.e., $\Delta H = k\Delta p$)

- Water droplets on filter increasing pressure drop and effecting isokinetics

- Dilution of impinger solutions thus effecting collection efficiency of analytes

- Condensation in pitot tube sample lines

Water Vapor and Testing

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The Problem: FRM 5
Isokinetic Rate Equation

$$\Delta H = \left\{ 846.72\, D_n^{\,4} \Delta H_{@}\, C_p^{2}\, (1 - B_{ws})^2 \quad \frac{M_d}{M_s}\, \frac{T_m}{T_s}\, \frac{P_s}{P_m} \right\} \Delta P$$

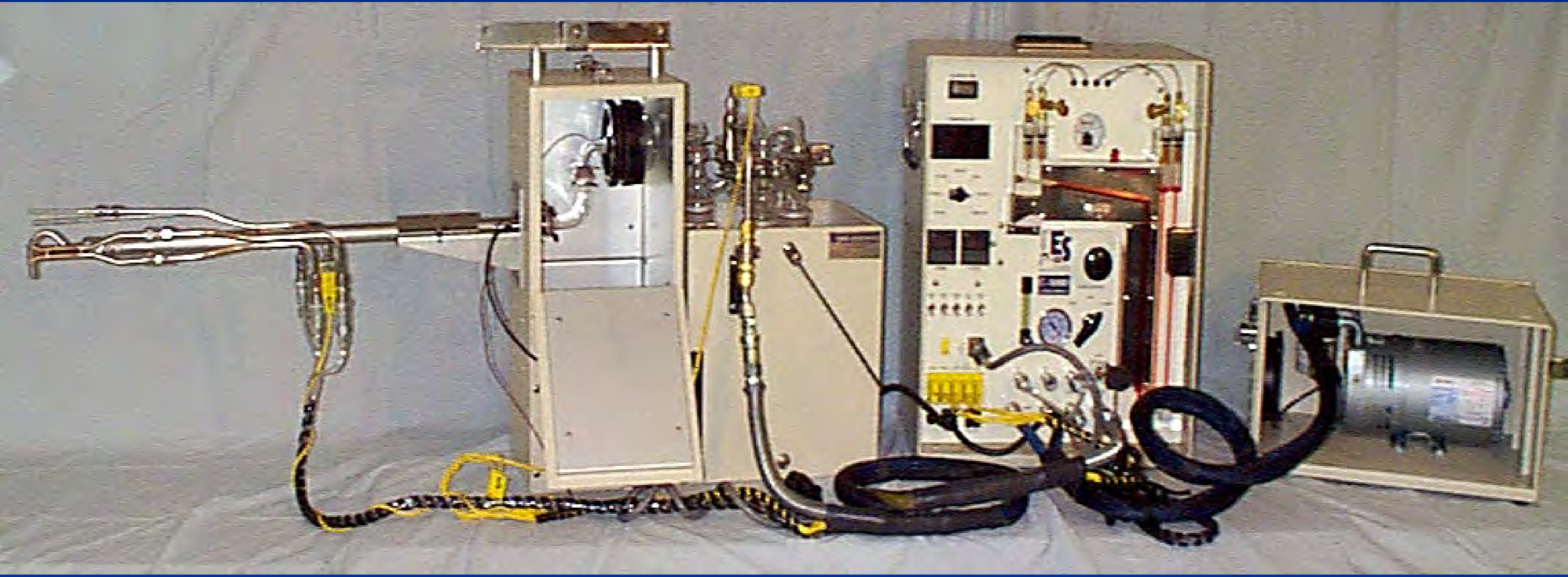
High Moisture Error

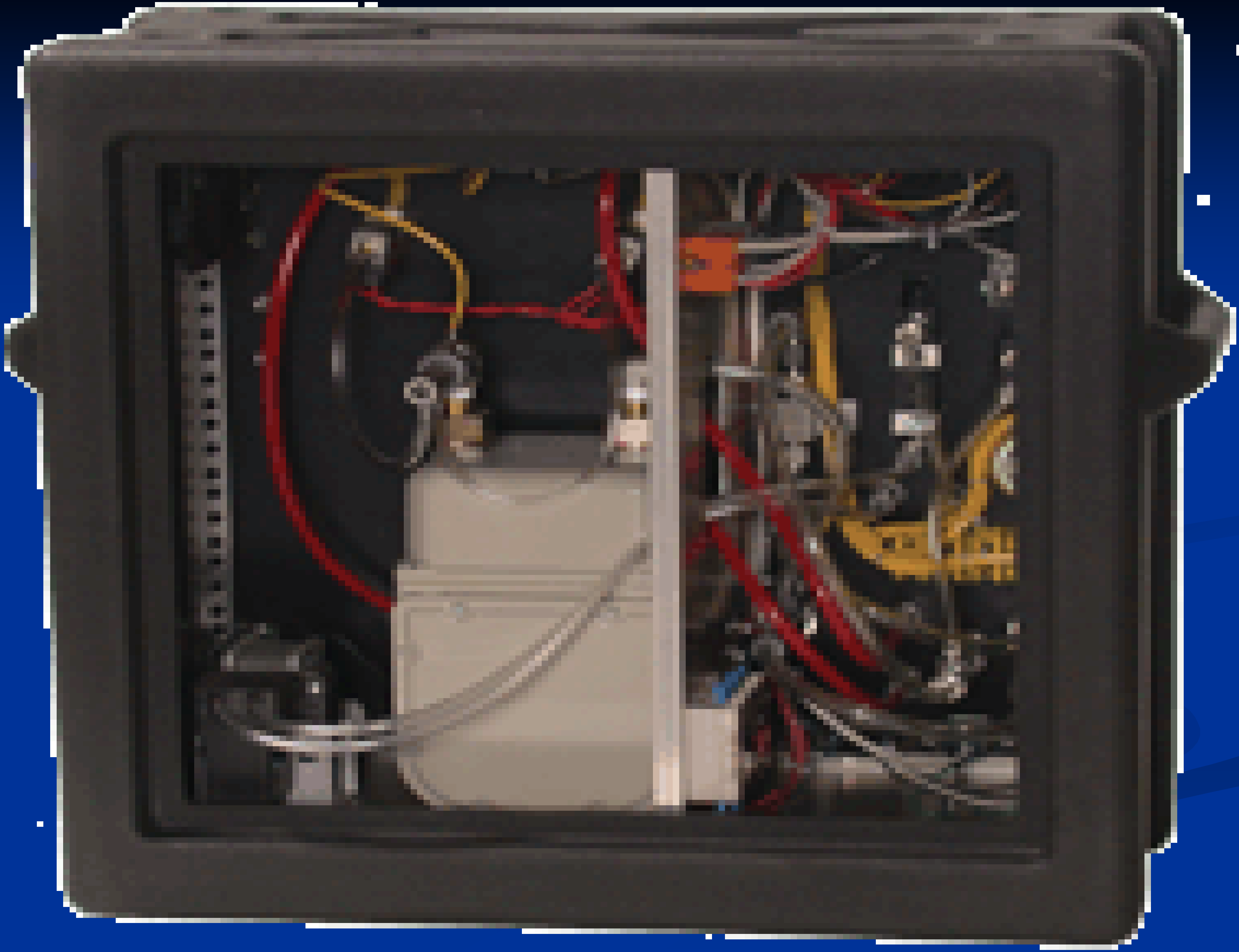
- With low moisture (i.e., <15 %), the error is rather small
- However, with high moisture (i.e., > 15 %, the error becomes small
- Typically, for every 1 % error in moisture determination reflects a 1 % error in isokinetics

Sampling Problems With High Moisture Stacks

- Erroneous readings due to low flow rate through orifice due to large volume of moisture drop-out in impingers
- Inaccurate control of sampling rate due to small volume of gas passing through control valves
- Non-isokinetic sampling due to fluctuations in moisture content of stack gas

What Approaches Can Be Taken To Sample Under High Moisture Situations?





General Solution #1 (Placement of Orifice Meter In Stack)

- Place orifice meter before impingers instead at end of sampling system
  - Total sample volume passes through orifice meter
  - Moisture content measurement unnecessary
  - Isokinetics not affected by moisture

EPA HIGH MOISTURE SAMPLING TRAIN

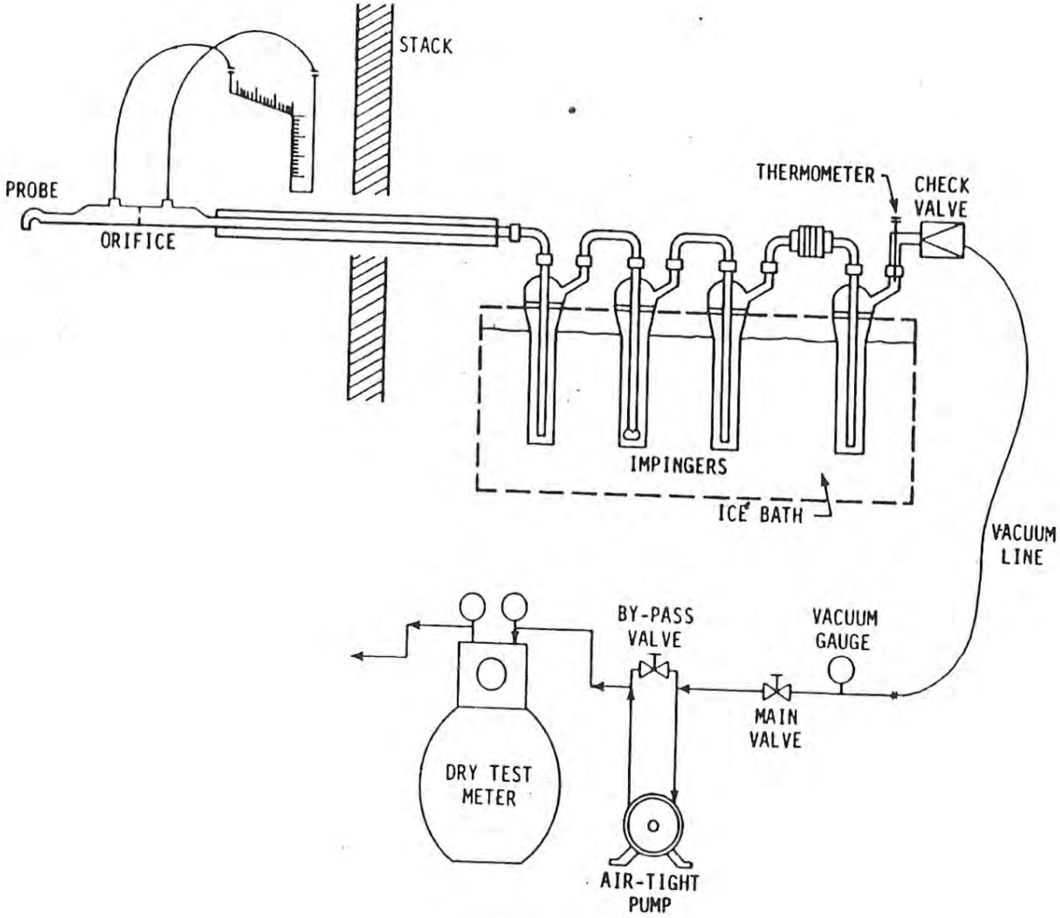


FIGURE 5-2.

General Solution #2 (Placement of Orifice Meter In Heated Filter Box)

- Orifice meter is located in heated sample box behind filter
    - Prevention of condensation at orifice
    - Protected from particulate fouling

JACA HIGH MOISTURE SAMPLING TRAIN

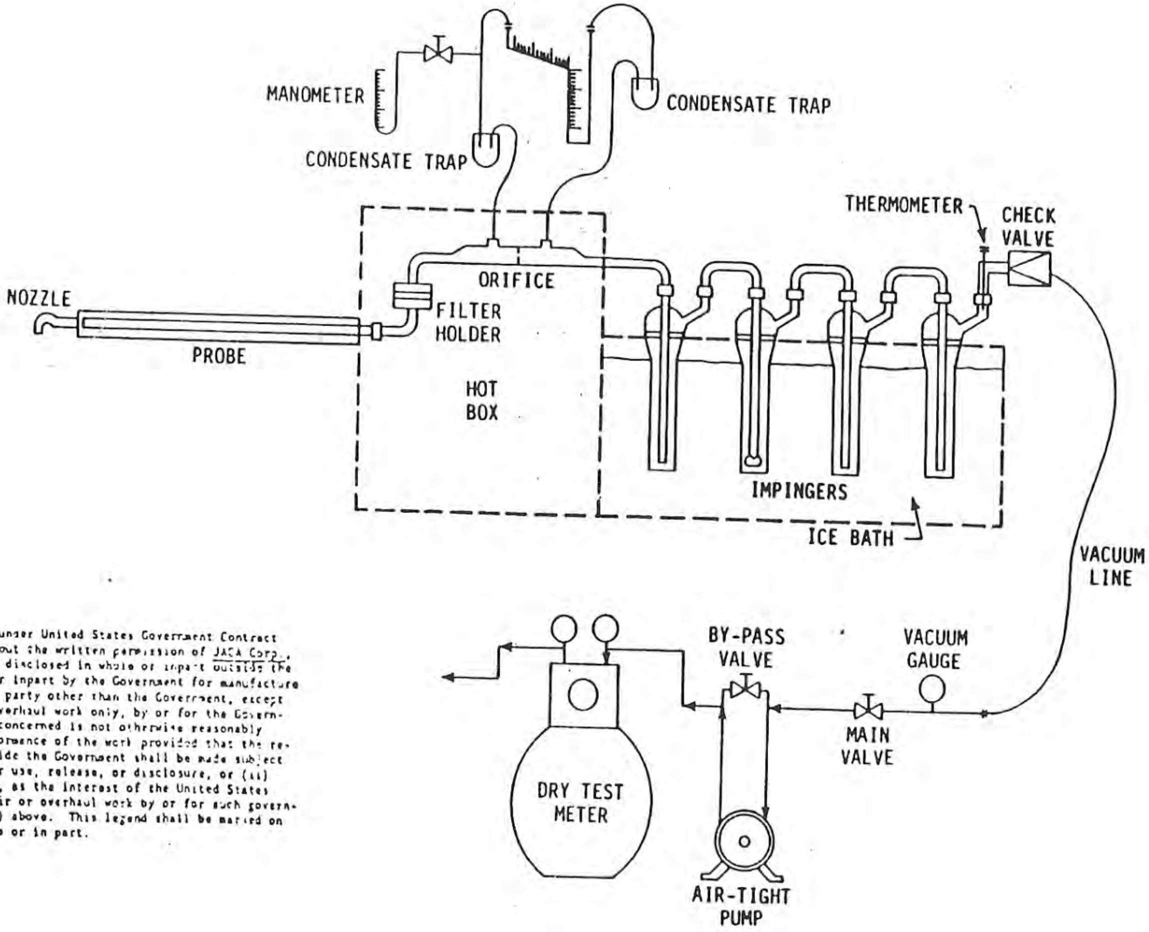


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FIGURE 5-1.

General Solution #3 (In-situ Orifice with Changeable Orifice Plates)

- Orifice meter is located in the stack with changeable orifice plates (i.e., In-situ)
- Filter located before silica gel impinger
- Probe heated to prevent condensation
- Developed for use at ammonium nitrate facilities

EPA HIGH MOISTURE SAMPLING TRAIN

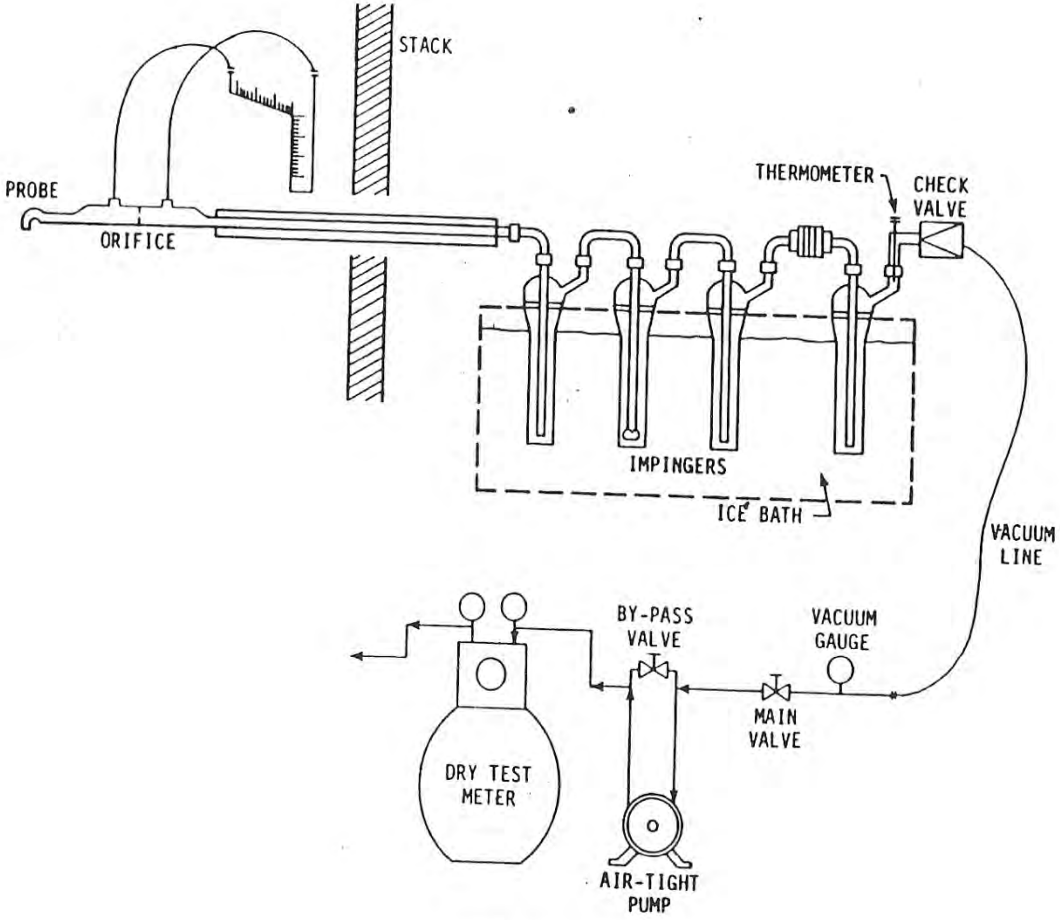


FIGURE 5-2.

General Solution #4 (Consultant's Approach)

- Orifice meter is located in the heated filter compartment of FRM 5 sampling train
- Filter located before silica gel impinger
- Probe heated to prevent condensation and pitot tube lines cleaned by pressurized air
- Developed for use at ammonium nitrate facilities

General Solution #5

- Use FRM 5 Sampling Train Except:
    - Install cyclone and drop-out impinger in sample train to catch larger volume of water
    - Use larger 1st impinger and change periodically during test (Must leak check during each change!)
    - Install drop-out traps in pitot tube lines or blow-back lines periodically during sampling

All of The Solutions Involve Removing B_{ws} From The Isokinetic Rate Equation

$$\Delta H = \left\{ 846.72\, D_n^{4}\, \Delta H_{@}\, C_p^{2}\ \frac{M_d}{M_s}\frac{T_m}{T_s}\frac{P_s}{P_m} \right\} \Delta P$$

Problems Common To All Three Approaches

- Entrained water droplets
- Condensation in manometer and pitot tube lines
- Improper condensation in impingers

General Solutions

- Use of larger knock-out impinger after heated filter compartment
- Use of condenser to aid in knocking out moisture coupled with larger impinger in sampling train
- Changing impingers frequently during testing (must leak check each time)

Compliance Test and Source Test Observation

Stack Testing Special Topics:

- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

Stack Testing At High Pressure Sources

William T. "Jerry" Winberry, Jr.
EnviroTech Solutions

Three Problem Areas With Stack Testing At High Pressure Stacks (> 5 “)

- Port Leakage
- Pressure Measurement Difficulties
- Sample Losses

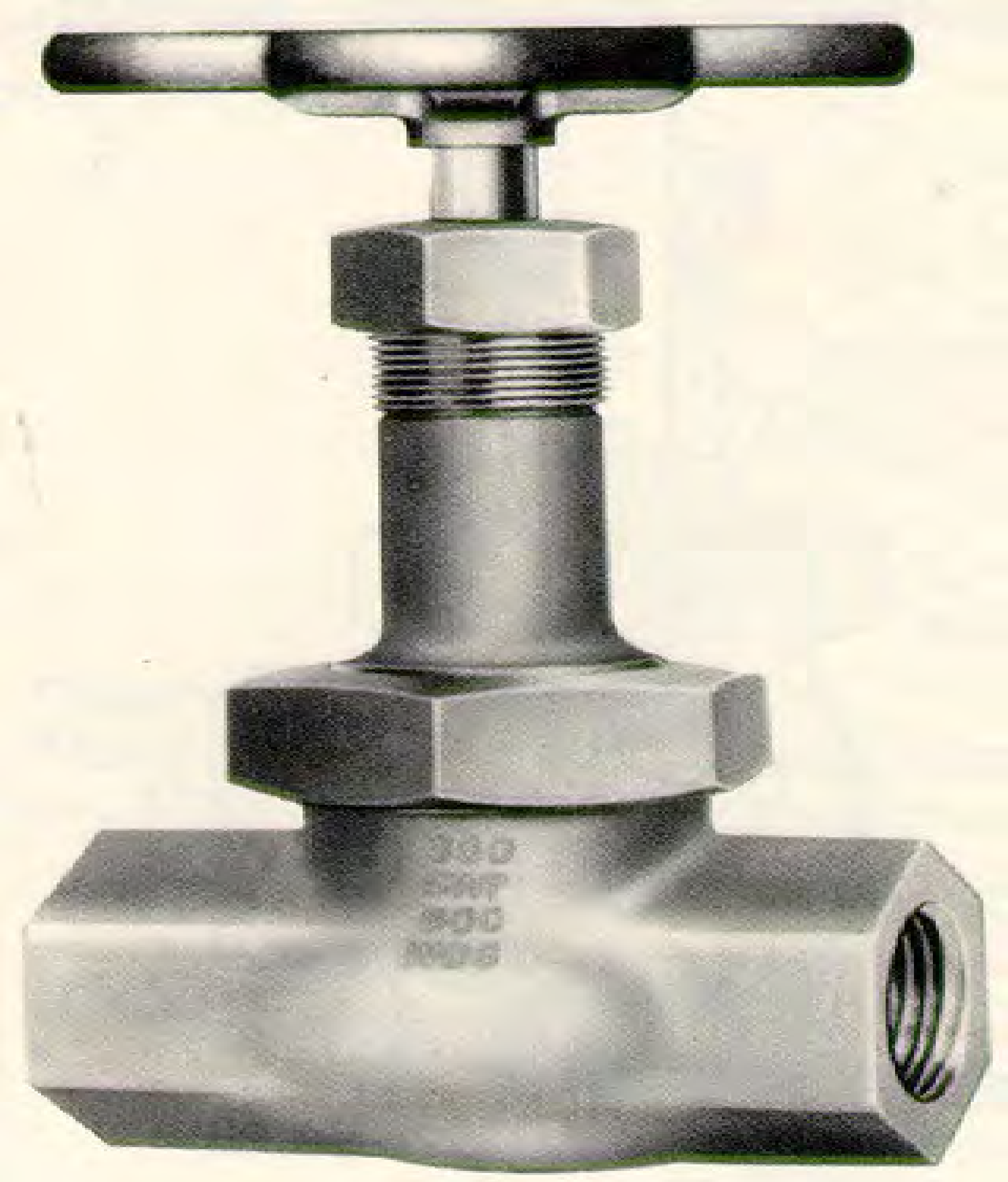
Port Leakage

- Locations with NEGATIVE STATIC PRESSURE
  - Ambient air (O_2 = 20.9 %) will be sucked into the duct
- Locations with POSITIVE STATIC PRESSURE
  - Flue gas will be blown out of port into the immediate test area

(As the magnitude of the static pressure increases, the effects become significant)

Minimizing Port Leakage

- Install gate valves or globe valves on ports for use during sample train insertion and removal
- Use port adapters with compression fittings around probe to seal off port during sampling



Pressure Measurement Difficulties

- During probe insertion/removal:
  - Pitot tube lines can be blown off the manometer from the force of the static pressure
  - Gauge oil in manometer can be pushed or pulled into the fluid reservoirs from the force of the static pressure
  - In extreme cases, the fluid can be pulled into pitot lines

Overcoming Pressure Measurement Difficulties

- Use compression fittings to attach pitot lines to manometer
- Install a series of shut-off valves to the pressure lines
- Measure static pressure with a magnahelic gauge

Sample Losses Can Occur

- During probe insertion/removal:
  - Filter can become unseated from the filter holder and sucked forward, along with any sample collected on the filter
  - Impinger contents can become sucked forward through the impinger train

Sample Losses Can Occur

- During sampling:
  - Probe (and all attached components of the sample train) can be inadvertently displaced by positive or negative pressure
  - Impinger train can burst from extreme positive pressure

Preventing Sample Losses

- Locations with NEGATIVE STATIC PRESSURE:
  - Engage the pump and allow a small amount of gas to flow through the sample train while putting the sample train into the port
- Locations with POSITIVE STATIC PRESSURE:
  - Engage the pump and allow a small amount of gas to flow through the sample train while taking the sample train out of the port

Preventing Sample Losses

- Use port adapters with compression fittings around probe to support sample train and keep it fixed in place
- Reduce positive pressure on impinger train
  - Insert a valve at the inlet of the impinger train to reduce gas flow
  - Use a coiled condenser at the inlet of the impingers train to rapidly cool the gas stream

Compliance Test and Source Test Observation

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- High Temperature Stacks
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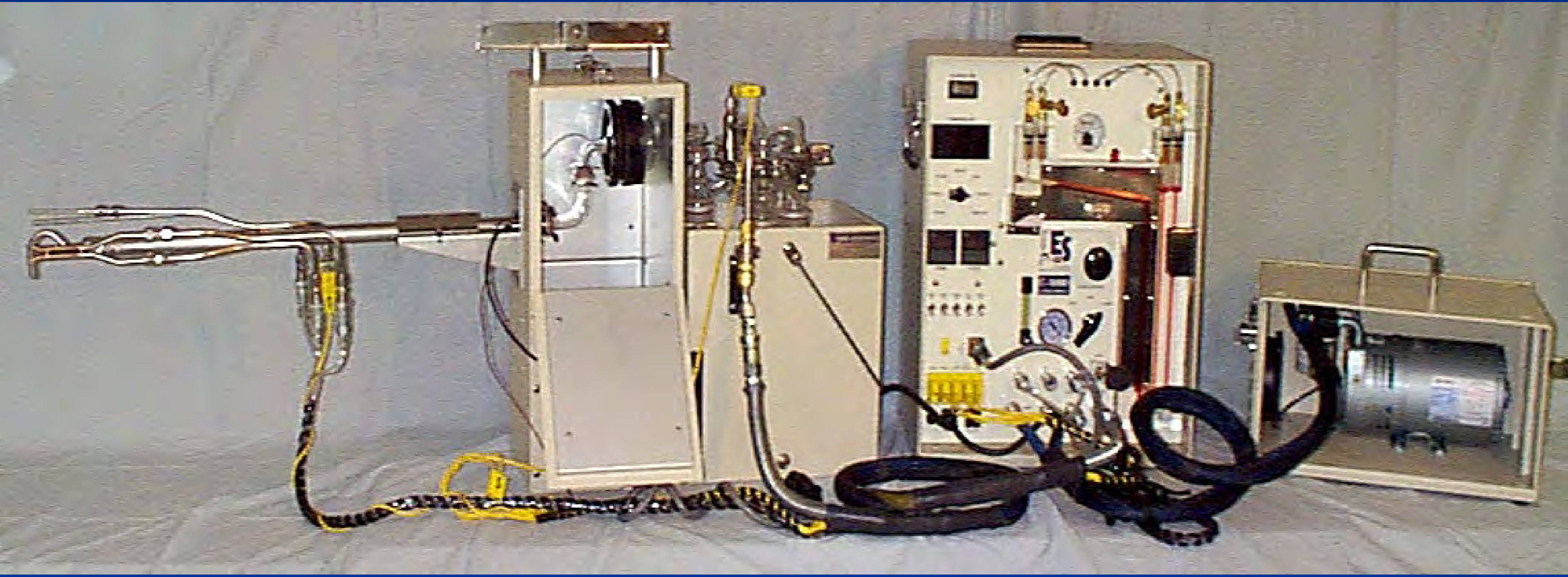

Typical Sources With High Moisture Content In Stack

- **Gas Turbines**
- **Municipal Incinerators**
- **Glass Furnaces**
- **Other Sources**


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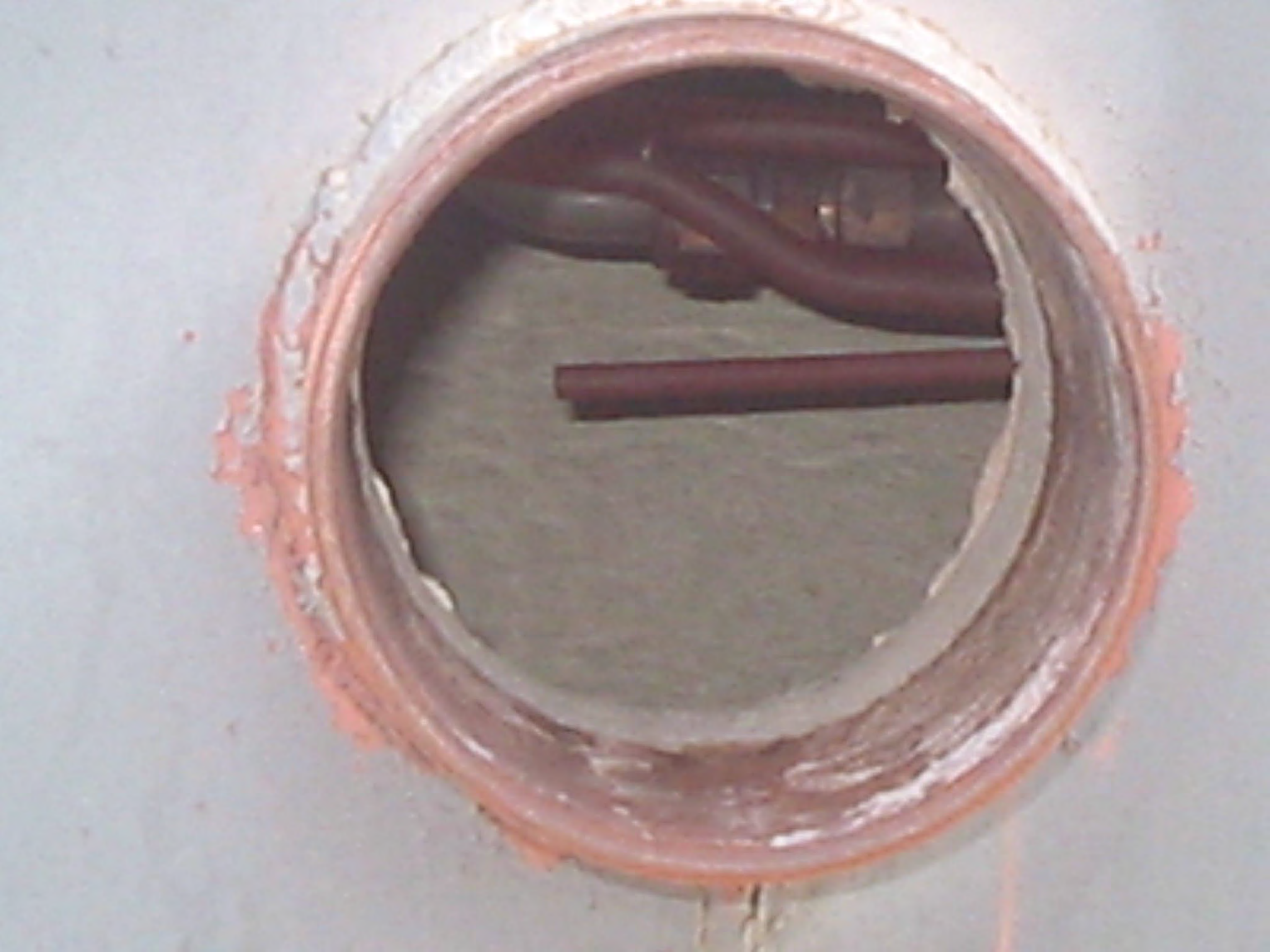
FOIL WRAP



TissuQuartz 82.6mm
Filter ID. 267
Tare Wt. 0.42618
7/11/06 Run #1 Filter #1

TissuQuartz 82.6mm
Filter ID. 268
Tare Wt. 0.4347
7/11/06 Run #2 Filter #2


IZOD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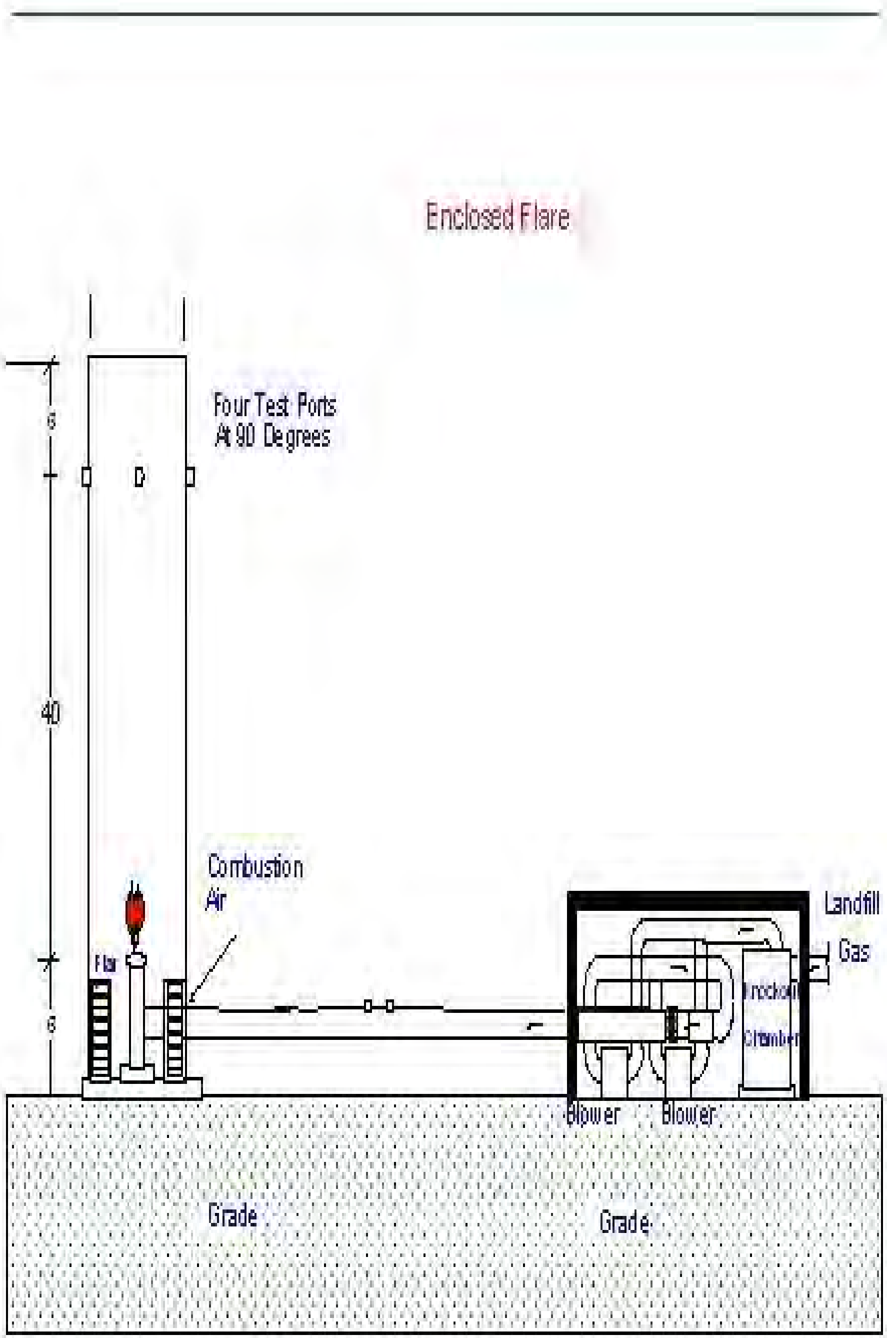
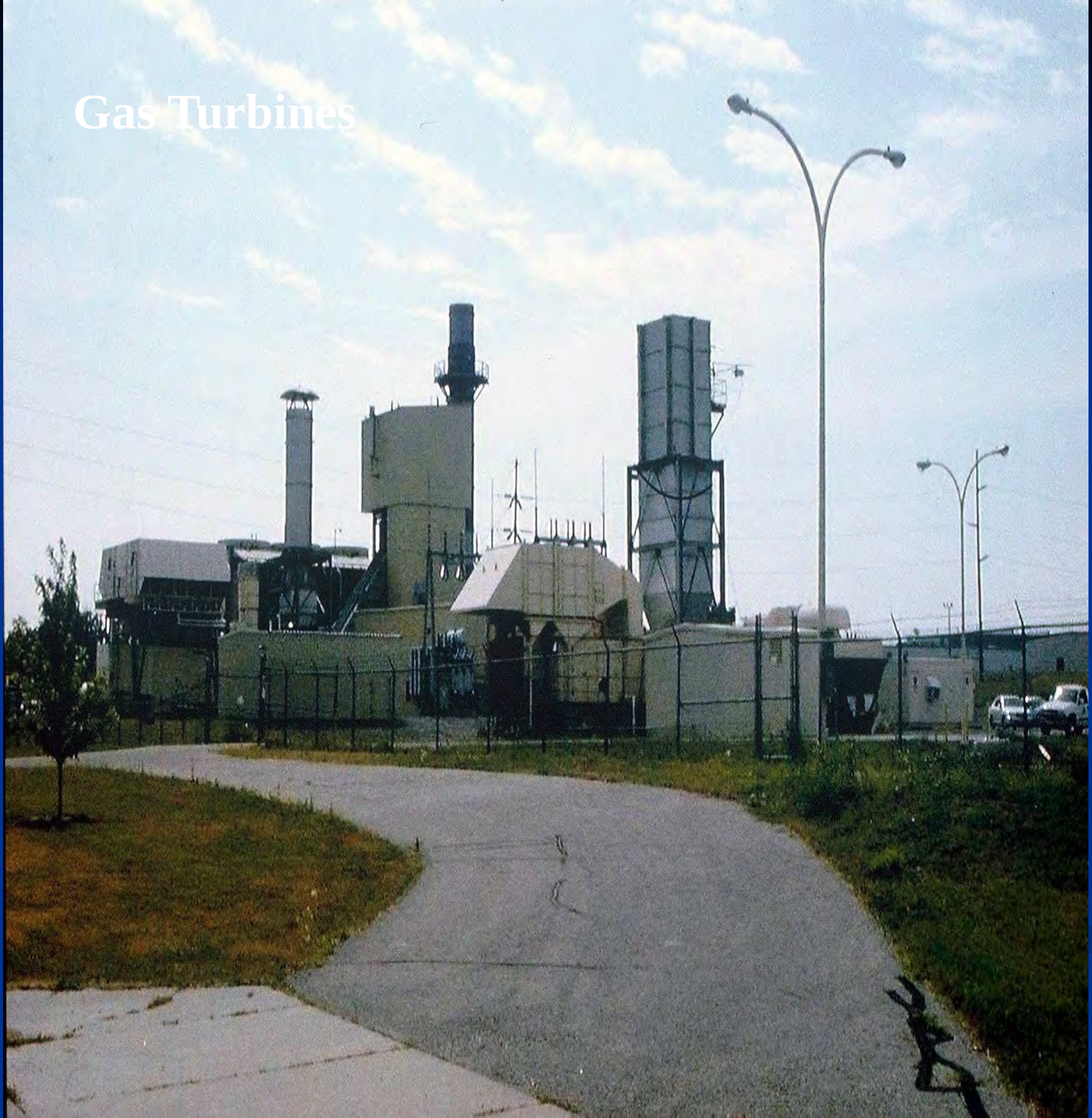
Vapor Recovery Unit



Gas Turbines



Rotary Kiln Incinerators

Other Sources

The Problem

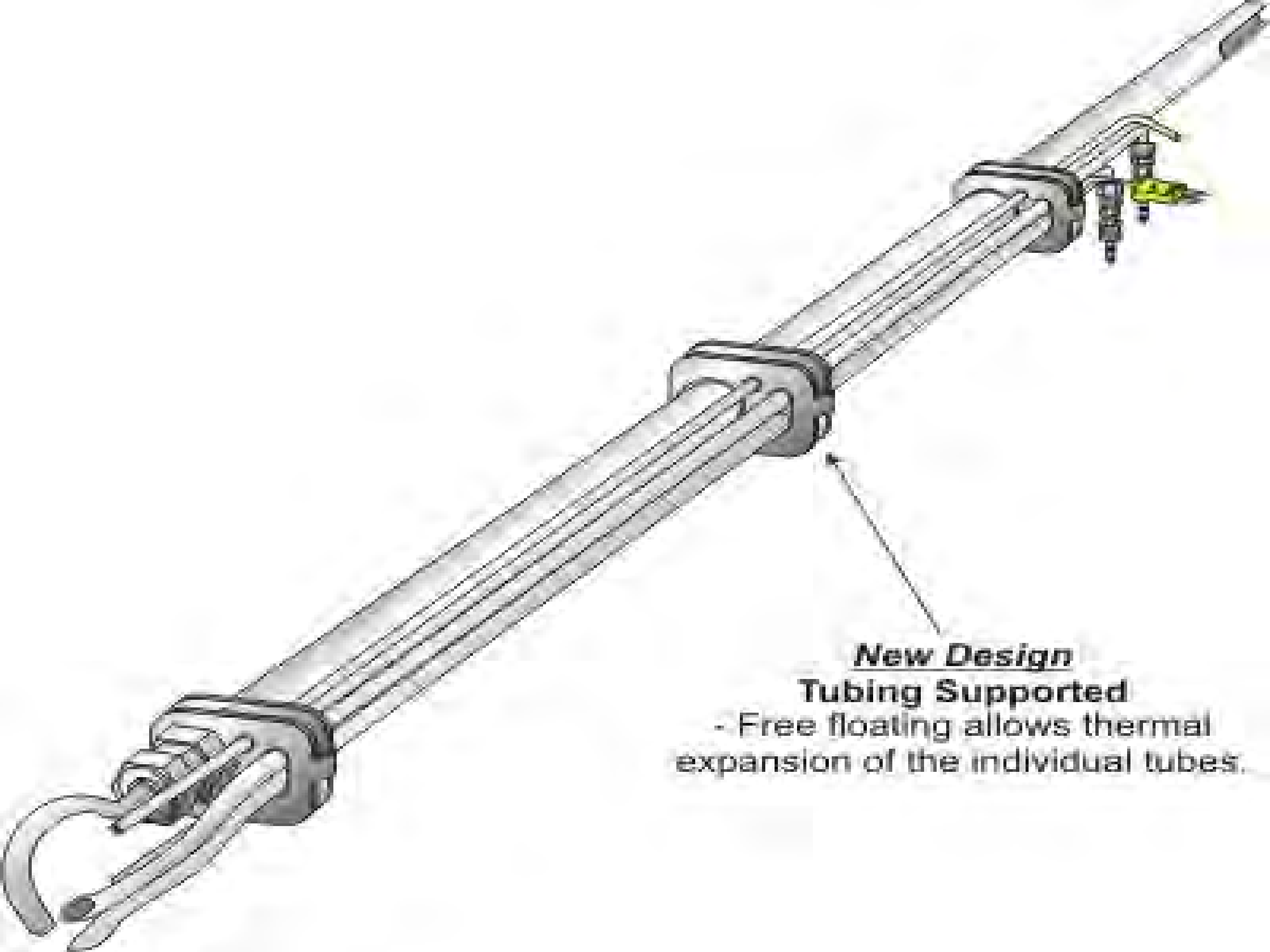
- High stack temperatures causes problems with obtaining proper leak check of sampling system and safety problems
- Problems with achieving airtight seal between nozzle and probe liner
- Breakage of glass probe liner due to different coefficients of thermal expansion between probe liner and stainless steel jacket

Stack Temperatures

- Traditional FRM 5 good to about 700 F
- Municipal incinerators and gas turbines usually emit effluents well in excess of 750 F, and up to 2000 F

Maximum Temperature of Various Materials

- Teflon: < 350 F
- Glass: < 900 F
- Stainless Steel: < 1210 F
- Quartz: < 1650 F
- Inconel: < 1800 F



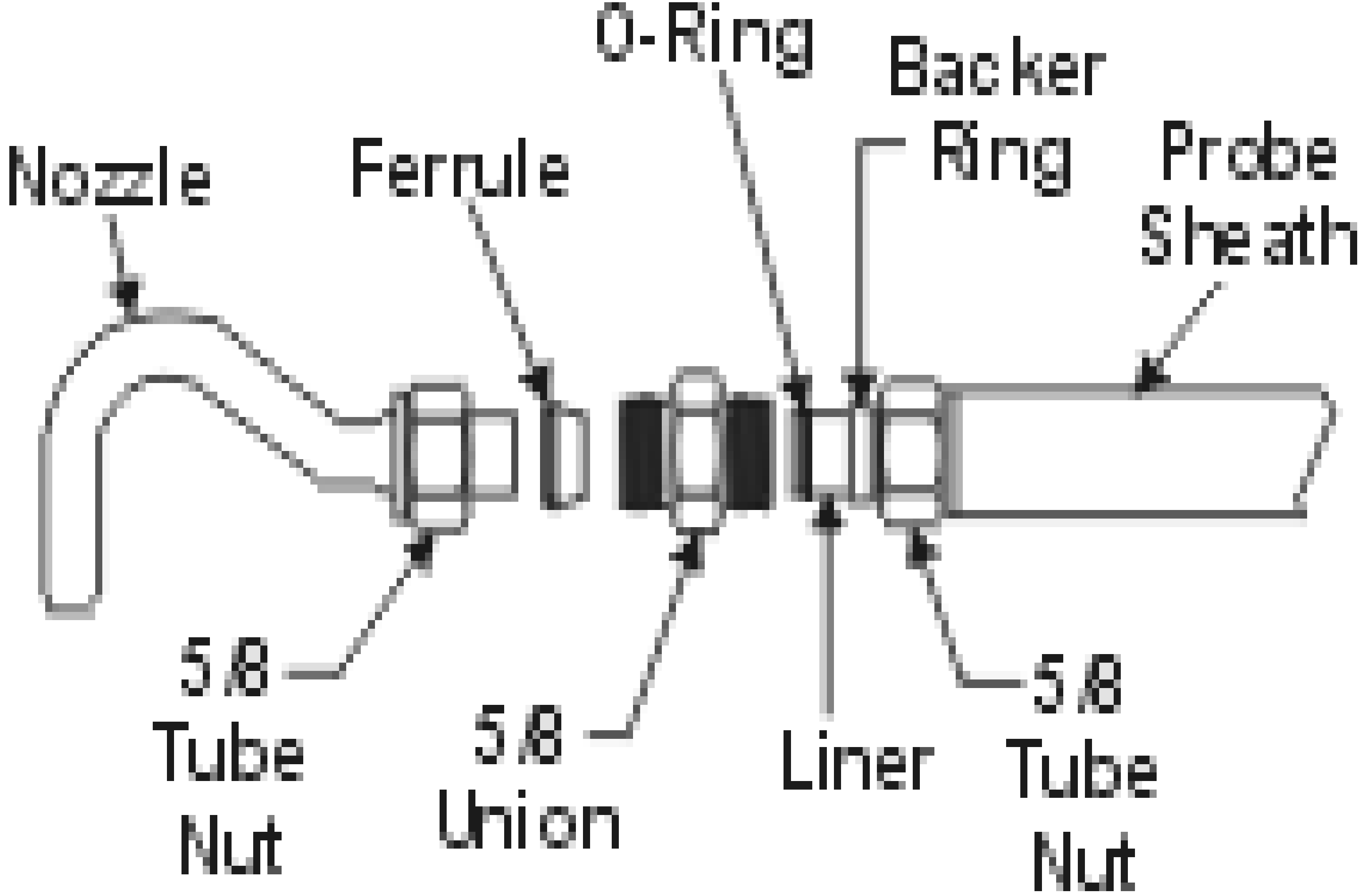
New Design

Tubing Supported

- Free floating allows thermal expansion of the individual tubes.

Sampling Problems

- Teflon ferrels and Viton-O rings must not be used at temperatures exceeding their softening point (i.e., seal between nozzle and probe liner etc.)
- The organic material in the glue on the tape used to wrap the heating wire on the probe can burn off and bias the test
- The probe should be free of tape since there is no reason to heat the probe


O-Ring
Backer Ring
Nozzle
Ferrule
Probe Sheath
5/8 Tube Nut
5/8 Union
Liner
5/8 Tube Nut

Sampling Problems

- Metal probes, at high temperatures, become catalyst (reactive surfaces) for substances in the stack gas (i.e., oxidation of metals, SO_2 to SO_3, etc.)
- High effluent gas temperature could cause softening of the nozzle, probe and pitot tube
- Difficulty of maintaining filter box temperature at 248 F

Solution #1 (Construction of High Temperature Probes)

- Devise a cooling system allowing use of standard construction materials (i.e., Glass, Teflon, Stainless Steel)
  - Ambient Air
  - Water
  - Steam (Very dangerous)

Solution #2 (Construction of High Temperature Probes)

- Construct probes of materials which can withstand high temperatures
  - Inconel
  - Special Alloys
  - Quartz

Use of Probe Cooling Techniques (Advantages)

- Durability of probe
- Unrestricted probe length
- Cooling of gases ensures that filter temperature can be maintained within limits
- Sensing lines (i.e., pitot tube) can be included within cooling jackets

Use of Probe Cooling Techniques (Disadvantages)

- Requires structural support equipment at sampling site
- Vapor pockets may form which may rupture jacket
- Condensation in probe may give problems with maintaining isokinetic sampling rate
- Cooling nozzle/pitot tube gives variable effects on stack gas flow

Use of Quartz Probe (Advantages)

- Stack gas effluents will not react probe material during sampling
- Absence of bulky cooling system
- No condensation in probe
- No heat expansion and distortion of probe and nozzle
- Gases not cooled below 248 F

Use of Quartz Probe (Disadvantages)

- Very brittle/may crack during adding probe nozzle
- Traditionally, fixed nozzle sizes
- Probe lengths greater than 5 ft are impractical
- If using quartz probe without probe liner, then can't attach pitot tube and thermocouple wires

Miscellaneous Sampling Problems

- Sagging of probe and pitot tubes in gas effluent
- Heat radiation from process affects temperature measurements (may have to shield stack gas components)
- General safety consideration for handling hot probe and working close to stack liner

Compliance Test and Source Test Observation

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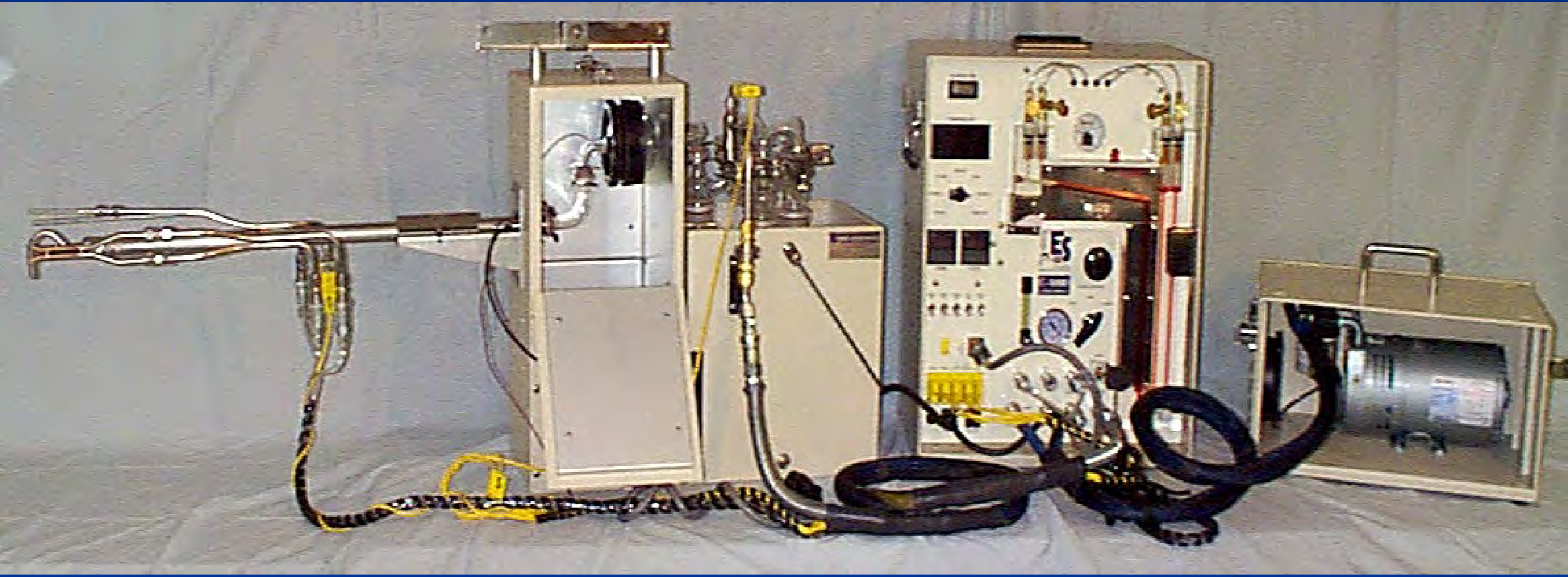

Velocity Measurement

- **Used in determination of nozzle size**
- **Used in obtaining K-factor for setting isokinetic rate conditions during testing**
- **Used in determining pollutant mass rate**

Federal Reference Method 2
Average Velocity Over Cross-Section

$$\overline{v}_{s} = K_{p} C_{p} \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s(avg)}}{M_{s} P_{s}}}$$

Average Stack Gas Dry Volumetric Flow Rate

$$Q_{std} = 3600 \left(1 - B_{ws(avg)}\right) v_{s(avg)} \, A \, \frac{T_{std}}{T_{s(avg)}} \frac{P_s}{P_{std}}$$

The Problem

- Pressure differential devices insensitive below 17 ft/second
- Unreliable pitot tube accuracy below 7 ft/second

The Problem

- FRM 5 typical incline manometer has incline range of 0-1 “ H_2O with 0.01 “ divisions, and vertical range of 1-10 “ H_2O with 0.10 “ divisions
- FRM 5 designed to monitor flows around 1.84 “ H_2O, not in the 0-0.5 “ H_20 range


MODEL 765
OFFSET CORRECT
PUSH RE-CIRK-IT
ometer Zero
Orsa
psed Time
CAUTION - CLEAN WITH SOAP AND WATER, OR KEROSENE ONLY. USE DWYER .826 SP. GR. RED GAGE OIL ONLY.
0
.1
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1.0
INCHES OF WATER
Dwyer
DWYER INSTRUMENTS, INC. MICHIGAN CITY, IND. 46360 U.S.A.
2
3
4
Coarse Open
osed
ONE REV. = 1 CU. FT
CUBIC FEET
10

Federal Reference Method 2 Guidelines

- A differential pressure gauge other greater sensitivity shall be used:
  - The arithmetic average of all Δp readings at the traverse points < 0.05 " H_2O
  - For traverse of 12 or more points, more than 10 % of the individual Δp readings < 0.05 " H_2O
  - For traverse of < 12 points, more than one Δp reading < 0.05 " H_2O

Federal Reference Method 2 Guidelines

- As an alternative to criteria (1) through (3) above, the following equation may be used to determine the necessity of using a more sensitive differential pressure gauge. If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

Determination of Sensitivity of Pressure Gauge

$$T = \frac{\sum_{i=1}^{n} \sqrt{\Delta p_i + K}}{\sum_{i=1}^{n} \sqrt{\Delta p_i}}$$

Using Magnehelic Gauges Etc.

- If differential pressure gauges other than inclined manometers are used (*e.g.*, magnehelic gauges), their calibration must be checked after each test series.
- To check the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of Δp values in the stack.


0
2
5
MAGNEHELIC
INDICATING TRANSMITTER
SPAN
ZERO
Dwyer
POINTER ZERO

Alternative Approaches for Low Velocity Measurements

- The use of techniques other than Type-S pitot tubes
- Modification of the source to effect a sufficiently high velocity for using the Type-S pitot tube
- Measure velocity at a different location and use data to calculate velocity at sampling site
- Compute flow and velocity using process parameters

Techniques For Measurement of Low Flows

- Standard pitot tube with portable inclined manometer (0-0.25 “ H_2O with 0.005 “ H_2O scale divisions) or digital manometer
- Standard pitot tube with dual scale portable inclined manometer with 0-1.0 “ H_2O with 0.01 “ H_2O scale divisions and 0-10 “ H_2O with 0.10 “ H_2O scale divisions

Techniques For Measurement of Low Flows

- Rotating vane anemometer with digital readout (0-100 ft/sec with 1 ft/sec accuracy)
- Thermal anemometer with digital readout (0-100 ft/sec with 1 ft/sec accuracy)

Other Low Flow Techniques

- Venturi Meters
- Orifice Meters
- Mass Flow Meters

Compliance Test and Source Test Observation

Stack Testing Special Topics:

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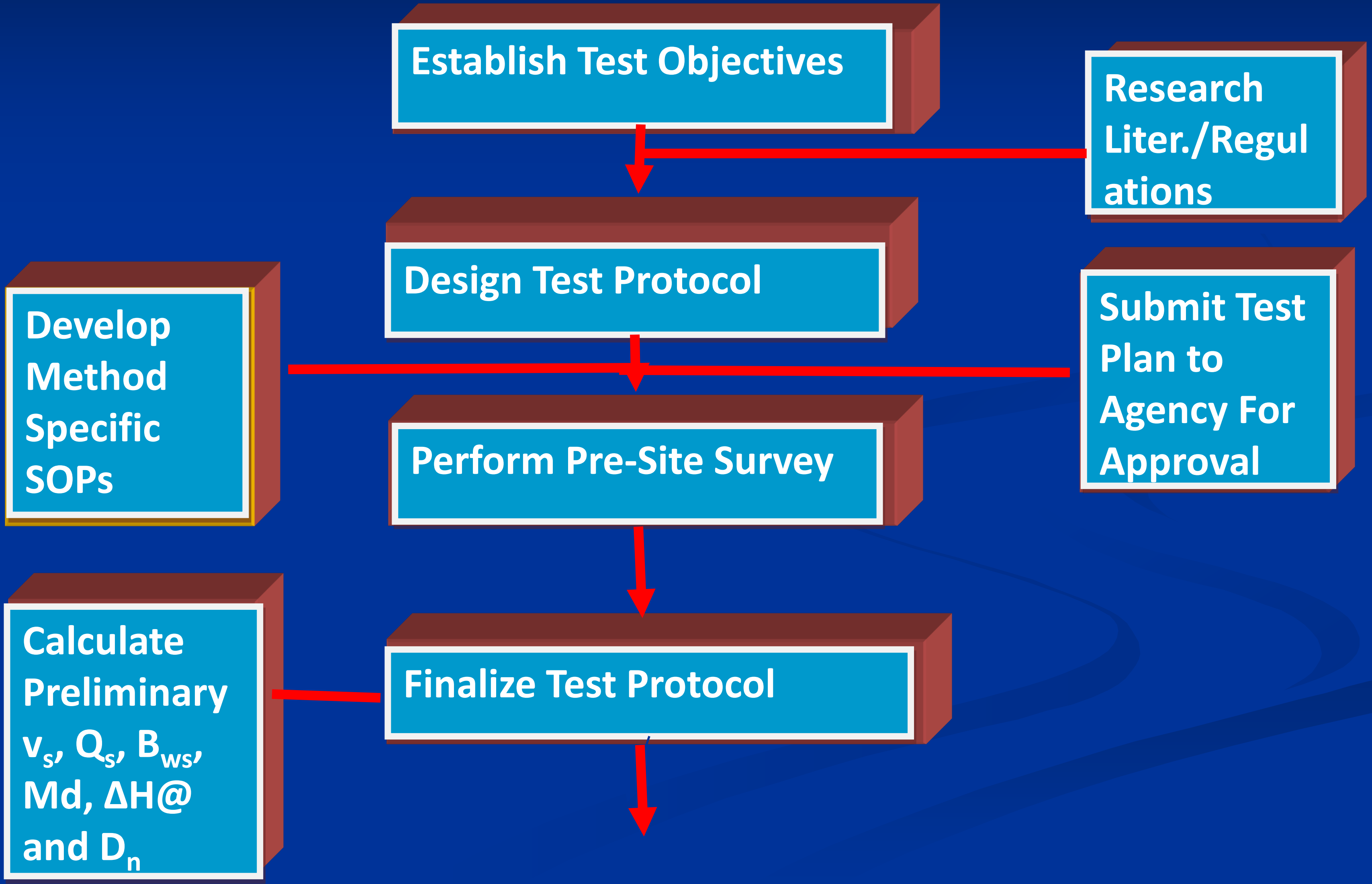
U.S. EPA APTI
Compliance Test and Source Test Observation

The Emission Test Report and Review

Step 1: Objectives, Protocols and Pre-site Survey



Establish Test Objectives

Research Liter./Regulations

Design Test Protocol

Develop Method Specific SOPs

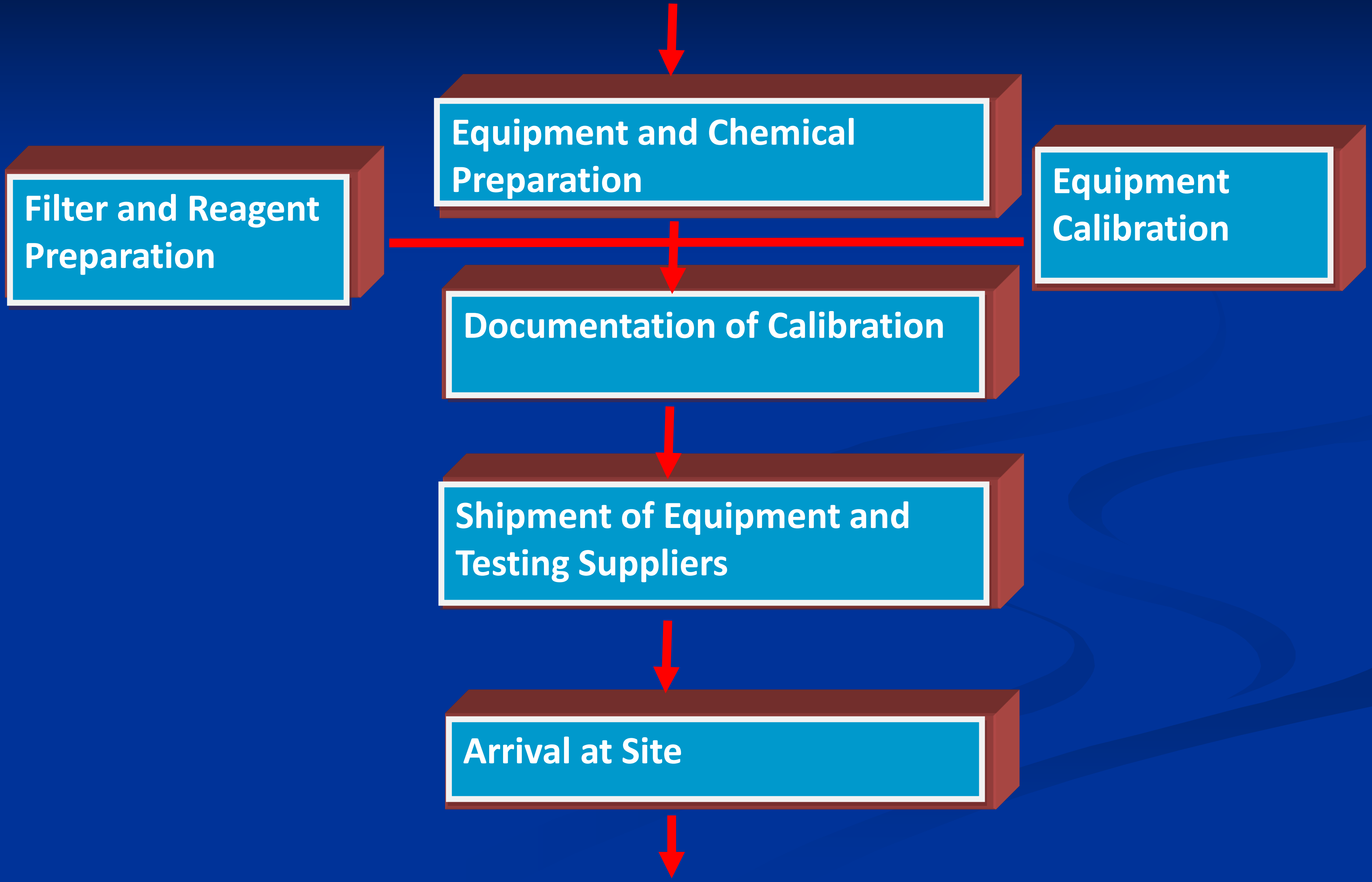
Submit Test Plan to Agency For Approval

Perform Pre-Site Survey

Calculate Preliminary v_s, Q_s, B_{ws}, Md, $\Delta H@$ and D_n

Finalize Test Protocol

Step 2: Equipment Preparation



Equipment and Chemical Preparation

Filter and Reagent Preparation

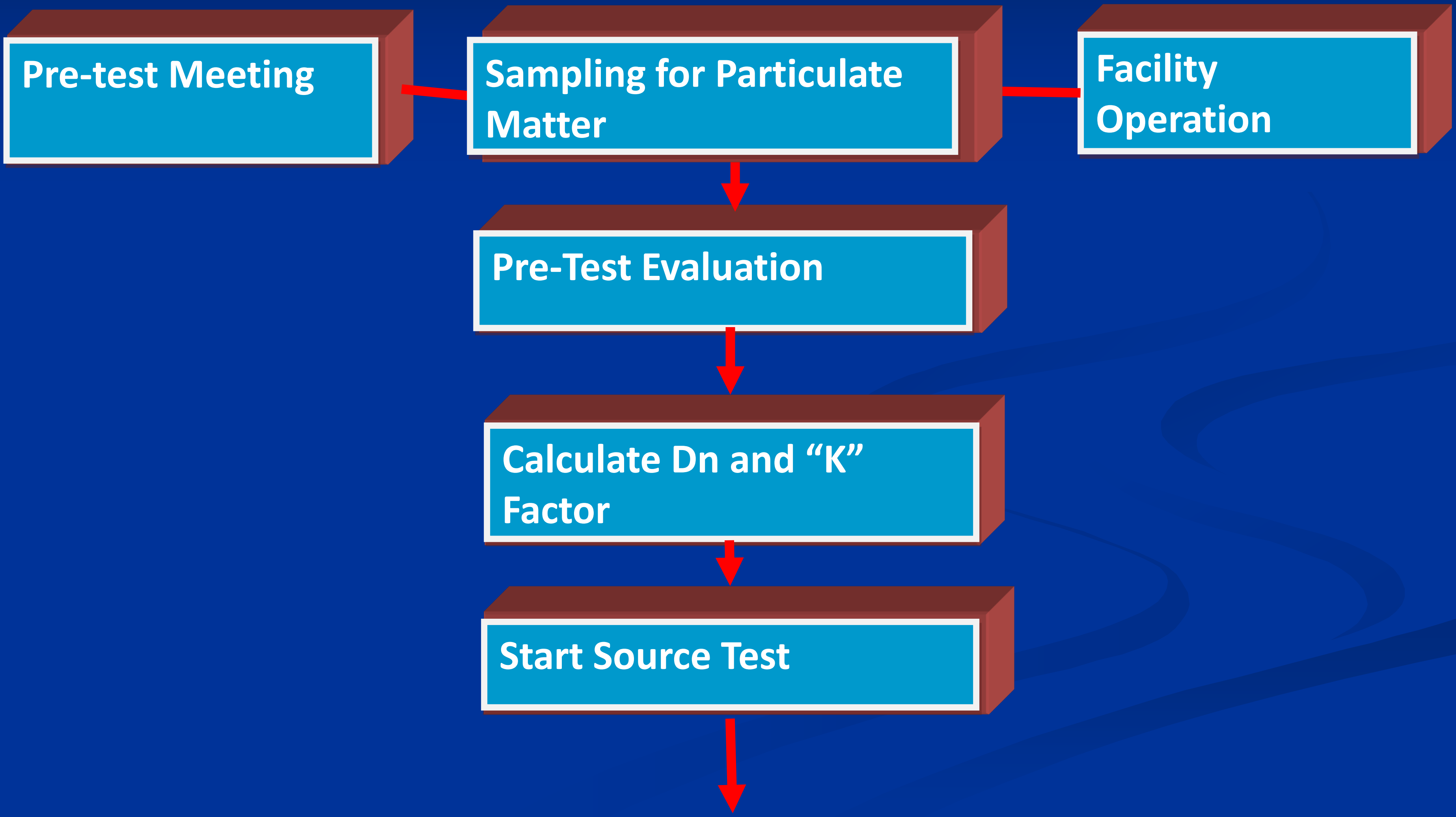
Equipment Calibration

Documentation of Calibration

Shipment of Equipment and Testing Suppliers

Arrival at Site

Step 3: Pre-test Conference and Evaluation



Pre-test Meeting

Sampling for Particulate Matter

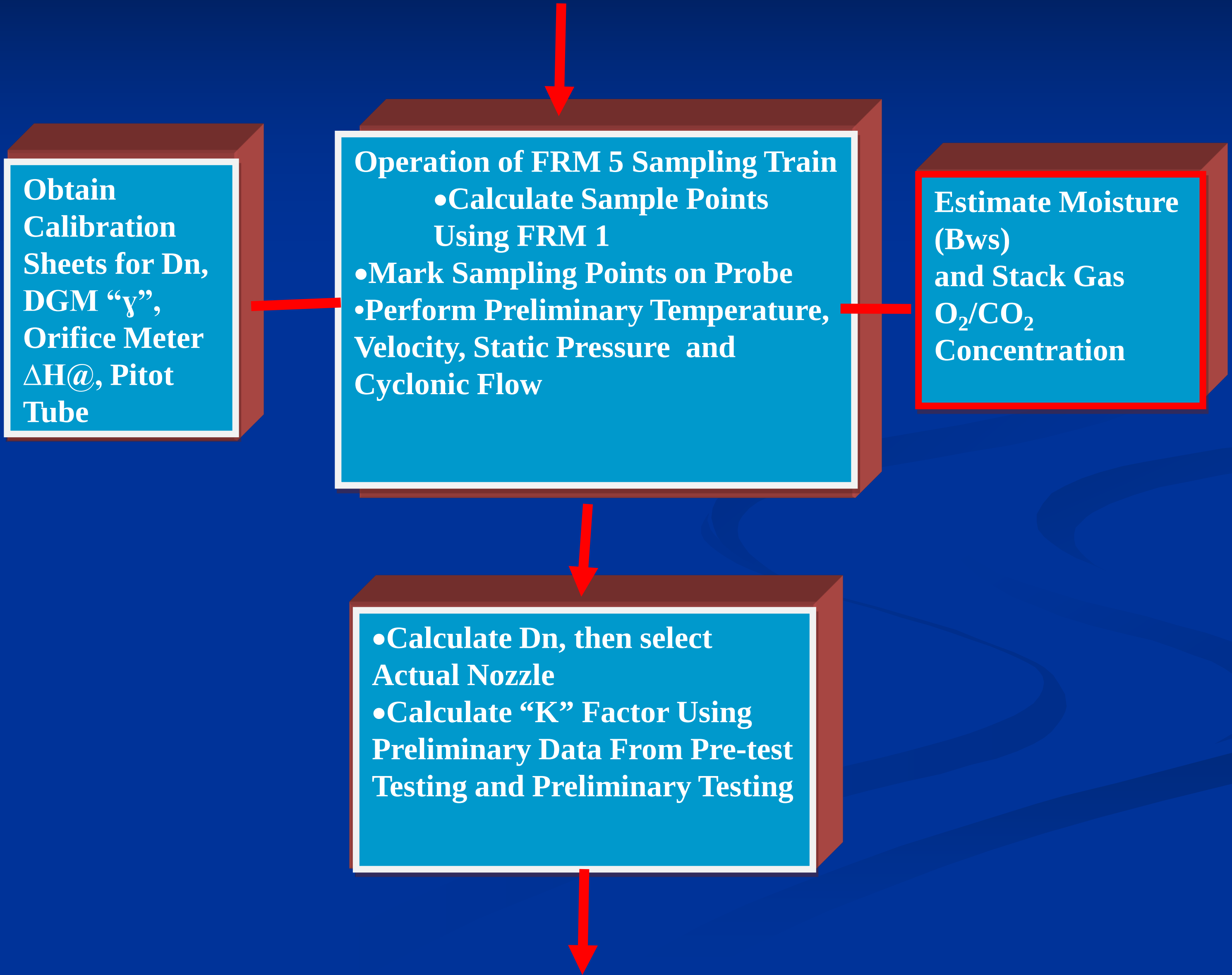
Facility Operation

Pre-Test Evaluation

Calculate Dn and “K” Factor

Start Source Test

Step 4: The Test



Obtain Calibration Sheets for Dn, DGM “γ”, Orifice Meter ΔH@, Pitot Tube

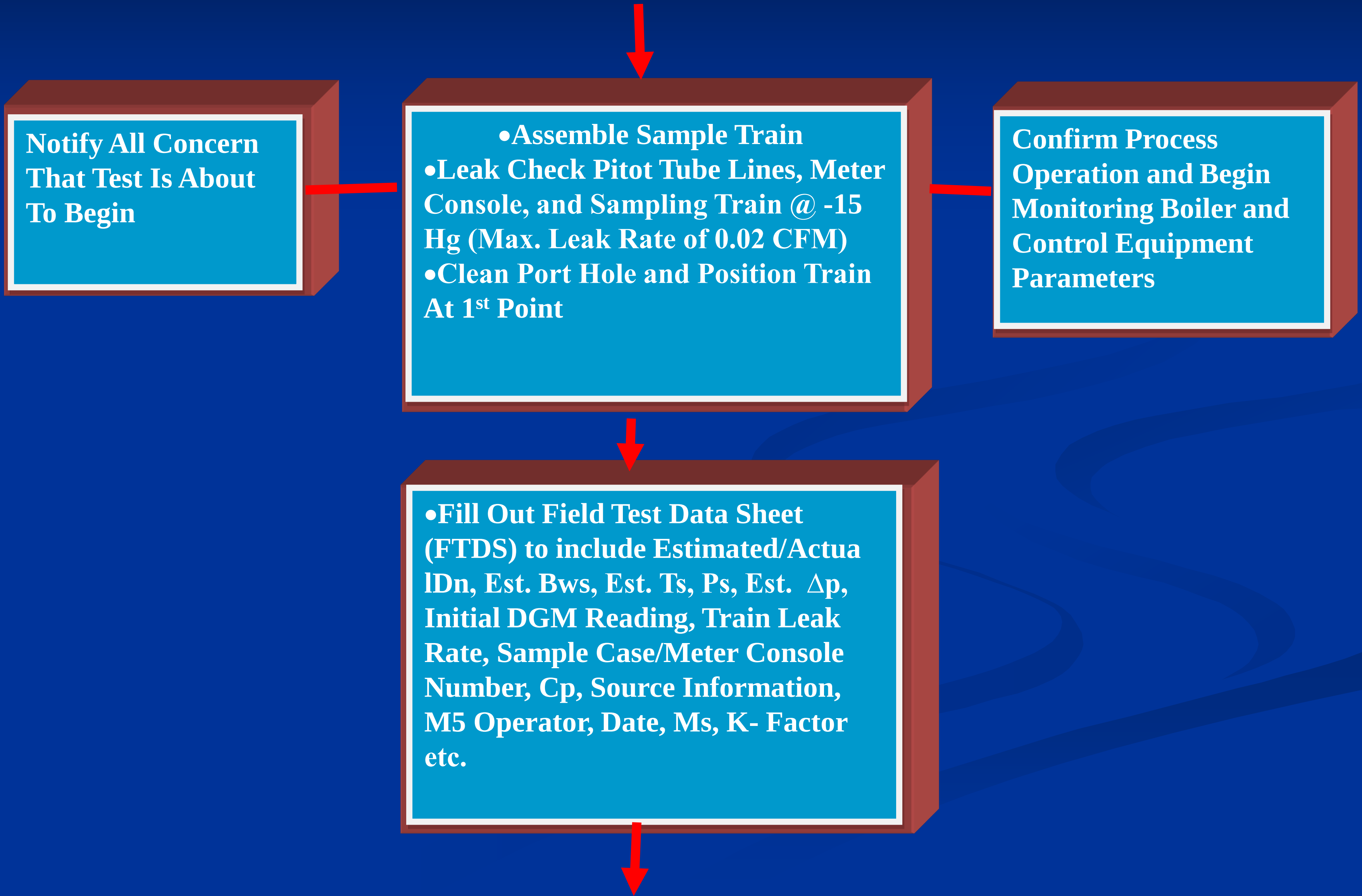
Operation of FRM 5 Sampling Train

- •Calculate Sample Points Using FRM 1
- •Mark Sampling Points on Probe
- •Perform Preliminary Temperature, Velocity, Static Pressure and Cyclonic Flow

Estimate Moisture (Bws) and Stack Gas O_2/CO_2 Concentration

- •Calculate Dn, then select Actual Nozzle
- •Calculate “K” Factor Using Preliminary Data From Pre-test Testing and Preliminary Testing

Step 4: The Test



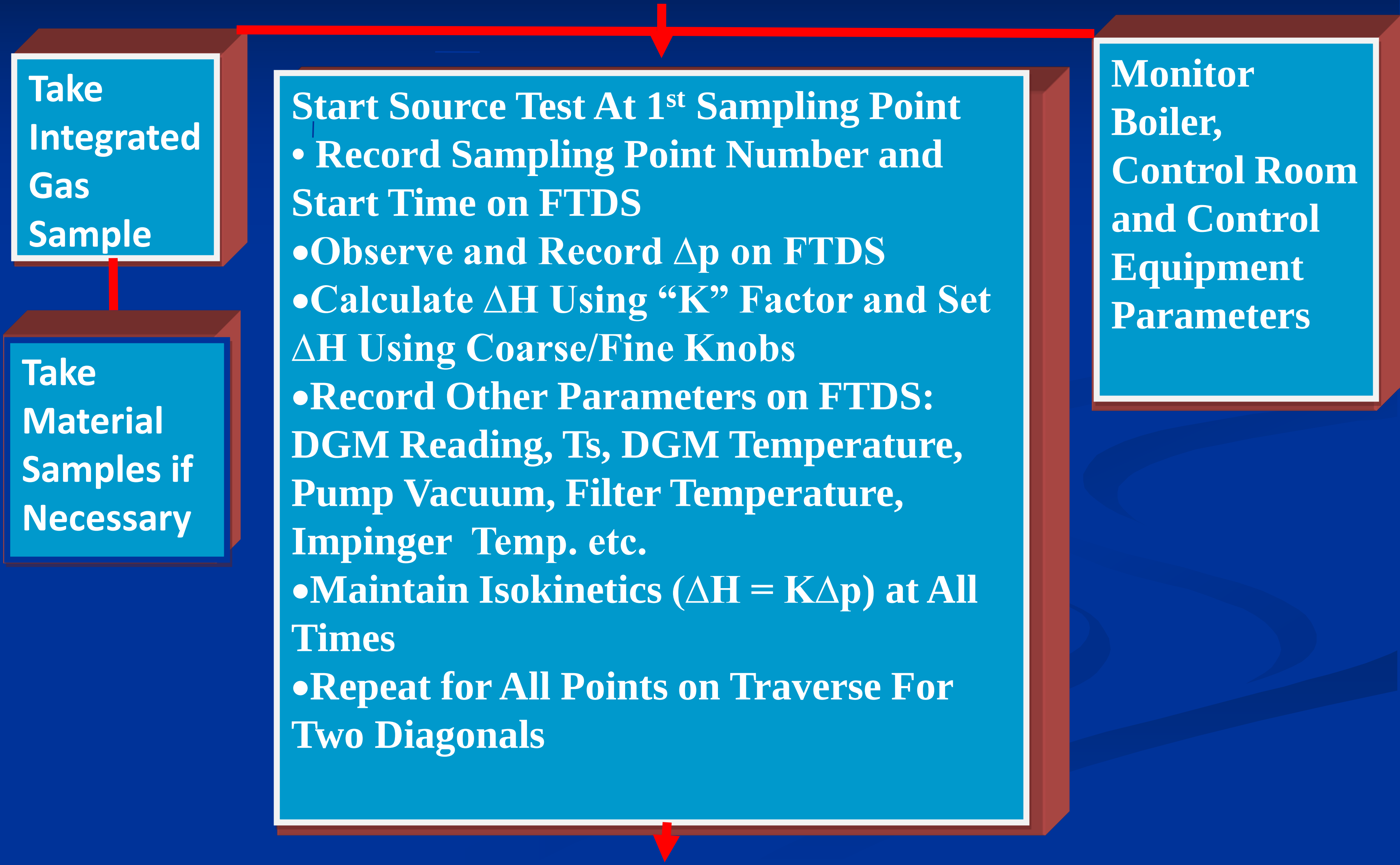
Notify All Concern That Test Is About To Begin

- Assemble Sample Train
- Leak Check Pitot Tube Lines, Meter Console, and Sampling Train @ -15 Hg (Max. Leak Rate of 0.02 CFM)
- Clean Port Hole and Position Train At 1st Point

Confirm Process Operation and Begin Monitoring Boiler and Control Equipment Parameters

- Fill Out Field Test Data Sheet (FTDS) to include Estimated/Actual Dn, Est. Bws, Est. Ts, Ps, Est. Δp, Initial DGM Reading, Train Leak Rate, Sample Case/Meter Console Number, Cp, Source Information, M5 Operator, Date, Ms, K- Factor etc.

Step 4: The Test (Cont'd)



Take Integrated Gas Sample

Take Material Samples if Necessary

Start Source Test At 1st Sampling Point

- Record Sampling Point Number and Start Time on FTDS
- Observe and Record Δp on FTDS
- Calculate ΔH Using "K" Factor and Set ΔH Using Coarse/Fine Knobs
- Record Other Parameters on FTDS: DGM Reading, Ts, DGM Temperature, Pump Vacuum, Filter Temperature, Impinger Temp. etc.
- Maintain Isokinetics ($\Delta H = K\Delta p$) at All Times
- Repeat for All Points on Traverse For Two Diagonals

Monitor Boiler, Control Room and Control Equipment Parameters

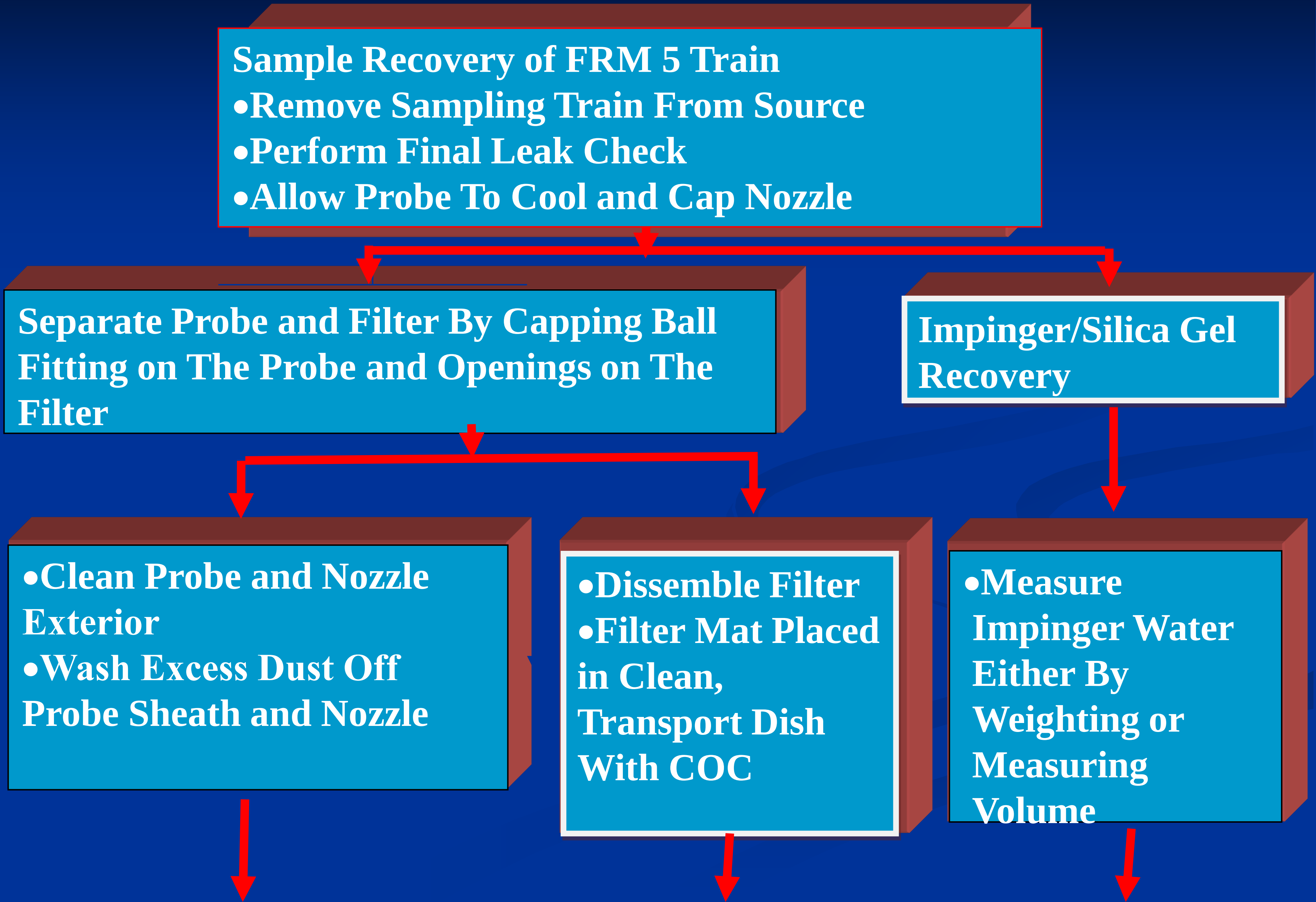
Step 4: The Test (Cont'd)

At Conclusion of Test (Last Point)

- Record Stop Time and Final DGM Reading
- Remove Sample Train From Source
- Leak Test Sampling Train at Highest Vacuum (in. Hg) Achieved During Test.
  Leak Rate Should Not Exceed 0.02 CFM
- Sample Clean-up and Recovery for Probe Rinse, Filter and Impinger/Silica Gel Components

Repeat Preceding Steps for A Total of Three Particulate Sampling Runs

Step 5: Sample Recovery



Sample Recovery of FRM 5 Train

- Remove Sampling Train From Source
- Perform Final Leak Check
- Allow Probe To Cool and Cap Nozzle

Separate Probe and Filter By Capping Ball Fitting on The Probe and Openings on The Filter

Impinger/Silica Gel Recovery

- Clean Probe and Nozzle Exterior
- Wash Excess Dust Off Probe Sheath and Nozzle

- Dissemble Filter
- Filter Mat Placed in Clean, Transport Dish With COC

- Measure Impinger Water Either By Weighting or Measuring Volume

Step 5: Sample Recovery (Cont’d)

- Remove Nozzle and Ball Fitting Caps
- Clean Probe With Nozzle In Place With Brush/Acetone and Brush 3 Times, Collect Into Marked Container

Remove Nozzle and Inspect Probe Liner

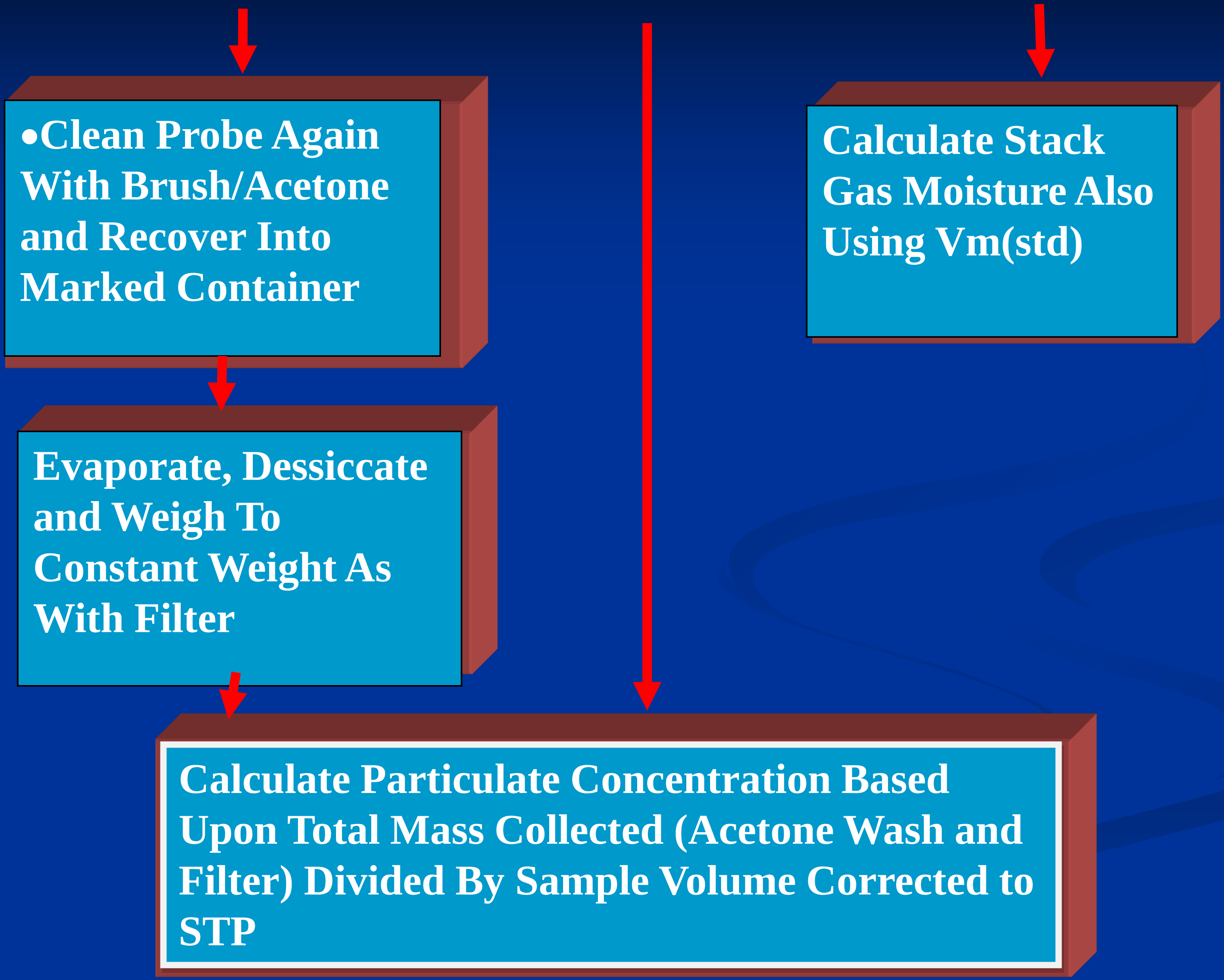
- Clean Nozzle Again With Brush/Acetone

- Filter Mat Conditioned, Then Weighted to Constant Weight ± 0.5 mg

- Store Impinger Water in Marked Container for Analysis (If Applicable)

- Observe Color of Silica Gel
- Weigh to Nearest 0.5 gm

Step 5: Sample Recovery (Cont’d)



- Clean Probe Again With Brush/Acetone and Recover Into Marked Container

Evaporate, Dessiccate and Weigh To Constant Weight As With Filter

Calculate Stack Gas Moisture Also Using Vm(std)

Calculate Particulate Concentration Based Upon Total Mass Collected (Acetone Wash and Filter) Divided By Sample Volume Corrected to STP

Emission Test Report

The emission test report serves as a legal record of the testing performed along with the calculations in determining the compliance status of the emission source. The emission test report must provide the information necessary to document the objectives of the test and determine whether proper procedures were used to accomplish these objectives.

Emission Test Report Guideline Documents

U.S. Environmental Protection Agency (EPA) has prepared a guideline document (GD-043) entitled:

"Preparation and Review of Emission Test Reports"

Purpose of GD-043

- The purpose of this guideline is to promote consistency in the preparation and review of test reports for emission test programs.
- The emission test report must provide the information necessary to document the objectives of the test and to determine whether the proper procedures were used to accomplish the objectives

Purpose of GD-043

- GD-043 presents a standard format for preparing the emission test report
  - Table of Content
  - Five Sections
  - Appendices

Emission Test Report

- Table of Content
- Section 1: Introduction
- Section 2: Plant and Sampling Location Descriptions
- Section 3: Summary and Discussion of Test Results

Emission Test Report

- Section 4: Sampling and Analytical Procedures
- Section 5: Internal QA/QC Activities
- Appendices

Section 1: Summary of Test Program and Results

- Responsible Organization
- Overall Purpose of Test
- Regulations
- Type of Industry
- Name of Plant and Location
- Summary of Test Results

Section 1: Summary of Test Program

- Process of Interest
- Air Pollution Control Equipment
- Emission Points and Sampling Location
- Pollutants to be Measured
- Dates of Emission Testing

Section 3: Summary and Discussion of Test Results

- Objectives and Test Matrix
- Field Test Changes and Problems
- Presentation of Results

Emission Test Report

Summary of Results

- Brief test method identification
- Regulatory agency approval of method
- Comments on process operation
- Emission rate determined by the test
- Emission rate limit given by law

Wesleyan College Pathological Incinerator Federal Reference Method 5 Test Results[1]					
Run Number		**Run 1**	**Run 2**	**Run 3**	**Average**
Identification	**Symbol Units**				
	Volumetric Flow Rate Data				
Avg. Stack Gas Velocity	V_s, ft/sec	33.52	39.59	39.13	37.41
Stack Gas Cross Sect Area	A_s, ft^2	1.58	1.58	1.58	1.58
Actual Stack Gas Flow	Q_{act}, acfm	3170	3745	3700	3538
Dry Std Stack Gas Flow	Q_{sd}, dscfm	760	864	856	827
Stack Gas Moisture Content	$B_{ws,}$ %	10.8	12.5	11.4	11.6
Stack Gas Oxygen (O_2)	%	10.9	12.2	12.2	11.8
Stack Gas Carbon Dioxide (CO_2)	%	9.0	7.0	7.0	7.7
Stack Gas Nitrogen (N_2)	%	80.1	80.8	80.8	80.6
Stack Gas Temperature, (T_s)	° F	1499.4	1524.9	1543.5	1522.6
Percent of Isokinetic Rate	**I, %**	**96.4**	**96.9**	**96.0**	**96.4**
EPA Allowed % I[2]	**I, %**	**90-110**	**90-110**	**90-110**	**90-110**
	Process Data				
Waste Charge Rate - Average	**P, lbs/hr**	**97.6**	**129.2**	**129.4**	**135.4**
	Emission Rate Data				
Total Mass of Particles	m_t, mg	37.7	28.2	23.9	29.9
Stack Particulate Conc.	c_s, g/dscf	0.001	0.001	0.001	0.001
	c_s, gr/dscf	0.015	0.010	0.008	0.011
Particulate Emission Rate	**E, kg/hr**	**0.031**	**0.024**	**0.020**	**0.025**
	E, lbs/hr	**0.068**	**0.053**	**0.044**	**0.055**
Allowable Emission Rate[3]	**E, lbs/hr**	**0.195**	**0.258**	**0.259**	**0.237**

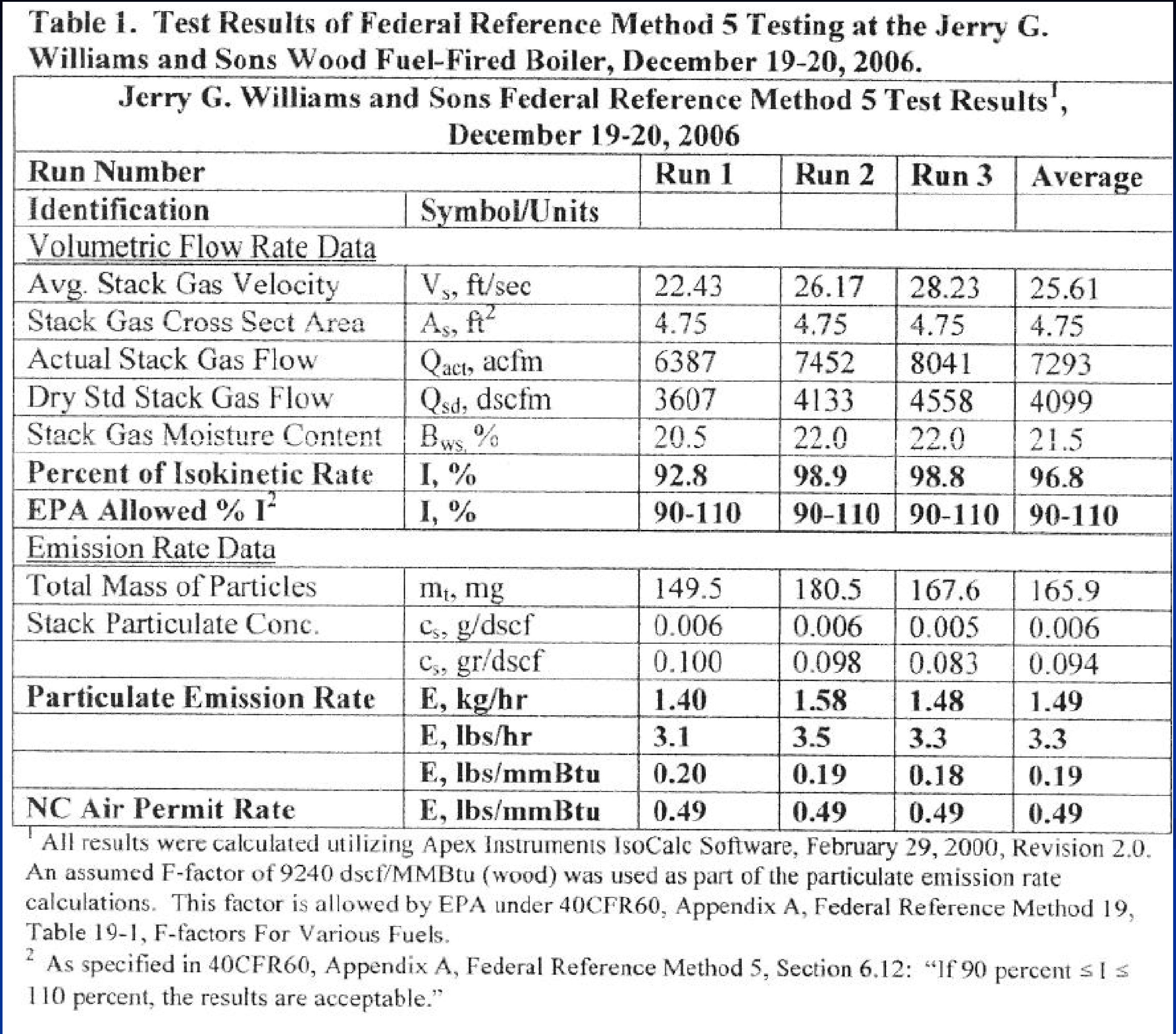
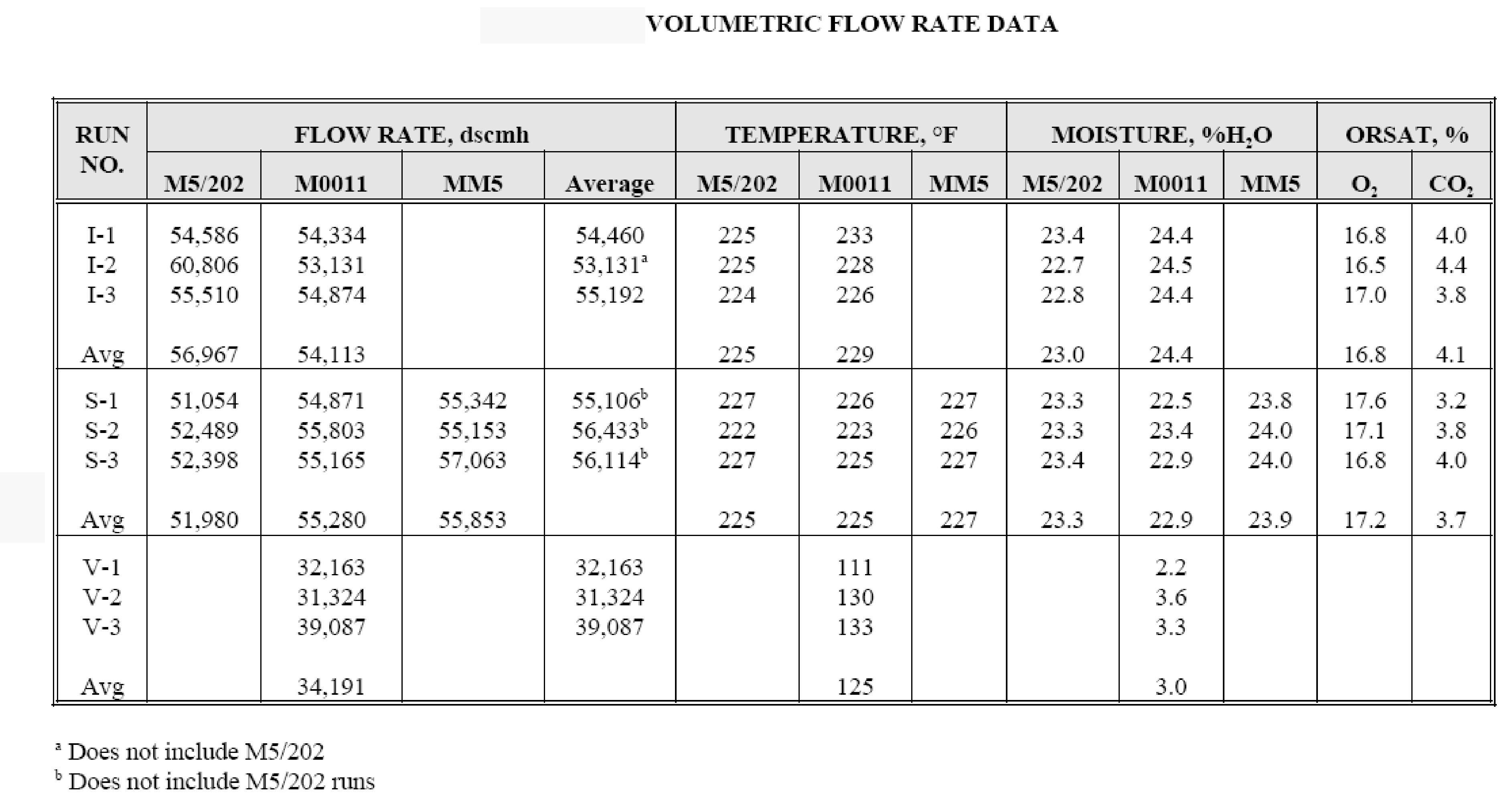


Table 1. Test Results of Federal Reference Method 5 Testing at the Jerry G. Williams and Sons Wood Fuel-Fired Boiler, December 19-20, 2006.

Jerry G. Williams and Sons Federal Reference Method 5 Test Results[1], December 19-20, 2006					
Run Number		**Run 1**	**Run 2**	**Run 3**	**Average**
Identification	**Symbol/Units**				
Volumetric Flow Rate Data					
Avg. Stack Gas Velocity	V_s, ft/sec	22.43	26.17	28.23	25.61
Stack Gas Cross Sect Area	A_s, ft^2	4.75	4.75	4.75	4.75
Actual Stack Gas Flow	Q_{act}, acfm	6387	7452	8041	7293
Dry Std Stack Gas Flow	Q_{sd}, dscfm	3607	4133	4558	4099
Stack Gas Moisture Content	B_{ws}, %	20.5	22.0	22.0	21.5
Percent of Isokinetic Rate	**I, %**	**92.8**	**98.9**	**98.8**	**96.8**
EPA Allowed % I[2]	**I, %**	**90-110**	**90-110**	**90-110**	**90-110**
Emission Rate Data					
Total Mass of Particles	m_t, mg	149.5	180.5	167.6	165.9
Stack Particulate Conc.	c_s, g/dscf	0.006	0.006	0.005	0.006
	c_s, gr/dscf	0.100	0.098	0.083	0.094
Particulate Emission Rate	**E, kg/hr**	**1.40**	**1.58**	**1.48**	**1.49**
	E, lbs/hr	**3.1**	**3.5**	**3.3**	**3.3**
	E, lbs/mmBtu	**0.20**	**0.19**	**0.18**	**0.19**
NC Air Permit Rate	**E, lbs/mmBtu**	**0.49**	**0.49**	**0.49**	**0.49**

[1] All results were calculated utilizing Apex Instruments IsoCalc Software, February 29, 2000, Revision 2.0. An assumed F-factor of 9240 dscf/MMBtu (wood) was used as part of the particulate emission rate calculations. This factor is allowed by EPA under 40CFR60, Appendix A, Federal Reference Method 19, Table 19-1, F-factors For Various Fuels.

[2] As specified in 40CFR60, Appendix A, Federal Reference Method 5, Section 6.12: "If 90 percent ≤ I ≤ 110 percent, the results are acceptable."



VOLUMETRIC FLOW RATE DATA

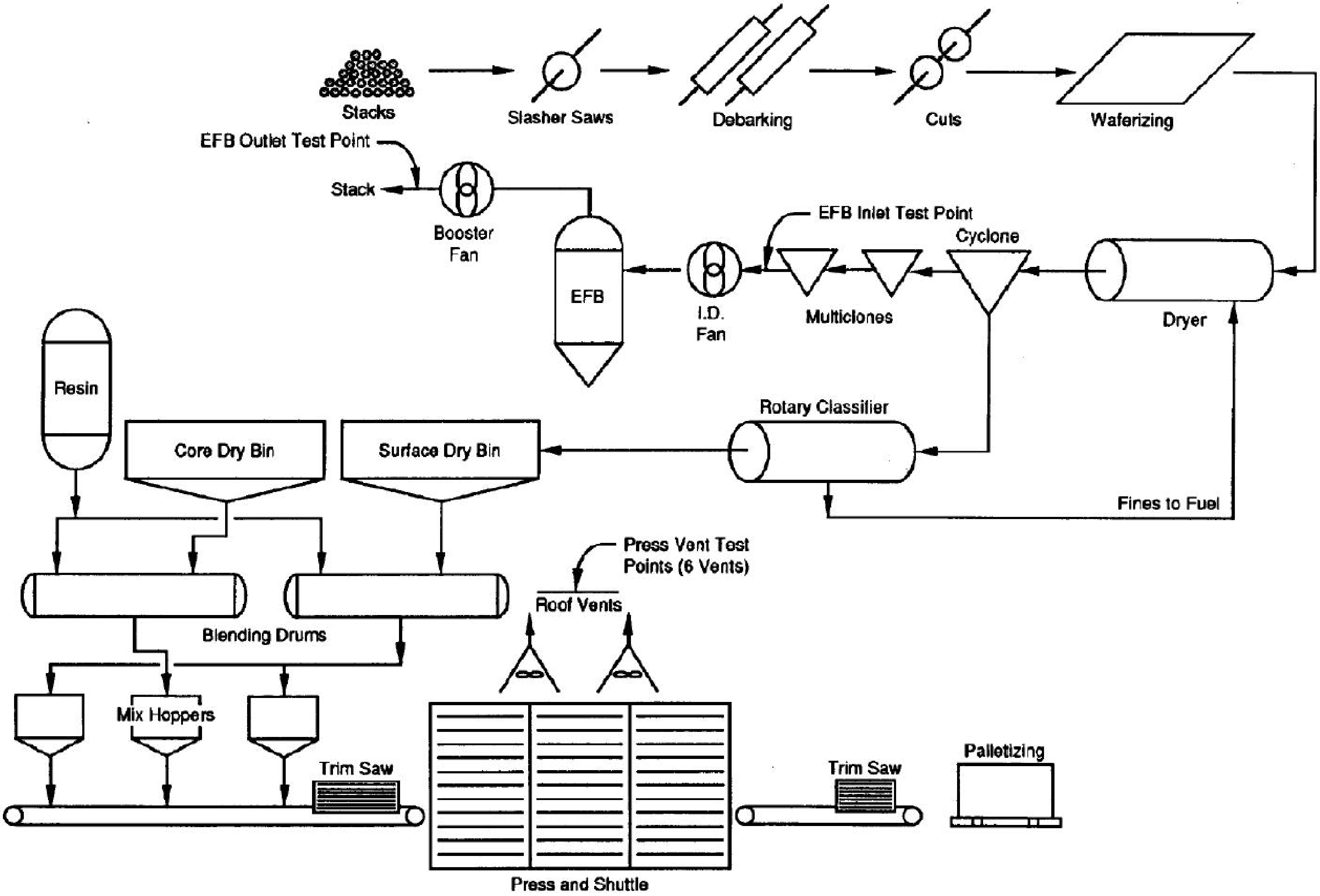
RUN NO.	FLOW RATE, dscmh				TEMPERATURE, °F			MOISTURE, %H_2O			ORSAT, %	
	M5/202	M0011	MM5	Average	M5/202	M0011	MM5	M5/202	M0011	MM5	O_2	CO_2
I-1	54,586	54,334		54,460	225	233		23.4	24.4		16.8	4.0
I-2	60,806	53,131		53,131[a]	225	228		22.7	24.5		16.5	4.4
I-3	55,510	54,874		55,192	224	226		22.8	24.4		17.0	3.8
Avg	56,967	54,113			225	229		23.0	24.4		16.8	4.1
S-1	51,054	54,871	55,342	55,106[b]	227	226	227	23.3	22.5	23.8	17.6	3.2
S-2	52,489	55,803	55,153	56,433[b]	222	223	226	23.3	23.4	24.0	17.1	3.8
S-3	52,398	55,165	57,063	56,114[b]	227	225	227	23.4	22.9	24.0	16.8	4.0
Avg	51,980	55,280	55,853		225	225	227	23.3	22.9	23.9	17.2	3.7
V-1		32,163		32,163		111			2.2			
V-2		31,324		31,324		130			3.6			
V-3		39,087		39,087		133			3.3			
Avg		34,191				125			3.0			

[a] Does not include M5/202

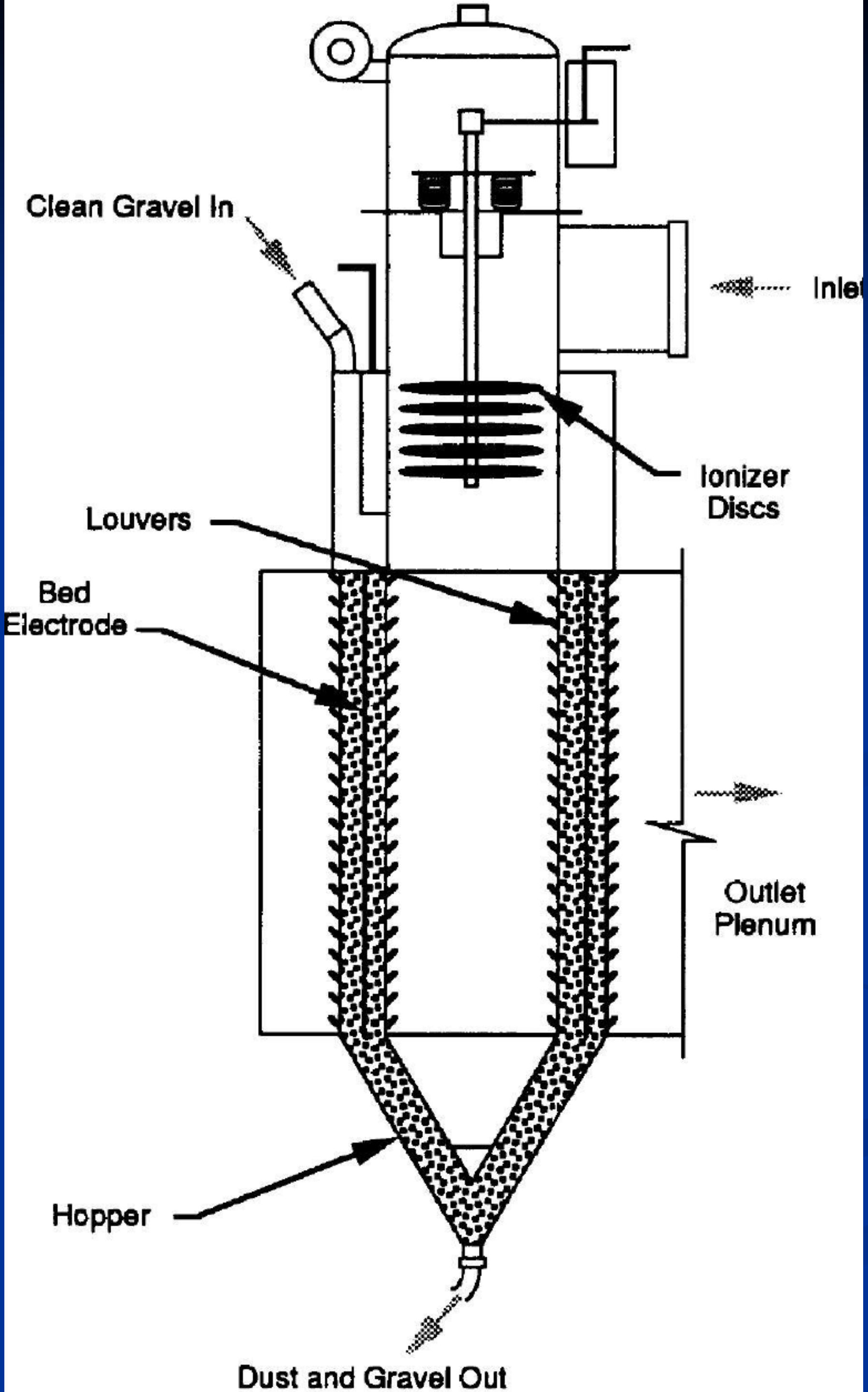
[b] Does not include M5/202 runs

Section 2: Plant and Sampling Location

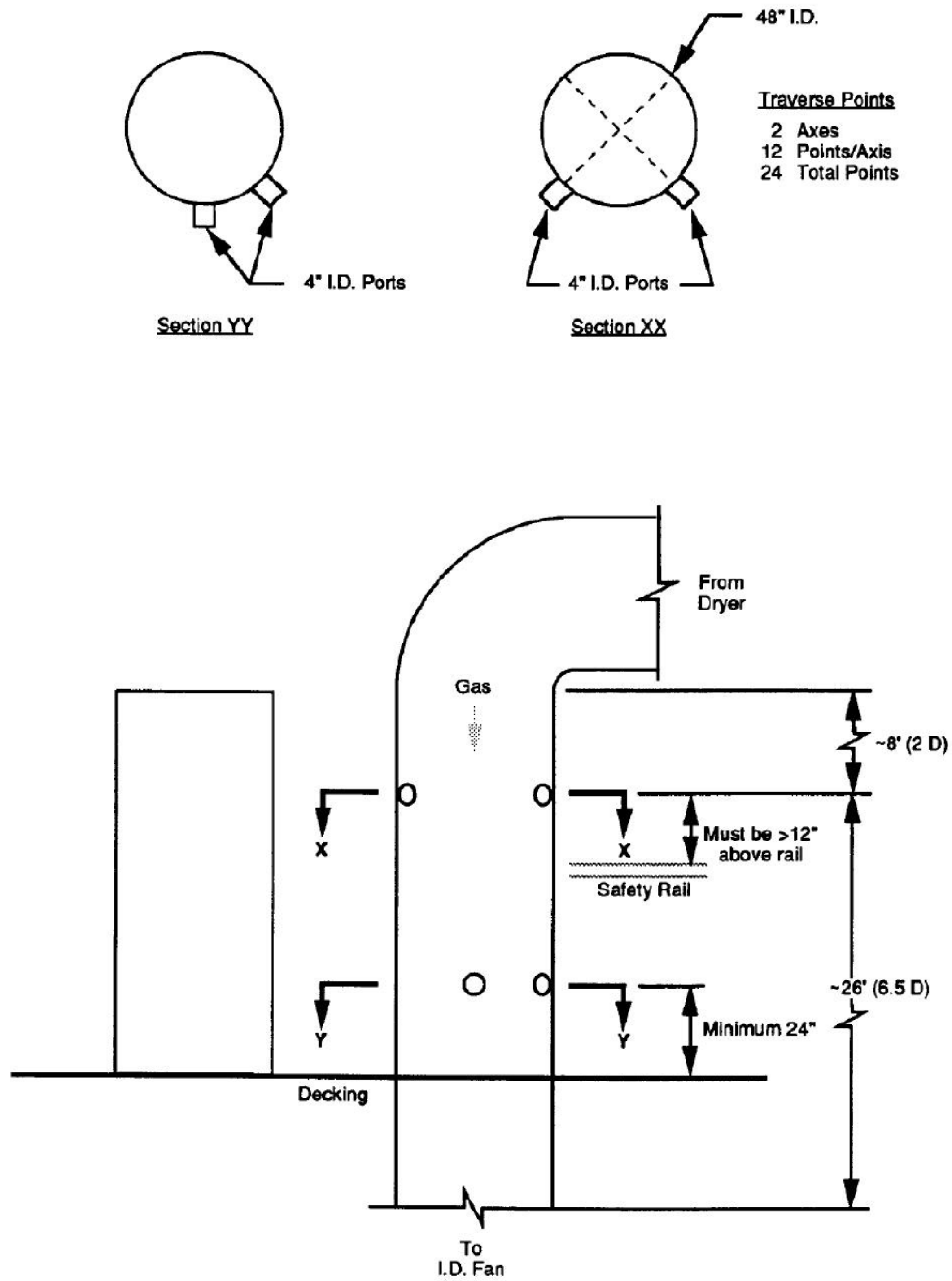
- Process Description and Operation
- Control Equipment Description
- Flue Gas Sampling Locations
- Process Sampling Locations



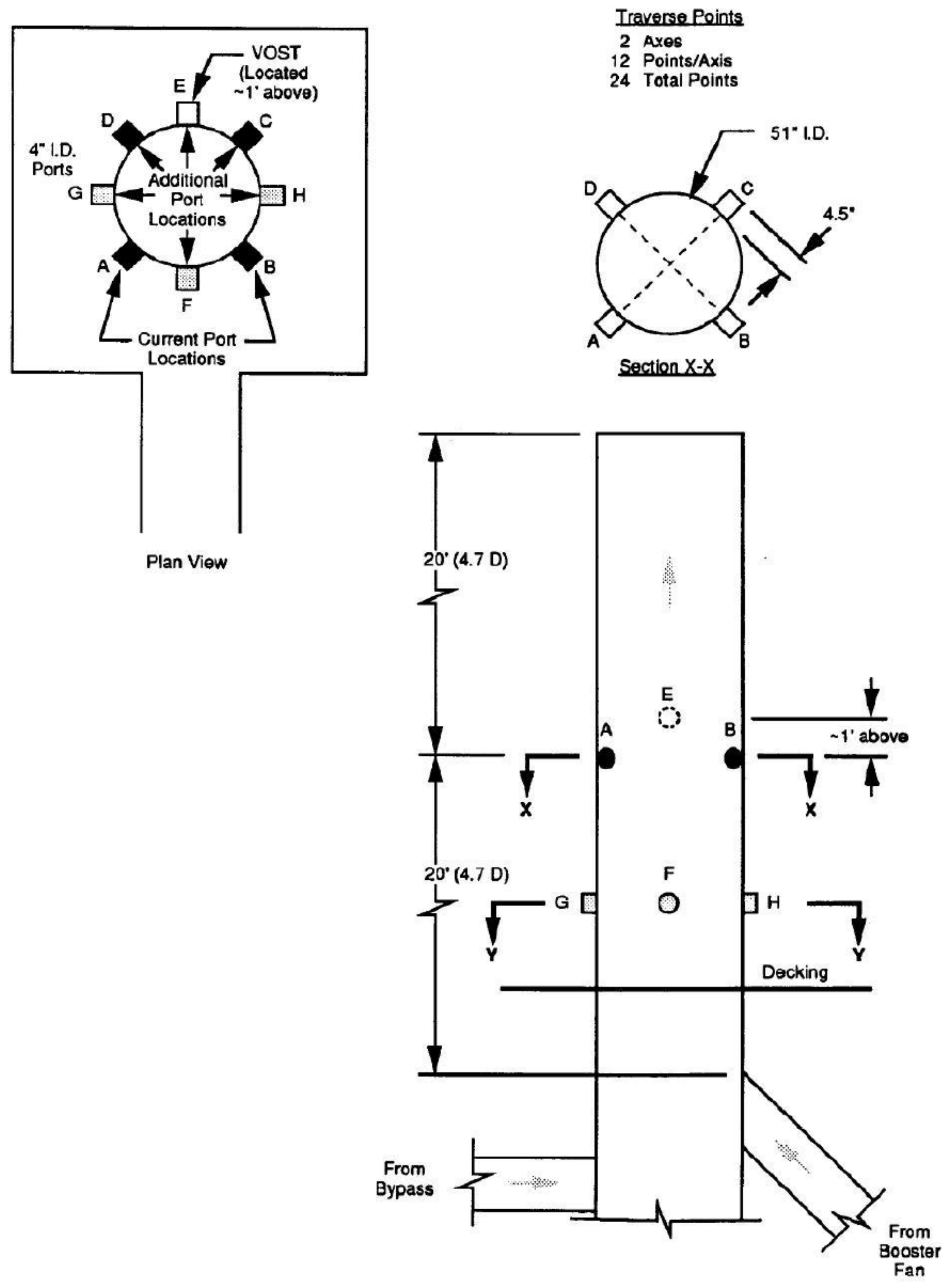
Oriented strand board (OSB) process flow diagram.


Clean Gravel In
Inlet
Ionizer Discs
Louvers
Bed Electrode
Outlet Plenum
Hopper
Dust and Gravel Out

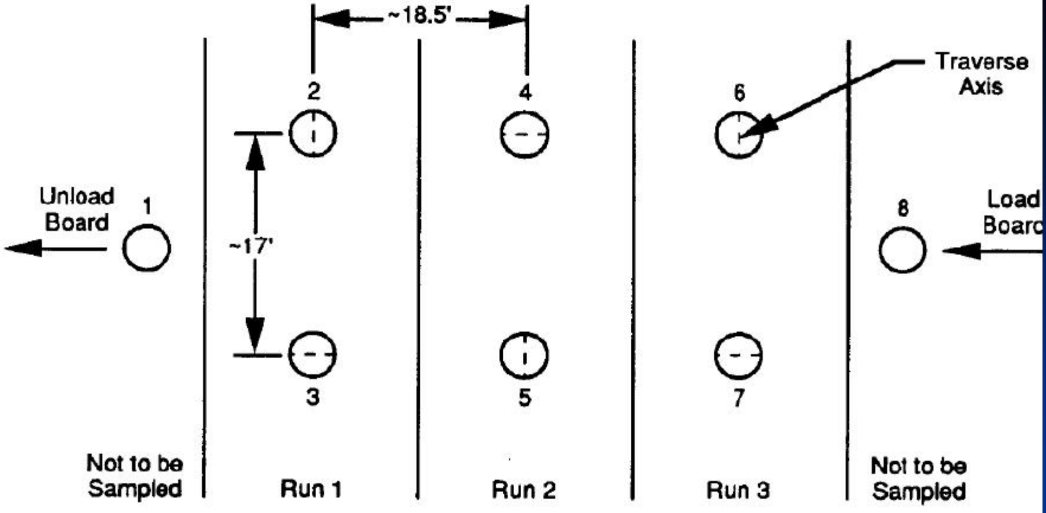
Schematic of Unit 1 Inlet Sampling Location

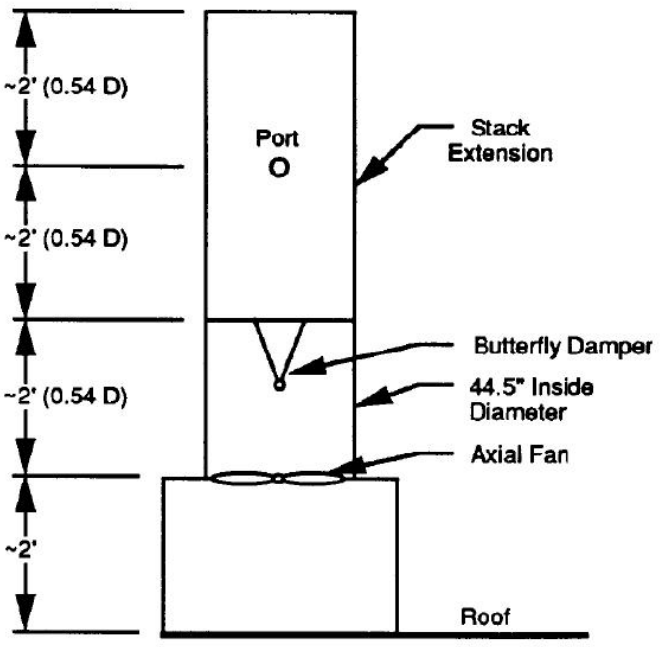


Schematic of Unit 1 Outlet Stack Sampling Location



Press Vents Sampling Location Configuration and Testing Scheme





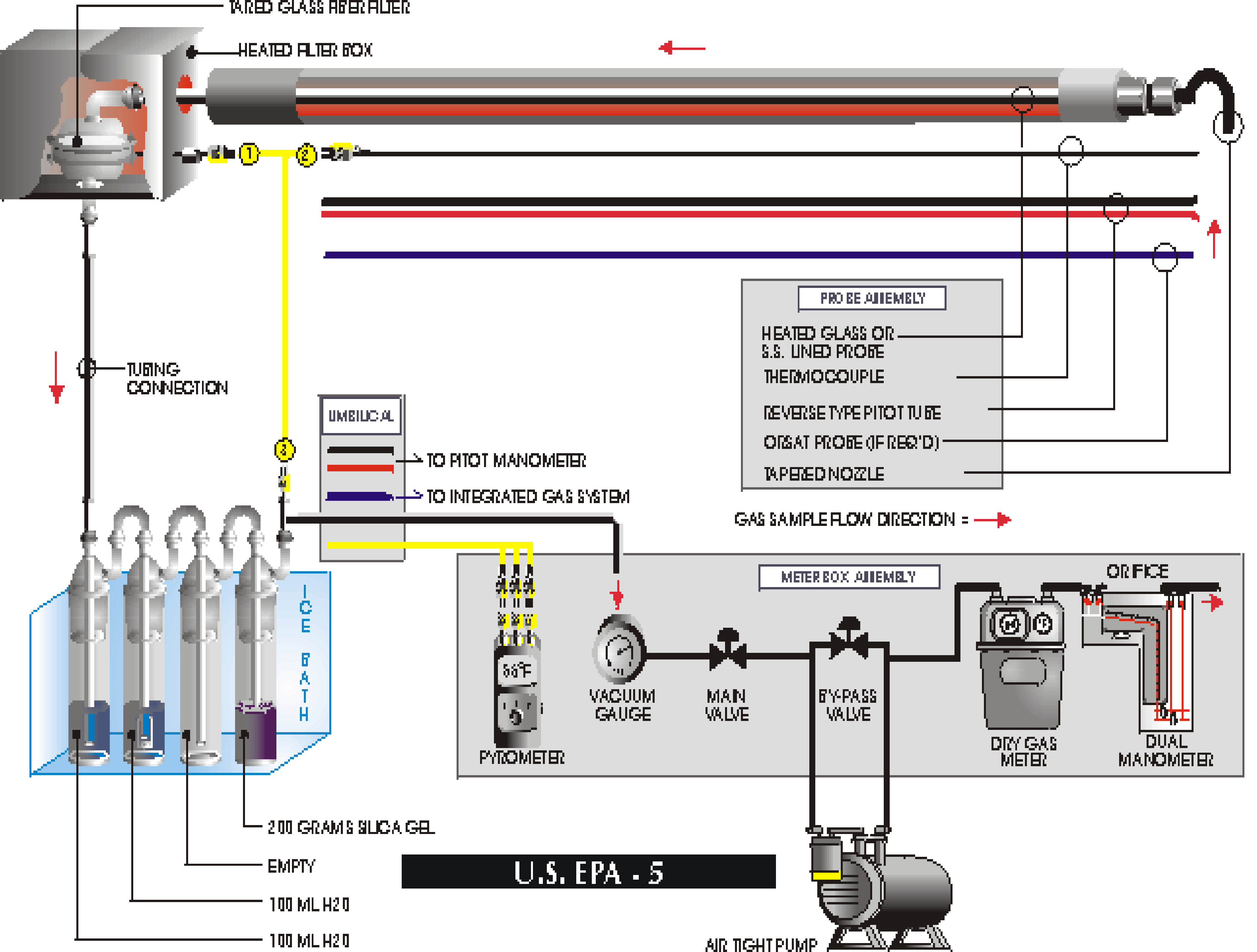
Section 4: Sampling and Analytical Procedures

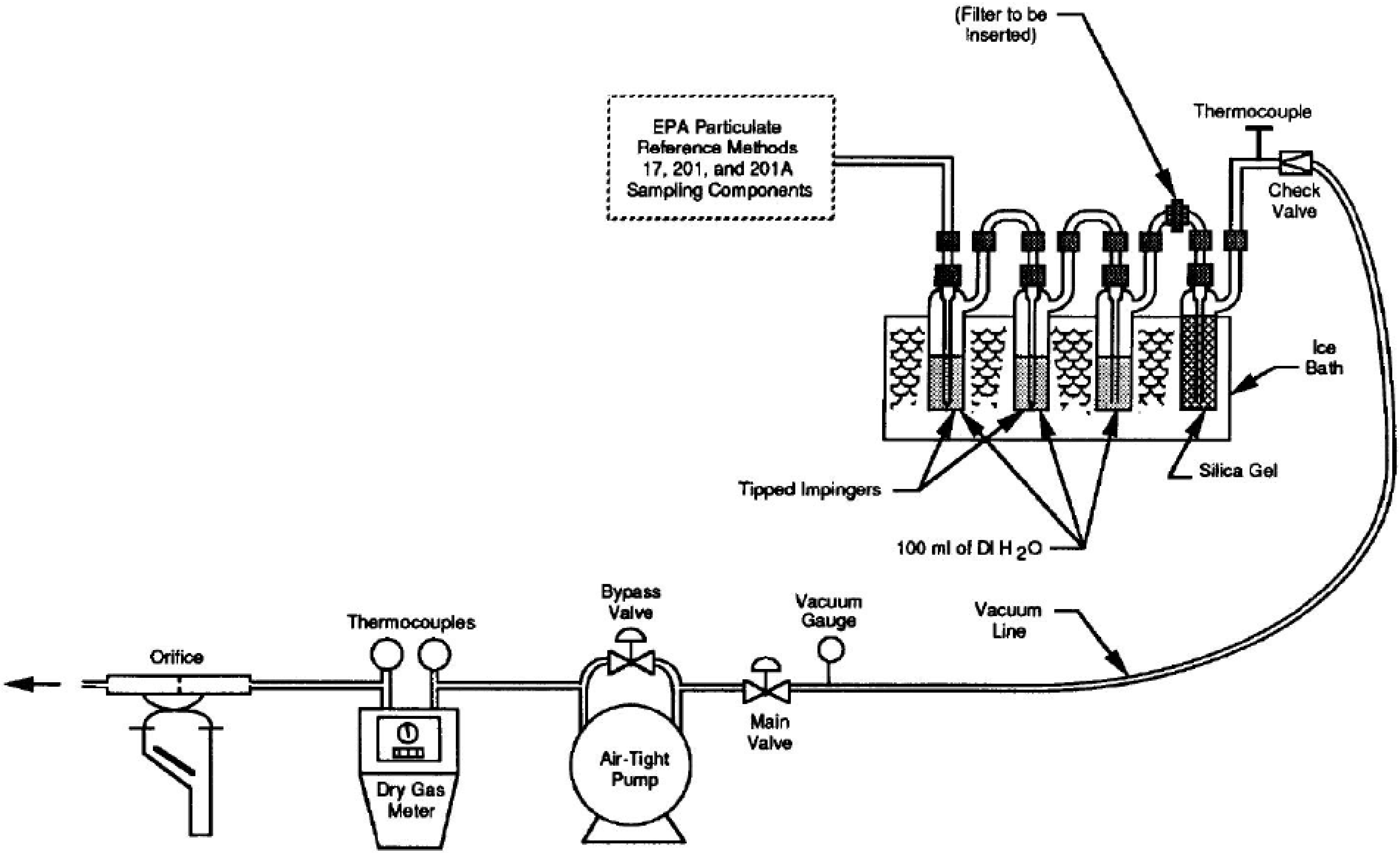
- Test Methods Discussion
- Process Test Methods Discussion

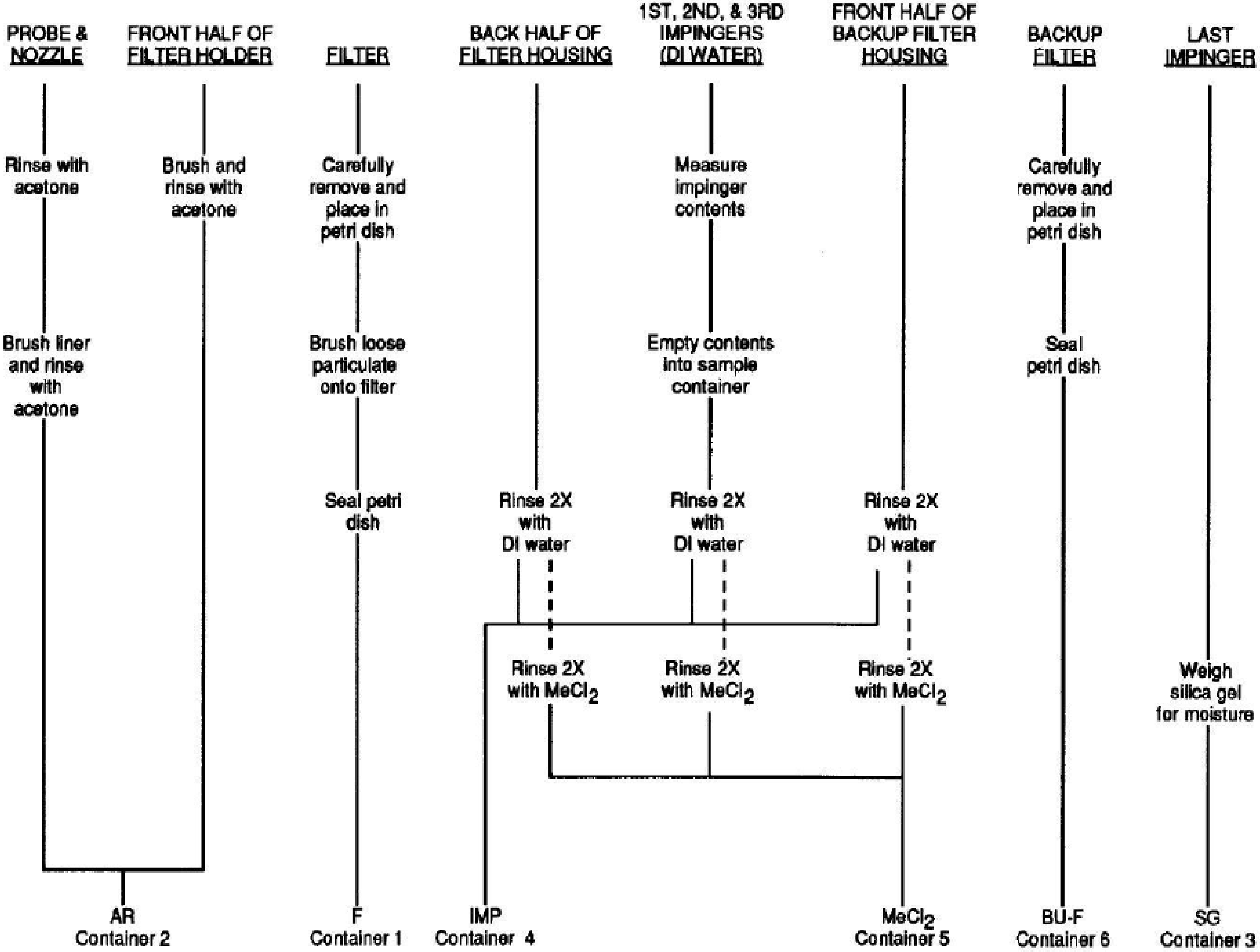
Emission Test Report

Test Methodology

- Sampling scheme with drawing and dimensions of site and sample points
- Description of sampling method
- Description of analytical method
- Modifications to methods and approved justification


TARED GLASS FIBER FILTER
HEATED FILTER BOX
1
2
3
TUBING CONNECTION
UMBILICAL
TO PITOT MANOMETER
TO INTEGRATED GAS SYSTEM
PROBE ASSEMBLY
HEATED GLASS OR S.S. LINED PROBE
THERMOCOUPLE
REVERSE TYPE PITOT TUBE
ORSAT PROBE (IF REQ'D)
TAPERED NOZZLE
GAS SAMPLE FLOW DIRECTION =
METER BOX ASSEMBLY
ORIFICE
ICE BATH
68°F
PYROMETER
VACUUM GAUGE
MAIN VALVE
BY-PASS VALVE
DRY GAS METER
DUAL MANOMETER
200 GRAMS SILICA GEL
EMPTY
100 ML H20
100 ML H20
U.S. EPA - 5
AIR TIGHT PUMP

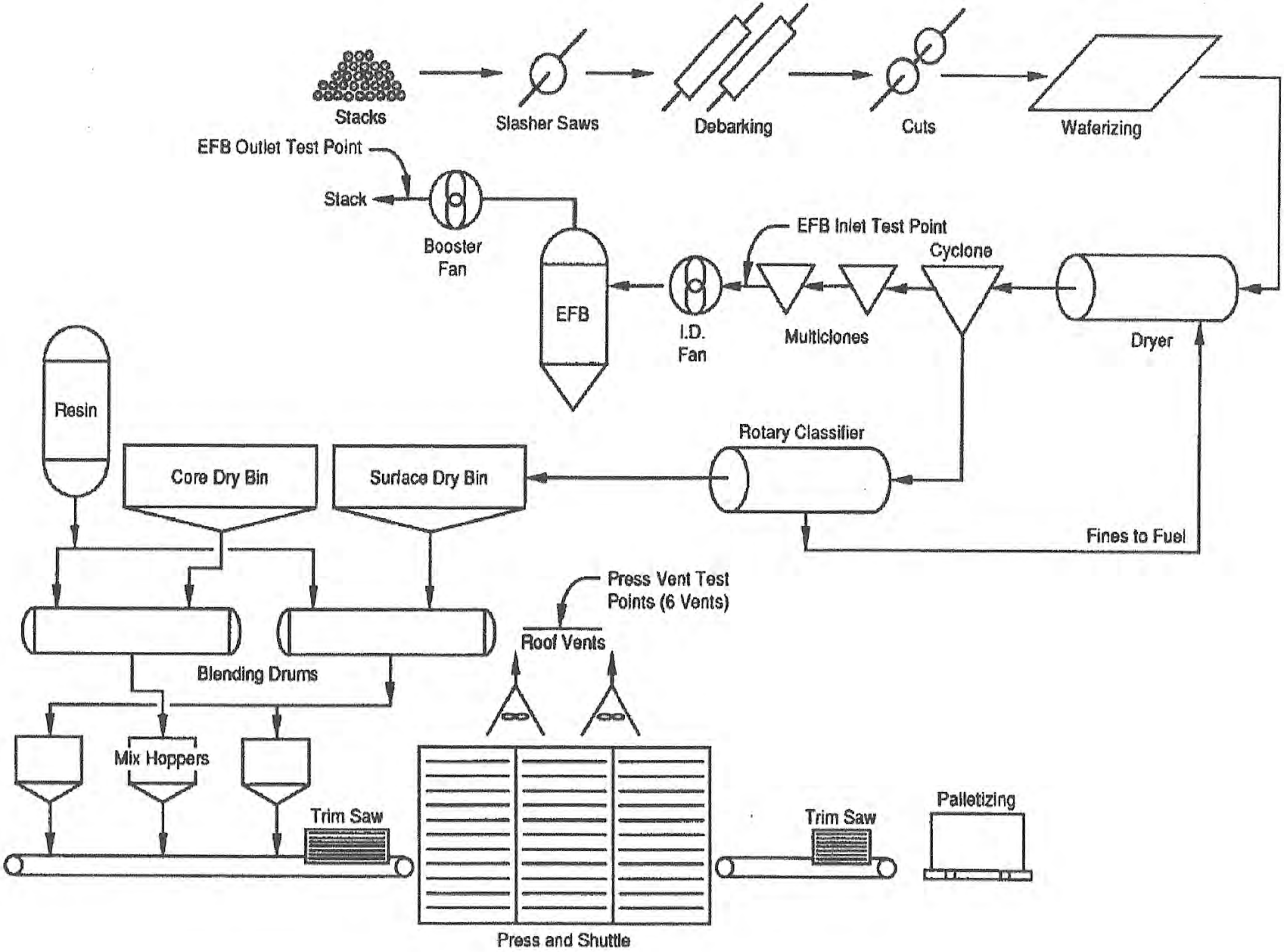

(Filter to be Inserted)
EPA Particulate Reference Methods 17, 201, and 201A Sampling Components
Thermocouple
Check Valve
Ice Bath
Silica Gel
Tipped Impingers
100 ml of DI H_2O
Vacuum Line
Vacuum Gauge
Main Valve
Bypass Valve
Air-Tight Pump
Thermocouples
Dry Gas Meter
Orifice


PROBE & NOZZLE
Rinse with acetone
Brush liner and rinse with acetone
FRONT HALF OF FILTER HOLDER
Brush and rinse with acetone
AR Container 2
FILTER
Carefully remove and place in petri dish
Brush loose particulate onto filter
Seal petri dish
F Container 1
BACK HALF OF FILTER HOUSING
Rinse 2X with DI water
Rinse 2X with $MeCl_2$
1ST, 2ND, & 3RD IMPINGERS (DI WATER)
Measure impinger contents
Empty contents into sample container
Rinse 2X with DI water
Rinse 2X with $MeCl_2$
FRONT HALF OF BACKUP FILTER HOUSING
Rinse 2X with DI water
Rinse 2X with $MeCl_2$
IMP Container 4
$MeCl_2$ Container 5
BACKUP FILTER
Carefully remove and place in petri dish
Seal petri dish
BU-F Container 6
LAST IMPINGER
Weigh silica gel for moisture
SG Container 3

Emission Test Report

Process Description

- Describe process
- Describe control equipment
- Flow diagram of entire process
- Flue gas sampling location


Stacks
Slasher Saws
Debarking
Cuts
Waferizing
EFB Outlet Test Point
Stack
Booster Fan
EFB
I.D. Fan
EFB Inlet Test Point
Multiclones
Cyclone
Dryer
Resin
Core Dry Bin
Surface Dry Bin
Rotary Classifier
Fines to Fuel
Press Vent Test Points (6 Vents)
Roof Vents
Blending Drums
Mix Hoppers
Trim Saw
Press and Shuttle
Trim Saw
Palletizing

Section #5: Internal QA/QC

- QA/QC Problems That Occurred During The Test
- Sample Identification and Custody Problems

Emission Test Report

Results

- Summary of data
- Charts and tables
- Example calculations

Wesleyan College Pathological Incinerator Federal Reference Method 5 Test Results[1]

Run Number		**Run 1**	**Run 2**	**Run 3**	**Average**
Identification	**Symbol** **Units**				
	Volumetric Flow Rate Data				
Avg. Stack Gas Velocity	V_s, ft/sec	33.52	39.59	39.13	37.41
Stack Gas Cross Sect Area	A_s, ft^2	1.58	1.58	1.58	1.58
Actual Stack Gas Flow	Q_{act}, acfm	3170	3745	3700	3538
Dry Std Stack Gas Flow	Q_{sd}, dscfm	760	864	856	827
Stack Gas Moisture Content	$B_{ws,}$ %	10.8	12.5	11.4	11.6
Stack Gas Oxygen (O_2)	%	10.9	12.2	12.2	11.8
Stack Gas Carbon Dioxide (CO_2)	%	9.0	7.0	7.0	7.7
Stack Gas Nitrogen (N_2)	%	80.1	80.8	80.8	80.6
Stack Gas Temperature, (T_s)	° F	1499.4	1524.9	1543.5	1522.6
Percent of Isokinetic Rate	**I, %**	**96.4**	**96.9**	**96.0**	**96.4**
EPA Allowed % I[2]	**I, %**	**90-110**	**90-110**	**90-110**	**90-110**
	Process Data				
Waste Charge Rate - Average	**P, lbs/hr**	**97.6**	**129.2**	**129.4**	**135.4**
	Emission Rate Data				
Total Mass of Particles	m_t, mg	37.7	28.2	23.9	29.9
Stack Particulate Conc.	c_s, g/dscf	0.001	0.001	0.001	0.001
	c_s, gr/dscf	0.015	0.010	0.008	0.011
Particulate Emission Rate	**E, kg/hr**	**0.031**	**0.024**	**0.020**	**0.025**
	E, lbs/hr	**0.068**	**0.053**	**0.044**	**0.055**
Allowable Emission Rate[3]	**E, lbs/hr**	**0.195**	**0.258**	**0.259**	**0.237**

Emission Test Report

Appendix

- Test log (record of events at site)
- Raw field data sheets
- Laboratory report including raw data, tables, and calibration graphs
- Testing equipment listing design and manufacturer
- Calibration procedures and data sheets
- Serial numbers of equipment used in test
- Copies of the methods applied from CFR Appendix A, or other reference procedure outline
- Copies of applicable statutes and regulations concerning the testing
- Results and Calculations

Emission Test Report Review

- Step 1: Obtain Emission Test Report, Test Protocol and Test Observation Report
- Step 2: Review Permit for Emission Standards and Test Requirements
- Step 3: Read Emission Test Report

Emission Test Report Review

- Step 4: Locate All Field Test Data Sheets
- Step 5: Conduct Independent Comprehensive Calculations of Emission Rates
- Step 6: Determine Correctable and Non-Correctable Errors

Emission Test Report Review

- Step 7: Compare Calculated Emission Rate to Standard
- Step 8: Complete Review Summary Checklist and Sign/Date
- Step 9: Notify Source of Acceptance and Compliance Status

Reviewing Stack Test Report

- Section 6.12 of FRM 5 states:

  "…If 90 %<I< 110 %, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or if I is less than 90 percent, the Administrator may opt to accept the results…"

Basic Approach to Reviewing

The basic approach of the procedure is to account for the inertial effects of particulate matter and to make a maximum adjustment on the measured particulate matter concentration

Step 1

- Check or calculate the percent isokinetic (I) and the particulate matter concentration (c_s) according to the procedure outlined in FRM 5
  - The c_s must be calculated using the volume of effluent gas actually sampled (in units of dry standard cubic feet, corrected for leakage).
  - Convert c_s to emission rate (E), units of the standard.

Step 2

- Compare E to the standard. Then accept or reject c_s using the criteria outlined below:
  - Case 1: I is between 90 and 110 percent. The concentration c_s must be considered acceptable. A variation of ± 10 percent from 100 percent isokinetic is acceptable.

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

  Situation 1: If E meets the standard, c_s should be accepted, since c_s can either be correct (if all particulate matter are less than 5 micrometers in diameter) or it can be biased high (if larger than 5 micrometer particulate matter is present) relative to the true concentration.

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

  Situation 2: If E is above the standard, multiply c_s by the factor (I/100) and recalculate E. If, on the one hand, this adjusted E is still higher than the standard, the adjusted c_s should be accepted (a maximum adjustment which accounts for the inertial effects of particulate matter has been made and E still exceeds the standard).

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

  Situation 2 (cont'd): On the other hand, if the adjusted E is lower than the standard, a retest should be done.

Step 2 (cont'd)

- Case 3 (I Is Greater Than 110 Percent)

  Situation 1: If E is above the standard, c_s should be accepted, since cs can either be equal to the true concentration or biased low relative to it. One has the assurance that E is definitely over the standard.

Step 2 (cont'd)

- Case 3 (I Is Greater Than 110 Percent) Situation 2: If E is below the standard, multiply c_s by the factor (I/100) and recalculate E. If, on the one hand, this adjusted E is still lower than the standard, the adjusted c_s should be accepted (a maximum adjustment which accounts for the inertial effects of particulate matter has been made and E still meets the standard).

Step 2 (cont'd)

- Case 2 (I Is Greater Than 110 Percent)

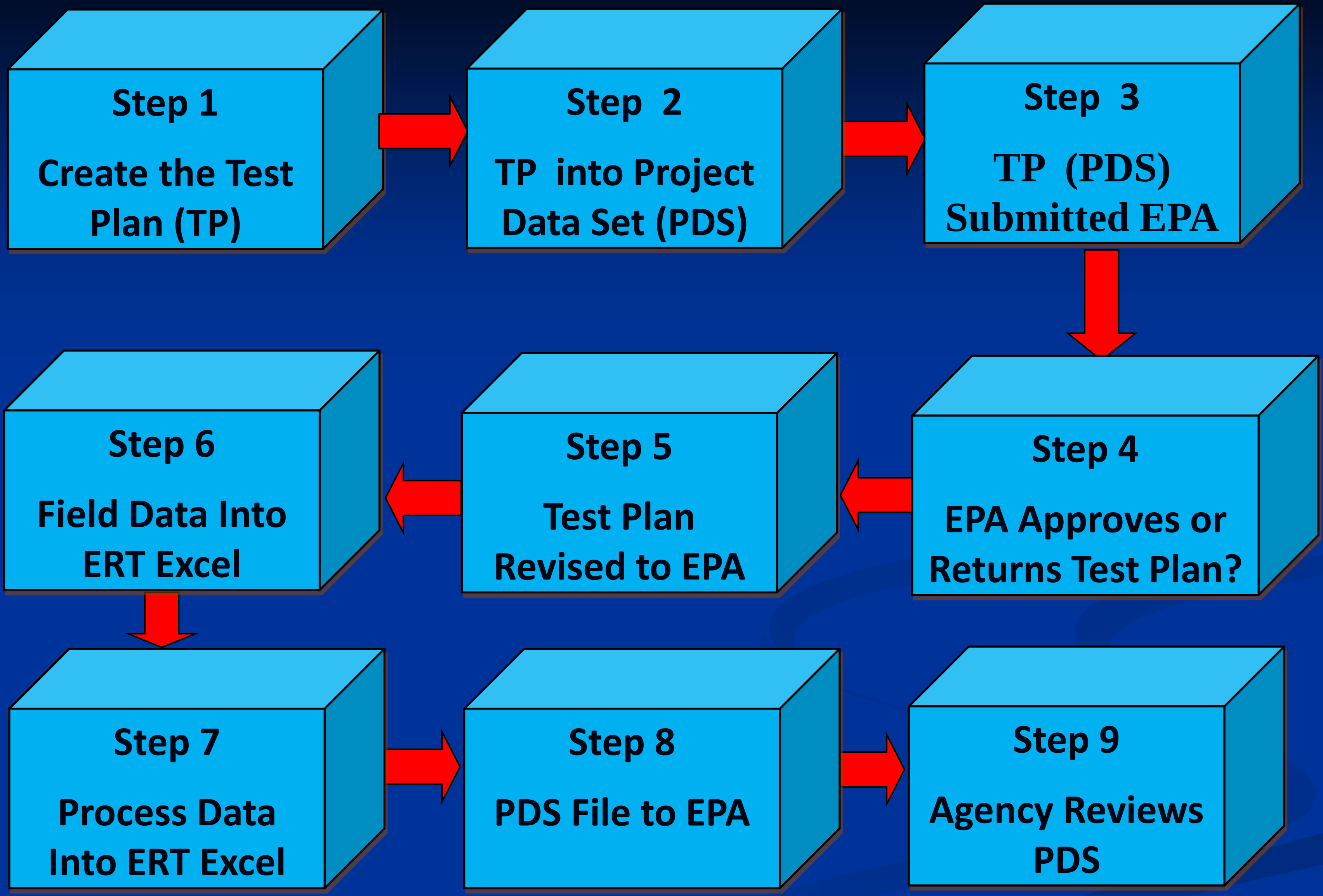
  Situation 2 (cont'd): On the other hand, if the adjusted E exceeds the standard, a retest should be done.

Summary of Acceptance

Case	I	Category	Decision
1	90-110 %		Accepted
2	< 90 %	E = ≤ Em. St.	Accepted
		C_s (I/100) = E_{adj} > Em. Std.	Accepted
		C_s (I/100) = E_{adj} < Em. Std.	Retest

Summary of Acceptance

Case	I	Category	Decision
3	> 110 %	E > Em. St.	Accept
		C_s (I/100) = E_{adj} < Em. Std.	Accept
		C_s (I/100) = E_{adj} > Em. Std.	Retest



Step 1

Create the Test Plan (TP)

Step 2

TP into Project Data Set (PDS)

Step 3

TP (PDS) Submitted EPA

Step 4

EPA Approves or Returns Test Plan?

Step 5

Test Plan Revised to EPA

Step 6

Field Data Into ERT Excel

Step 7

Process Data Into ERT Excel

Step 8

PDS File to EPA

Step 9

Agency Reviews PDS

Step 1

Obtain Emission Test Report, Test Protocol, and Test Observers Report

Step 2

Review Permit for Emissions Standards and Test Requirements

Step 3

Read Emission Test Report

- Complete Agency Emission Report Test Review Checklist
- Note Discrepancies

Step 4

Locate All Data Sheets

- Compare to Test Observers Report
- Note Discrepancies

Step 5

Conduct Independent Calculations

- Complete Comparison Data Evaluation Checklist
- Note Discrepancies

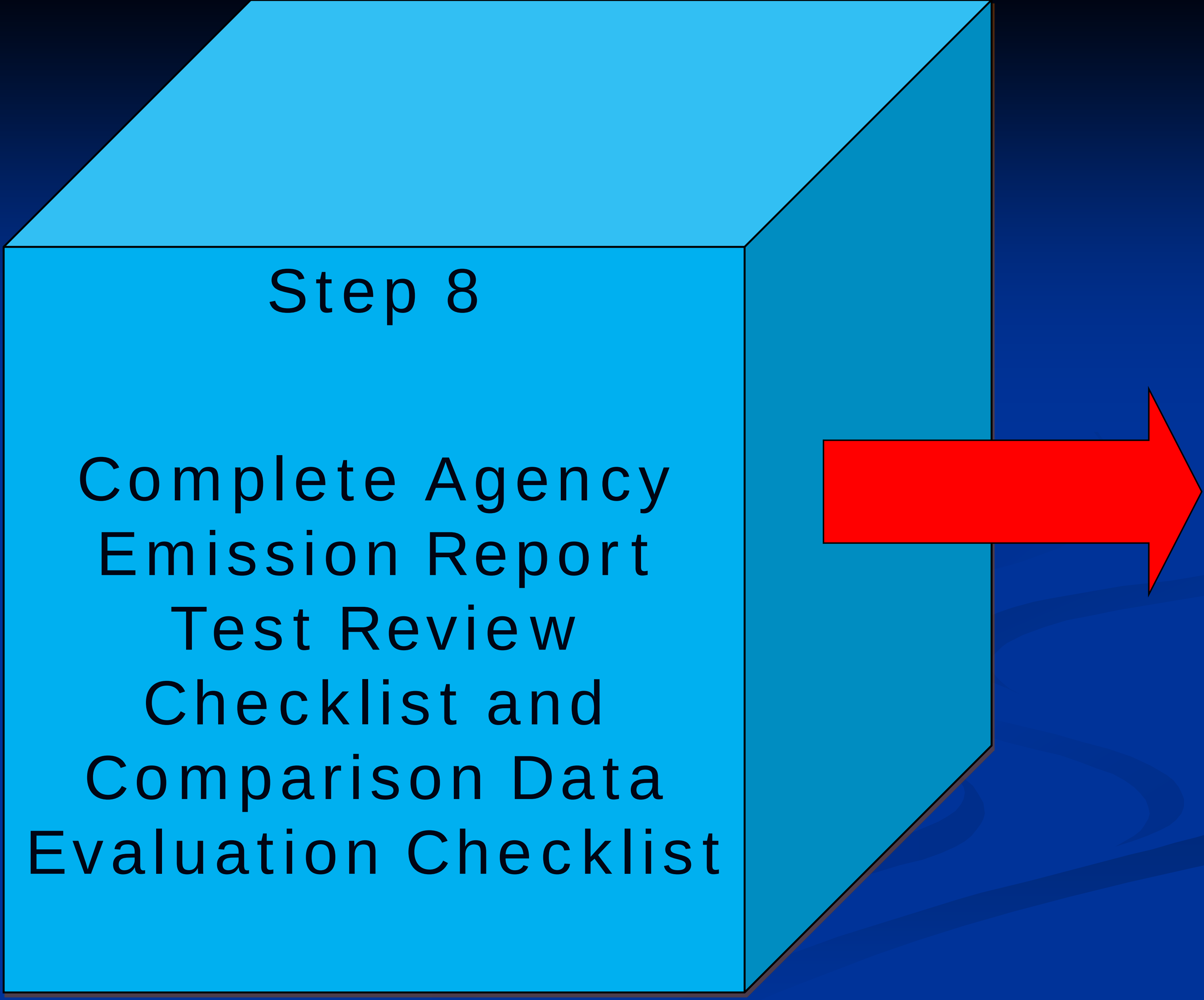
Step 6

Any Errors?

- Errors not Correctable, Reject Report
- If Corrections Possible, Return To Source

Step 7

Compare Calculated Emission Rate To Standard To Determine If Source Is In Violation or Compliance

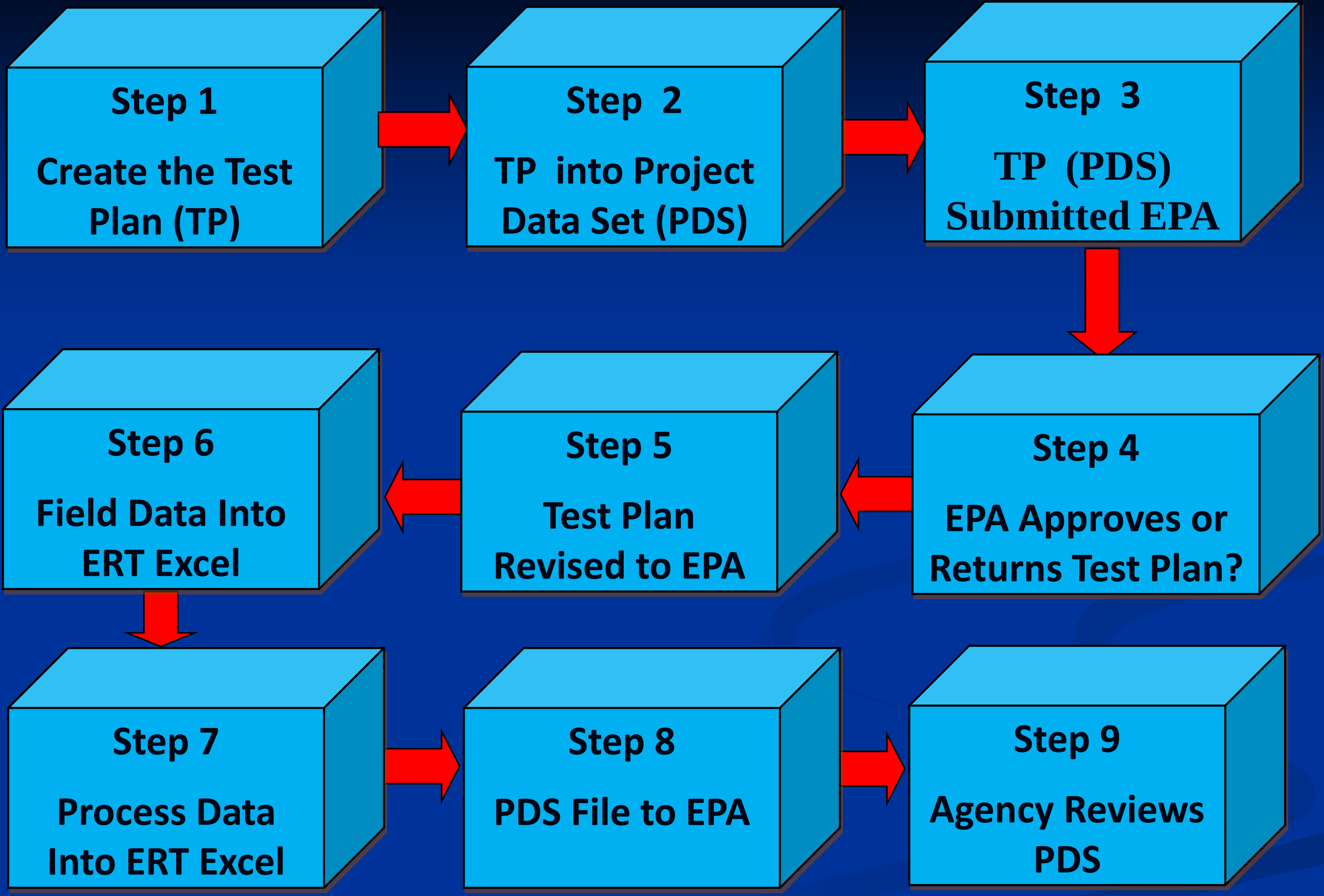


Step 8

Complete Agency Emission Report Test Review Checklist and Comparison Data Evaluation Checklist

Step 9

Notify Source of Acceptance Status of Report and Compliance Status



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Process Data Into ERT Excel

Step 8

PDS File to EPA

Step 9

Agency Reviews PDS

EPA's Electronic Reporting Tool

- Part of EPA's Electronic Stack Testing and Assessment Project
- ERT Version 3 Accepts Data from FRMs 1-4, 3A, 5, 6C, 7E, 25A, 26A, 29, 101A, 201A, and 202

Three Parts to ERT Application

#1: The Application

#2: The Project Data Set

#3: An Excel Spreadsheet

ERT Users Guide

http://www.epa.gov/ttn/chief/ert/ert_tool.html

Also includes template for importing test data to EPA's WebFire

U.S. EPA APTI
Compliance Test and Source Test Observation

F-Factors and Units of the Standard

Emission Standards for Sources

- Concentration of stack gas (C_S)
- Pollutant mass rate (pmr)
- Emission rate (E)
- Process weight rate (R)

Concentration of Stack Gas (c_s)

Can be expressed in:

- ppm
- g/dscm
- gr/dscf

For example:

The New Source Performance Standards (NSPS) for asphalt concrete plants is:

0.04 gr/dscf <=> 90 mg/dscm

Pollutant Mass Rate (pmr)

Can be expressed in:

- lb/hr
- g/hr

pmr = Concentration x Stack gas volumetric flow rate

$$= \frac{\text{lb}}{\text{dscf}} \times \frac{\text{dscf}}{\text{hr}}$$

$$= \frac{\text{lb}}{\text{hr}}$$

Emission Rate (E)

Can be expressed in:

- lb/10^6 Btu heat input
- ng/joule heat input

$$E = \frac{\text{Pollutant mass rate}}{\text{Heat input rate}}$$

$$= \frac{\text{lb /hr}}{10^6 \text{ Btu/hr}}$$

$$= \frac{\text{lb}}{10^6 \text{ Btu}}$$

For example:

The NSPS emission rate for fossil-fuel fired steam generators (FFFSG) is:

Particulate emissions limited to

$0.03\ \text{lb}/10^6\ \text{Btu}$.

Process Weight Rate (E)

Can be expressed in:

- lb/tons of product
- kg/metric tons of product

For Example:

The NSPS for sulfuric acid plants is:

SO_2 emissions limited to 2 kg SO_2/ metric ton H_2SO_4 produced.

$$\text{Combustion} = \frac{\text{Pollutant mass rate}}{\text{Heat input Rate}}$$

$$\text{Process} = \frac{\text{Pollutant mass rate}}{\text{Item of mass process rate}}$$

$$C_{corr} = C_S \frac{P_{std} T_s}{P_s T_{std}}$$

$$\overline{C}_{S_{12}} = \overline{C}_{S} \frac{12}{\%CO_2}$$

$$\overline{C}_{S6\%O2} = \frac{\overline{C}_{S}\ [\,20.9 - 6.0\,]}{20.9 - \%O_2}$$

$$\%EA = \frac{\%\ O_2 - 0.5\ (\%CO)}{0.264(\%N_2) - [\%O_2 - 0.5\ (\%CO)]} \times 100$$

Method 19

F Factor Methods

$$E = \frac{pmr_s}{Q_H} = \frac{c_s Q_s}{Q_H} = \frac{\dfrac{\text{lbs}\ \cancel{\text{ft}^3}}{\cancel{\text{ft}^3}\ \cancel{\text{hr}}}}{10^6\ \text{Btu}/\cancel{\text{hr}}}$$

$$= \frac{\text{lbs}}{10^6\ \text{Btu}}$$

$$E = c_s F \left(\begin{array}{c} \text{Dilution} \\ \text{correction} \\ \text{term} \end{array} \right)$$

$$\mathrm{E} = \frac{\cancel{\mathrm{ft}^3}}{10^6\ \mathrm{Btu}}\,\frac{\mathrm{lbs}}{\cancel{\mathrm{ft}^3}} = \frac{\mathrm{lbs}}{10^6\ \mathrm{Btu}}$$

Dilution correction term is dimensionless.

$$E = \bar{c}_s F_d \left[\frac{20.9}{20.9 - \%O_2} \right]$$

$$E = c_{ws} F_d \left[\frac{20.9}{20.9(1 - B_{ws}) - \%O_{2w}} \right]$$

$$E = \bar{c}_s F_c \frac{100}{\%CO_2}$$

$$E = \bar{c}_{sw} F_w \left[\frac{20.9}{20.9(1 - B_{ws}) - \%O_{2w}} \right]$$

Table 19-1-F: Factors for Various Fuels[illegible]

Fuel Type	F[illegible] dscm/J	F[illegible] dscf/10[illegible] Btu	F[illegible] wscm/J	F[illegible] wscf/10[illegible] Btu	F[illegible] scm/J	F[illegible] scf/10[illegible] Btu
Coal:						
Anthracite[illegible]	2.71x10-[illegible]	10,100	2.83x10-[illegible]	10,540	2.71x10-[illegible]	1,970
Bituminous[illegible]	2.63x10-[illegible]	9,760	2.66x10-[illegible]	10,640	2.63x10-[illegible]	1,800
Lignite	2.65x10-[illegible]	9,660	3.21x10-[illegible]	10,950	2.65x10-[illegible]	1,910
Oil[illegible]:	2.47x10-[illegible]	9,190	2.77x10-[illegible]	10,320	2.47x10-[illegible]	1,420
Gas:						
Natural	2.43x10-[illegible]	8,710	2.85x10-[illegible]	10,610	2.43x10-[illegible]	1,040
Propane	2.34x10-[illegible]	8,710	2.74x10-[illegible]	10,200	2.34x10-[illegible]	1,190
Butane	2.34x10-[illegible]	8,710	2.79x10-[illegible]	10,390	2.34x10-[illegible]	1,250
Wood	2.48x10-[illegible]	9,240			2.48x10-[illegible]	1,830
Wood bark	2.58x10-[illegible]	9,600			2.58x10-[illegible]	1,920
Municipal Solid Waste	2.57x10-[illegible]	9,570			2.57x10-[illegible]	1,820

[redacted]

[redacted]

[redacted]

U.S. EPA APTI
Compliance Test and Source Test Observation

FRM 316 and SW-846, Method 0011: Sampling and Analysis for Formaldehyde

40CFR63, Subpart NNN: National Emission Standards for Wool Fiberglass Manufacutring

- 3/31/97: Proposed rule and notice of public hearing
- 2/12/99: Proposed supplemental rulemaking
- 6/14/99: Final rule

Test Methods Identification

- FRM 1: Port location
- FRM 2: Volumetric flow rate
- FRM 3 or 3A: Correct conc. meas.
- FRM 4: Moisture content
- FRM 5: Particulate matter (PM); Each run 2 hours with min. 60 dscf; Probe temperature set to 350 °F
- FRM 316/FRM 318: Formaldehyde; Each run 1 hour with min. 30 dscf; Probe temperature set to 248 °F

What Is Formaldehyde?

- Formaldehyde (CH_2O) is an organic aldehyde compound having a terminal carbonyl group (R-CHO)
- Formaldehyde is a gas a room temperature (BP-20 ^{o}C; VP 2700 mm Hg @25 ^{o}C)
- Odor: Pungent, penetrating; Odor threshold of 27 ppb
- Very reactive compound

Sources of Formaldehyde?

- Products of incomplete combustion (e.g., vehicles, incineration of waste, combustion of fuels)
- Formed in photochemical reactions
- Production sources: Formaldehyde manufactures, product sources, mineral wool and wool fiberglass

Mineral Wool Process

- Mineral wool made in cupola furnaces charged with blast furnace slag, silica rock, and coke
- Charge heated to 3000 °F and fed to a blow chamber where steam atomizes the molten rock into globules that develop into long fibrous tails as they are drawn to the other end of the chamber

Mineral Wool Process

- Temperature of between 150-250 °F is maintained in the blow chamber
- Wool blanket formed is conveyed to an oven to cure the binding agent and then to a cooler
- A batting operation normally follows the cooler

Questions to Ask In Selecting A Method

- Is the sampling for indoor, ambient or stack emissions?
- Is the source regulated under a specific regulation (i.e., NAAQS, NSPS, SIP, BIF, MACT, NESHAP)?
- If it is a source emission, does the source have liquid droplet?
  - If yes, then isokinetic sampling!
  - If no, then constant sampling rate!

Questions to Ask

- If the source is wet, what type of source is it?
  - Incinerator (e.g., hazardous waste, cement kiln, BIF, thermo oxidizers etc.)? Use SW-846, Method 0011
  - Mineral wool or wool fiberglass industry? Use FRM 316 or FRM 318
- Do you need to know about other aldehydes and ketones?
  - SW-846, Method 0011 speciates
  - FRM 316 doesn't

Questions to Ask

- Do you need to know about other aldehydes and ketones?
  - SW-846, Method 0011 speciates
  - FRM 316 doesn't
- If the source is dry, what type of source?
  - Pulp and Paper Industry: NCASI Chilled Impinger/Silica Gel Test
  - Other sources, FRM 316 or SW-846, Method 0011

Questions to Ask

- Are the concentrations high (> 50,000 ppm_v) or low (< 50,000 ppm_v)?
  - SW-846, Method 0011 becomes saturated resulting in low bias
  - FRM 316 has slightly better detection limits
- Do the formaldehyde measurements need to be continuous or time-integrated?

Questions to Ask

- Do special sampling and recovery considerations need to addressed:
  - Reagent certified "organic-free formaldehyde free"
  - Recovery of samples in polyehtylene bottles with no head-space and dry ice storage
  - Clean-up step during analysis to remove interference of acetylacetone
  - Analysis of second impinger to determine "breakthrough"

History of Formaldehyde

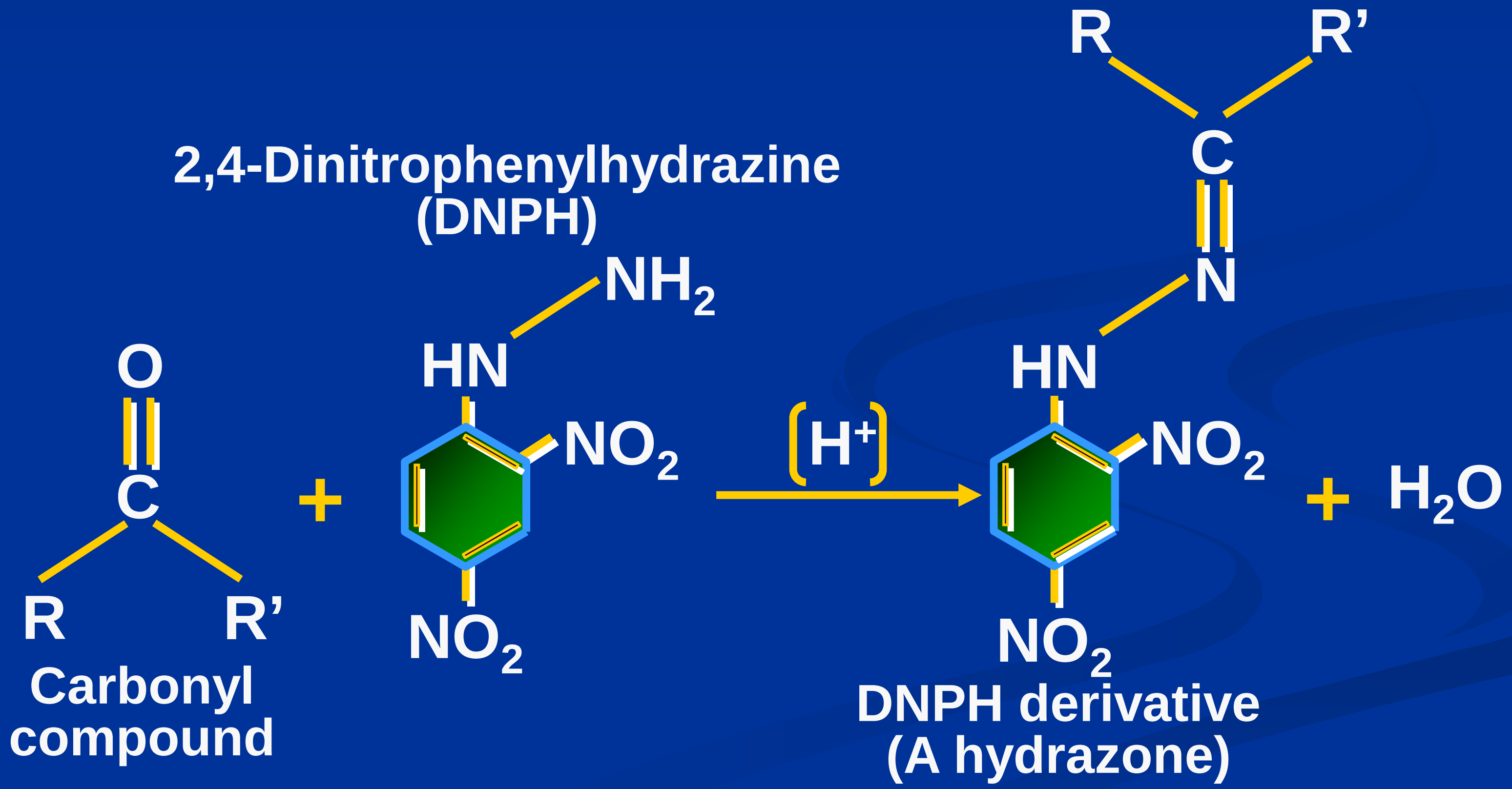
- 1990 EPA Ambient Air Method (EPA/600/3-90/005)
  - Constant Rate Sampling: DNPH Cartridges
  - Constant Rate Sampling: DNPH Impingers
  - EPA's Compendium of Methods
    - Indoor Compendium
    - Organic Compendium

Compendia

- Indoor (IP-1 through IP-10)
  - EPA-600/4-90-010
- Inorganic (I0-1 through IO-5)
  - EPA-625/R-96/010a
- Organic-Second Edition (TO-1 through TO-17)
  - EPA-625/R-96/010b

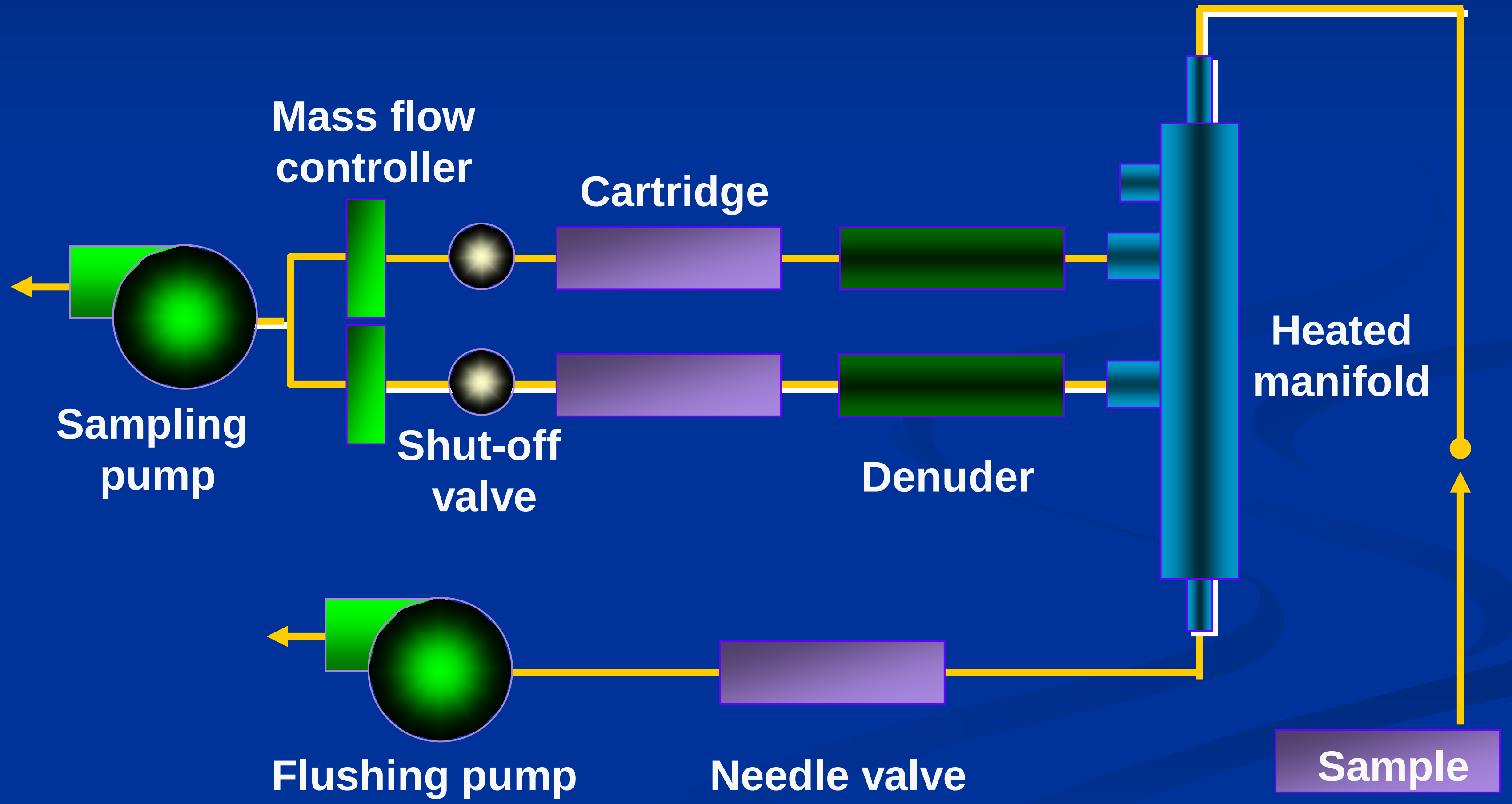
Compendium Method TO-11A

Derivatization Reaction

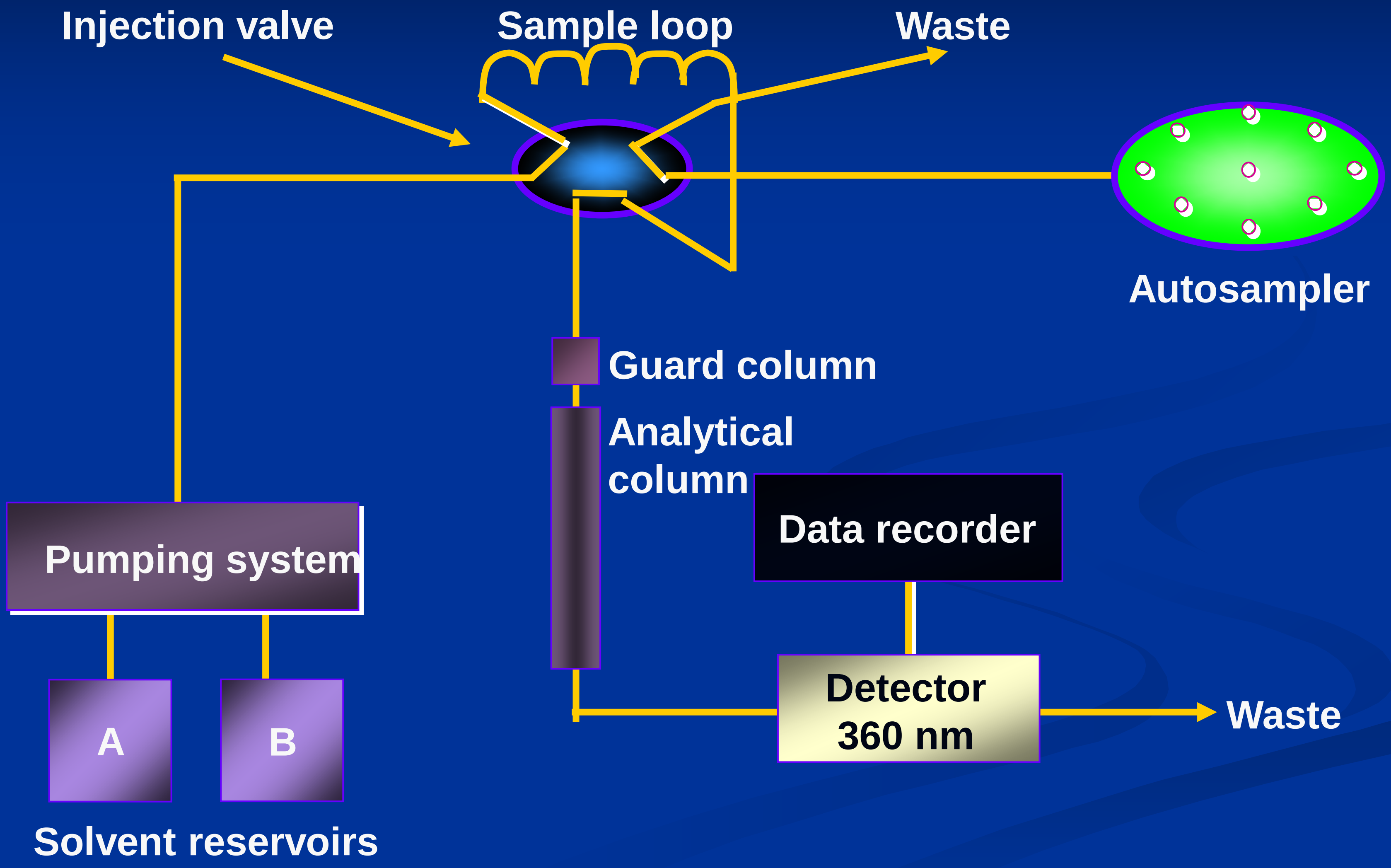


Example of Commercially Available DNPH-Cartridge

Example of Dual-port Carbonyl Sampler



Basic HPLC System



Injection valve

Sample loop

Waste

Autosampler

Guard column

Analytical column

Data recorder

Pumping system

Detector 360 nm

Waste

A

B

Solvent reservoirs

HPLC Chromatogram

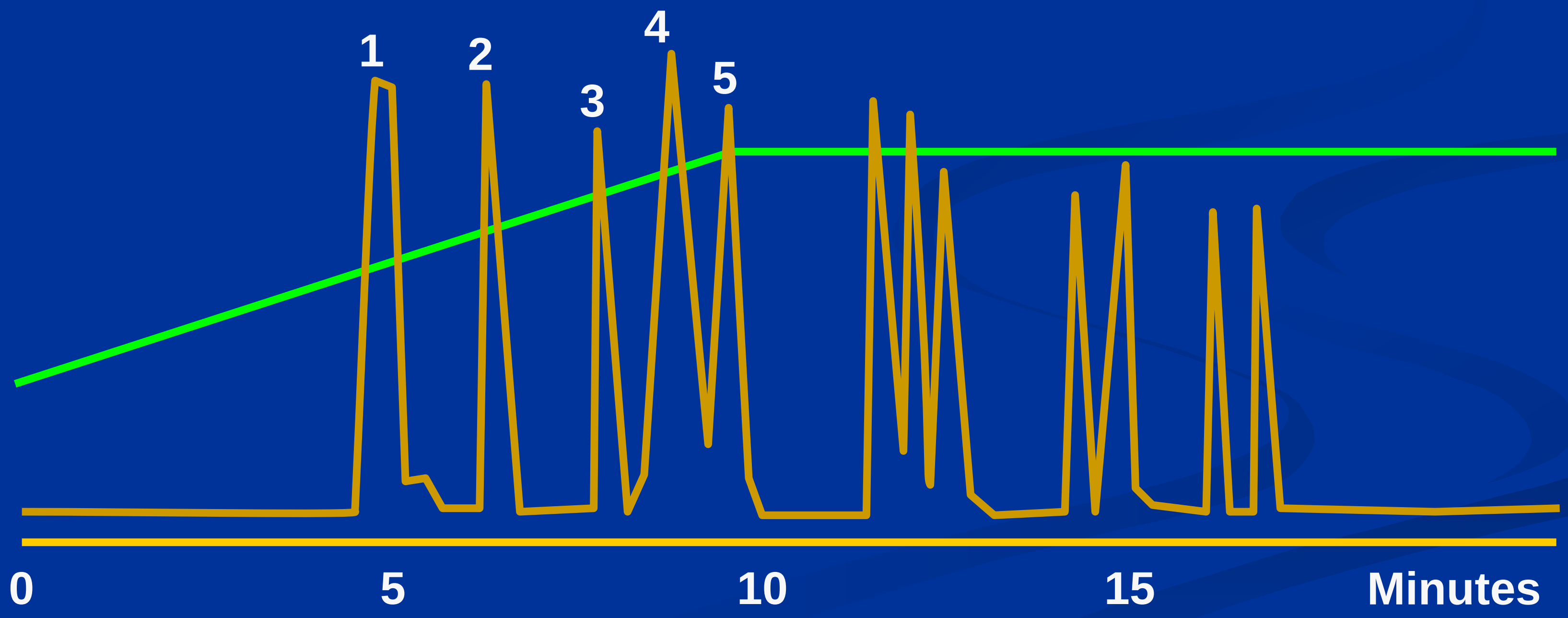
1 Formaldehyde

2 Acetaldehyde

3 Acetone

4 Acrolein

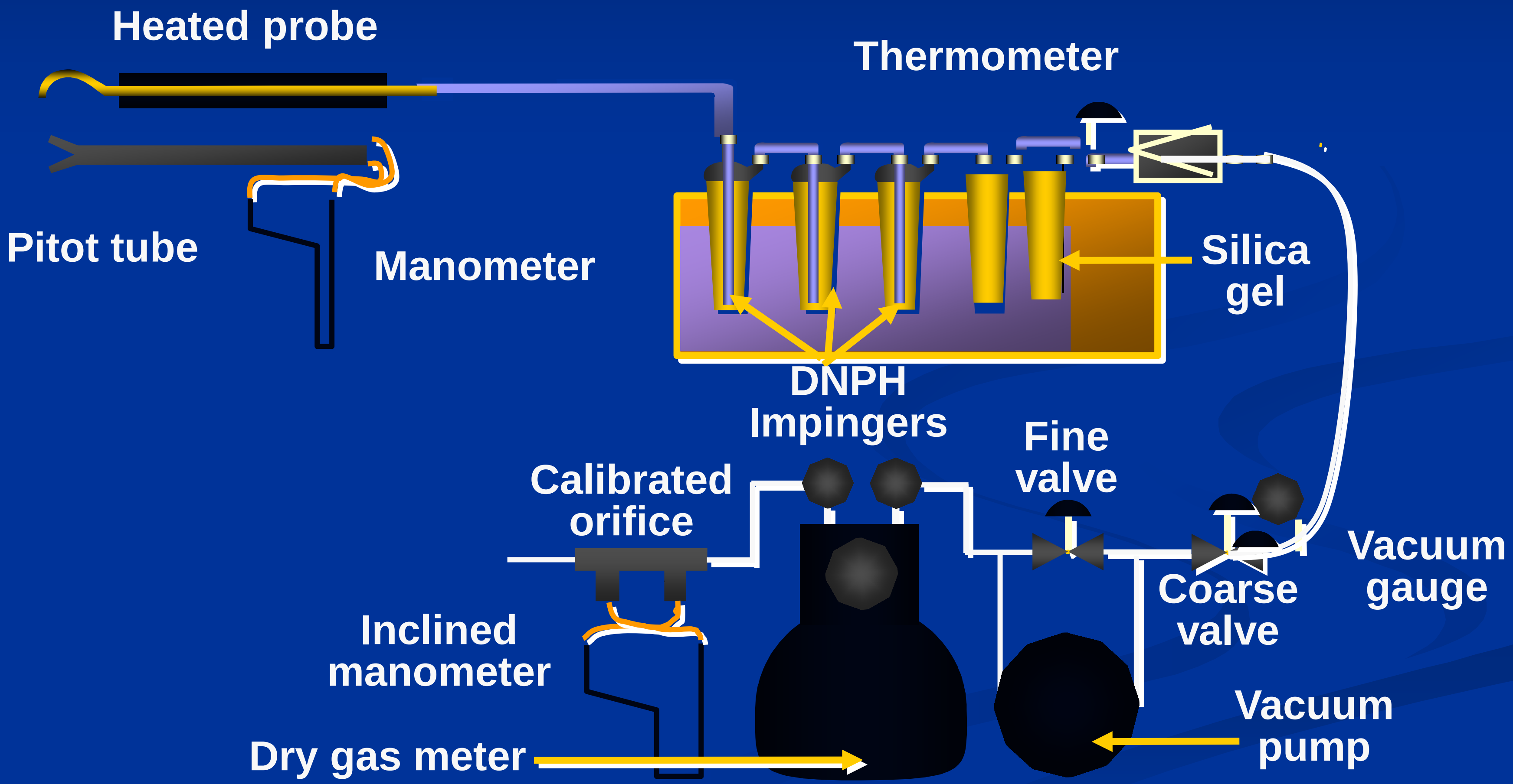
5 Propionaldehyde



History of Formaldehyde

- 1991 Boiler and Industrial Furnaces Regulations (BIF)
- Method 0011 (SW-846)
  - Federal Reference Method 5 Sampling Train With 5 Impingers
  - Isokinetic Sampling
  - DNPH Impingers (opt. breakthrough check)

SW-846, Method 0011 Sampling Train



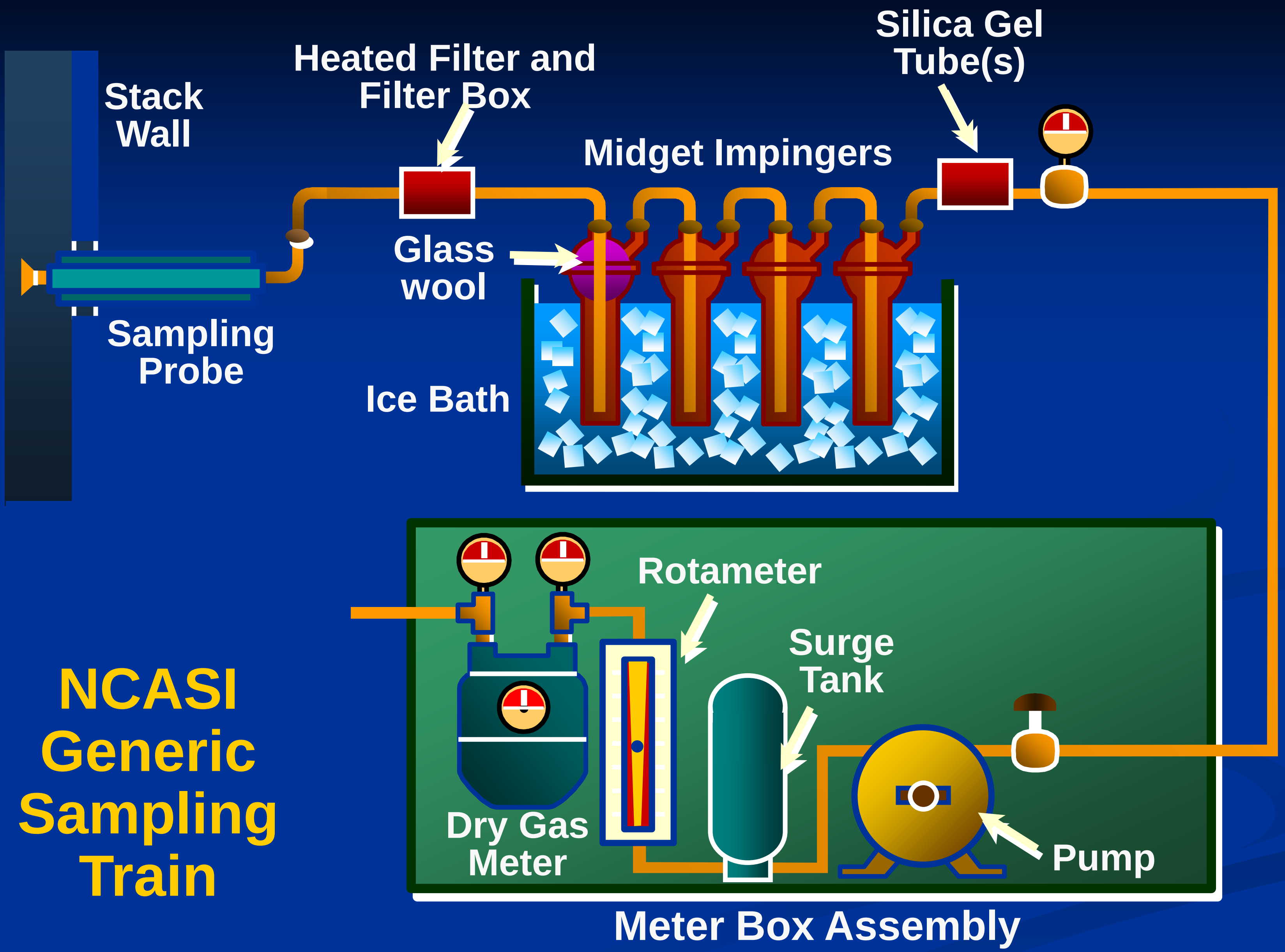
BIF Formaldehyde Method (SW846, Method 0011)

- FRM 5 sampling train without heated filter and filter compartment
- Isokinetic sampling; FRM 1-4 apply
- Impinger solutions DNPH (~100 mL)
- Analysis: HPLC @ 360 nm
- Methylene chloride rinse
- Sample volume of 40 cf for 1 hour

History of Formaldehyde

- NCASI Chilled Impinger Methods
  - Constant Rate Sampling (400±50 cc/min); Water
    - CI/SG/PULP-94.02 (pulp & paper mills)
      - No filter; Midget Impingers; Silica Gel
    - CI/WP-98.01 (wood products mills)
      - Hot probe/filter; Impingers
    - IM/CAN/WP-99.01 (wood prod mills)
      - Hot probe/filter; Impingers, Canister
  - EPA Method 301 Validation

NCASI Generic Sampling Train



Stack Wall

Sampling Probe

Heated Filter and Filter Box

Glass wool

Midget Impingers

Ice Bath

Silica Gel Tube(s)

Rotameter

Surge Tank

Dry Gas Meter

Pump

Meter Box Assembly

NCASI Formaldehyde Method (CI/SG/Pulp-94.02 and 98.01)

- FRM 6 sampling train without glass wool filter
- Constant sampling rate of 400 cc/min for 60 minutes
- Impinger solutions of water with back-up two (2) silica gel traps (n-propanol/water extraction)
- Analysis: GC/FID
- Water rinse

History of Formaldehyde

- Federal Reference Method 316: Mineral Wool Manufacturing Industry
  - Promulgated and published with the MACT mineral wool regulations, May 1999: Impinger Technique
- Federal Reference Method 318: Industries Using Phenolic Resins (Mineral Wool and Fiberglass)
  - Promulgated and published with the MACT regulations, May 1999: Instrumental FTIR

Applicability

- FRM 316 is applicable for the determination of formaldehyde emissions from stationary sources in the mineral wool and wool fiberglass industries

Applicability

- Method requires the use of FRMs 1-4
- Method uses standard FRM 5 equipment except elimination of the heated filter

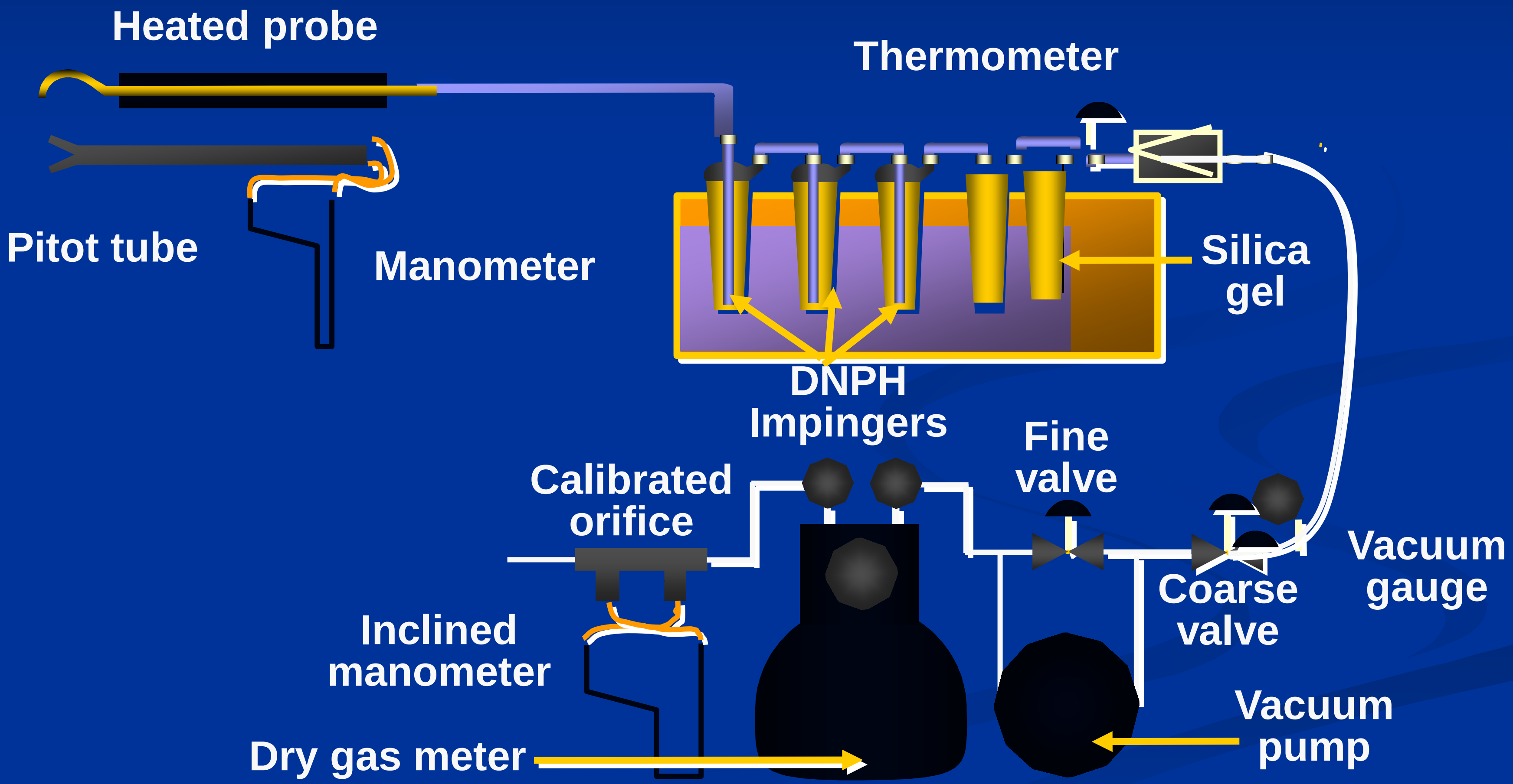
Principle
FRM 316

- Gaseous and particulate pollutants of formaldehyde are withdrawn isokinetically from the source and collected in a series of impingers containing high purity water
- Formaldehyde collected in the impingers is determined by the modified acidic pararosaniline method

FRM 316 Sampling Train

- Nozzle/heated probe
- No heated filter box assembly
- Impinger assembly containing DI water
- Meter box assembly

SW-846, Method 0011 Sampling Train



Heated probe

Thermometer

Pitot tube

Manometer

Silica gel

DNPH Impingers

Fine valve

Calibrated orifice

Vacuum gauge

Coarse valve

Inclined manometer

Vacuum pump

Dry gas meter

FRM 316 Principle

- Formaldehyde and particulate matter/formaldehyde are withdrawn isokinetically from the source through a nozzle and heated probe
- Formaldehyde and particulate matter are trapped in the impingers containing DI water

FRM 316 Principle

- Formaldehyde is highly soluble in high purity water
- Concentration of the soluble formaldehyde in the water is determined using the modified acidic pararosaniline colorimetric method

FRM 316 Principle

- Formaldehyde reacts with acidic pararosaniline and the sodium sulfite forming a purple chromophore
- Intensity of the purple chromophore is measured spectrophotometrically
- Detecton limit is 11 ppb_v and as high a 23,000,000 ppb_v for a 1-hr sample (~ 30cf)

FRM 316 Objective

- The objective of performing FRM 316 is to determine the pollutant mass rate (pmr) or emission rate (E) of formaldehyde from the regulated source
  - $pmr = (c_s)(Q_s)$
  - $E = pmr/Q_h$

FRM 316 Interferences

- Sulfites
- Cyanides

FRM 316 Sample Nozzle

- Seamless stainless steel tubing, quartz or glass
- Other materials approved by administrator
- Button-hook/elbow design
  - Sharp/tapered leading edge (< 30 Angle)
  - Constant internal diameter

FRM 316 Sample Nozzle

- Range of nozzles (0.32-1.27 cm I.D.)
  - Nozzles must be calibrated
  - Measure 3 reading using micrometer (take average)
  - Low/high reading not exceed 0.004 in

FRM 316 Sample Nozzle

- Nozzles that have been nicked, dented, or corroded must be reshaped and recalibrated
- Each nozzle must have a permanent identification

FRM 316 Pitot Tube

- Must be constructed according to FRM 2
- Position of pitot tube with reference to nozzle
  - nozzle entry plane must be even or below pitot orifice
  - Centerline of orifice and nozzle must agree

FRM 316 Pitot Tube

- Minimum spearation for 1.3 cm I.D. nozzle and pitot is 1.90 cm
- Position of pitot tube with reference to probe sheath/thermocouple
  - Probe sheath end and pitot tube separated by 7.62 cm
  - Thermocouple must either be offset 1.90 cm or no closer than 5.08 cm

FRM 316 Pitot Tube

- Must develop calibration factor
- Manometer/magnahelic usually attached to indicate differential pressure

FRM 316 Sampling Probe

- Typical diameter of 2.54 cm
- Probe liner should be borosilicate or quartz with heating system to prevent “visible” condensation
  (do not use metal probe liners!)

FRM 316 Sampling Probe

- Pitot tube must be
  firmly welded to probe
- Probe designed to prevent accidental
  misalignment in
  gas stream

FRM 316 Sampling Probe

- Probe designed to protect liner
- Material of construction
  - Borosilicate Glass liners up to 480°C
  - Quartz liners up to 900°C

FRM 316 Sampling Probe

- Must have heating system capable of maintaining gas temperature of 120°C ± 14°C
- Temperature must be calibrated

FRM 316 Impinger System

- Material of construction
    - Glass, Teflon, stainless steel
- Minimum of 4 impingers
- Design may allow for additional space for impingers beyond FRM 5 requirements
- Need for water drain tap

FRM 316 Impinger System

- Ball joints with Teflon® compression rings
  - Silicone grease not required
  - Reduced contamination probability
  - Favorable to most stack testers
- Screw type fittings
  - Convenient
  - Reduced contamination probability

FRM 316 Impinger System

- First and Second Impingers: 100 mL of high purity water (May go to 200 mL if formaldehyde concentration in stack is high)
- Third Impinger: Dry
- Fourth Impinger: 200-300 g of silica gel

FRM 316 Umbilical Cord

- Contains vacuum lines, pitot tube lines, and electrical connections
- Keep bundle simple and light
- Use heavy rubber vacuum tubing for pump/impinger connection
- Use tygon or Teflon® for pitot tube lines (color coded)

FRM 316 Meter Console Desirable Features

- Light weight
- Reliable leak-free pump
- Good temperature controls
- Rugged construction/ good carrying handles

FRM 316 Meter Console Desirable Features

- Accessibility to components and fuse compartment
- Communication system
- Easy to read digital readouts

FRM 316 Meter Console Required Calibrations

- Leak check both positive and negative (< 0.04 cfm)
- Dry gas meter γ value of 0.98-1.02
- Therometers calibrated to ±2°F
- Orifice meter "$\Delta H_{@}$" documented and verified

FRM 316 Isokinetic Rate Equation

- The relationship between “v_s” and “v_n” is the core understanding of FRM 316 isokinetic sampling
- Reading the “Δp” from the pitot tube and setting the proper “ΔH” on the meter box allows one to sample isokinetically

FRM 316 Isokinetic Rate Equation (Simplified)

- $\Delta H = (K)(\Delta p)$
- Isokinetics must be between 90 to 110%

FRM 316 Causes for not Meeting 100% Isokinetics

- Moisture value wrong in setting preliminary isokinetic rate equation
- Inability to follow rapid fluctuations in Δp and corresponding calculating/setting ΔH

FRM 316 Causes for not Meeting 100% Isokinetics

- Large temperature variations not corrected in isokinetic rate equation
- Leak in pitot or sampling lines (broken probe)
- Preliminary selection
  of wrong nozzle size

Difficulty in Maintaining Isokinetics

- Impinger stem too restricted
- Buildup of particles in impinger #1, thus plugging tip
- Nozzle too small/large for velocity of stack gas

FRM 316 Pre-test Preparation

- Calibrate the meter system
- Determine the number and location of sampling points
- Prepare sampling train
  - Add 100 mL of high purity water to first and second impinger
  - Third impinger dry
  - Add 200 g silica gel in last impinger

FRM 316 Pre-test Preparation

- Place ice and water around bubbler/impingers
- Adjust probe heater to desired temperature

FRM 316 Sampling

- Leak check the sampling system (Optional)
- Record initial DGM reading and barometric pressure
- Position tip of probe at first traverse point

FRM 316 Sampling

- Adjust flow rate to isokinetic conditions during the entire sampling run (Sampling rate should not exceed 1.0 cfm)
- Traverse taking reading every 2 minutes and recording on FTDS

FRM 316 Sampling

- Add more ice during run to maintain last impinger outlet < 68°F
- At conclusion of run, turn off the pump, remove probe from stack, and record final DGM reading
- Leak check the sampling train (mandatory)

FRM 316 Leak Check

- Similar to FRM 5, if the leak rate exceeds 0.02 cfm, then the tester has two options:
  - Adjust final sample volume as outlined in Section 6.3 of FRM 5
  - Void the sample run
- If change components during sample run, then must perform leak check prior to component change

FRM 316 Sample Recovery

- Drain the ice bath
- Allow probe to cool, then disconnect from sampling train. Cap inlet to first impinger and both ends of probe
- Measure to the nearest 1.0 mL the solutions in the three impingers and transfer to polyethylene bottle

FRM 316 Sample Recovery

- Rinse impingers with additional water and recover in bottle
- Also rinse nozzle and probe line with water and collect in bottle. Use brushes to clean nozzle and probe liner
- Weigh silica gel impinger

FRM 316 Sample Recovery

- Seal, identify the sample container, and mark liquid level
- Complete “chain-of-custody” for sample run
- Complete field test data sheet (FTDS)
- Collect high purity water as reagent blank

FRM 316 Sample Recovery

- Seal, identify the sample container, and mark liquid level
- Complete “chain-of-custody” for sample run
- Complete field test data sheet (FTDS)
- Collect high purity water as reagent blank

FRM 316 Analysis

- Develop working formaldehyde standards to generate calibration curve
- Formaldehyde reacts with acidic pararosaniline and the sodium sulfite forming a purple chromophore

FRM 316 Analysis

- Color development period is 60 minutes
- Intensity of the purple chromophore is measured spectrophotometrically at 570 nm in cuvettes

FRM 316 Post-test Calibration Requirements

- Post-test calibration check procedure same as initial calibration check for orifice meter and DGM

FRM 316 Post-test Calibration Requirements

- If the calibration factor does not deviate by more than 5 percent from the initial calibration factor, then the DGM volumes obtained during the test series are acceptable

FRM 316 Other Components Needing Calibration

- Thermometers: Calibrated against mercury-in-glass thermometers
- Barometer: Calibrated against a mercury barometer

FRM 316 Audit Vial

- Obtained from EPA
    - Emission Measurement Center
      Research Triangle Park, NC 27711

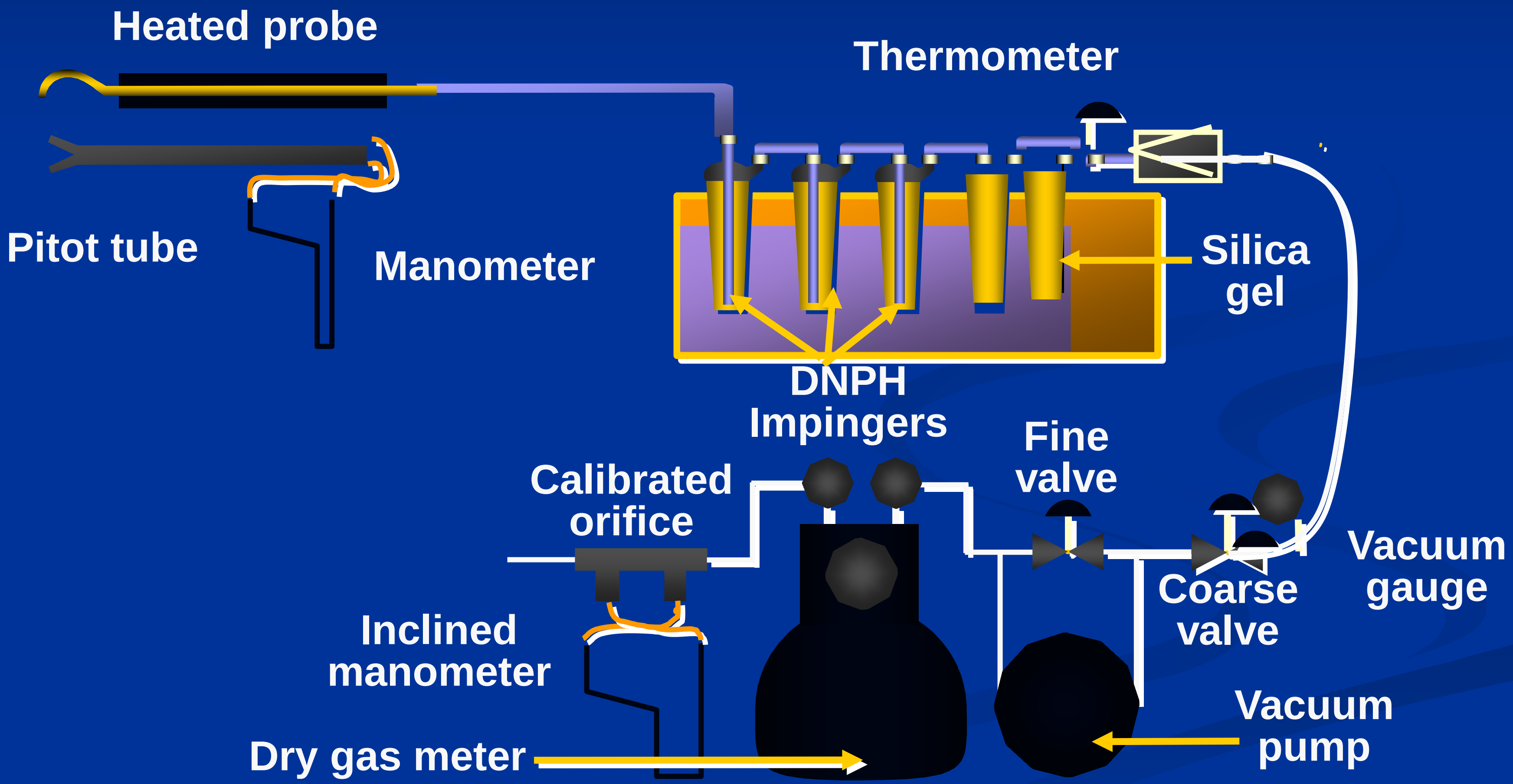
FRM 316 Audit Vial

- Analyze vial with each set of samples
- Acceptable limits of ±5% of stated value

SW-846, Method 0011

- Uses FRM 5 sampling train (Isokinetic) except without the heated filter
- Extends the impinger train to five (5) impingers
  - 200 mL first impinger
  - 100 mL in second and third impinger
  - Fourth impinger dry
  - Fifth impinger contains 200-300 g silica gel

SW-846, Method 0011 Sampling Train

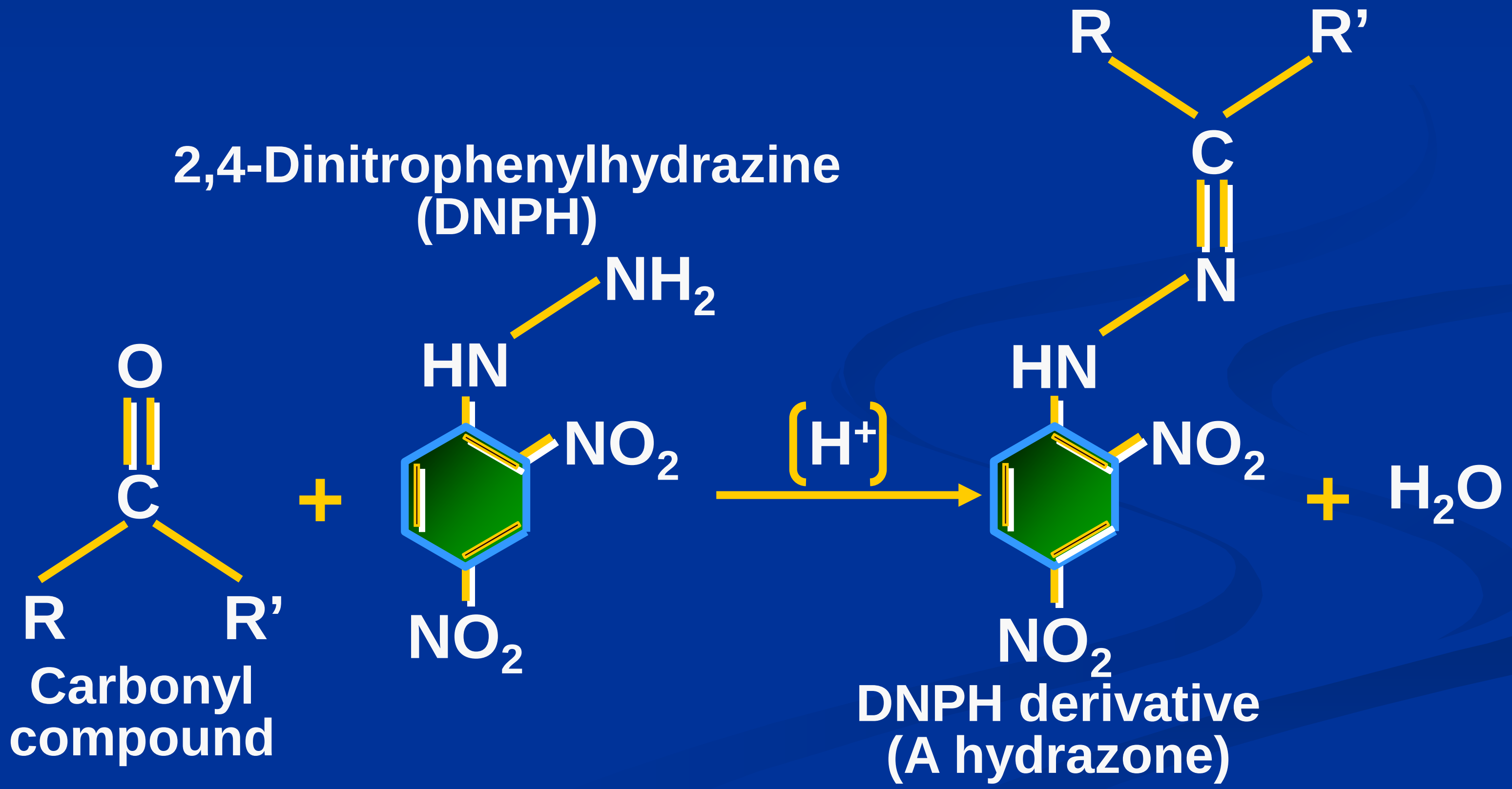


SW-846, Method 0011

- Uses 2,4-dinitrophenylhydrazine (DNPH) as the absorbing solution rather than high purity water in FRM 316
- Use methylene chloride as the rinse solution
- Analysis by HPLC @ 360 nm
- Must chill samples prior to analysis
- Can also analyze for other aldehydes and ketones

Method 0010 Reaction

Derivatization Reaction



Carbonyl compound

DNPH derivative (A hydrazone)

SW-846, Method 0011 Analyte List

- Formaldehyde
- Acrolein
- Propionaldehyde
- Butyraldehyde

Acetaldehyde
Acetone
Crotonaldehyde
Benzaldehyde

SW-846, Method 0011 Analyte List

- Isovaleraldehyde Valeraldehyde
- o-Tolualdehyde m-Tolualdehyde
- p-Tolualdehyde Hexanaldehyde
- 2,5-Dimethylbenzaldehyde
- Methyl ethyl ketone

Allegheny Particleboard Tests

- 06/94 1990 EPA Method (constant rate) and 08/94 BIF Method 0011 (isokinetic)
  - Board Press & Cooler results were substantially lower
- Results were considerablely different?
  - Process Variability?
  - Difference in Sampling Rate?
  - Breakthrough?

Yorktowne Department Tests

- Waste Wood-Fired Boilers w/common stack
  - 5 MMBtu/hour heat input (per unit)
  - Cyclones used for particulate control
- 07/96 BIF Method 0011
  - 2 impingers, each with 150 mL of DNPH
  - 31.6% of CH_2O in last impinger; probable breakthrough

Yorktown Department Tests

- 10/96 BIF Method 0011
  - 4 impingers, each with 150 mL of DNPH
  - 0.1% of CH_2O in last impinger; no breakthrough
  - Mass emission rate was 2.7x higher
  - CH_2O emissions much higher than AP-42 Factor
    - 2 lbs/ton versus 0.019 lbs/ton (assuming HHV of 8500 btu/lb)

Wood-Mode Department Tests

- Virgin or Waste Wood-Fired Boiler
  - 30MMBtu/hour heat input
  - Cyclone used for particulate control
- 08/96 BIF Method 0011
  - 4 impingers, each with 150 mL of DNPH
  - 0.1% of CH_2O in last impinger; no breakthrough
    - 5 lbs/ton versus 0.019 lbs/ton (assuming HHV of 8500 btu/lb)

Wood-Mode Department Tests (Contd)

- 08/96 BIF Method 0011
  - Fuel had no appreciable impact on CH_2O emissions
    - Some aldehyde emissions increased for waste wood
  - CH_2O emissions much higher than AP-42 Factor
    - 5 lbs/ton versus 0.019 lbs/ton (assuming HHV of 8500 btu/lb)

Testing at MDF Plants (BIF Method 0011)

- 10/97 Allegheny MDF
  - 57.3% of formaldehyde in last (2nd) impinger
  - Probable breakthrough
- 11/97 MacMillan Bloedel Clarion
  - 4.4% of formaldehyde in last (3rd) impinger
  - No breakthrough

Testing at MDF Plants (NCASI Method CI/WP-98.01)

- 12/98 Masonite Corporation
  - 2-58% of formaldehyde in last (2nd) impinger
    - 10% for Die Form Press
    - 38% for Resin Blender
    - 46% for Felter Scrubber
    - 58% for Board Cooler
    - 46% for First Stage Dryer
    - 2% for Second Stage Dryer
  - Probable breakthrough when sampled at 650 cc/min

Issues of Concern

- Do the various test methods produce data that is comparable?
- If the test methods are not comparable, how does one decide which procedure is appropriate?
- Is breakthrough a problem?
- Is formaldehyde being accounted for?
- Would audit samples help validate the data?

FRM 318

Extractive FTIR Method for Measurement of Emissions from Mineral Wool and Wool Fiberglass Industries

- See FTIR Video

EPA's FTIR Support

- FRM 318: Extractive FTIR Method for Measurement of Emissions from Mineral Wool and Wool Fiberglass Industries
- FRM 320: Vapor Phase Organic and Inorganic Emissions by FTIR (Extractive)
- FRM 321: Determination of HCl from Portland Cement Industries

EPA’s FTIR Support

- Performance Specification 15 for Extractive FTIR CEMS in Stationary Sources (www.epa.gov/ttn)
- Protocol for Extractive FTIR for Analysis of Gas Emissions (www.epa.gov/ttn)
- EPA/EMC FTIR Database (www.epa.gov/ttn)

U.S. EPA APTI
Compliance Test and Source Test Observation

FRM 13A and 13B: Determination of Total Fluoride Emissions

Test Methods Identification

- FRM 1: Port location
- FRM 2: Volumetric flow rate
- FRM 3 or 3A: Correct conc. meas.
- FRM 4: Moisture content
- FRM 13A or 13B: Determination of Total Fluoride Emissions

FRM 13A or 13B Applicability

- This method is used to determine the concentration of particulate matter (PM) fluoride and gaseous fluoride emissions from stationary sources
    - FRM 13A: SPADNS Zirconium Lake
    - FRM 13B: Specific Aion Electrode
- Sources comprise mostly of the: phosphoric acid phosphate fertilizer MACT and the aluminum MACT

Summary of Method

- FRM 5 sample train with Stainless steel or glass nozzle and probe liner
- Filter temperature maintained @ 248°F and interchangeable
- Particulate fluorides caught on filter while gaseous fluorides caught in impingers
- Analysis by SPADNS zirconium lake colorimetric @ 570 nm for FRM 13A

FRM 13A or 13B Design Requirements

- Gas flow measurement system (FRM 1-4)
- FRM 5 sampling train
- Operated isokinetically, but below 1 cfm
- Optional filter location

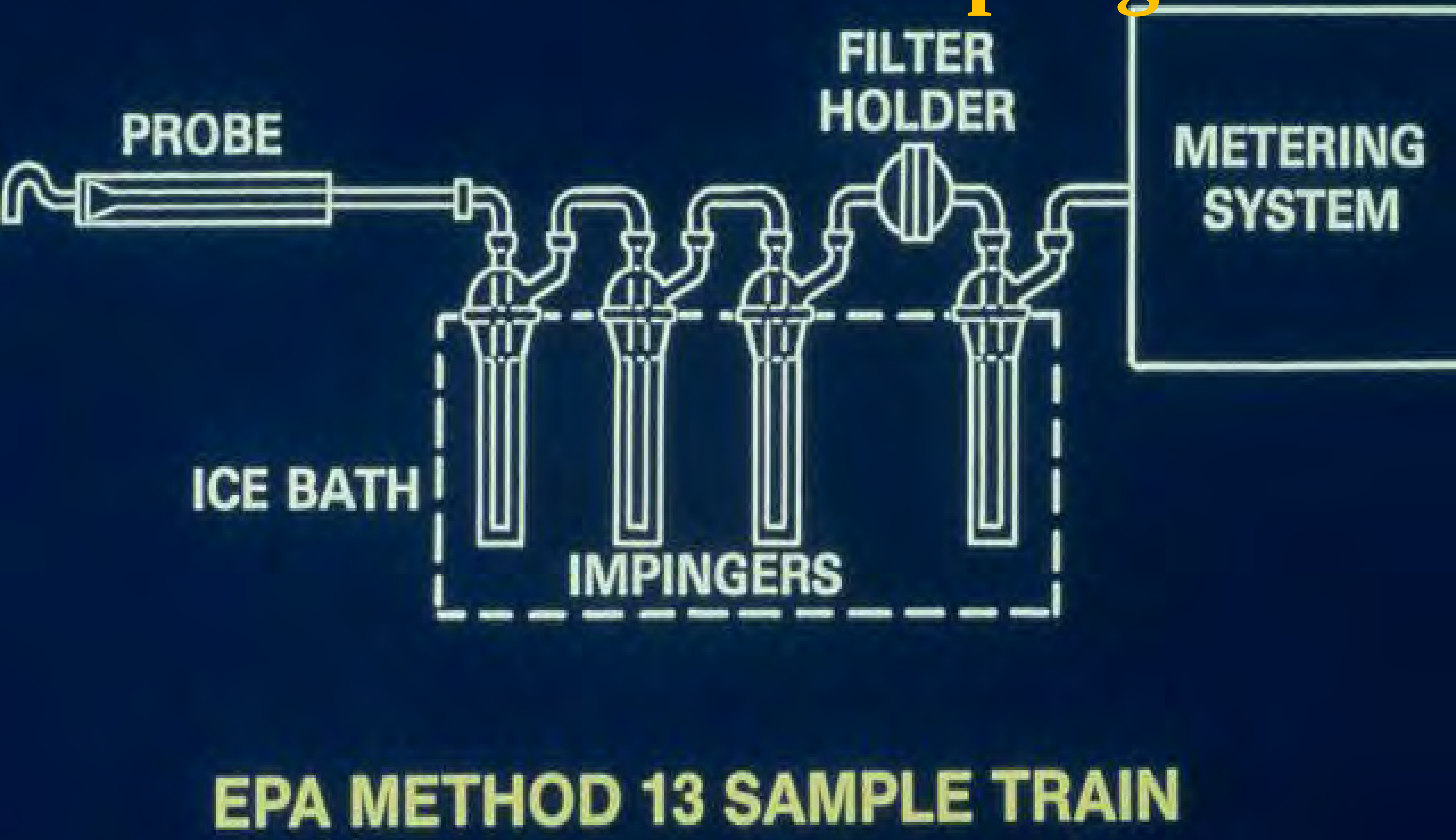
FRM 13A or 13B Sampling Train

- Heated probe (248 °F) with nozzle (glass or stainless steel)
- Pitot tube/temperature sensor array
- Heated filter assembly maintained at 248 °F +/- 25 °F
- Standard FRM 5 impingers
- Pump/dry gas meter/orifice assembly

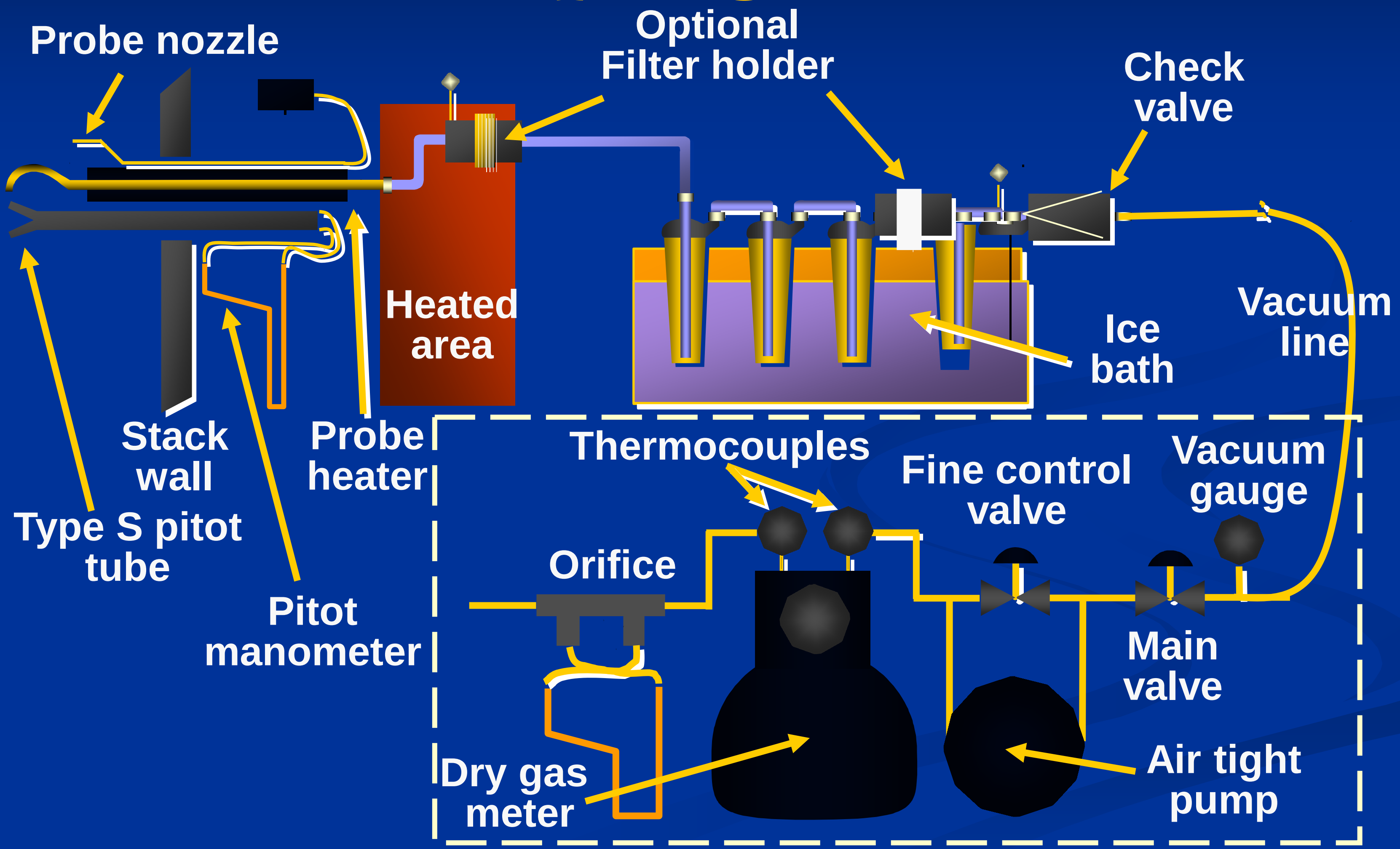
Historical FRM 13 Sampling Train

EPA METHOD 13 SAMPLE TRAIN

Historical FRM 13 Sampling Train



FRM 13A or 13B Sampling Train



FRM 13A or 13B Sample Recovery

- Container #1: Probe, filter and impinger catches, including DI water rinses of all active components (must not exceed 500 mL total volume)
- Container #2: Sample blank plus same volume of DI water Container #1
- Container #3: Note color of silica gel to determine whether it has been completely spent. Transfer the silica gel to its original container, weigh on site or transport back to laboratory for weighting

FRM 13A Sample Preparation

- Container #1: Observe level, then filter contents in 1-L volumetric flask. This is the filtrate.
- Filtered material:
  - Nickel crucible plus DI water
  - Add 100 mg CaO, 2 drop phenolphthalein, hot plate evaporate to dryness, then char
  - Muffle furnace to ash; 4 g NaOH, fuse, DI water transfer to filtrate flask

FRM 13A Sample Preparation

- Containers #2: Treated same as Container #1

FRM 13A Analysis Preparation

- Distillation
  - Adjustment of acid/water ration in distillation flask
    - 400 mL of DI water/200 mL of H_2SO_4
    - Heat to 175 °C; Discard distillate
  - Add separate aliquots from sample preparation Containers #1 and #2 to fluoride distillation flask, add DI water to make 220 mL total, heat rapidly to 175 °C, collect distillate in 250 volumetric flask

FRM 13A Sample Analysis

- Sample Preparation Containers # 1 and #2
  - Dilute distillate with DI water to exactly 250 mL
  - Pipet aliquot to beaker, add 50 mL of DI water, add 10 mL of SPADNS reagent
  - Mix thoroughly
  - Place in a constant-temperature bath for 30-minutes

FRM 13A Sample Analysis

- Spectrophotometer
  - Calibrated using fluoride standard solutions (F mg/50 mL) plotting absorbance vs. concentration @ 570 nm
  - Daily zero spectrophotometer using zero reference solution
  - Read absorbance of sample preparation Containers #1 and #2 and determine concentration
  - A calibration standard must be run with each set of sample analysis

FRM 13A Analysis Interferences

- Large quantities of chloride will interfere; Add silver sulfate into distillation flask
- After sample and colorimetric reagent are mixed, the color formed is stable for ~ 2 hours
- Temperature of standard solutions and sample solutions must be within 3 °C of each other or else a 0.005 mg F/L error may occur

FRM 13B Sample Analysis

- Sample Preparation Containers # 1 and #2
  - Dilute distillate with DI water to exactly 250 mL
  - Pipet 25-mL aliquot to separate beakers, add 25-mL of TISAB and mix
  - Maintain sample and calibration temperatures the same
  - Insert fluoride and reference electrode into the solution, record millivolt reading and determine concentration from calibration curve

FRM 13B Sample Analysis

- Fluoride Standardization Solutions
  - Serial dilution of 0.1 M fluoride standard. Make 10^{-1} to 10^{-5} standard solutions
  - Add 50 mL of each standard solution to a beaker, add 50 mL of TISAB solution and record millivolt reading (Start with most dilute standard and proceed to strongest standard)
  - Plot millivolt reading on linear axis vs. concentration of standard on log axis

FRM 13A or 13B
Operational Requirements

- See Field Observation Checklist for FRM 5
- Multi-point integrated sampling
- Isokinetic sampling rate but below 1 cfm
- 1-hr sample with minimum sample volume of 45 cf

FRM 13A or 13B
Operational Requirements

- Probe/filter at 120°C (248°F)
- Optional filter placement; However, gaseous fluorides collected in impingers

FRM 13A or 13B
Impinger Arrangement

- 1st and 2nd Impinger- 100 mL DI water
- 3rd Impinger- Dry
- 4th Impinger- 200-300 g silica gel

FRM 13A or 13B Operation

- See Field Observation Checklist for FRM 5
- Preliminary field determination (sample location, nozzle size,
  probe length) same as FRM 5
- Sample train preparation (charging of impingers etc.) same as FRM 5

FRM 13A or 13B Operation

- Pre-/post leak check in accordance with FRM 5
- Sample collection in general accordance with FRM 5
- Sample recovery in general agreement with FRM 5 except all active components are rinsed with DI water and the filter is place with the impinger catch

FRM 13A or 13B Key Points

- All active sample train components can be made of glass or stainless steel (no mention of Teflon components)
- All active sample train components must be cleaned

FRM 13A or 13B Key Points

- EPA audit vial available for quality control evaluation

U.S. EPA APTI
Compliance Test and Source Test Observation
FRMs 6C, 7E, and 3A Instrumental

Applicability

- "…controlled and uncontrolled emissions from sources specified in the regulations…"
- Fossil fuel-fired boilers
- Municipal waste combustors

Principle

- "…sample continuously extracted and conveyed to an instrumental analyzer…"

How the Method Works

- Inject calibration gases directly to analyzers
- Inject calibration gases through sampling system
- Conduct a sampling run and record data

How the Method Works

- Inject calibration gases through sampling system again
- Use average values from sampling system calibrations to correct the sample data
- YOU CORRECT EMISSION DATA!

Eight Major Points

- Calibration Error (Both Analyzer): Zero, mid-, high (2%)
- Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span or Reject
- Sampling System Bias Check/Recovery Check(Both Analyzers): Zero, Mid-/High Range at Probe and Analyzer (5% of span)

Eight Major Points

- Interference Check (SO2 Analyzer): Use Modified Method 6 (3 Runs/1 L/min) vs. Analyzer at Vent (7%)
- Converter Check (NOx Analyzer): Introduce CO @ 500 ppm, SO2@200 ppm, CO2@10% and O2@20.9%; < 2% of span response, pass

Eight Major Points

- Calibration Error (Both Analyzer): Zero, mid-, high (2%)
- Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span or Reject
- Sampling System Bias Check/Recovery Check(Both Analyzers): Zero, Mid-/High Range at Probe and Analyzer (5% of span)

Interesting Points

- Perform Calibration Curve: High (80-100% span), Mid (40-60% span), Zero (<0.25% span)
- Calibration Gas Certification: Protocol 1 or Method 6 (3 Runs/1 L/min), 5%

Interesting Points

- Span of instrument: Emission standard at 30% of span
- Calibration gases can be SO2/N2, SO2/Air,SO2/CO2, or SO2/CO2/O2
- Emission data corrected with determined bias number
- No EPA Method 6 audit vial required due to "Interferece Check"

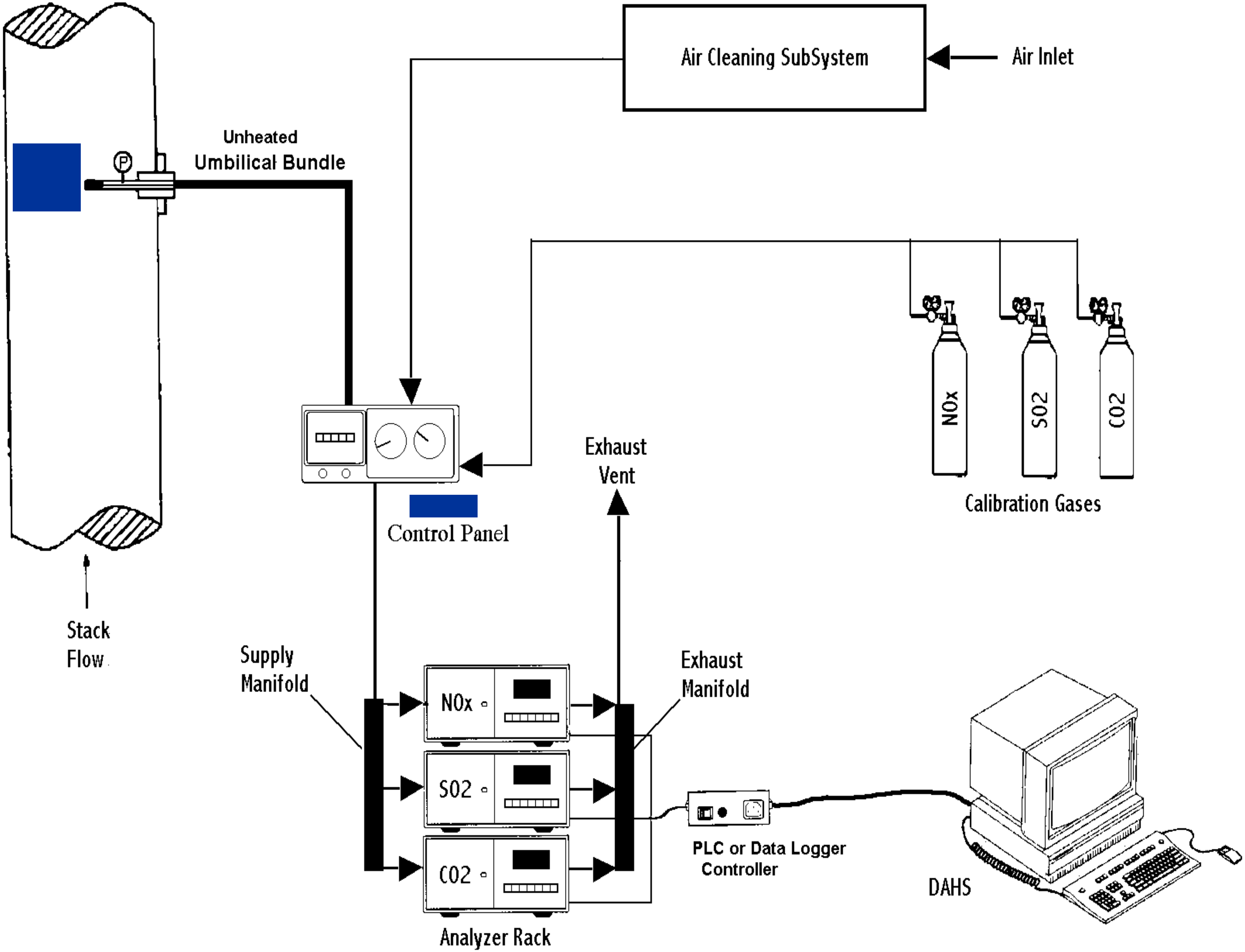
Interesting Points

- Sampling system bias test done before and after test, then average, and apply value to emission data to correct
- Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span; May not reject if pass bias check!

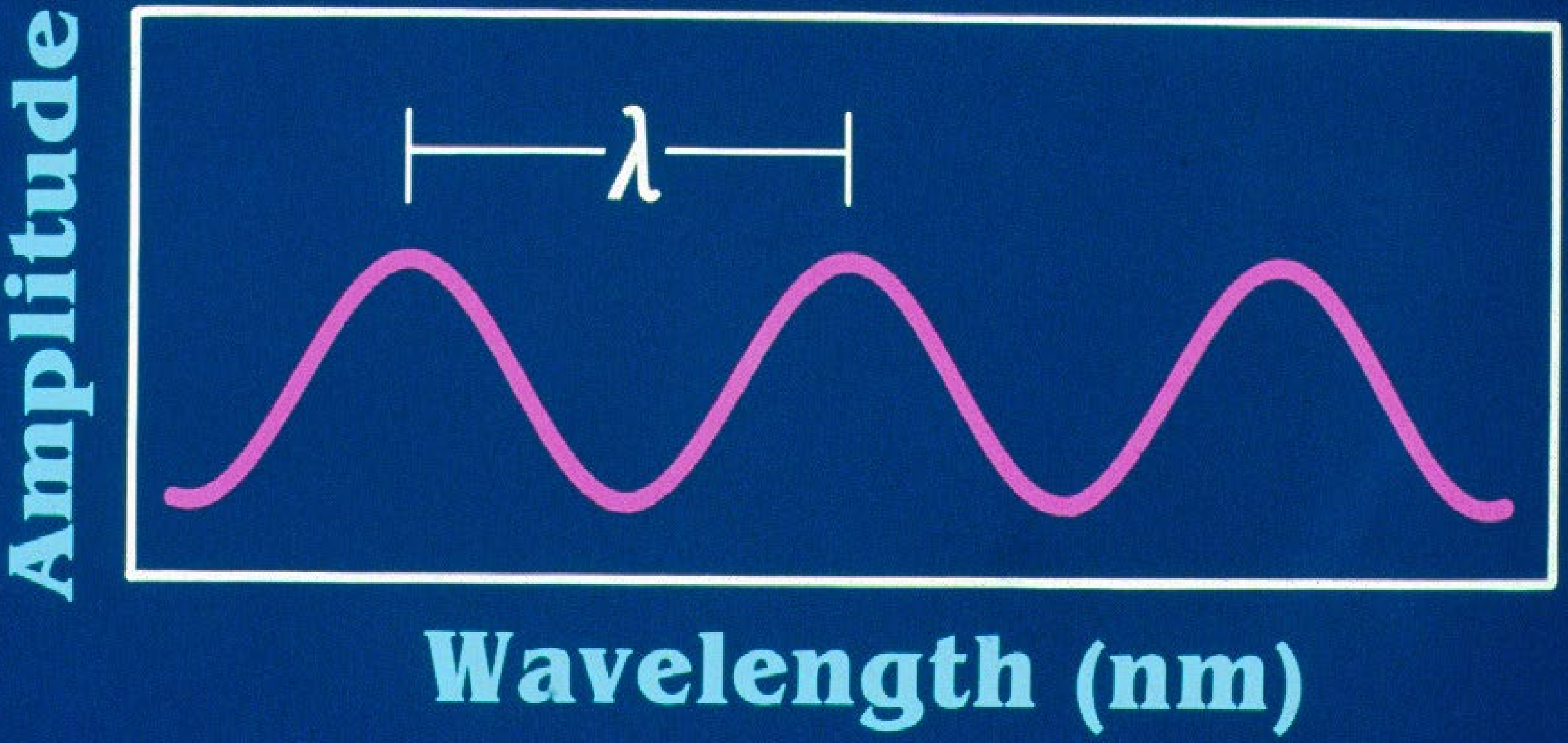

EXTRACTIVE MONITORS

Method 6C
Only Analytical Techniques Allowed Now!

- Ultraviolet Absorption (UV)
- Nondispersive Infrared (NDIR)
- Fluorescence

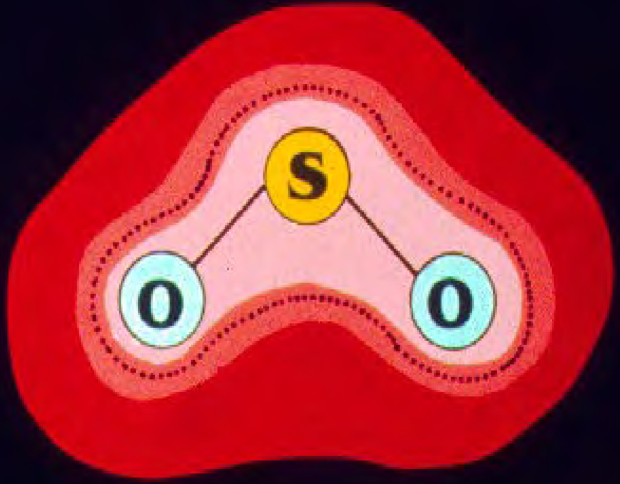

Air Cleaning SubSystem
Air Inlet
[redacted]
Unheated
Umbilical Bundle
P
NOx
SO2
CO2
Exhaust
Vent
Calibration Gases
[redacted]
Control Panel
Stack
Flow
Supply
Manifold
Exhaust
Manifold
NOx
SO2
CO2
Analyzer Rack
PLC or Data Logger
Controller
DAHS

OPTICAL PRINCIPLES and SPECTRA


λ
Amplitude
Wavelength (nm)

Vibration

Rotation

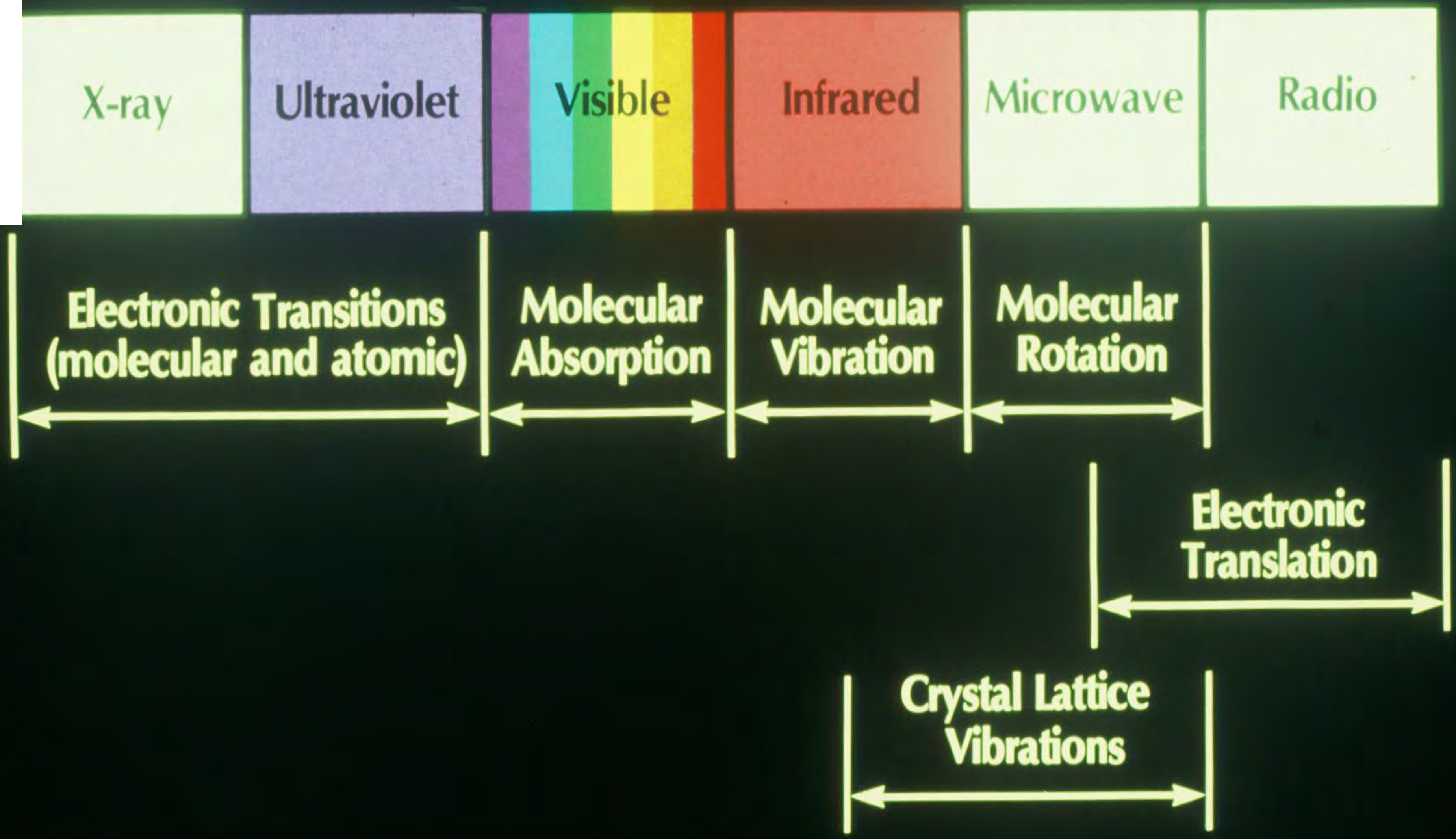


Electronic

CHARACTERISTICS OF THE EM SPECTRUM

X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio

TRANSITION REGIONS



X-ray

Ultraviolet

Visible

Infrared

Microwave

Radio

Electronic Transitions (molecular and atomic)

Molecular Absorption

Molecular Vibration

Molecular Rotation

Electronic Translation

Crystal Lattice Vibrations

ELECTROMAGNETIC SPECTRUM

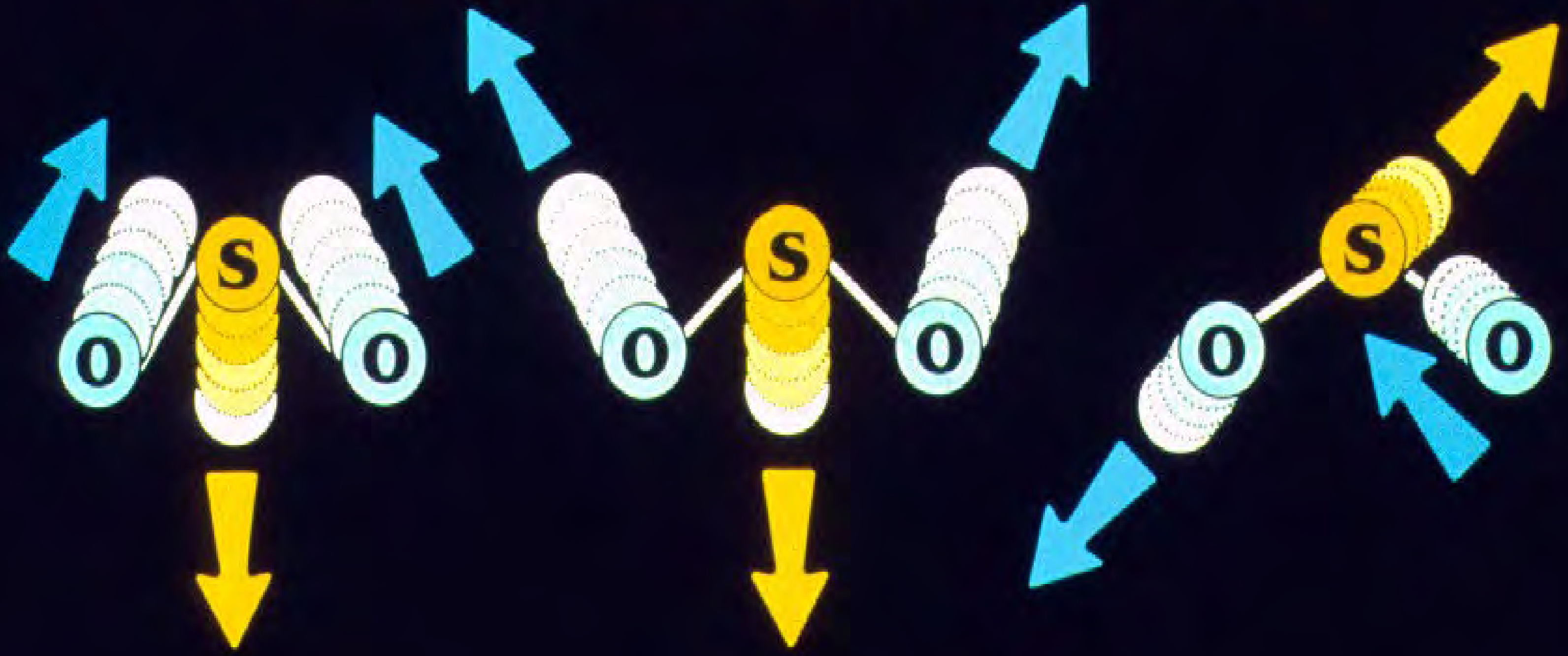
X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio

001μm
.1μm
.4μm
.7μm
22μm
400μm
250,000μm

$$E = h\upsilon$$

$$= h\left(\frac{c}{\lambda}\right)$$

Normal Vibrations of SO_2



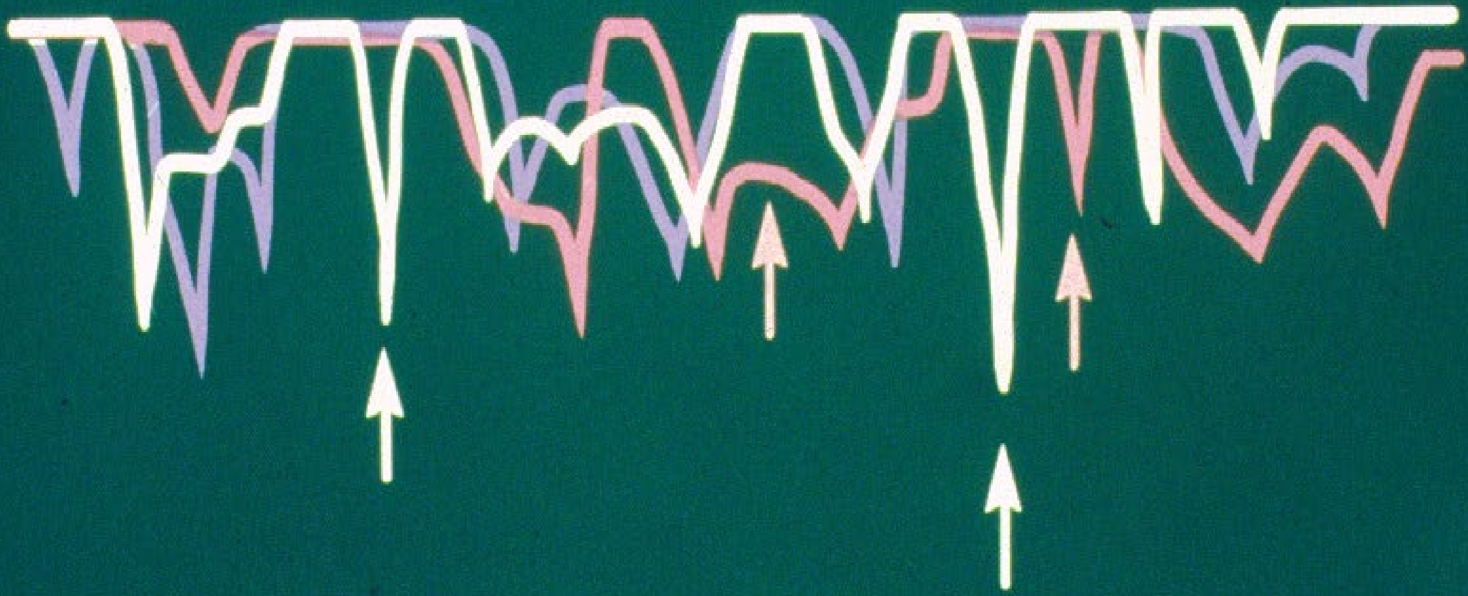
$\lambda = 8.69\,\mu m$
$\bar{\nu} = 1150.5\ cm^{-1}$

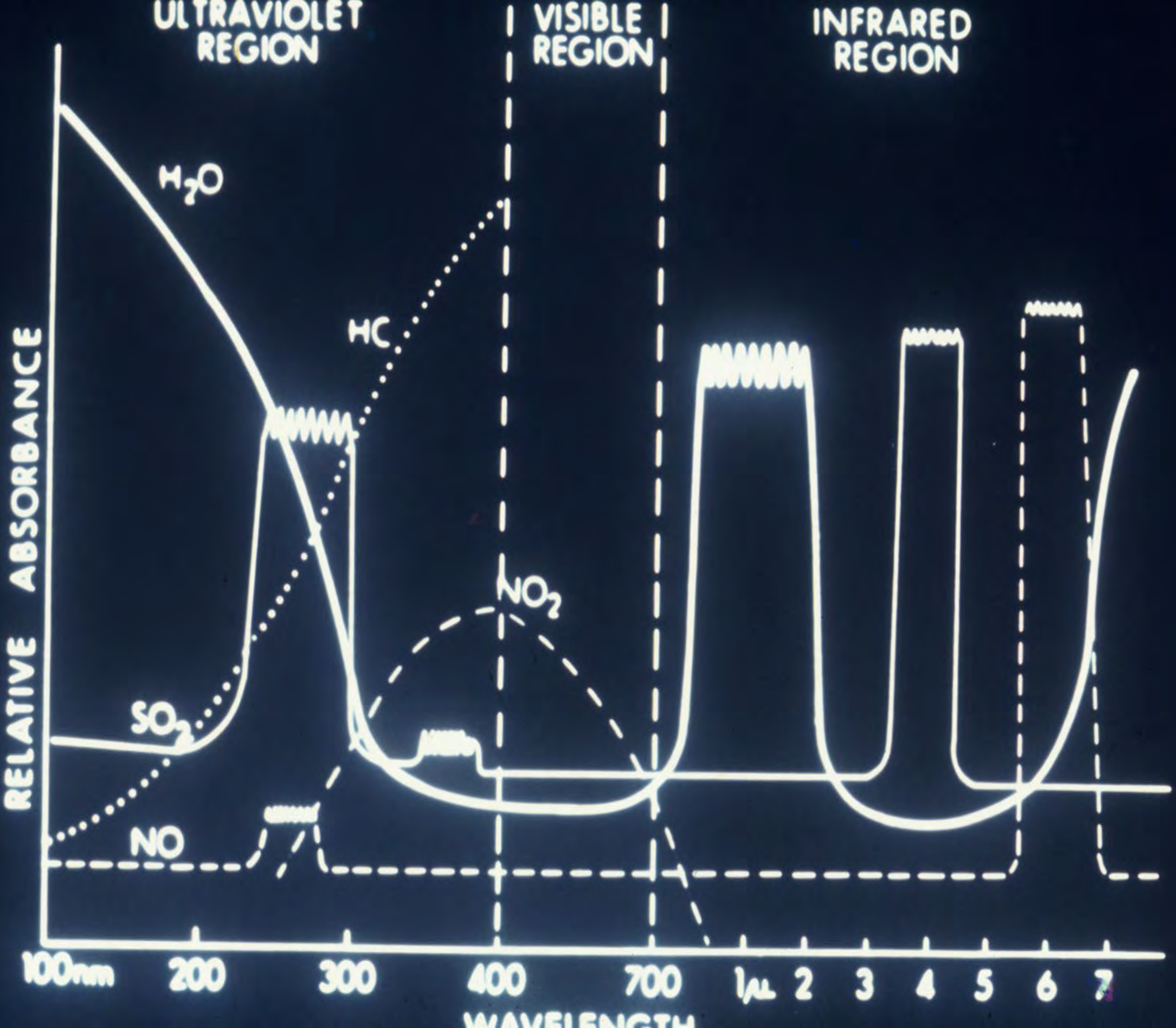
$\lambda = 7.48\,\mu m$
$\bar{\nu} = 1336.0\ cm^{-1}$

$\lambda = 19.1\,\mu m$
$\bar{\nu} = 524.5\ cm^{-1}$

Molecules Absorb Light at Specific Wavelengths

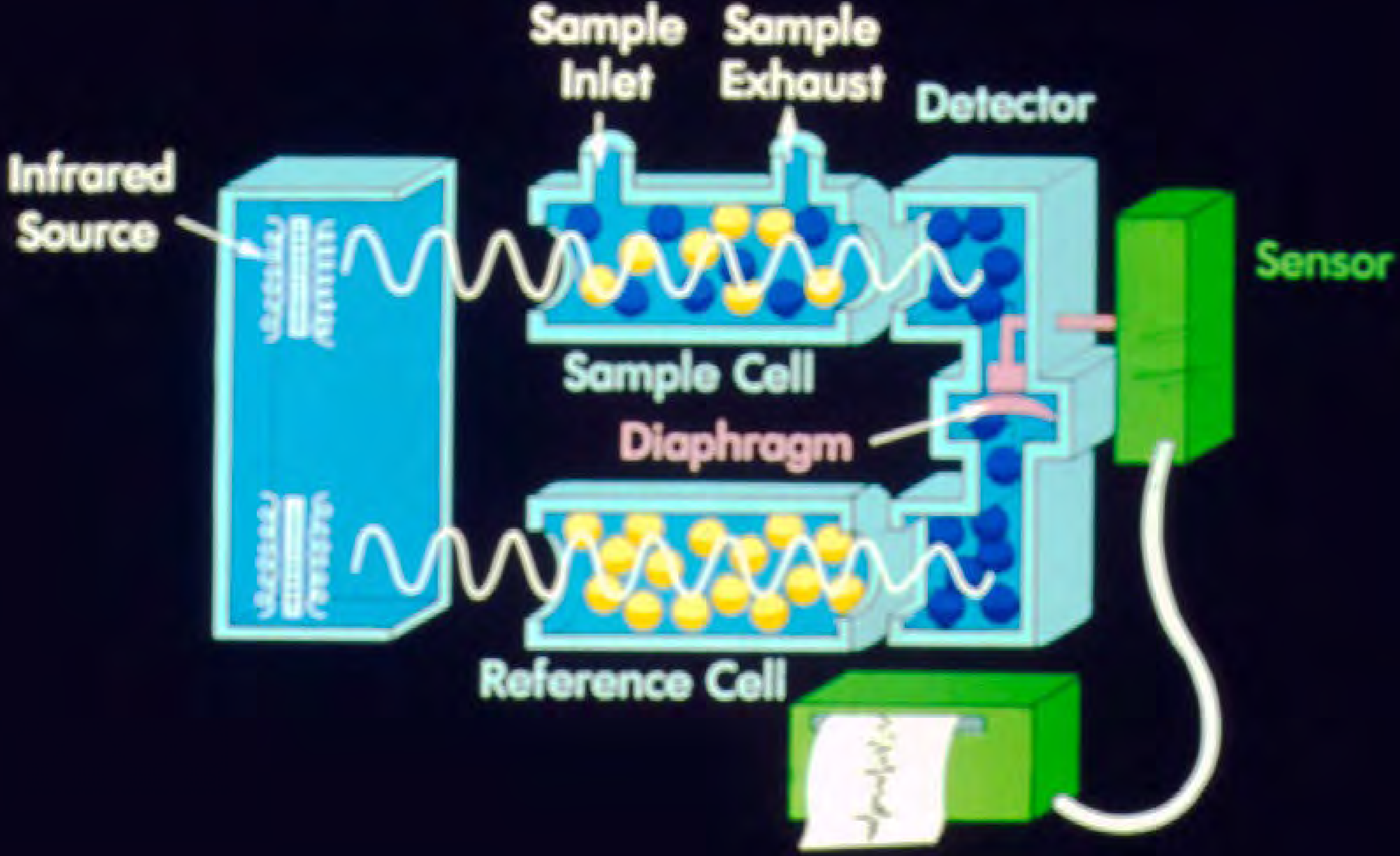
Spectra of Different Molecules Can Overlap



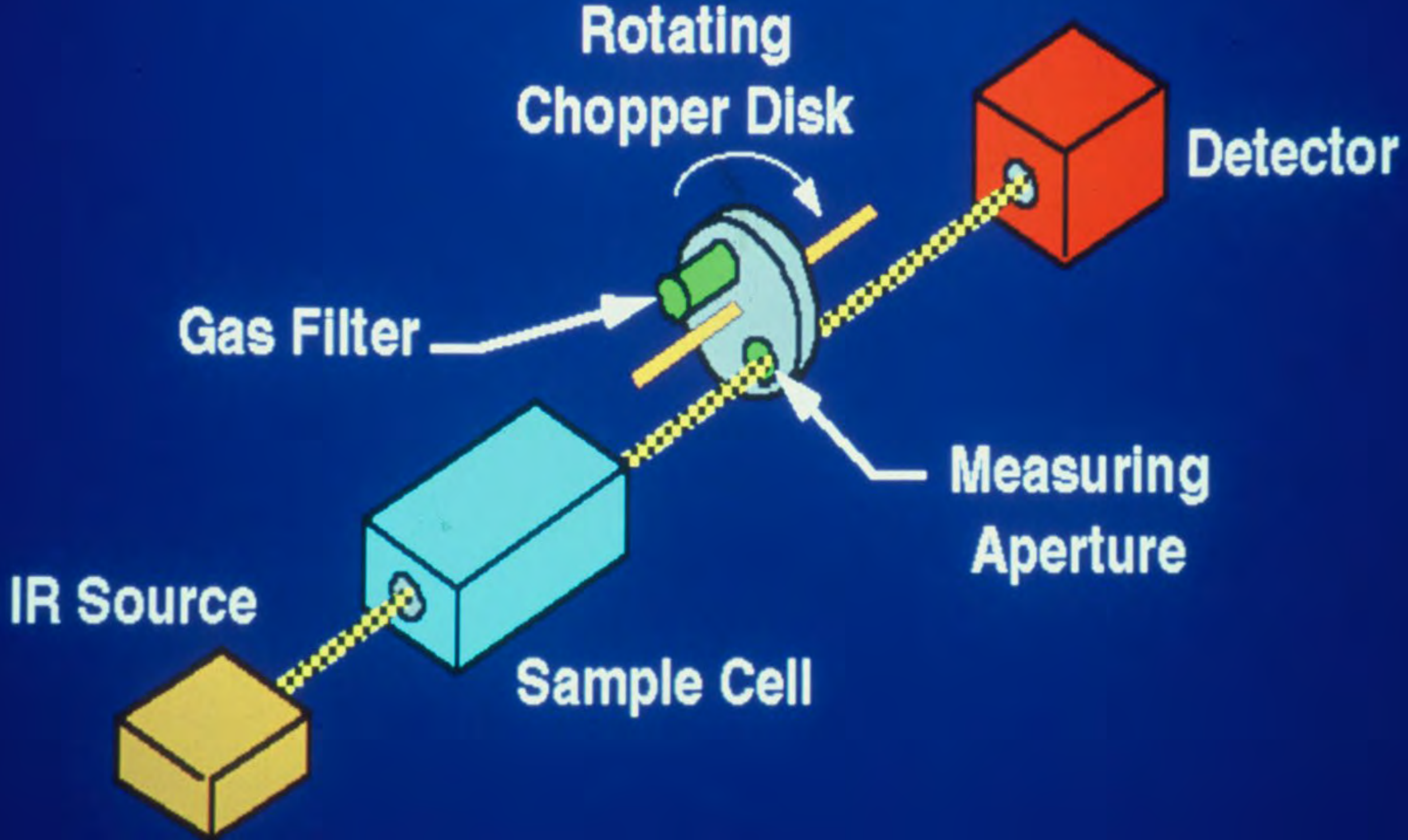

ULTRAVIOLET REGION
VISIBLE REGION
INFRARED REGION
H_2O
HC
NO_2
SO_2
NO
RELATIVE ABSORBANCE
100nm
200
300
400
700
1μ
2
3
4
5
6
7
WAVELENGTH

ight → $E = h\upsilon$ → Absorption → Beer-Lambert Law → Instrument

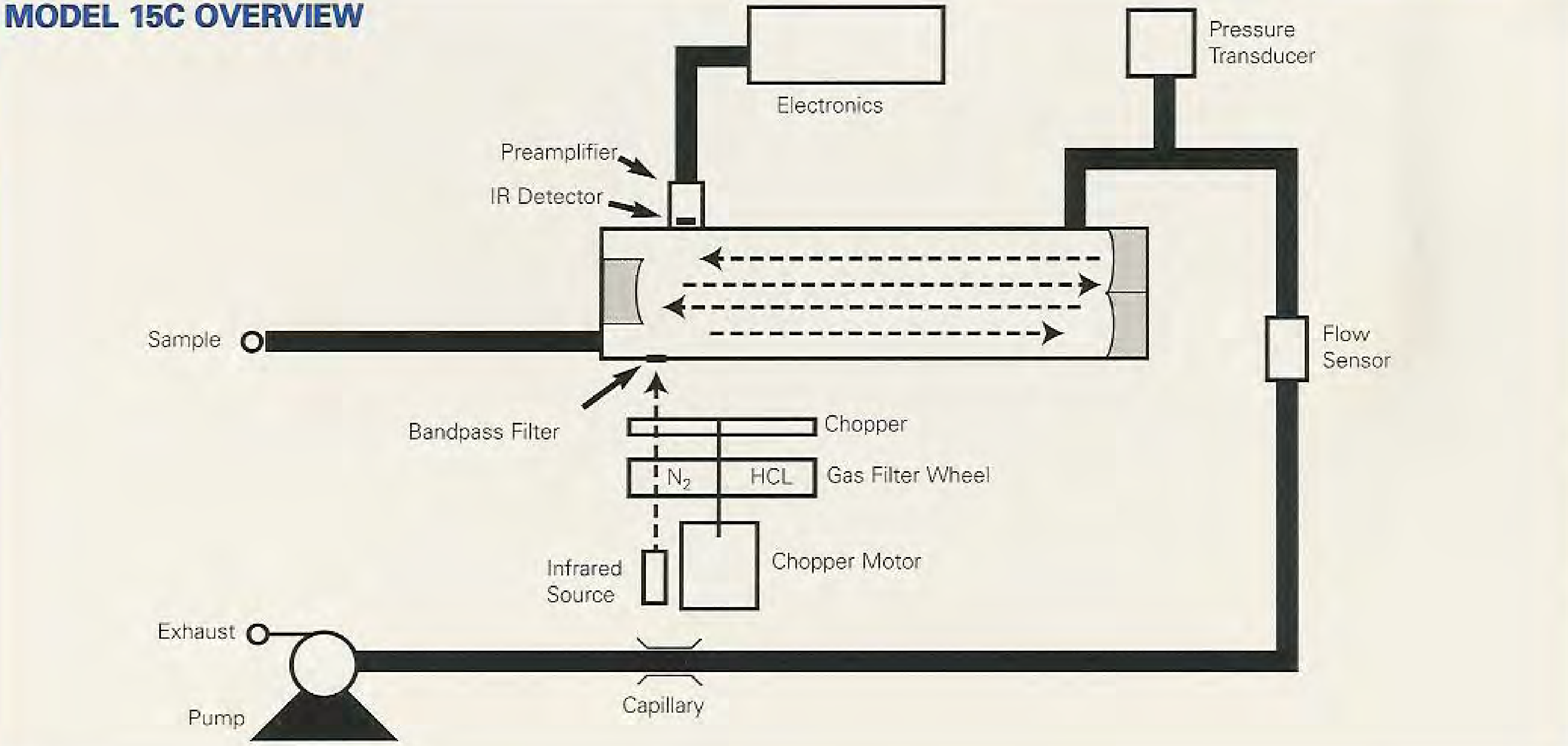
NDIR ANALYZER FOR CO



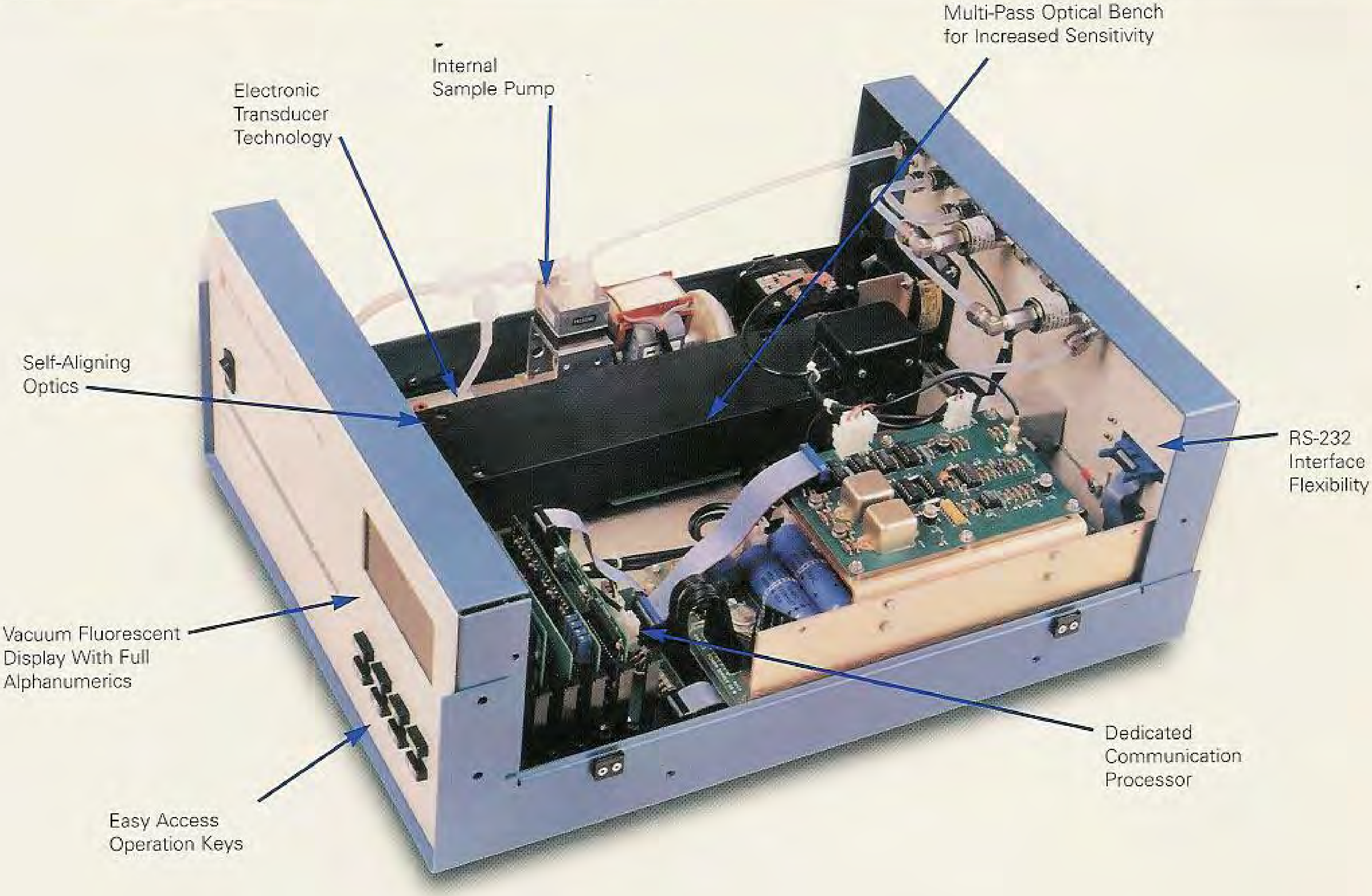
Extractive Type Gas Filter Cell Correlation Analyzer



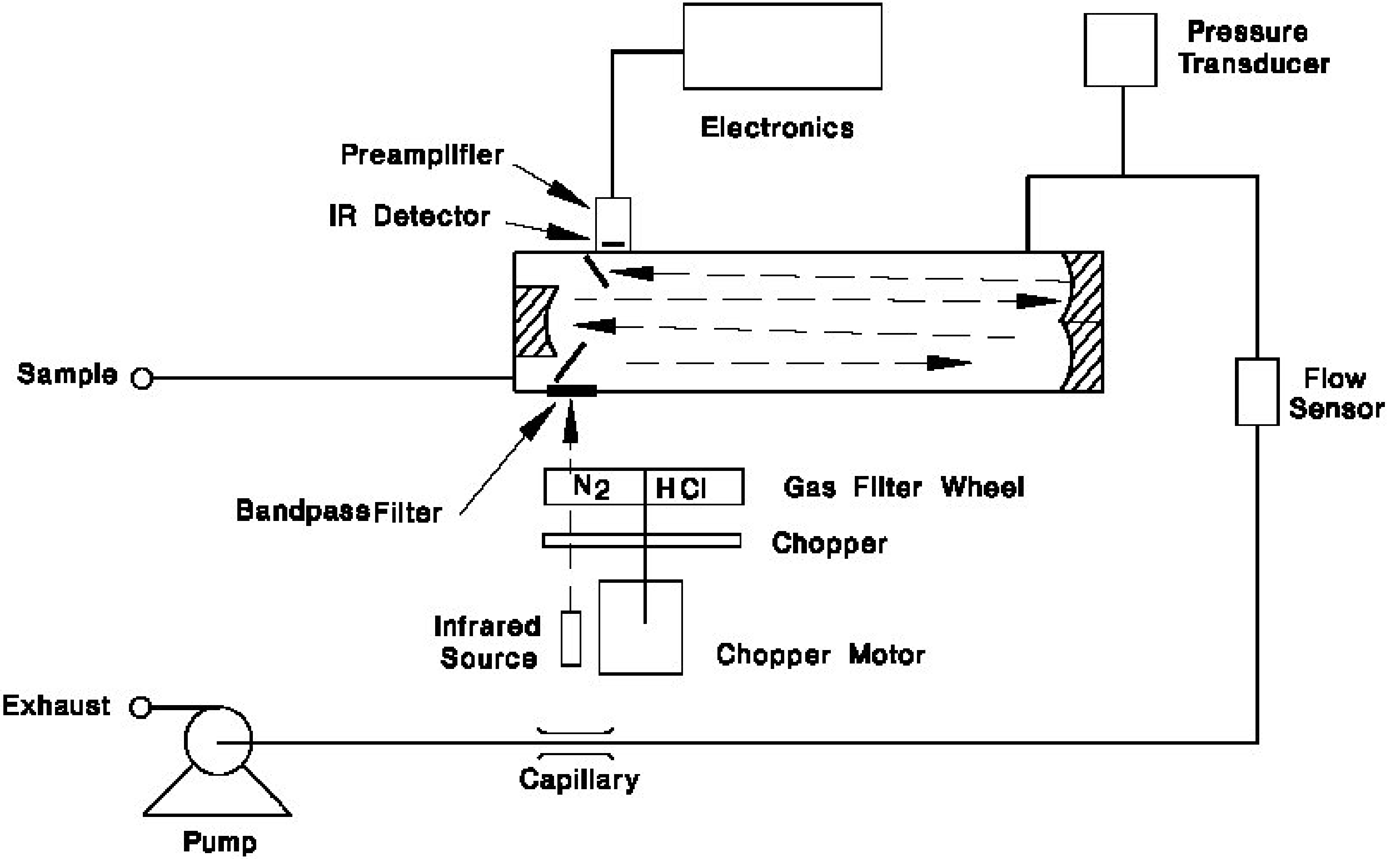
MODEL 15C OVERVIEW



KEY DESIGN FEATURES

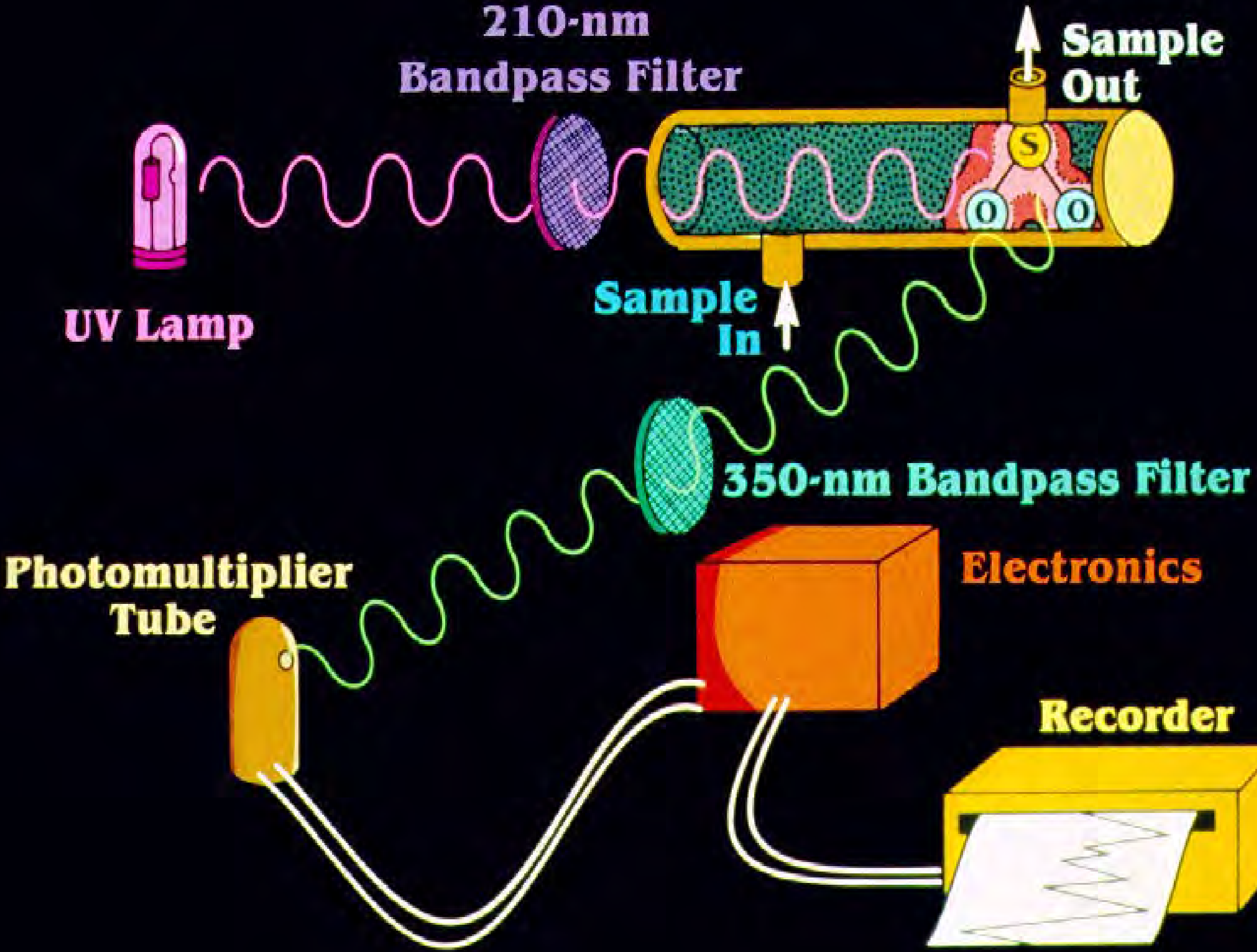


ADVANCED TECHNOLOGY **Model 15 Gas Filter Correlation HCl Analyzer**



Model 15C Flow Schematic


Thermo
THERMO ENVIRONMENTAL
INSTRUMENTS
Model 15C HCl Analyzer


210-nm
Bandpass Filter
Sample
Out
UV Lamp
S
O
O
Sample
In
350-nm Bandpass Filter
Photomultiplier
Tube
Electronics
Recorder

MODEL 43C- SO_2 ANALYZER

- Microprocessor control
- SO_2 Specific
- Reflective U.V. filtering
- Hermetically sealed U.V. lamp
- No consumables

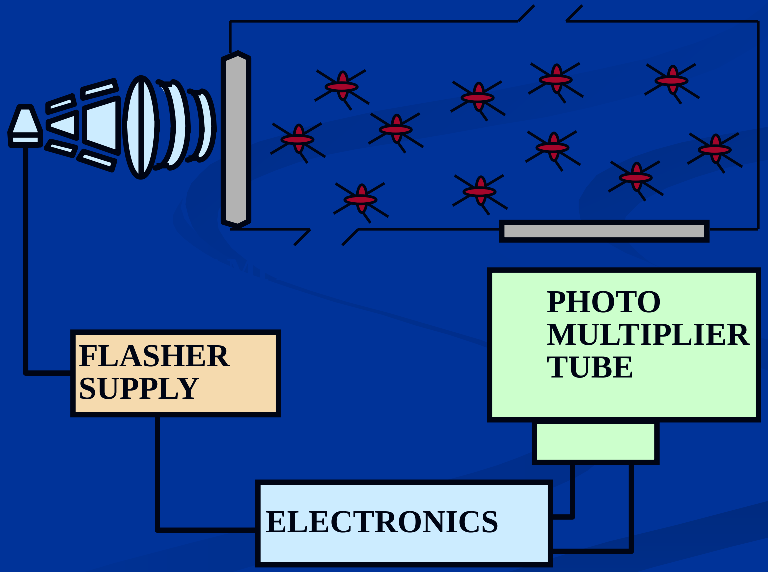
MODEL 43C-SO2 Analyzer

$$SO_2 + h\nu_1 \xrightarrow{I_a} SO_2^*$$

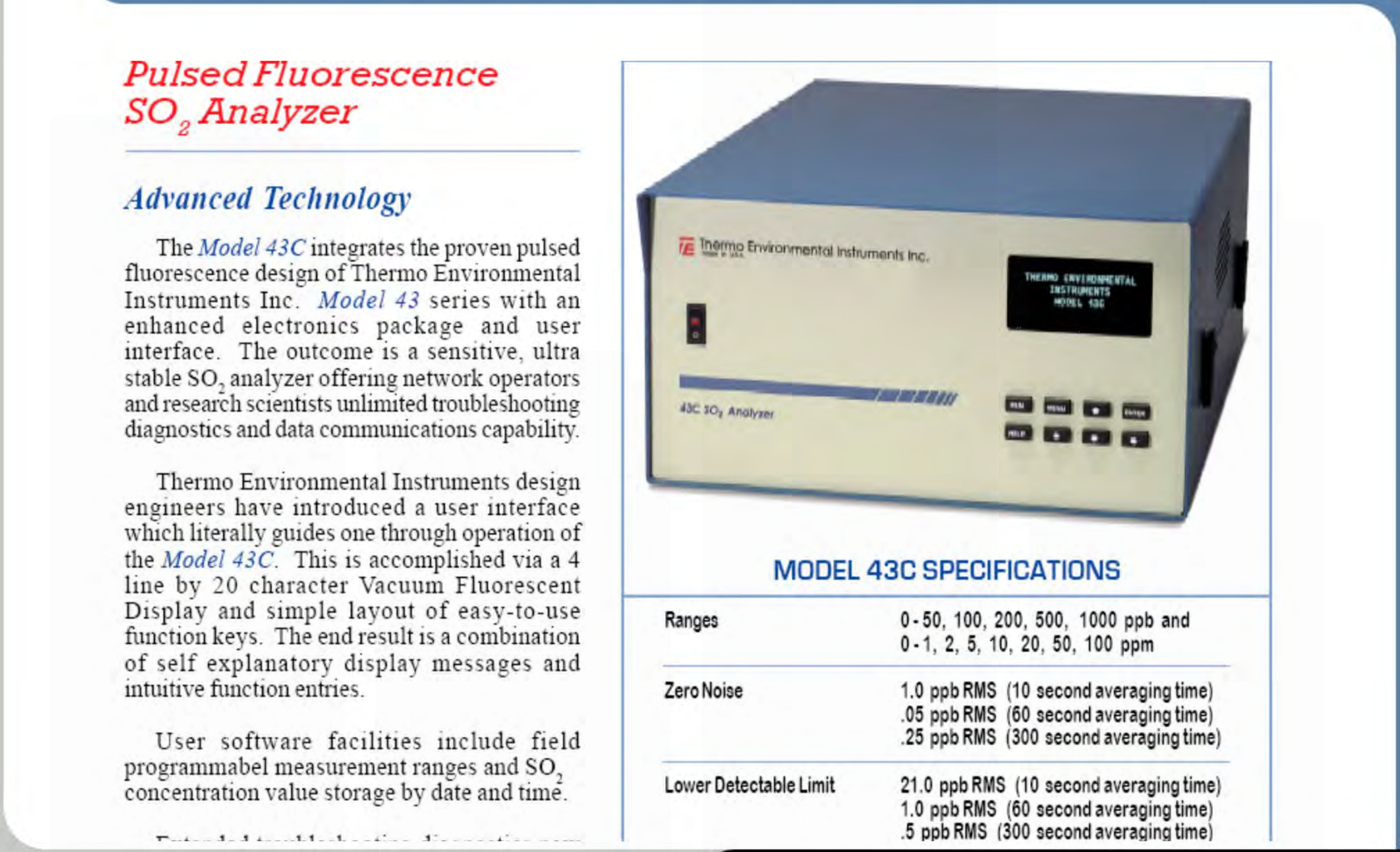
$$SO_2^* \xrightarrow{K_f} SO_2 + h\nu_2$$

$$I_a = I_o[I-e^{-\{ax(SO_2)\}}]$$

$$I_f \propto I_o ax(SO_2) \text{ or } K\,(SO_2)$$



Thermo Model 43C SO2 Analyzer



Pulsed Fluorescence SO$_2$ Analyzer

Advanced Technology

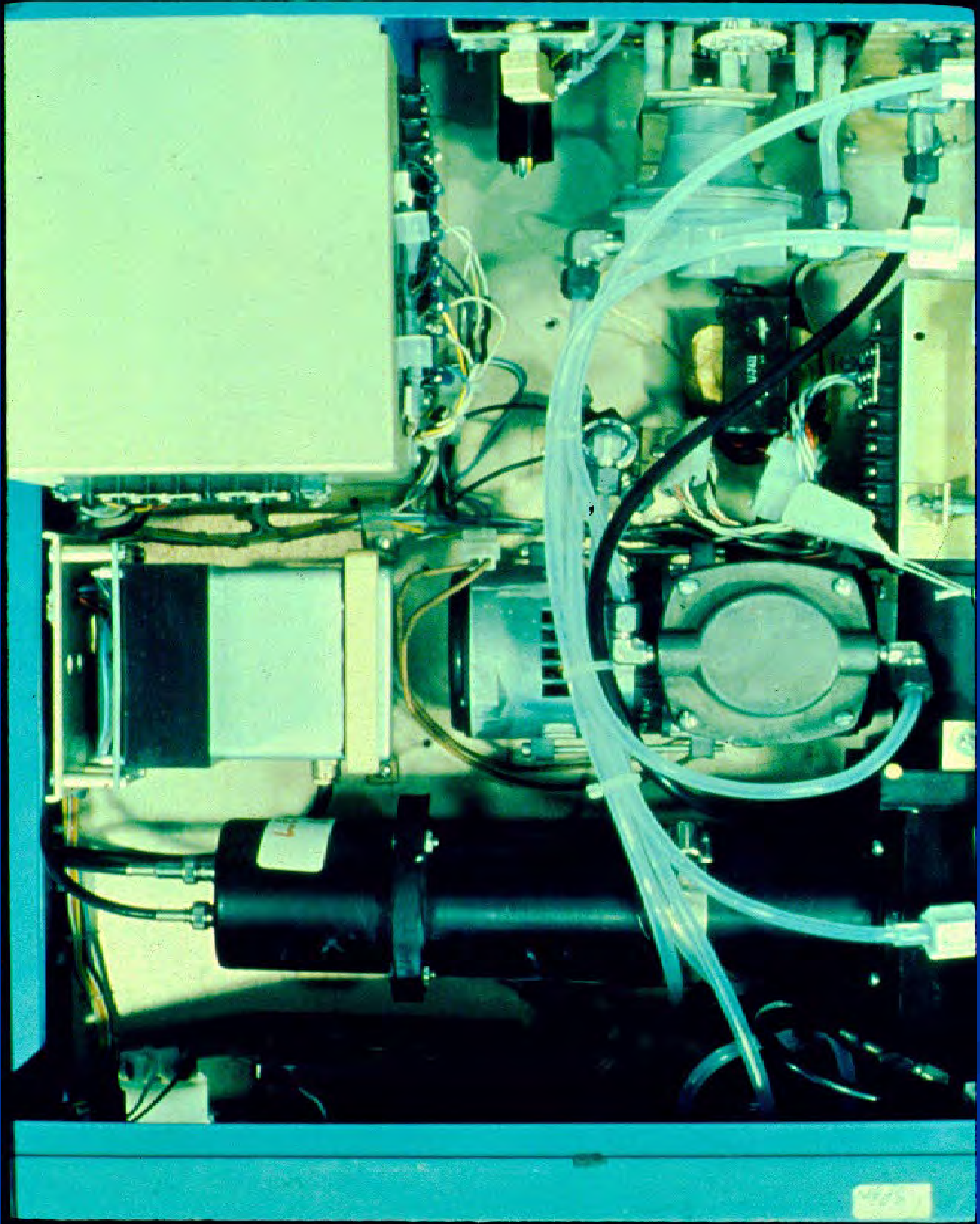
The *Model 43C* integrates the proven pulsed fluorescence design of Thermo Environmental Instruments Inc. *Model 43* series with an enhanced electronics package and user interface. The outcome is a sensitive, ultra stable SO$_2$ analyzer offering network operators and research scientists unlimited troubleshooting diagnostics and data communications capability.

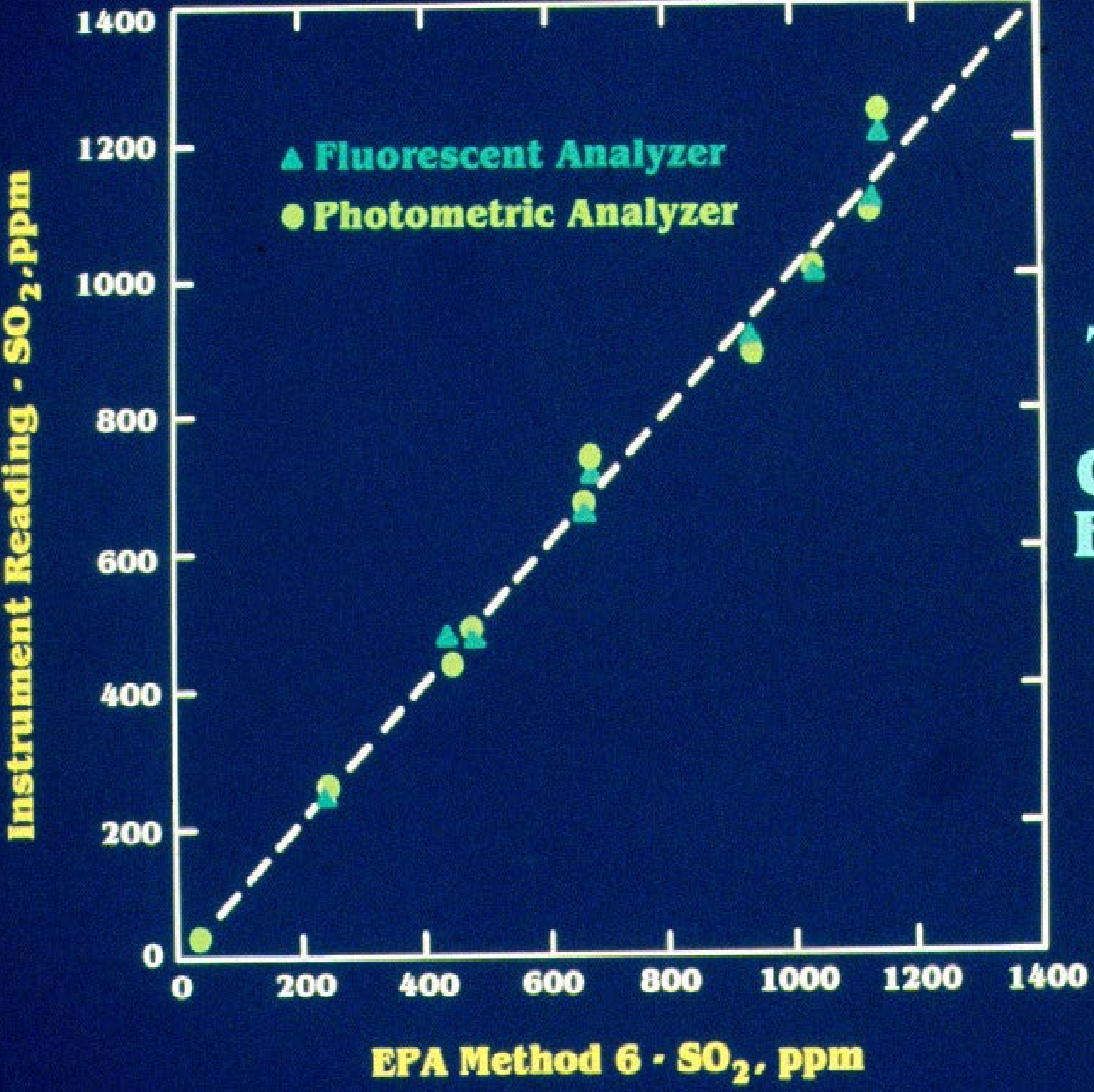
Thermo Environmental Instruments design engineers have introduced a user interface which literally guides one through operation of the *Model 43C*. This is accomplished via a 4 line by 20 character Vacuum Fluorescent Display and simple layout of easy-to-use function keys. The end result is a combination of self explanatory display messages and intuitive function entries.

User software facilities include field programmabel measurement ranges and SO$_2$ concentration value storage by date and time.

MODEL 43C SPECIFICATIONS

Ranges	0 - 50, 100, 200, 500, 1000 ppb and 0 - 1, 2, 5, 10, 20, 50, 100 ppm
Zero Noise	1.0 ppb RMS (10 second averaging time) .05 ppb RMS (60 second averaging time) .25 ppb RMS (300 second averaging time)
Lower Detectable Limit	21.0 ppb RMS (10 second averaging time) 1.0 ppb RMS (60 second averaging time) .5 ppb RMS (300 second averaging time)

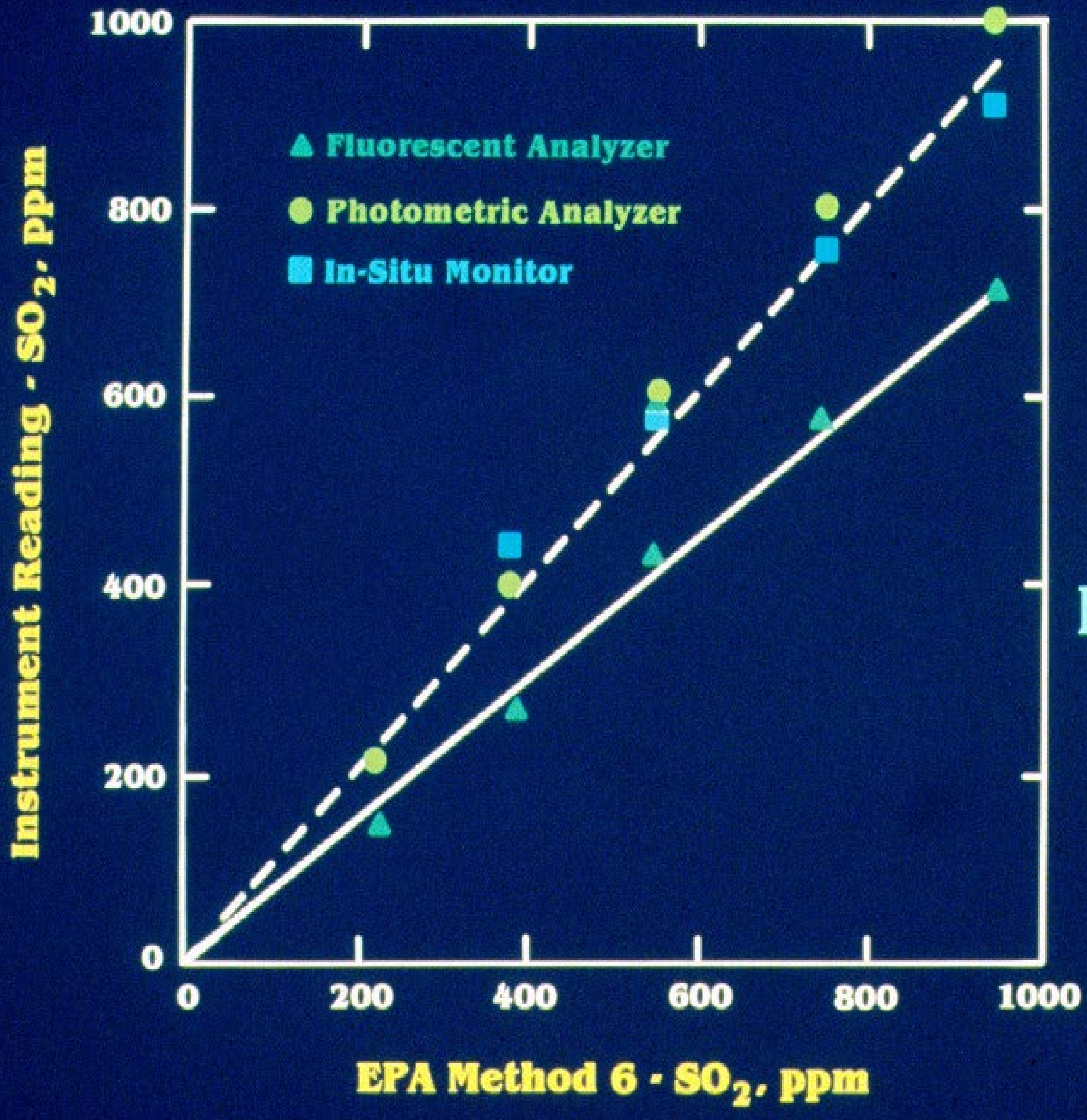




Twenty-one Percent O_2 Calibration Experiment

SO$_2$ in Nitrogen Span Gas Experiment

(371 ppm SO$_2$ in N$_2$)
Span Gas




Thermo
THERMO ENVIRONMENTAL
INSTRUMENTS
Model 42C NO-NO2-NOx Analyzer

HOW IS NO MEASURED?

Chemiluminescence Technique

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + hn$$

Intensity of emitted light is proportional to NO concentration

Chemiluminescent

Reduction of NO_2 to NO

$$3\,NO_2 + Mo \longrightarrow 3\,NO + MoO_3$$

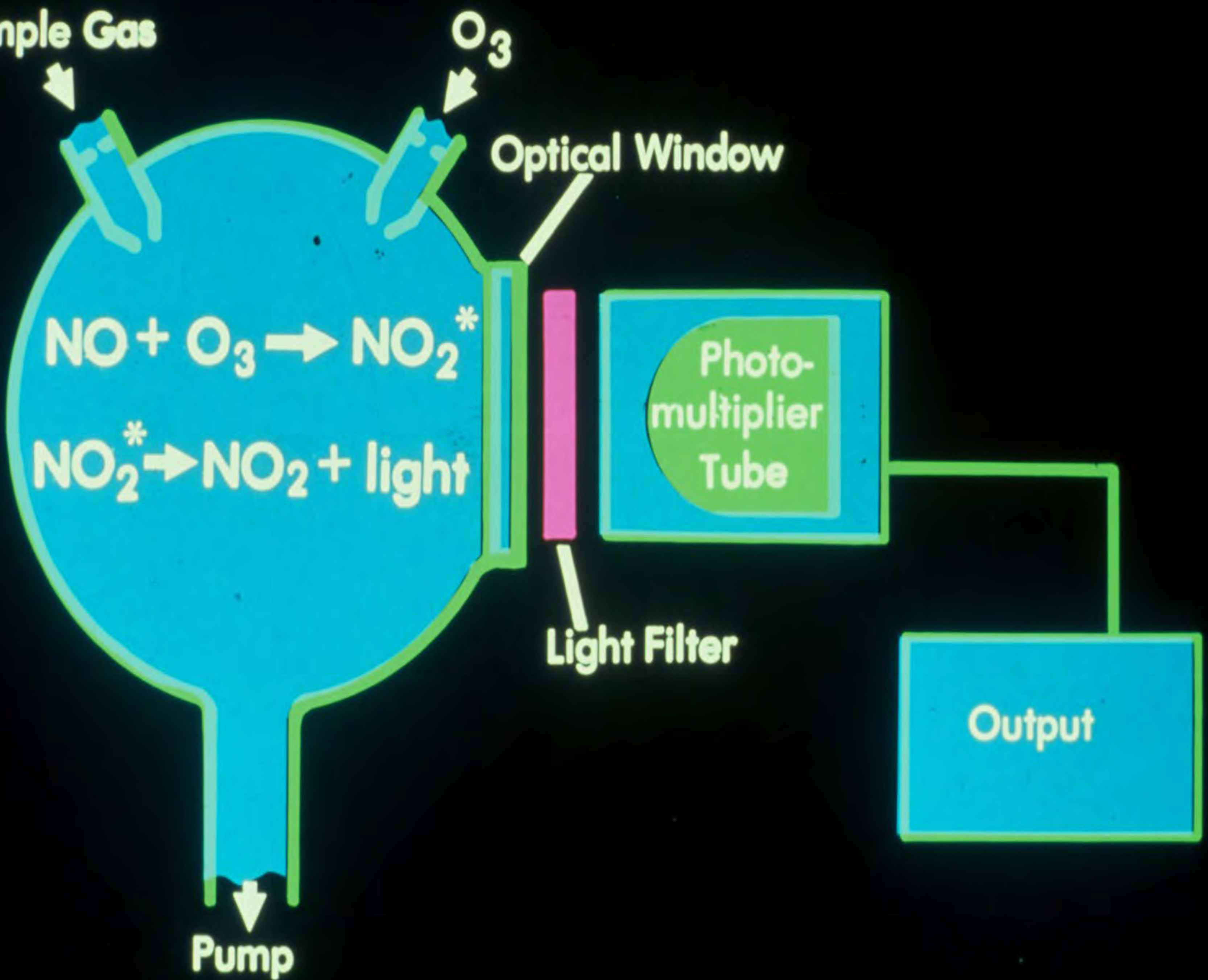
A molybdenum catalyst, heated to ~325°C, is used to Convert NO_2 to NO

Measurement Principle

CHEMILUMINESCENCE

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$



Sample Gas

O_3

Optical Window

$NO + O_3 \rightarrow NO_2^*$

$NO_2^* \rightarrow NO_2 + \text{light}$

Photo-multiplier Tube

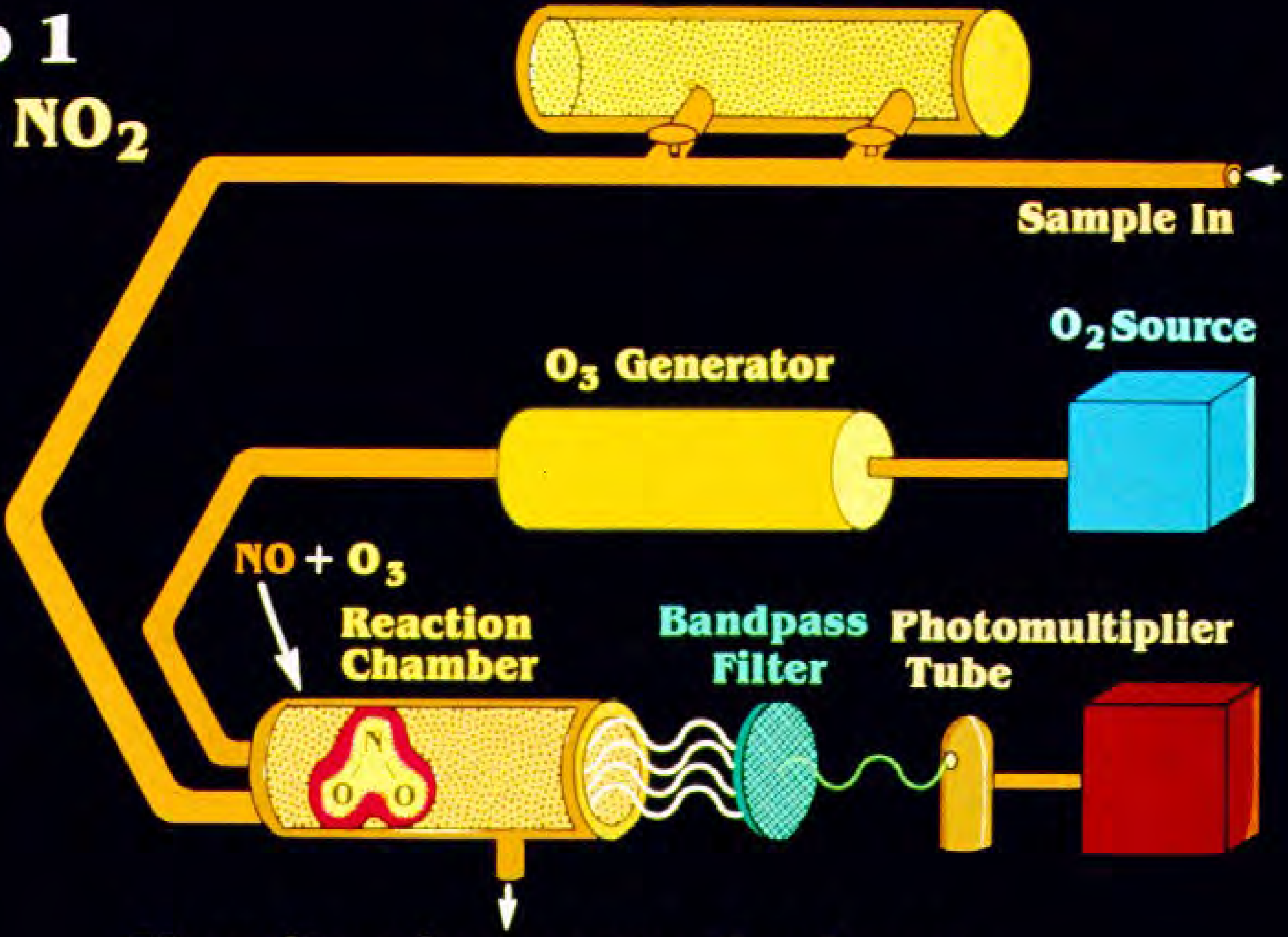
Light Filter

Output

Pump

Step 1

$NO + NO_2$



Sample In

O_2 Source

O_3 Generator

$NO + O_3$

Reaction Chamber

Bandpass Filter

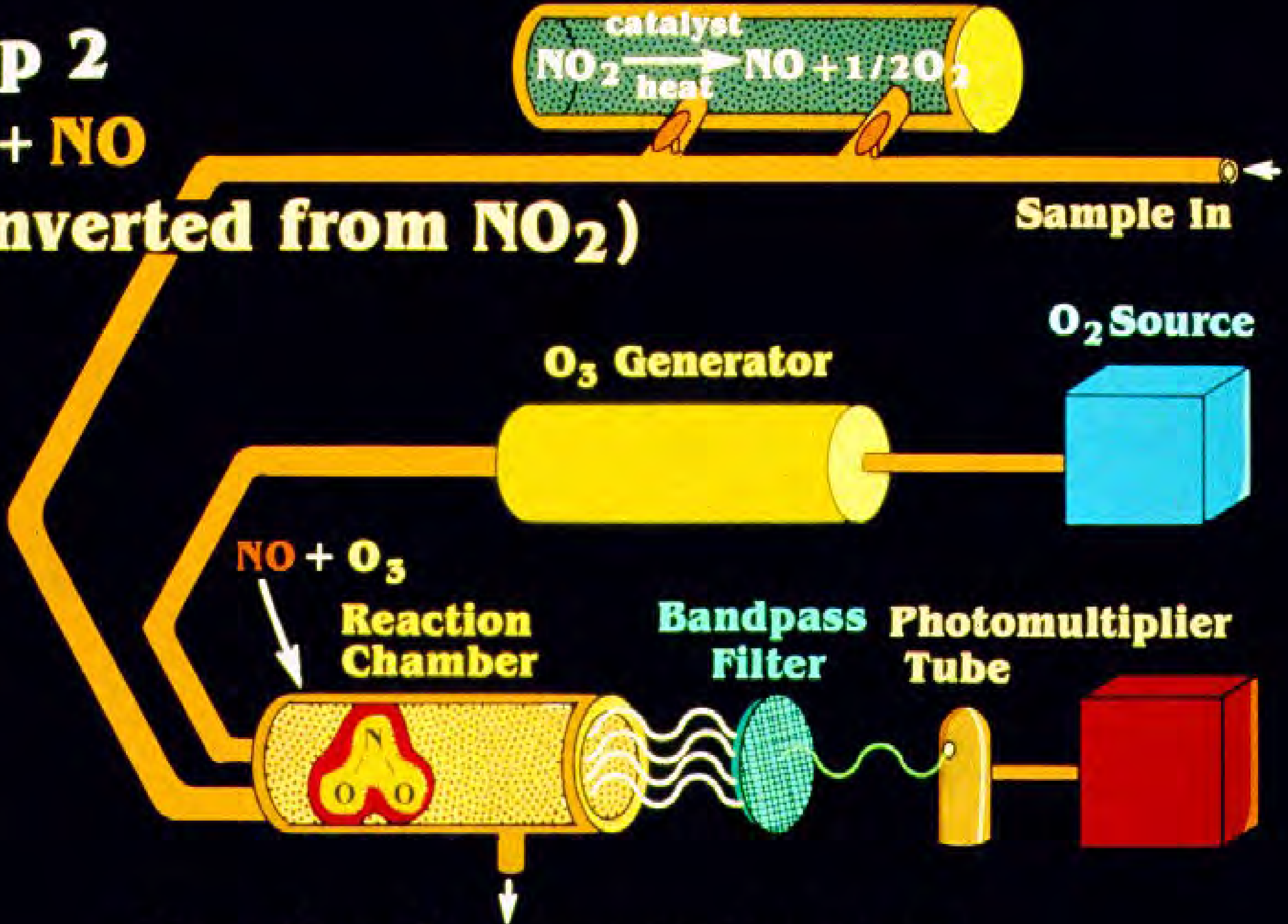
Photomultiplier Tube

Chemiluminescence Analyzer

Step 2

NO + NO

(Converted from NO_2)



$NO_2 \xrightarrow[\text{heat}]{\text{catalyst}} NO + 1/2O_2$

Sample In

O_2 Source

O_3 Generator

NO + O_3

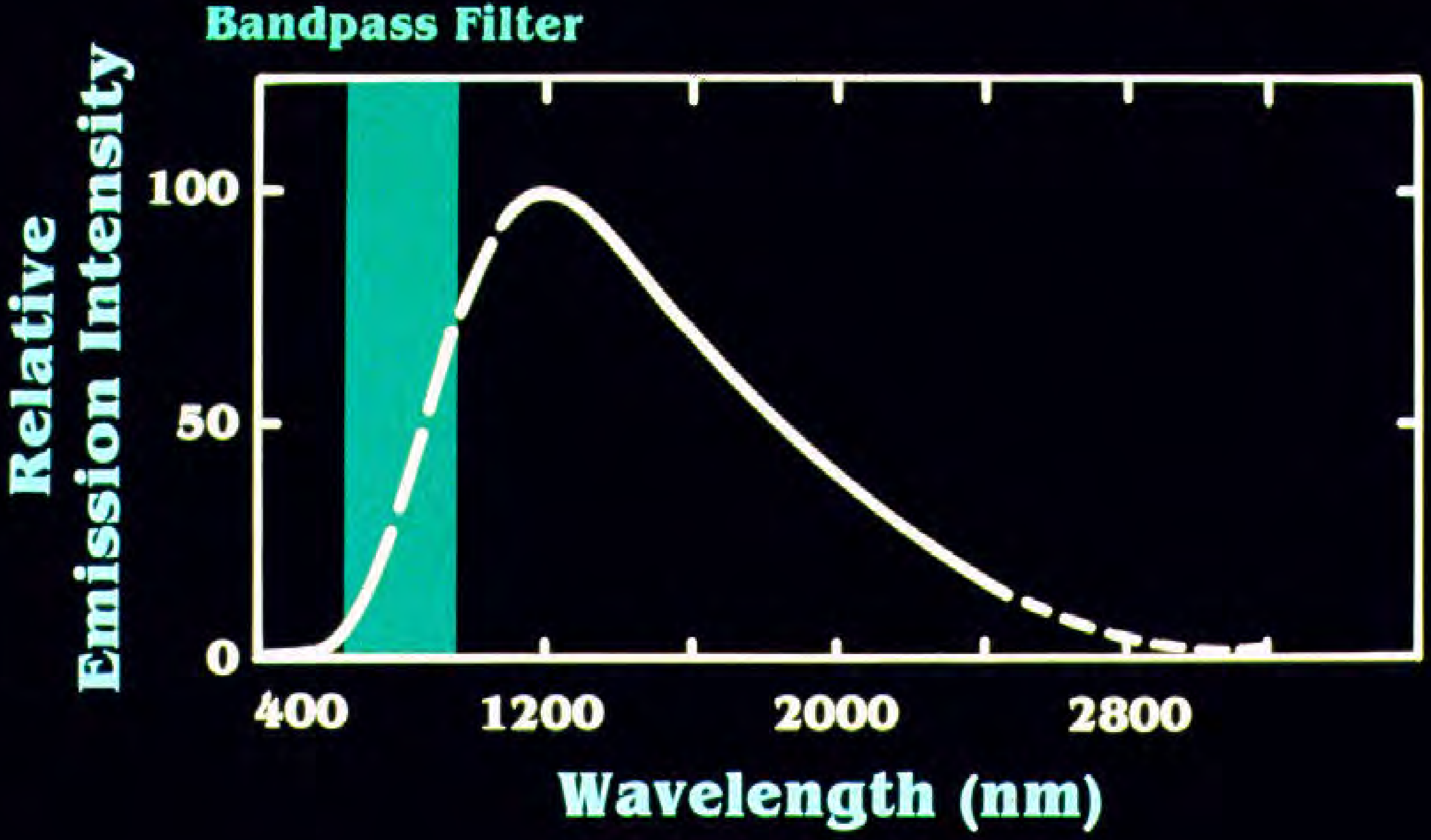
Reaction Chamber

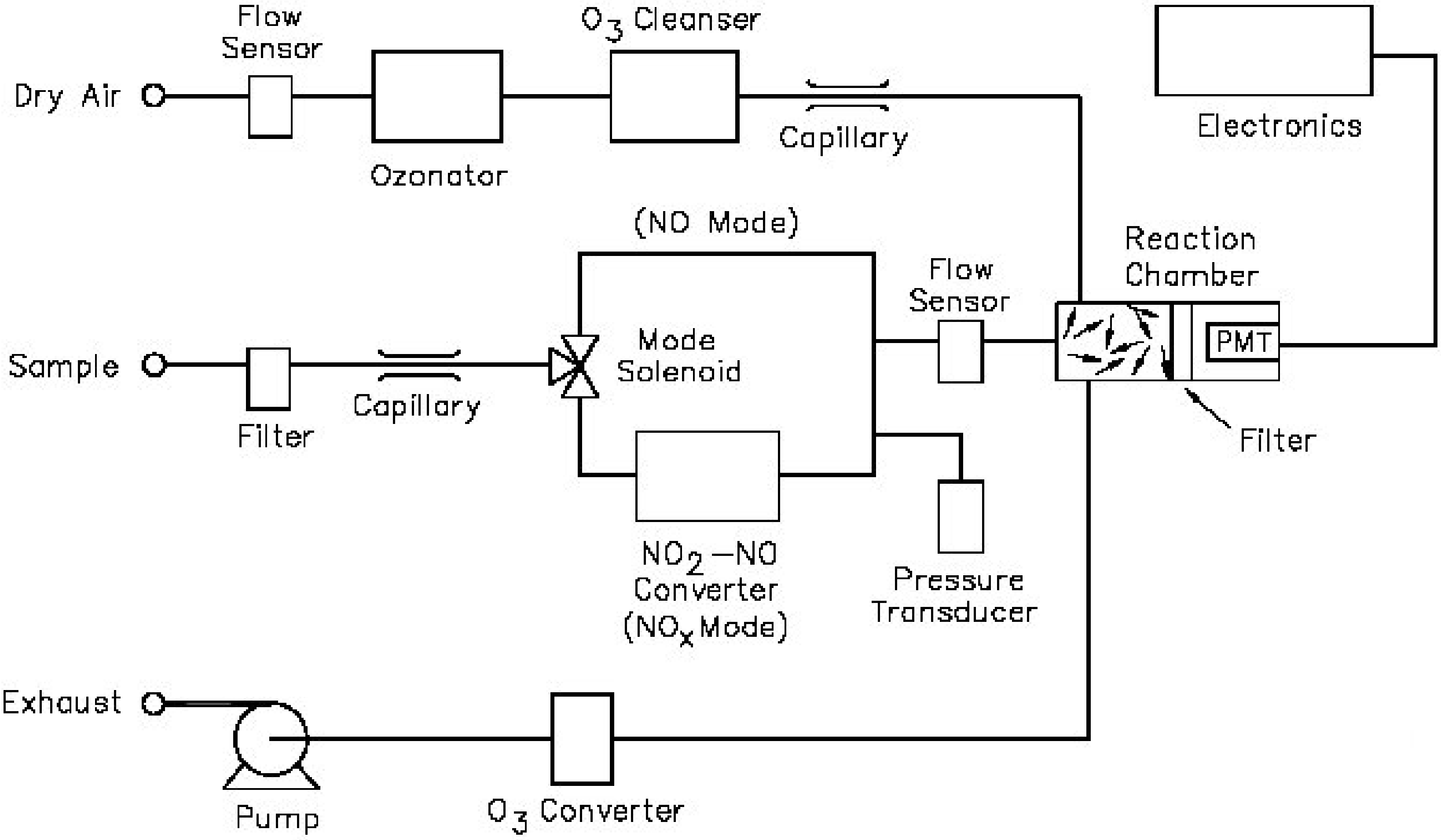
Bandpass Filter

Photomultiplier Tube

Chemiluminescence Analyzer

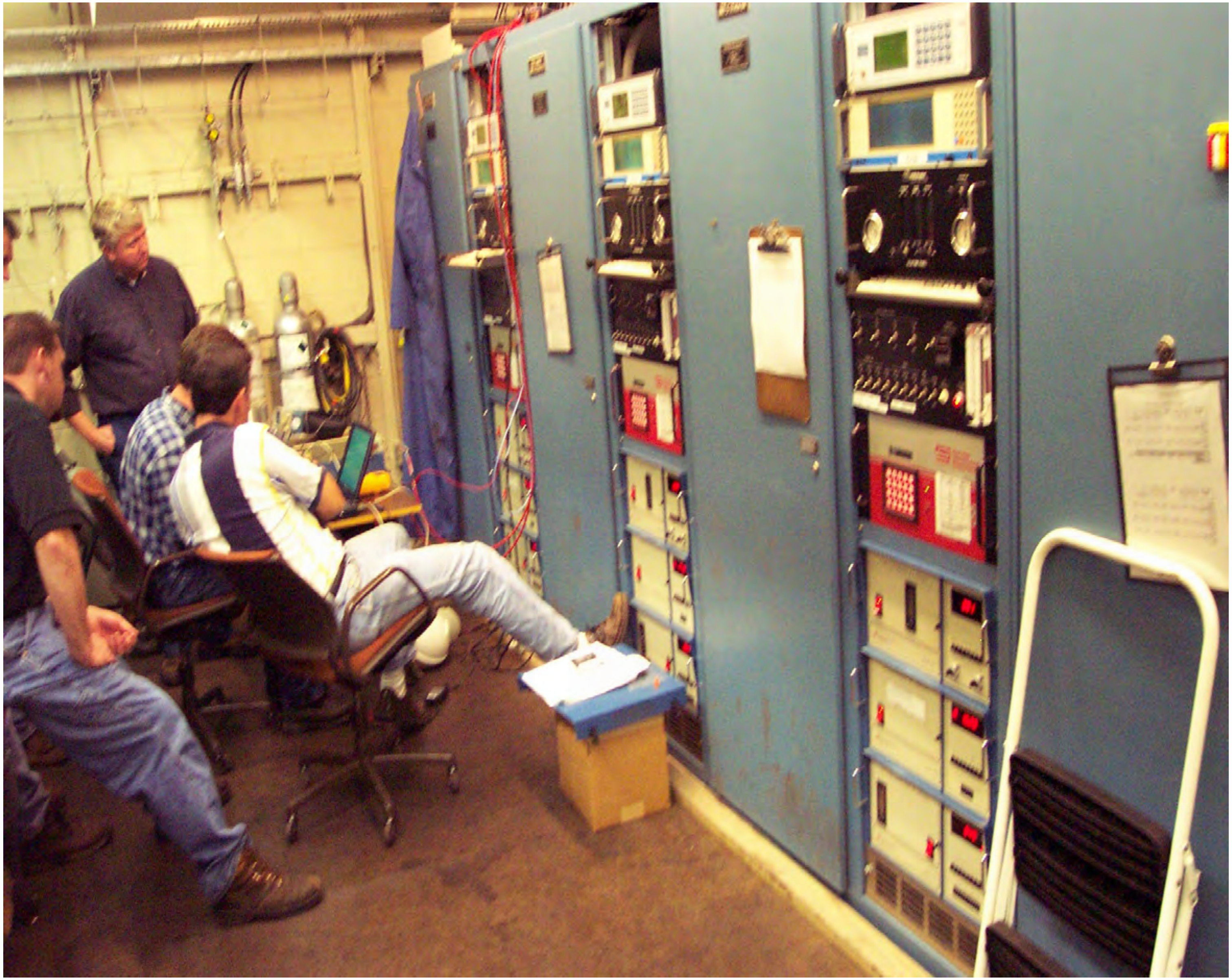
NO_2^* Chemiluminescent Emission Spectrum





Model 42C Flow Diagram


Thermo
ELECTRON CORPORATION
Thermo
Thermo
Thermo
Thermo



Analytical Range

- "…Select span so that concentration equivalent to emission standard is not less than 30 percent of span…"
- "If gas concentration exceeds the span, the run is invalid…"

Performance Specifications

- Analyzer calibration error
  - Less than ± 2% of span for zero, mid, and high-range gases
- Sampling system bias
  - Less than ± 5% of span for zero and mid or high-range gases

Performance Specifications

- Zero drift and calibration drift
  - Less than ± 3% of span over the period of the run

Calibration Gases

- High-range = 80-100% of span
- Mid-range = 40-60% of span
- Zero gas = < 0.25% of span

Calibration Gases

- Protocol 1, or triplicate analysis using Method 6
- SO_2 in N_2 or $SO_2/CO_2/O_2$ in N_2
- Beware use of triple-blends in dilution systems

For Fluorscence-based Analyzers

- O_2 and CO_2 concentrations of calibration gases and effluent samples as introduced to analyzer must be within ±1% O_2 and CO_2

Measurement System Performance Test Procedures

- Measurement system preparation
  - Acquire equipment/calibration gases
  - Set-up the components
  - Warm up the analyzers
  - Adjust flow rates

Recommended Sampling System Design Criteria

- Remove particulate
- Remove moisture or otherwise lower the dew point of the sample
- Minimize sample loss through leaks, absorption, and reaction

Recommended Sampling System Design Criteria

- Allow for introduction of calibration gas through as many components as possible

Recommended Particulate Removal

- In-stack filter at probe tip or probe outlet
- Filter after moisture removal system to catch condensable particulate
- Final filter at analyzer inlet

Sample Handling

- Maintain the sample above the dew point temperature except in the condensers
- Use only non-reactive wetted surfaces (i.e., glass, Teflon, and stainless steel)

Moisture Removal Condensers

- Use ice bath, refrigerated, or thermoelectrically cooled impingers or coils
- Design condenser to minimize contact area between sample and condensate

Moisture Removal
Condensers

- Continuously remove condensate from traps to further reduce contact with sample and limit absorption of SO_2 and NO_2

Other Methods of Lowering Sample Dew Point

- Semi-permeable membrane dryers (Perma-Pure®)
- Dilution probes

Injecting Calibration Gases Into the Sampling system

- One of the most common problem areas
- Calibration gases should be introduced under flow conditions that are as close as possible to the sampling conditions
- Testers hate to waste calibration gas

Three Suggested Ways to Introduce Calibration Gases

- Straight Tee
- Closed Loop
- Closed Loop with Vent

Calibration Gas Introduction - Straight Tee

- No 3-way valve required
- Will not pressurize sampling system if probe filter is clean
- Uses analyzer zero readings to establish adequate calibration gas flow

Calibration Gas Introduction - Closed Loop

- Uses 3-way valve to isolate sampling system from probe
- Sample flow meter is used to match calibration gas and sample gas flows
- Pressurizing the sampling system can disguise leaks

Calibration Gas Introduction - Closed Loop with Vent

- Uses 3-way valve to isolate sampling system from probe
- Vent with rotameter ensures that calibration gas is introduced under vacuum

Leak Check

- Not required by the method due to bias test procedure
- Should be conducted from probe tip to analyzers before and after each test

Analyzer Calibration Error

- Less than ± 2% of span for zero, mid and high-range gases
- Demonstrates accuracy and linearity

Sampling System Bias Check

- Less than ± 5% of span for zero and mid or high-range gases
- Check integrity of system; cannot adjust monitor calibration after calibration error (CE) test

Emission Testing

- Same sampling points as Method 6
- Sample run duration plus twice the sampling system response time

Sampling Procedures

- Conduct sampling system bias checks before and after each run
- Make no calibration adjustments prior to recording bias results after a run

If System Exceeds Bias Specifications

- Run is invalid
- Fix system (maybe just re-calibrate analyzer)
- Repeat analyzer calibration error and sampling system bias checks before proceeding

If System Meets Bias Specification

- Use average of bias results before and after the run to correct the measured effluent gas concentration

If System Exceeds Zero or Calibration Drift Limits

- Run is still valid if
  bias limits were met
- Repeat analyzer calibration error and sampling system bias checks before next run

Data Recording

- Strip chart or computer data acquisition system with resolution of at least 0.5% of instrument span
- Commonly done with PC-based data acquisition systems

Emission Calculations

- Data corrected for errors observed in calibration error bias checks

Interference Check

- Difference of less than ± 7% of the modified Method 6 results
- Method 6 sampling at the analyzer manifold

Known SO_2 Analyzer Interferences

- Some earlier model NDIR SO_2 analyzers demonstrated a high bias due to residual moisture in the sample (after condenser)
- Some earlier model UV analyzers demonstrated a high bias when NO_2 concentrations were high relative to the SO_2 concentrations

Known SO_2 Analyzer Interferences

- Fluorescence analyzers suffer from quenching effects from CO_2 and O_2

Sampling in the Presence of Ammonia

- Ammonia reacts with SO_2 in the condenser causing a low bias
- Amount of bias depends on the relative concentrations of SO_2 and ammonia

Sampling in the Presence of Ammonia

- Some success reported using dilution sampling systems
- Used modified Method 6 or modified Method 8 instead of Method 6C to ensure good results

Alternative Techniques for Method 6C

- The following techniques have been approved by EPA in limited applications
  - Dilution probes for sampling
  - Calibration gas dilution systems (Not Part 75)

Dilution Probes for Method 6C

- EMTIC Guidance Document GD-012
- All gases introduced
  at the probe tip
- Wet basis concentration results

Dilution Probes for Method 6C

- Initial 3-point calibration still required
- Bias calculated as deviation from gas value

Calibration Gas Dilution Systems

- EMTIC Conditional Test Method CTM-007
- Proposed as Method 205, FR 8/3/94, Vol. 59, No. 148
- Dilute high level Protocol 1 gases to achieve desired concentrations

Calibration Gas Dilution Systems

- Not approved for acid rain (40CFR75) testing
- Field verification procedure for at least five dilution ratios
- Yearly lab calibration procedure for flowmeters (NIST traceable)

Method 7E - NO_x

- Must use chemiluminescence analyzer
- No field interference check (use Method 20 laboratory interference test)
- NO_2 to NO converter efficiency test (same as Method 20)

Method 7E - Ammonia (NH_3) Interference Problems

- Use low temperature (molybdenum or activated carbon) NO_2 to NO converter to prevent conversion of NH_3 to NO
- Molybdenum converters lose efficiency quickly and need to
  be regenerated often

Method 7E - High NO_2/NO Ratio in Sample

- NO_2 is readily absorbed by the sampling system, causing low bias
- Most NO_x calibration gases contain little NO_2

Method 7E - High NO_2/NO Ratio in Sample

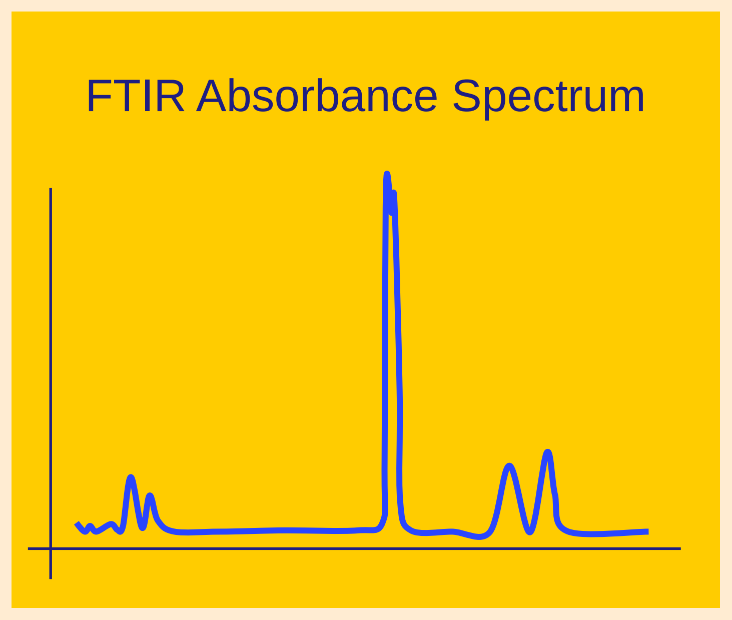
- NO_2 to NO converter efficiency becomes much more important
- Tester should perform NO/NO_2 balance adjustment

Method 3A - O_2 and CO_2

- Any analytical technique
- Less rigorous sampling system material specification
- Option to substitute low-range check for zero gas for O_2 analyzers
- Laboratory interference check same as Method 20


Scott

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 320 and 321 FTIR



FRM 320

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - 1.0 Introduction
  - 2.0 Summary of Method
  - 3.0 Definitions
  - 4.0 Interferences
  - 5.0 Safety
  - 6.0 Equipment and Supplies

FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - 7.0 Reagents and Standards
  - 8.0 Sampling and Analytical Procedure
  - 9.0 Quality Control
  - 10.0 Calibration and Standardization
  - 11.0 Data Analysis and Calculations
  - 12.0 Method Performance

FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - 13.0 Method Validation Procedure
  - 14.0 Pollution Prevention
  - 15.0 Waste Management
  - 16.0 References
  - Addendum to Test Method 320
    - Protocol for the Use of Extractive FTIR for the Analyses of Gaseous Emissions from Stationary Sources

FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - Addendum A to Test Method 320
    - Protocol for the Use of Extractive FTIR for the Analyses of Gaseous Emissions from Stationary Sources
  - Addendum B to Test Method 320
    - Identifying Spectral Interferants
  - Addendum C to Test Method 320
    - Estimating Noise Levels

FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - Addendum D to Test Method 320
    - Estimating Minimum Concentration Measurement Uncertainties
  - Addendum E to Test Method 320
    - Determining Fractional Reproducibility Unceertainties
  - Addendum F to Test Method 320
    - Determining Fractional Calibration Uncertainties
  - Addendum G to Test Method 320
    - Measuring Noise Levels

FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - Addendum H to Test Method 320
    - Determining Sample Absorption Pathlength and Fractional Analytical Uncertainty
  - Addendum I to Test Method 320
    - Determining Fractional Model Uncertainties

FRM 320 Sampling Types

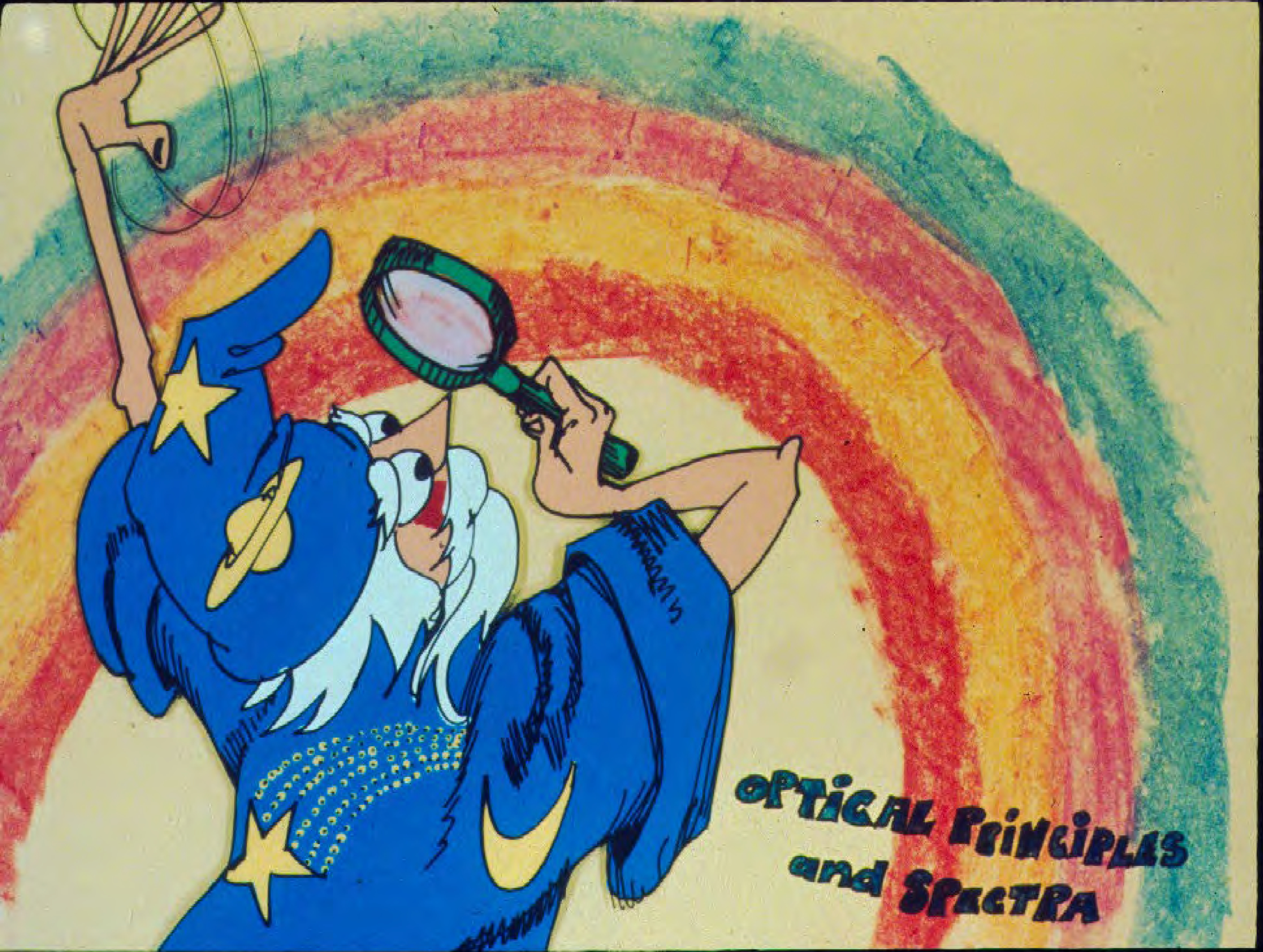
- Screening
- Emission Test
- Validation

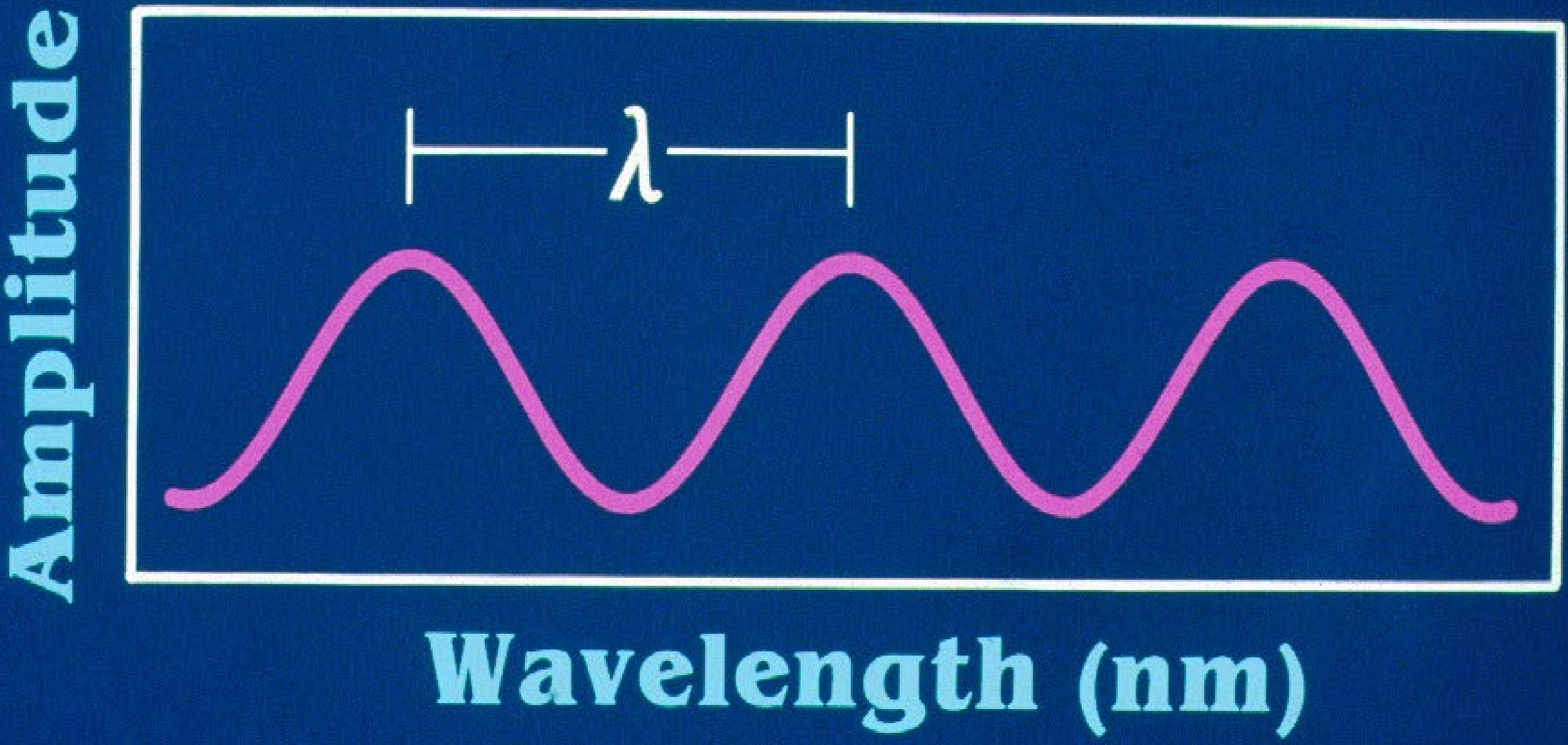
FRM 320 (cont'd)

- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - System involves typical CEM probe and pump to extract the sample to the FTIR analytical bench
  - An IR spectra of the sample is digitized from the FTIR gas cell
  - "Reference spectra" prepared in the laboratory of the standard samples of interest compared to the digitized FTIR spectra of the sample
  - Self-validation method in utilizing a QA analyte spike of the extracted sample at the probe

FRM 320

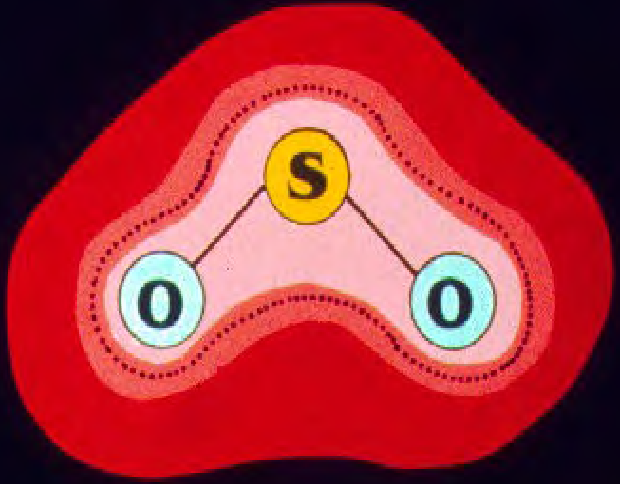
- *"…This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm*$^{-1}$ *(25 to 2.5 um). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations."*


OPTICAL PRINCIPLES
and SPECTRA


λ
Amplitude
Wavelength (nm)

Vibration

Rotation

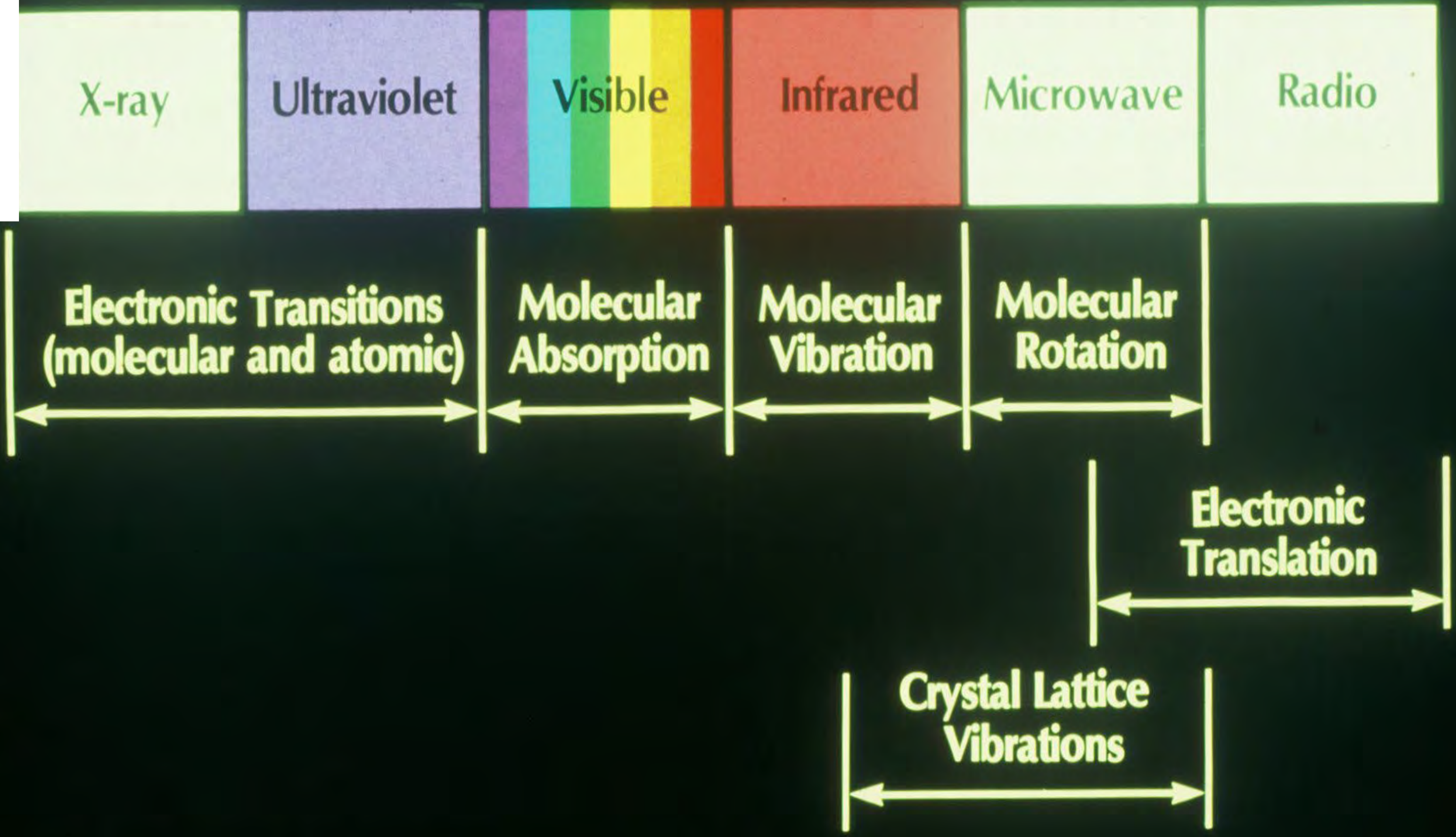


Electronic

CHARACTERISTICS OF THE EM SPECTRUM

X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio

TRANSITION REGIONS



X-ray

Ultraviolet

Visible

Infrared

Microwave

Radio

Electronic Transitions (molecular and atomic)

Molecular Absorption

Molecular Vibration

Molecular Rotation

Electronic Translation

Crystal Lattice Vibrations

ELECTROMAGNETIC SPECTRUM

X-ray

Ultraviolet

Visible

Infrared

Microwave

Radio

001 μm

.1 μm

.4 μm

.7 μm

22 μm

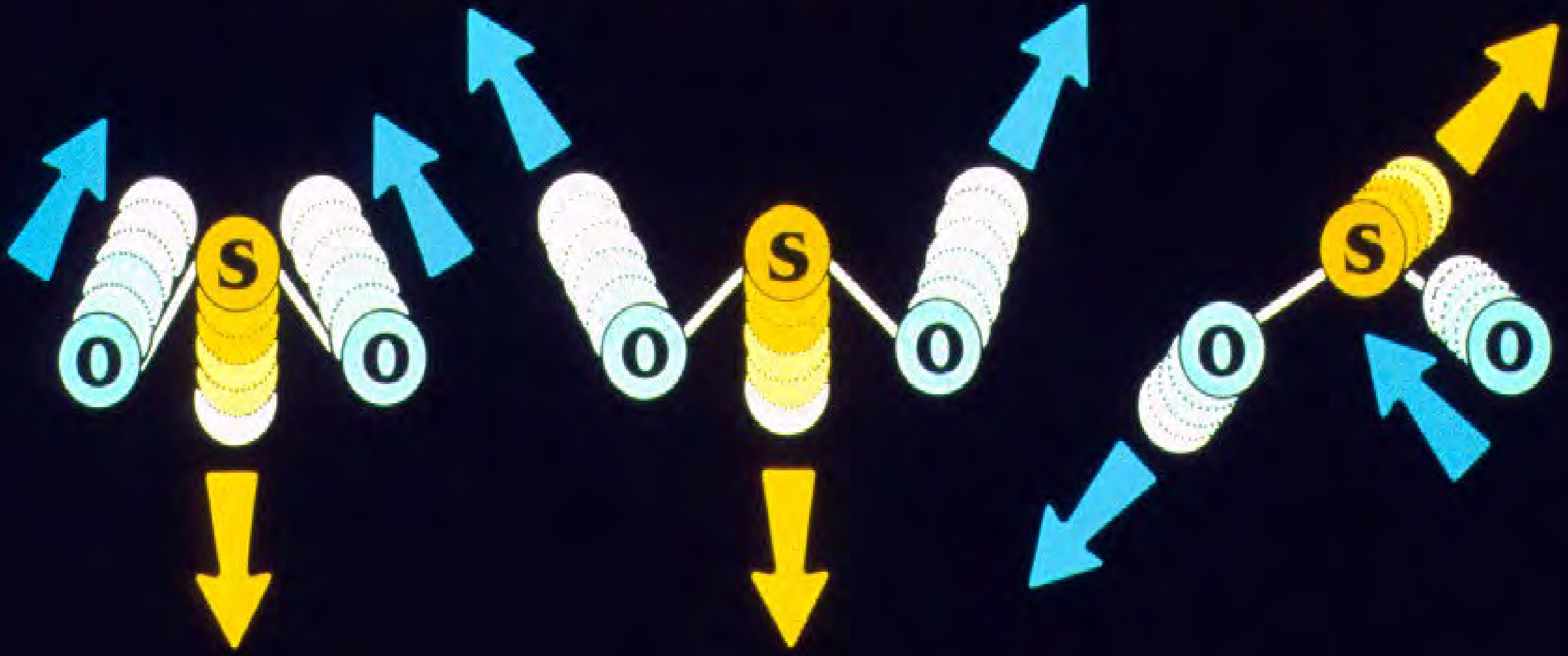
400 μm

250,000 μm

$$E = h\nu$$

$$= h\left(\frac{c}{\lambda}\right)$$

Normal Vibrations of SO_2

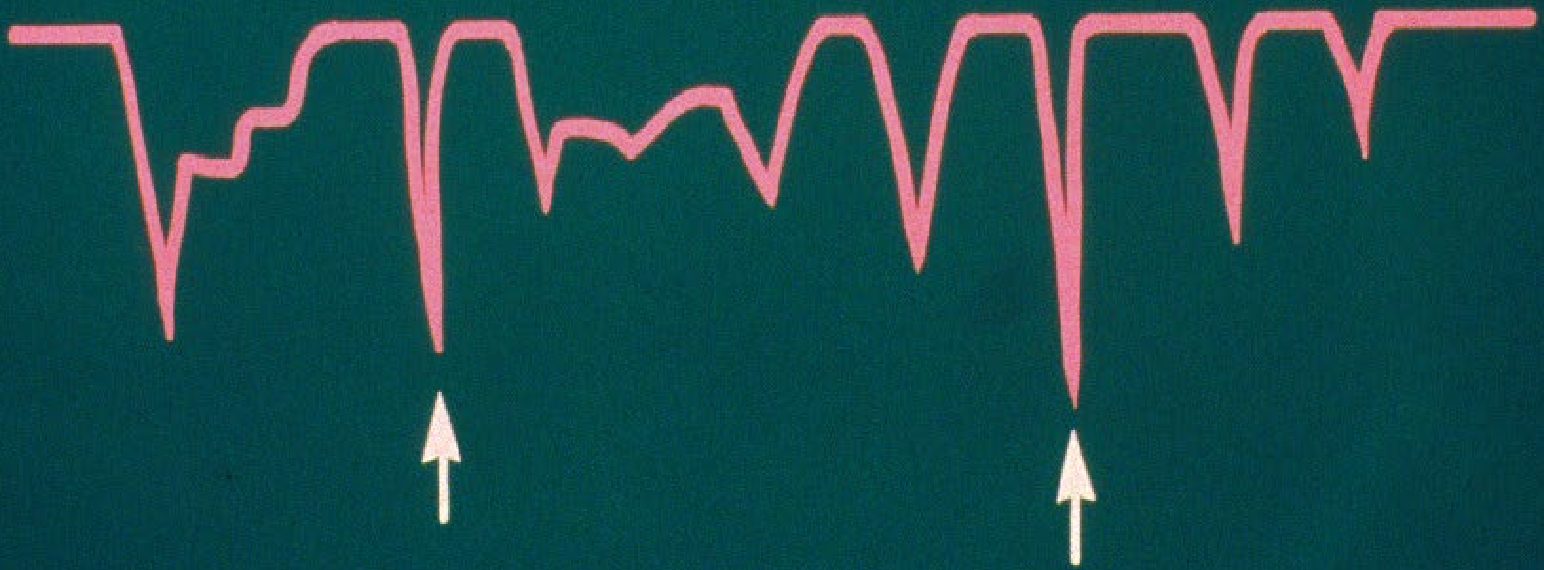


$\lambda = 8.69\,\mu\text{m}$
$\bar{\nu} = 1150.5\ \text{cm}^{-1}$

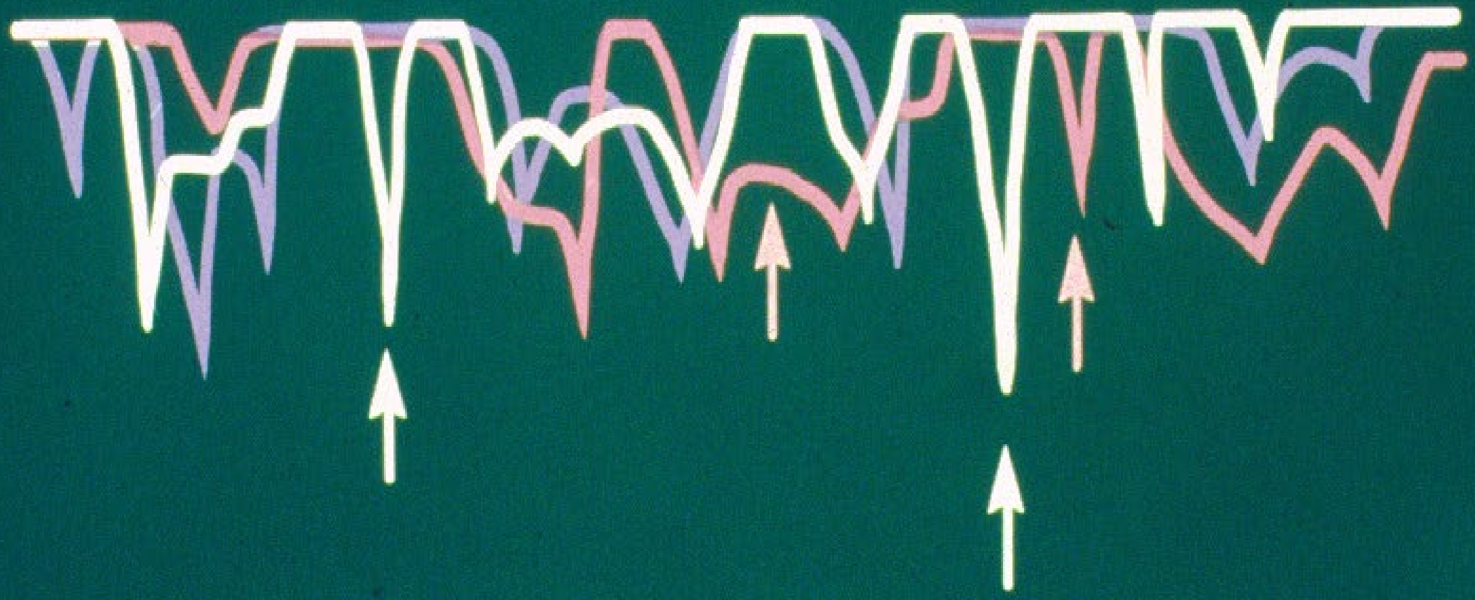
$\lambda = 7.48\,\mu\text{m}$
$\bar{\nu} = 1336.0\ \text{cm}^{-1}$

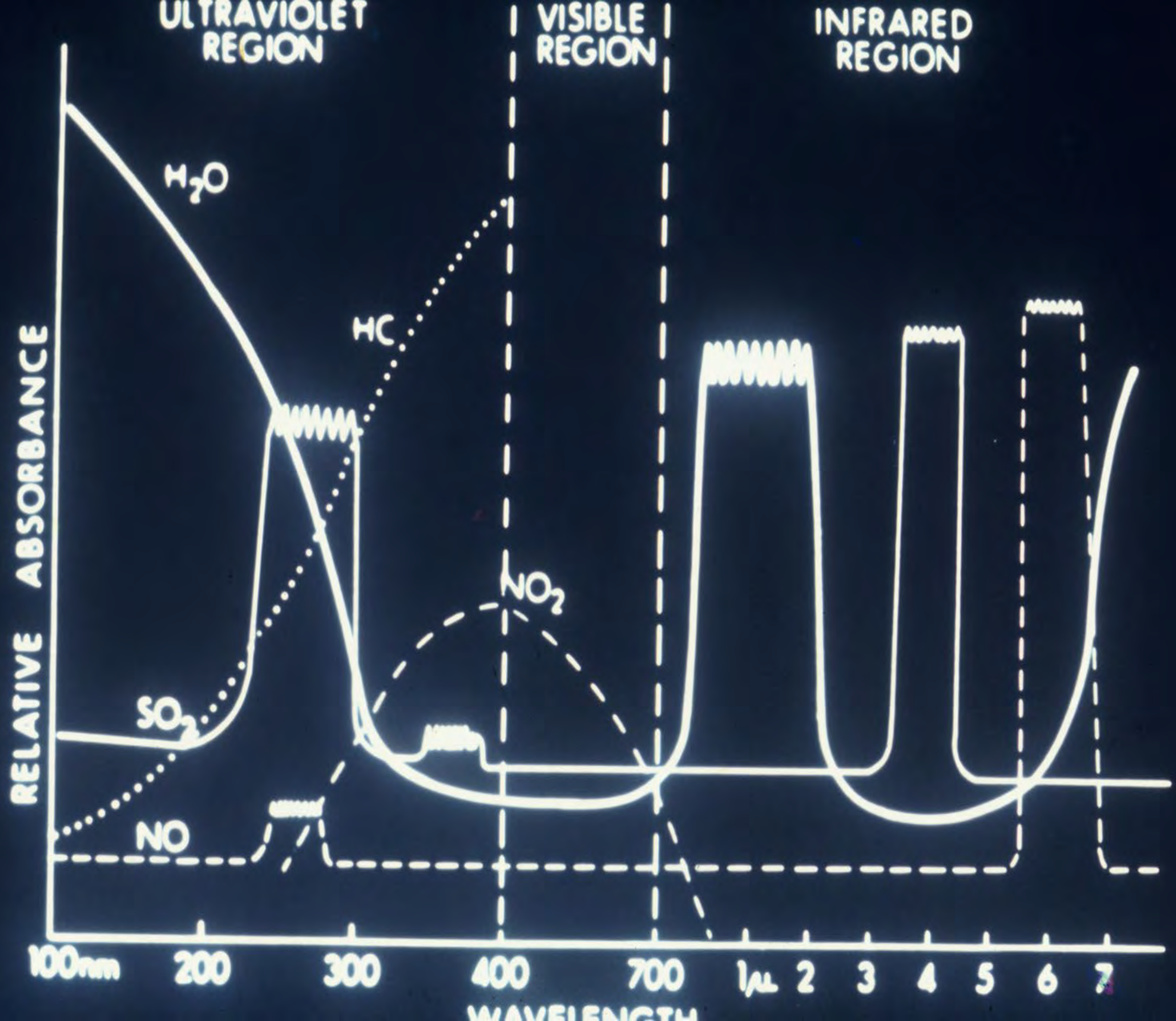
$\lambda = 19.1\,\mu\text{m}$
$\bar{\nu} = 524.5\ \text{cm}^{-1}$

Molecules Absorb Light at Specific Wavelengths



Spectra of Different Molecules Can Overlap




ULTRAVIOLET REGION
VISIBLE REGION
INFRARED REGION
RELATIVE ABSORBANCE
H_2O
HC
SO_2
NO_2
NO
100nm
200
300
400
700
1µ
2
3
4
5
6
7
WAVELENGTH

ight → $E = h\upsilon$ → Absorption → Beer - Lambert Law → Instrument

Beer-Lambert Law

$$I = I_o e^{-\alpha c \ell}$$

I = intensity of radiation through the sample

I_o = intensity of radiation with $c = 0$ or $\alpha = 0$

α = absorption coefficient

c = gas concentration

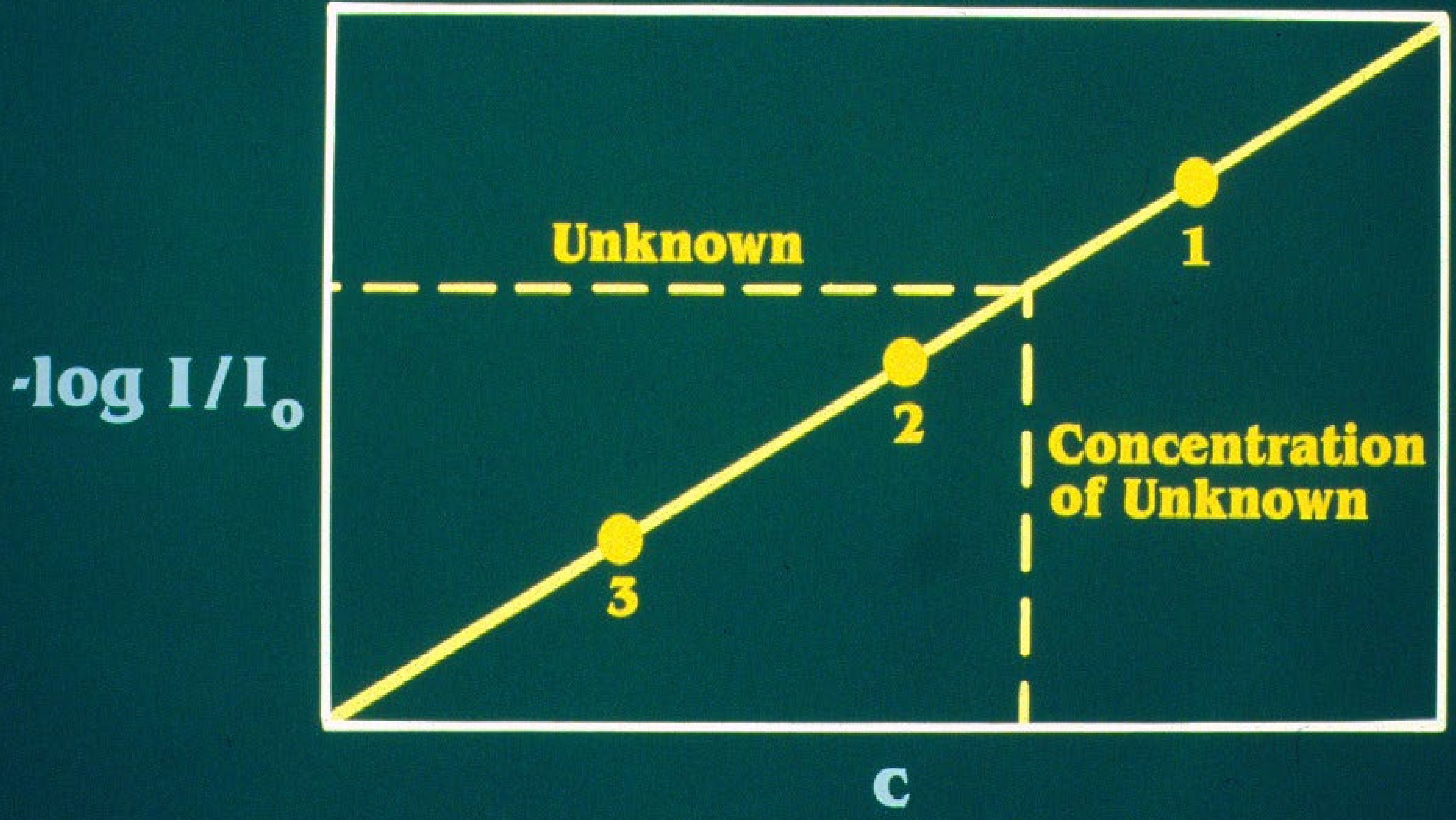
ℓ = pathlength of radiation through the gas

From Beer-Lambert Law:

$$A = \log I/I_0 = \alpha c \ell$$

Direct Relationship

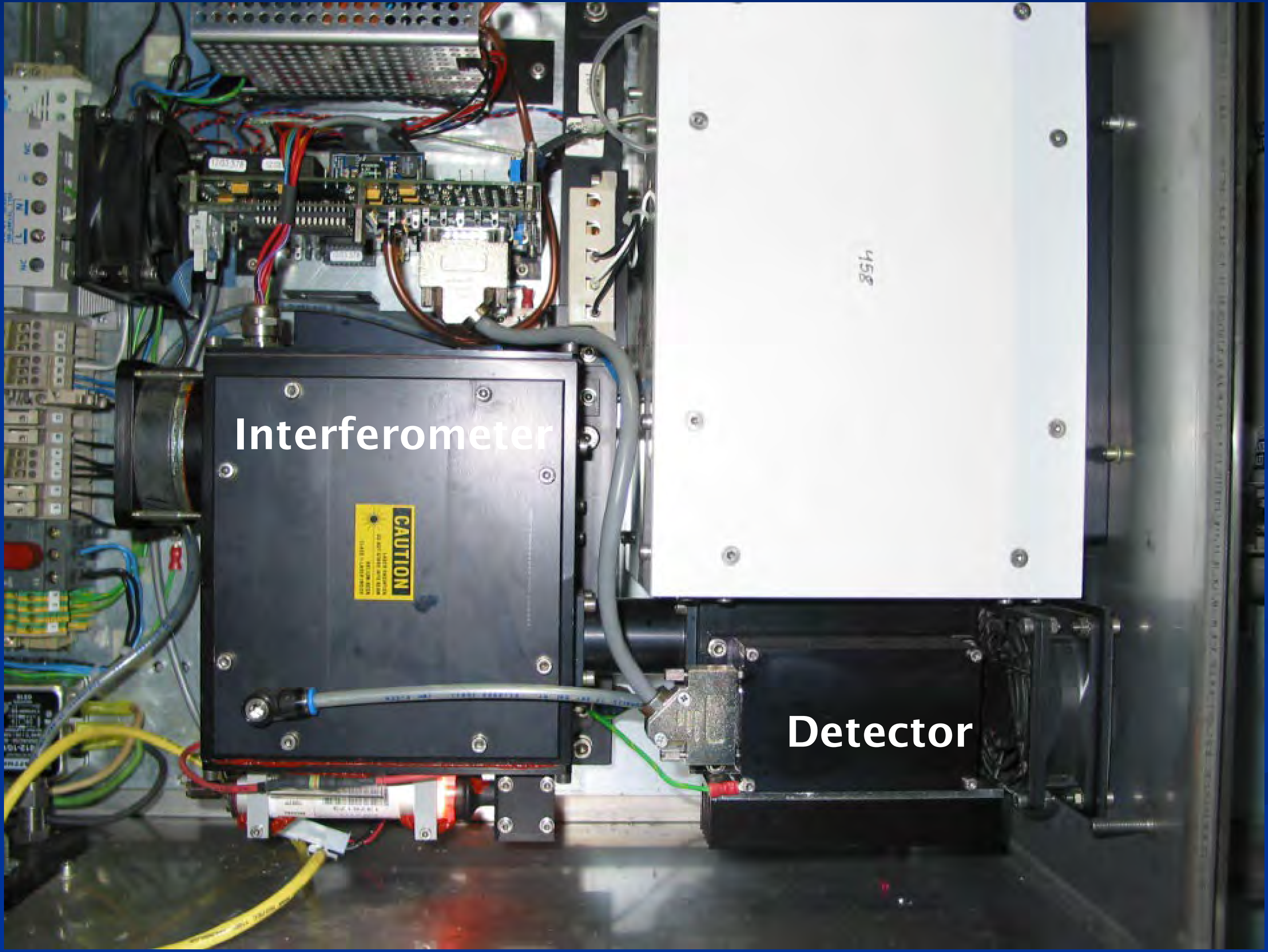
Calibrating a Spectrometer



INFRARED BAND CENTERS OF SOME COMMON GASES

Gas	Band Center (µm)	Wave Number (cm^{-1})
NO	5.0-5.5	1800-2000
NO_2	5.5-20	500-1800
SO_2	8-14	700-1250
H_2O	3.1, 5-5.5, 7.1-10	1000-1400 1800-3200
CO_2	2.7, 5.2, 8-12	850-3700
NH_3	10.5	950

FTIR Interferometer Cell



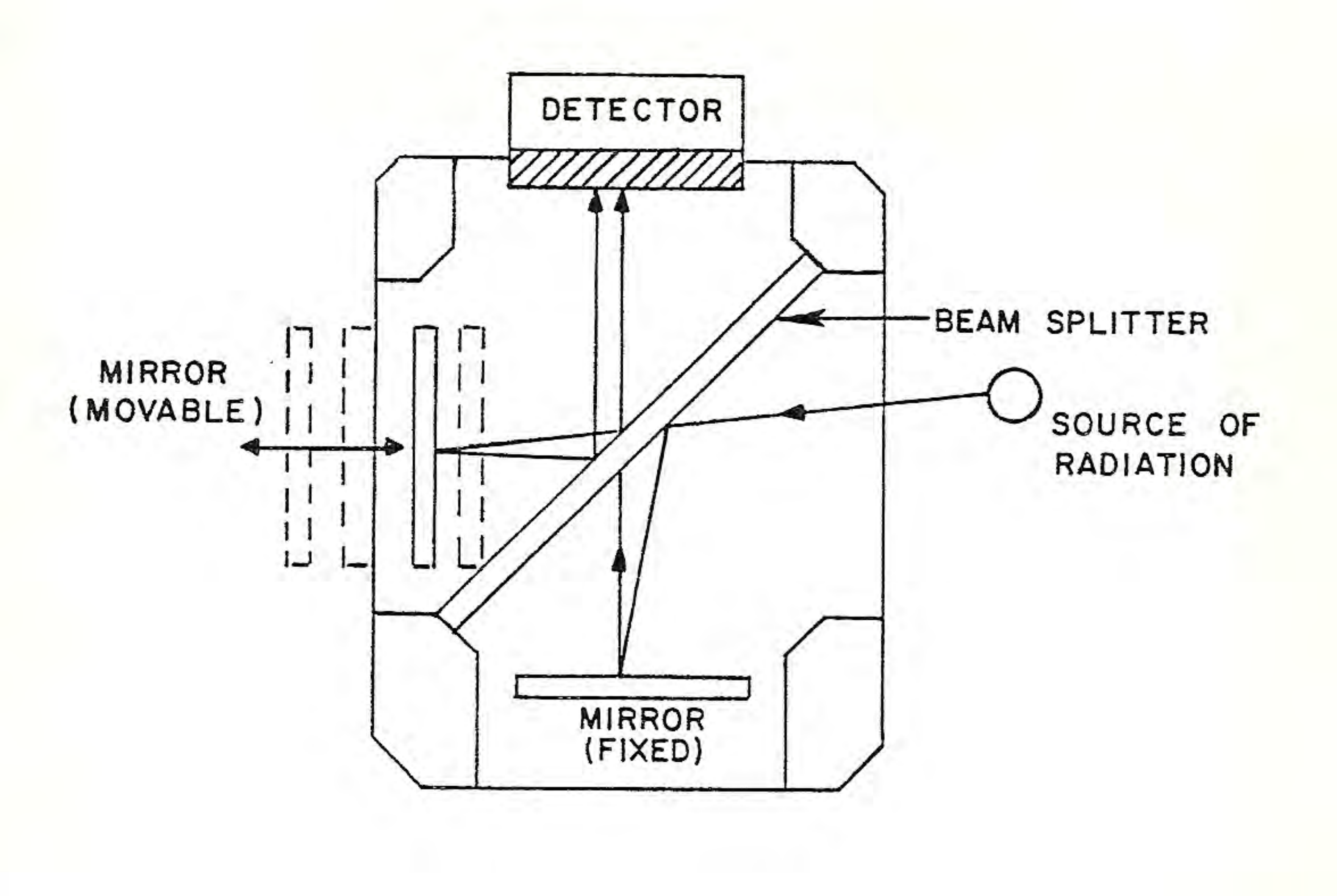
Operation of the FTIR Spectrometer

- IR energy enters the spectrometer
- A beam splitter reflects back 50 percent and transmits 50 percent of the incoming infared radiation
- The two beams are then reflected back to the beam splitter by a moving mirror and a stationary mirror
- Depending on the position of the moving mirror, these two beams recombine with a specific path difference between them

Operation of the FTIR Spectrometer

- This produces the interferogram
- The interferogram is generated by the interferometer modulating the infrared beam as the moving mirror is translated
- The modulated frequencies depend on the wavelength of the incident radiation and the velocity of the moving mirror
- The interferogram is produced after absorption by the sample and is detected by the detector

Operation of the FTIR Mirror



How Gasmet - USA™ FTIR works

FTIR spectrometer

infrared source

continuous infrared spectrum

interferometer

moduled infrared spectrum

sample cell

transmitted infrared light

detector

meas. signal

Electronics / µC

Fourier analysis

absorption spectrum

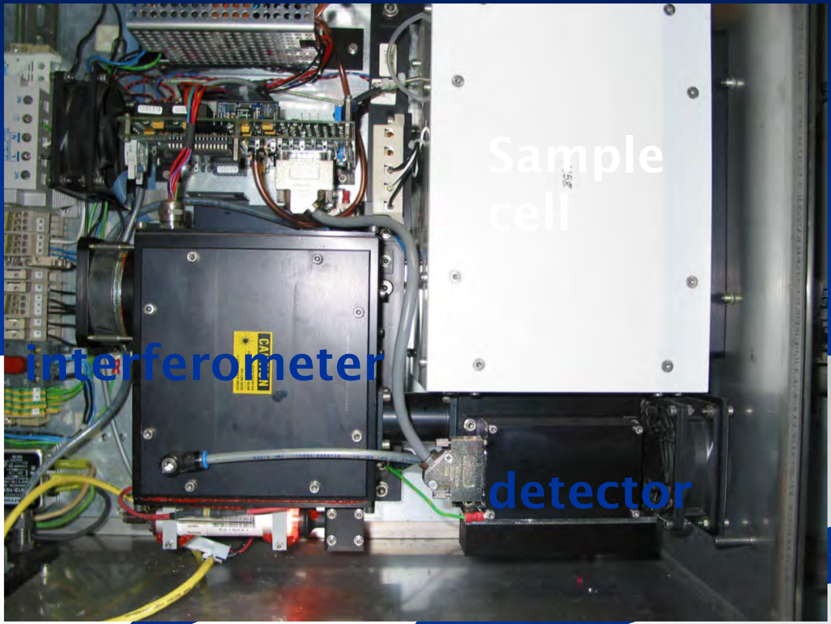
CALCMET™ software

results

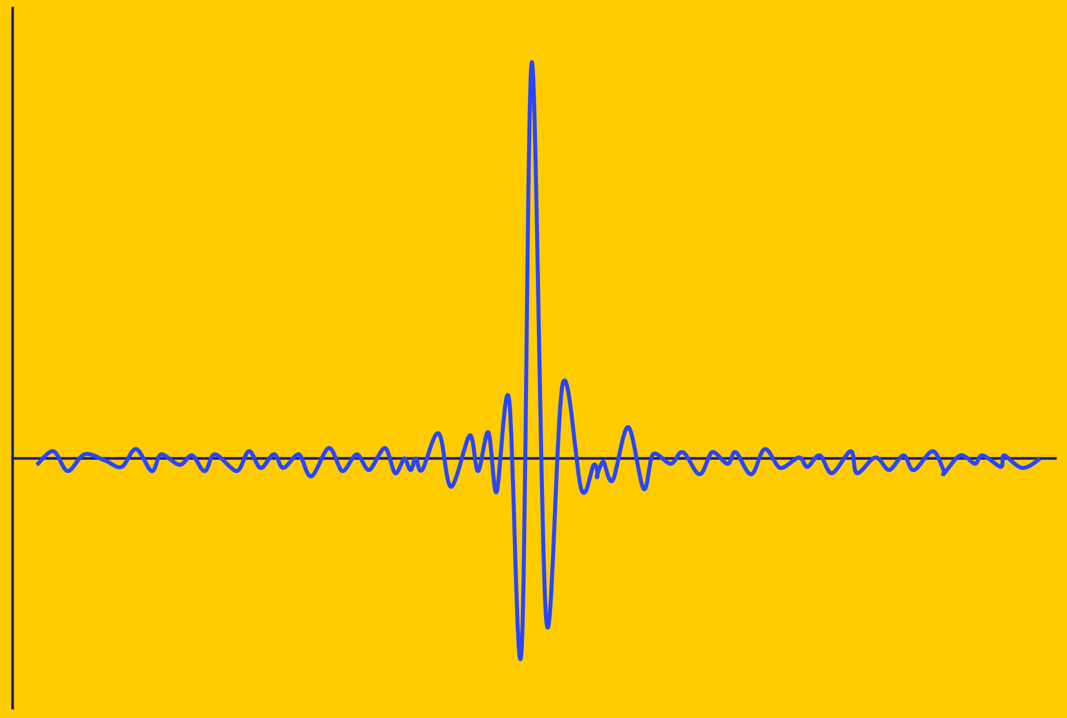
measuring value displays

external eductor

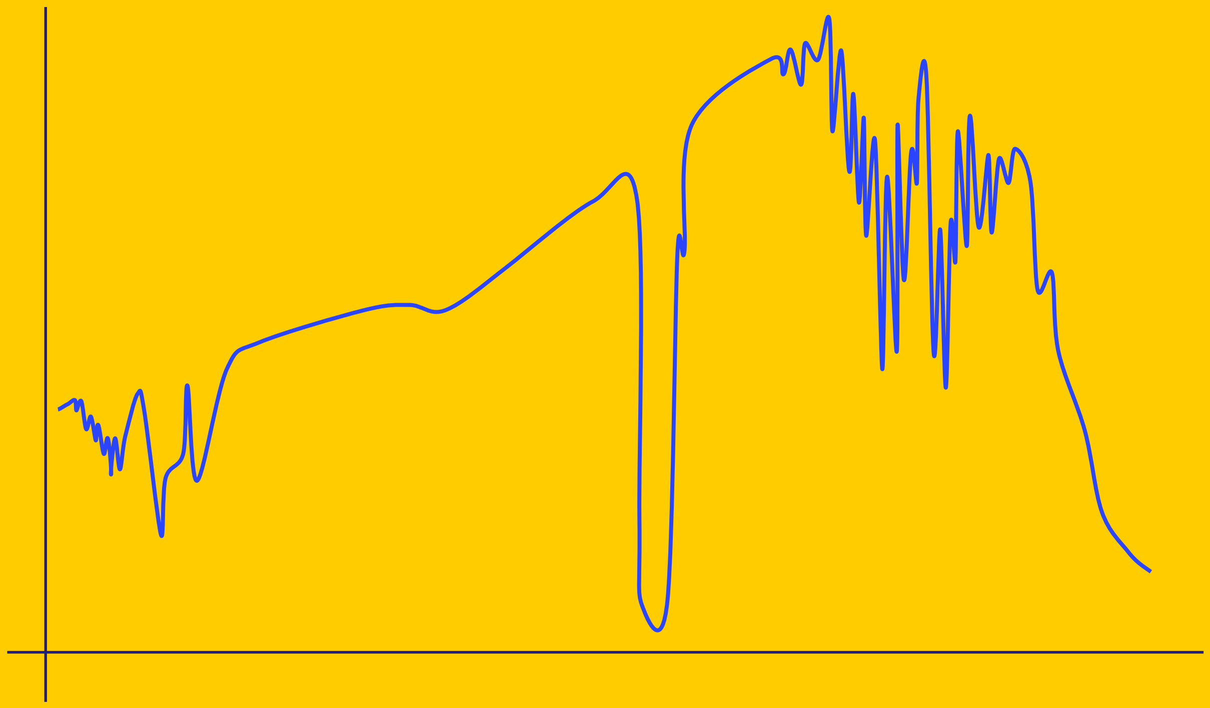
external computer data storage



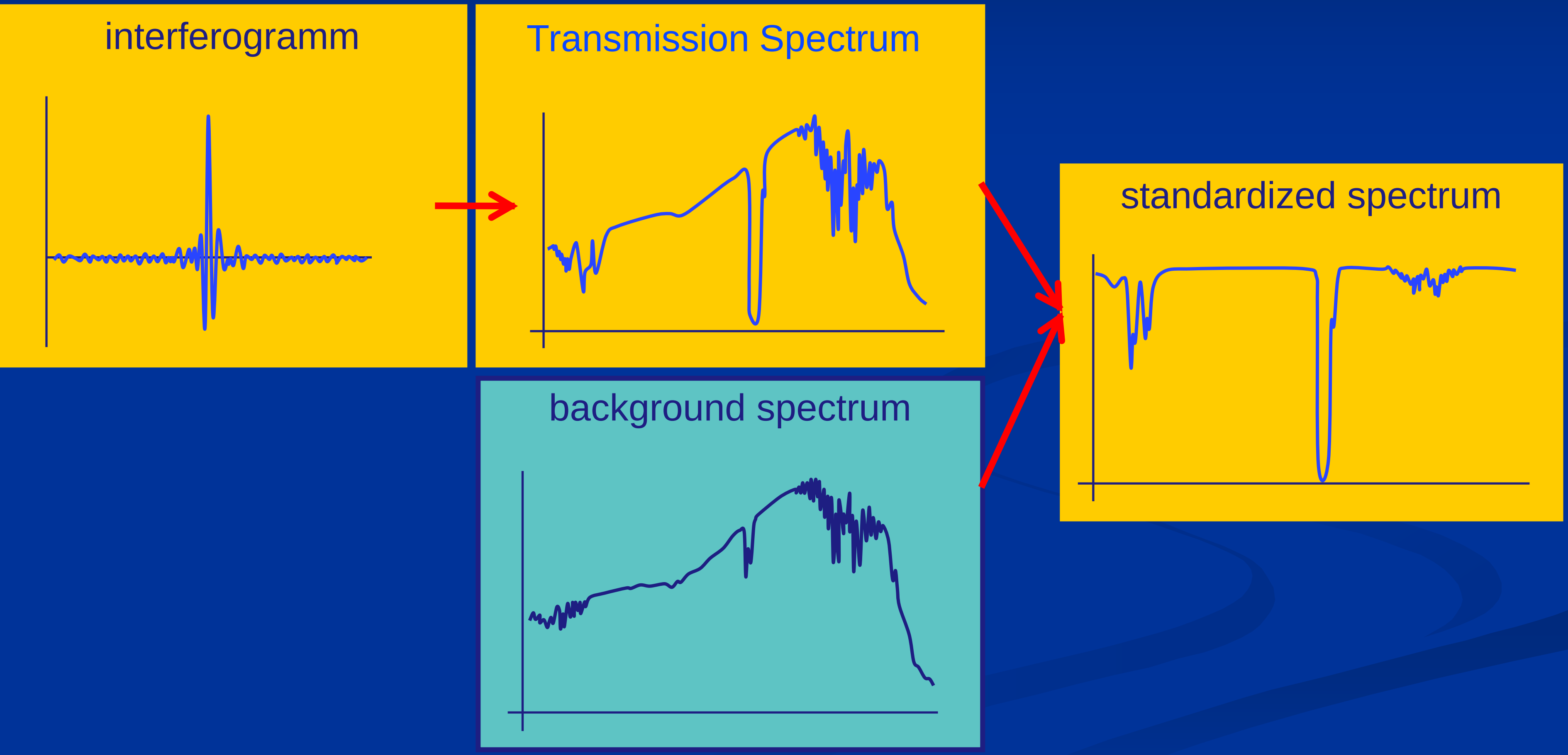
FTIR Interferogram



FTIR Transmission Spectrum



FTIR Generated Standardized Spectrum



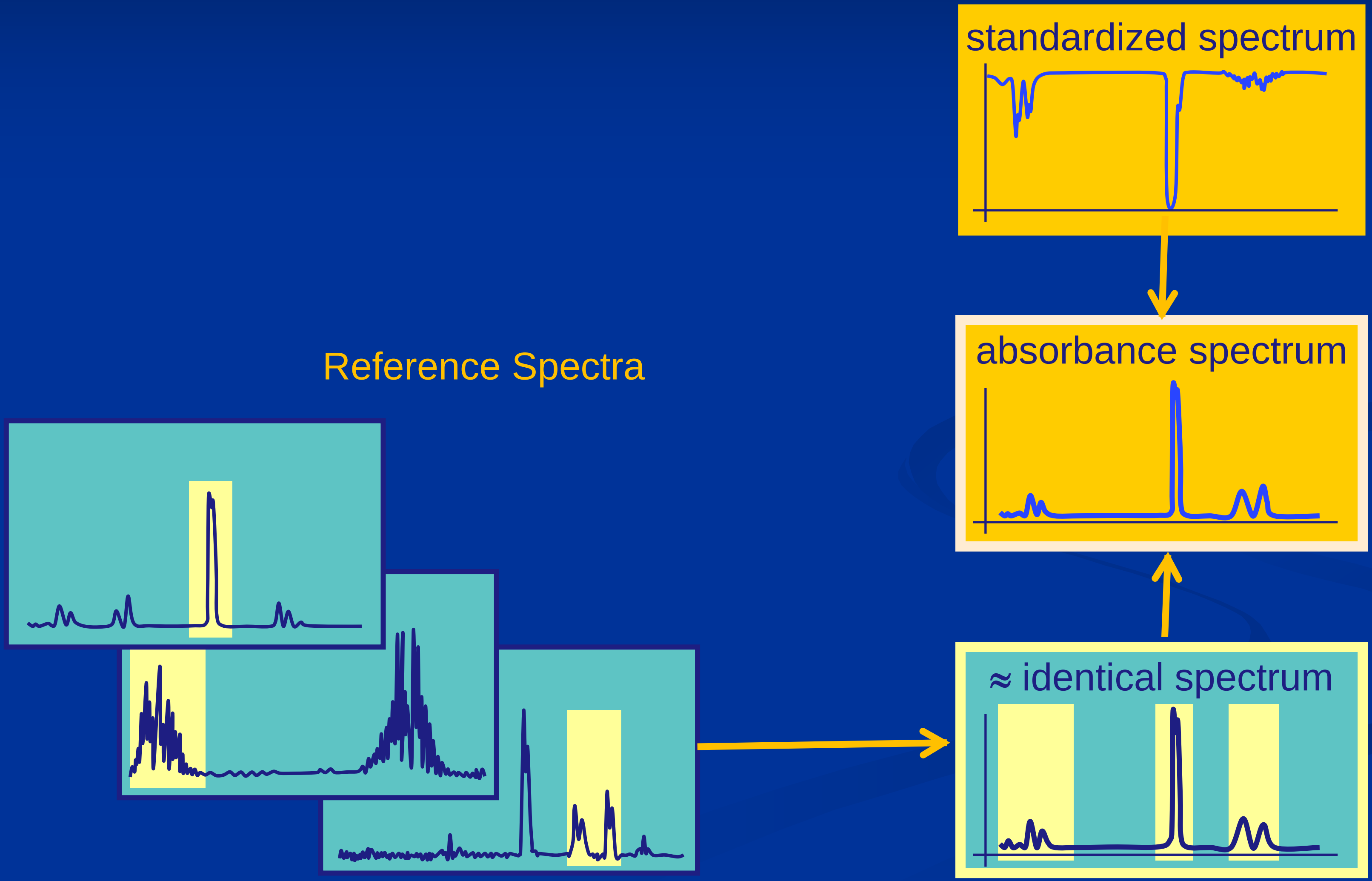
interferogramm

Transmission Spectrum

background spectrum

standardized spectrum

FTIR Identification Process



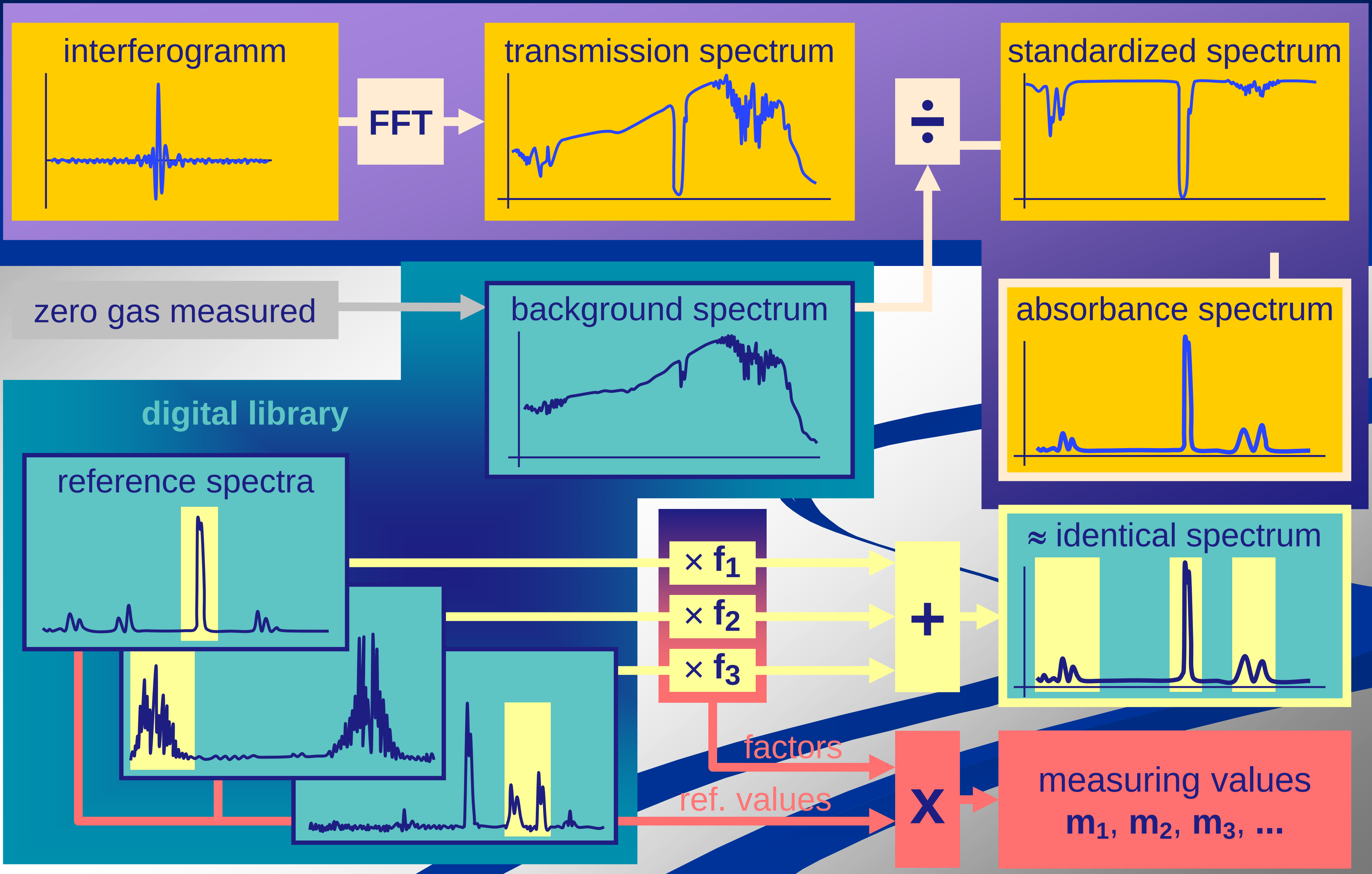
standardized spectrum

absorbance spectrum

Reference Spectra

≈ identical spectrum

How Gasmet - USA™ FTIR works



interferogramm

FFT

transmission spectrum

÷

standardized spectrum

zero gas measured

background spectrum

absorbance spectrum

digital library

reference spectra

× f_1

× f_2

× f_3

+

≈ identical spectrum

factors

ref. values

X

measuring values

m_1, m_2, m_3, ...

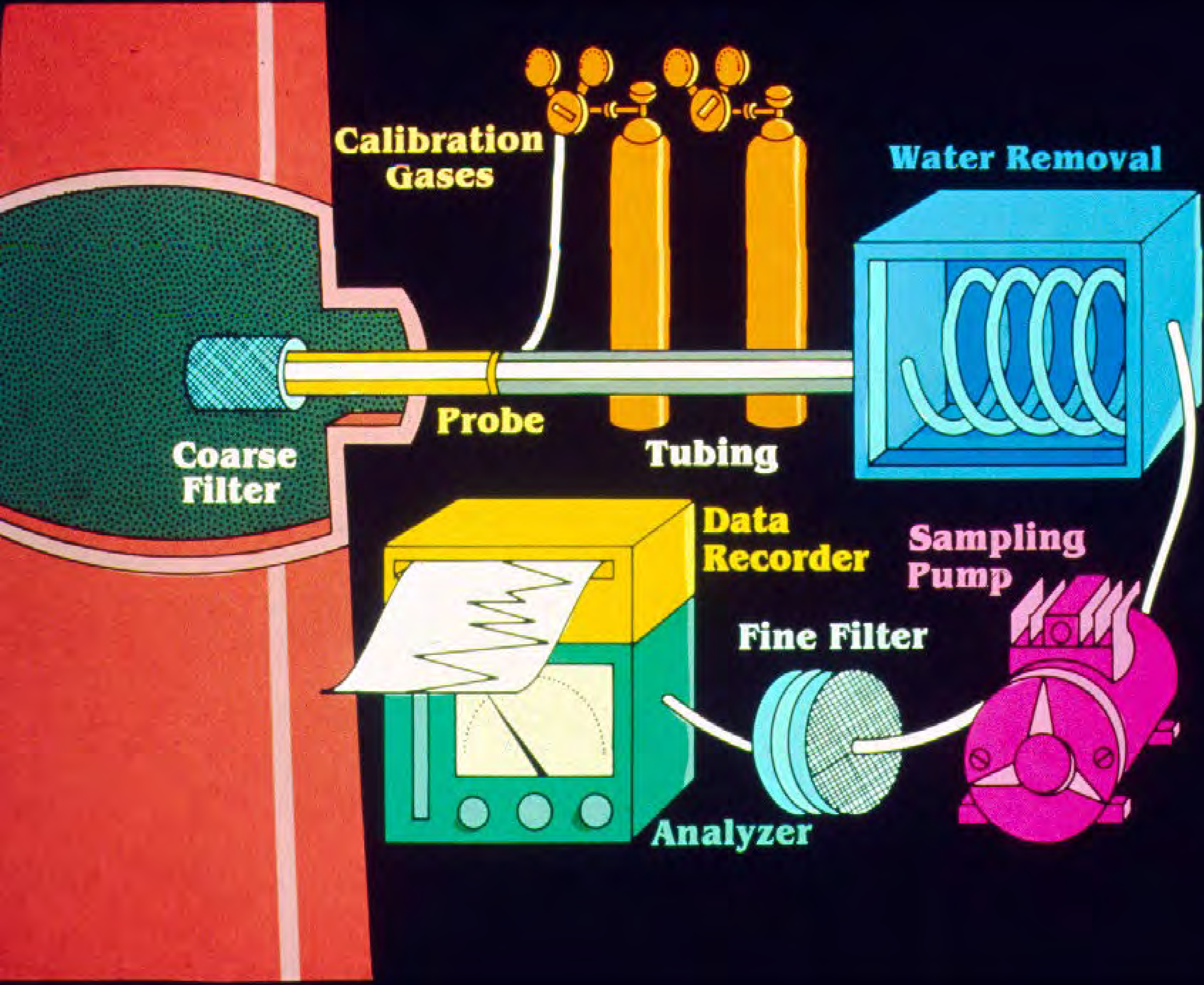

EXTRACTIVE MONITORS

Components of FRM 320

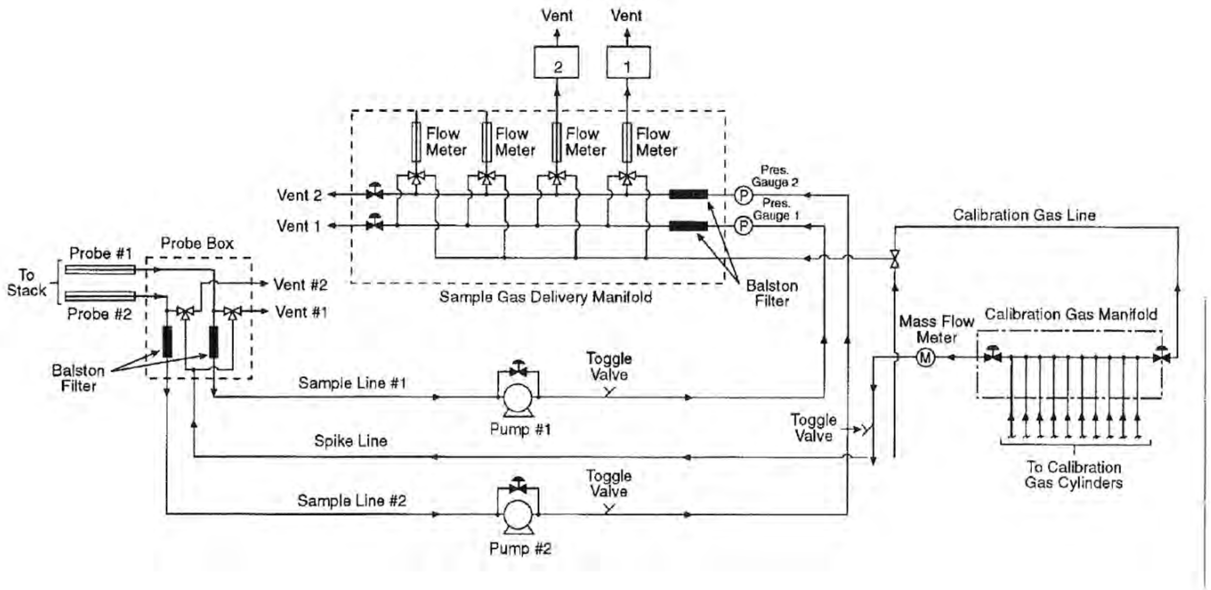
- Sample probe: Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating.
- Particulate filter: A glass wool plug inserted at the probe tip and a filter to remove particulate matter.
- Heat trace sample line: Heated sufficiently to prevent condensation.

Components of FRM 320

- Gas Distribution Manifold: A heated manifold allowing the operator to control flows of gas standards and samples directly to the FTIR system or through sample conditioning system. May use heated flow meters, heated valves etc.
- Calibration/Analyte Spike Assembly: A three-way valve assembly to introduce analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack filter and the FTIR analytical system.
- FTIR Analytical Bench


Calibration Gases
Water Removal
Probe
Tubing
Coarse Filter
Data Recorder
Sampling Pump
Fine Filter
Analyzer

FRM 320 Extractive FTIR Sampling System



Sampling and Analysis Procedures

- Set-up Sampling System
- Pre-test Preparation and Evaluation
  - Select required detection limit (DL_i) and maximum permissible Analytical Uncertainty (AU_i) for each analyte. Estimate maximum expected concentration of each analyte.
  - List potential interferences
  - Determine Fractional Reproducibility Uncertainty (FRU_i)

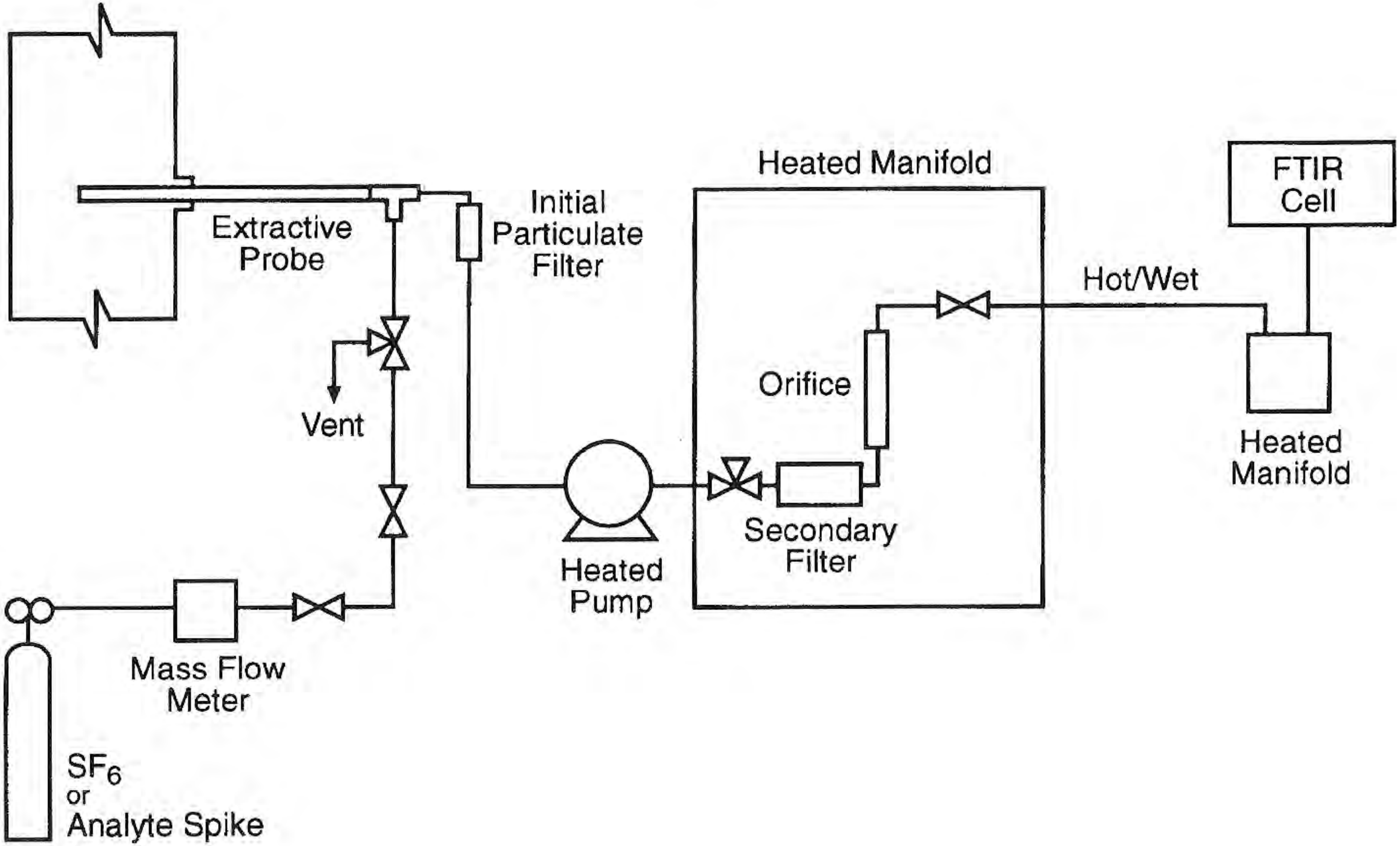
Sampling and Analysis Procedures

- Pre-test Preparation and Evaluation (Cont'd)
  - Calculate Minimum Analyte Uncertainty (MAU)
  - Prepare computer program and input reference spectra for all analytes
- Leak-Check Sampling System
  - From probe to pump
  - FTIR cell
- Determine Linearity of Detector

Sampling and Analysis Procedures

- Perform Background Spectrum with dry nitrogen in FTIR cell
  - Also have in data base spectra of major interferences
- Pre-test Calibrations
  - Fill FTIR cell with Calibration Transfer Standard (CTS). CTS should be certified ± 2% by manufacturer. Record spectra
  - QA Spike to probe to FTIR analytical bench using certified standard (70-130 % recovery)
- Begin Sampling

FRM 320 FTIR Sampling/Spiking Configuration



Sampling and Analysis Procedures

- Post-test QA
  - Verify instrument parameters
  - Perform post-test CTS spectra (± 5 %)

FRM 320 QA Activities

- Analytical Spike (Section 9)-Three spiked samples, analyte concentration in the spike sample compared to expected spike concentration to verify that the sampling/analytical system is working properly
- QA Spike Procedure (Section 8.6.2)- QA Spike to probe to verify that sampling/analytical system is working.
- Response Time Determination (Section 9.2.2)-
- Validation Procedure (Section 13)-

FRM 320 QA Activities

- Method Validation Procedure (Section 13)- Similar to QA Spike procedure in that one acquires two un-spiked samples, then introduces QA Spike gas into continuous flow of sample gas. Collect spectra of two sample gases.
  - Use FRM 301 to calculate bias as:

$$B = S_m - CS$$

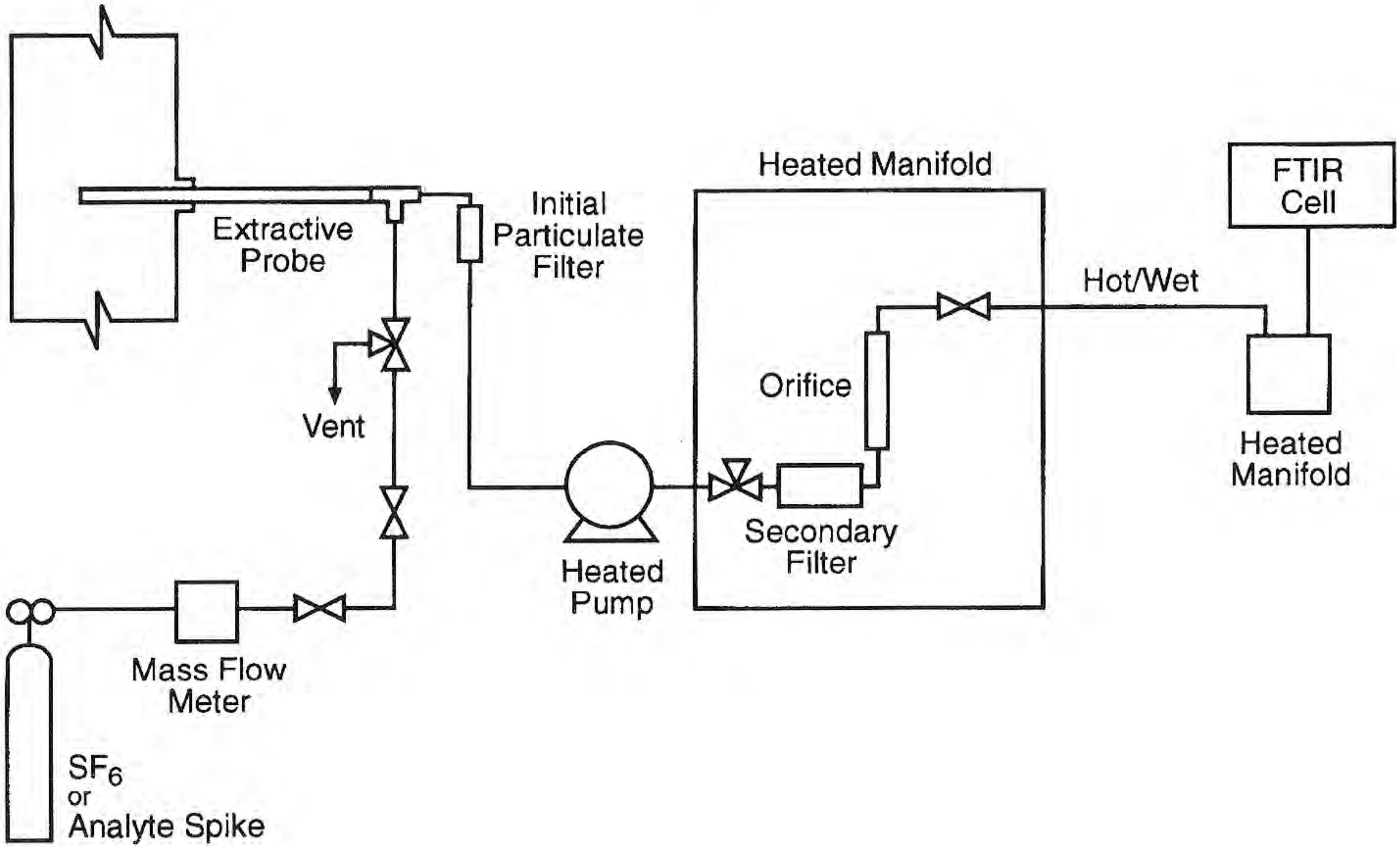
Where:

B = Bias at spike level

S_m = Mean concentration of the analyte spiked samples

CS = Expected concentration of the spiked samples

FRM 320 FTIR Sampling/Spiking Configuration



FRM 320 QA Activities

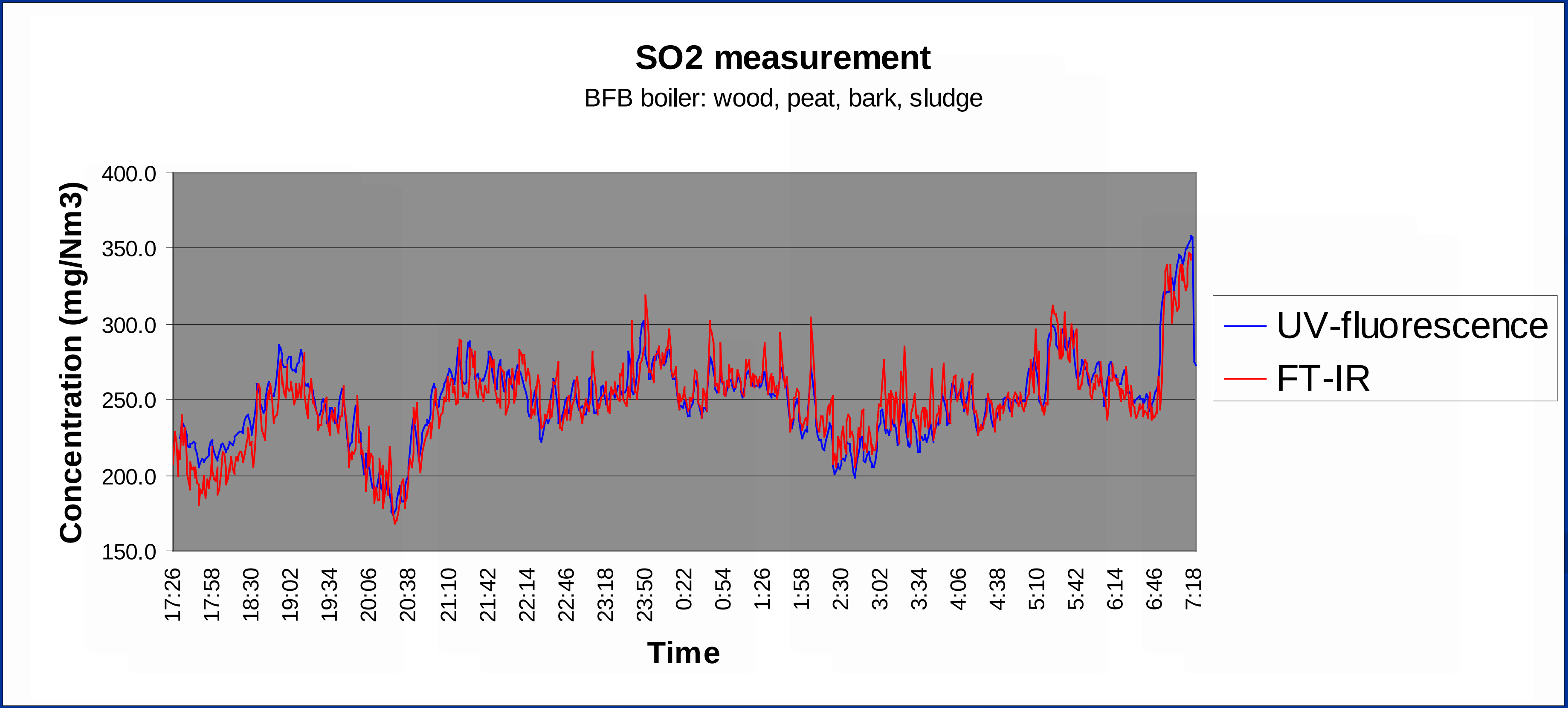
- Method Validation Procedure (Section 13)-
  - Use Method 301 to evaluate statistical significance of the bias.
  - If bias is significant ($0.7 \leq CF \leq 1.3$), then develop a correction factor (CF) is calculated and emission results are multiplied by the CF for final analyte concentration.
  - If CF $\geq \pm$ 30 percent, then the test method is considered to be “not valid.”

FRM 320 Interferences

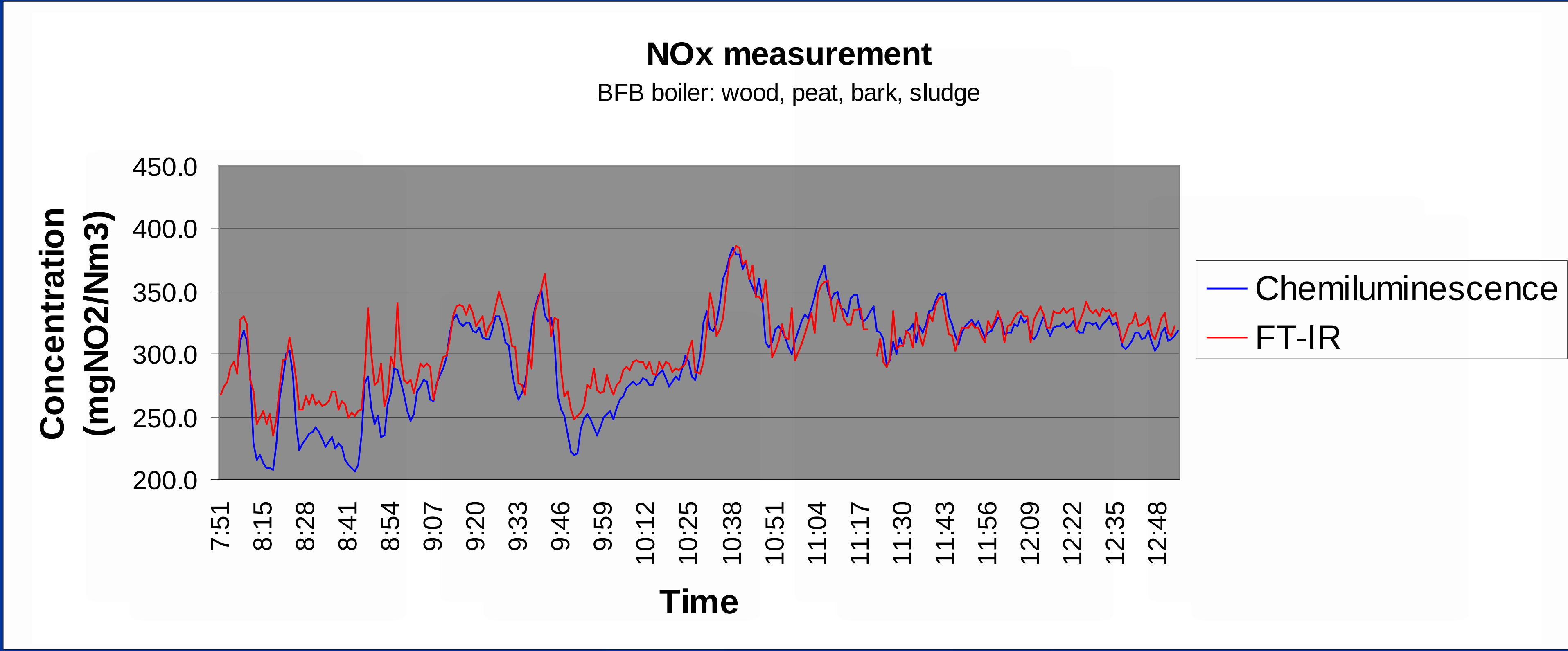
- Analytical Interferences (Background and Sampling)
    - Background interference occurs when unexpected change in background spectra from dirt on lenses, changes in detector sensitivity, changes in infrared source etc. This requires a new background to be generated.
    - Spectral interferences from mostly water and CO_2 which causes interferences with measurement analyte wavelength.

GASMET CEMS APPLICATIONS

Gasmet CEMS and reference measurements:

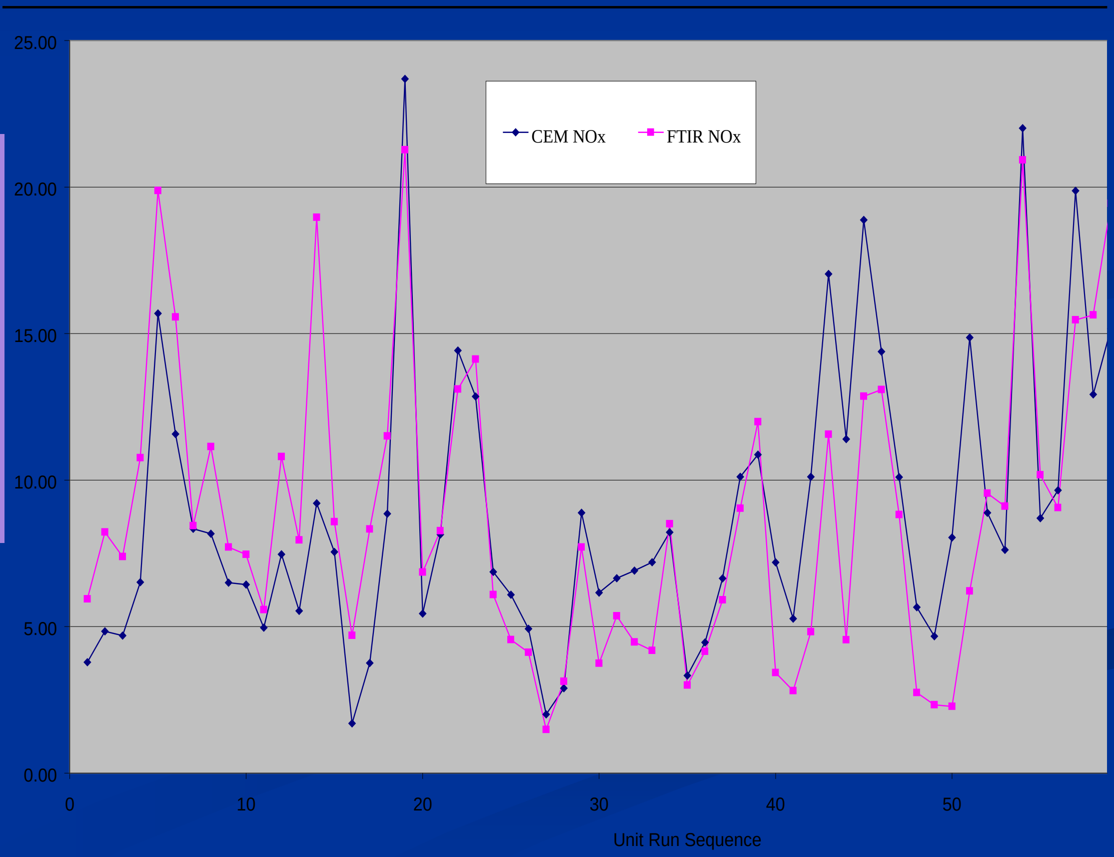


GASMET CEMS APPLICATIONS



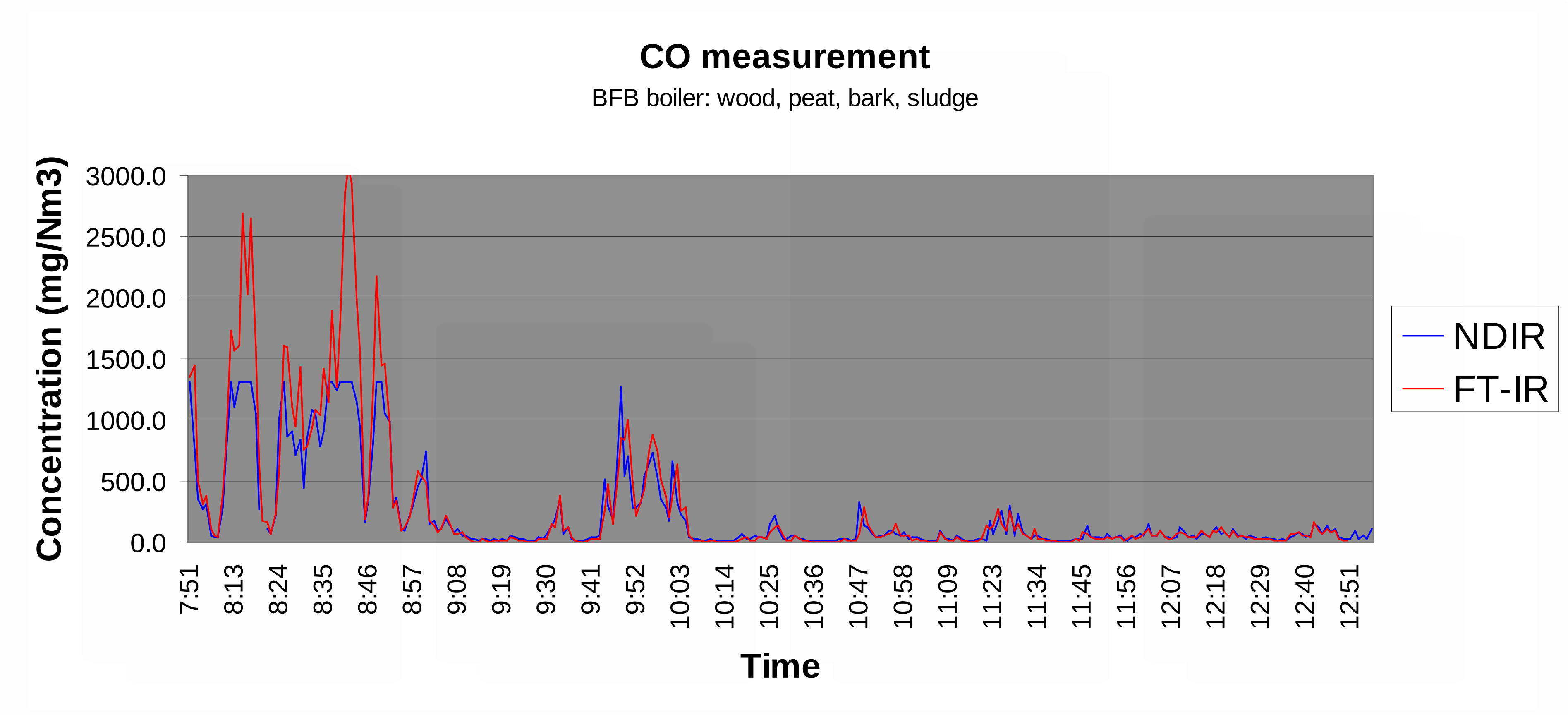
Austin Energy Sandhill Unit #1 Demonstration Results

	CEM NOx	**FTIR NOx**	**FTIR Dev**
Average	9.38	9.25	**-0.29**
Min	1.70	1.19	**-9.45**
Max	24.87	35.65	**10.78**
Std Dev	5.21	5.89	**3.61**
CI			**0.82**

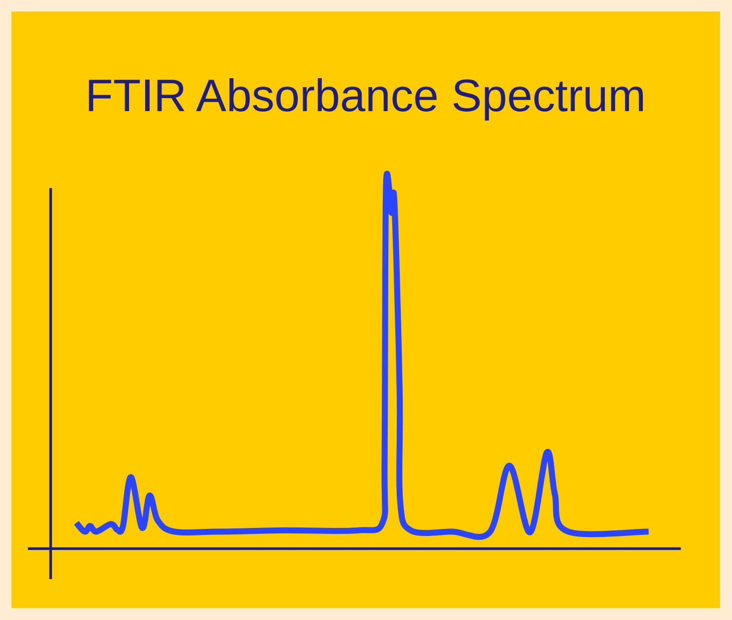


GASMET CEMS APPLICATIONS

Gasmet CEMS and reference measurements:



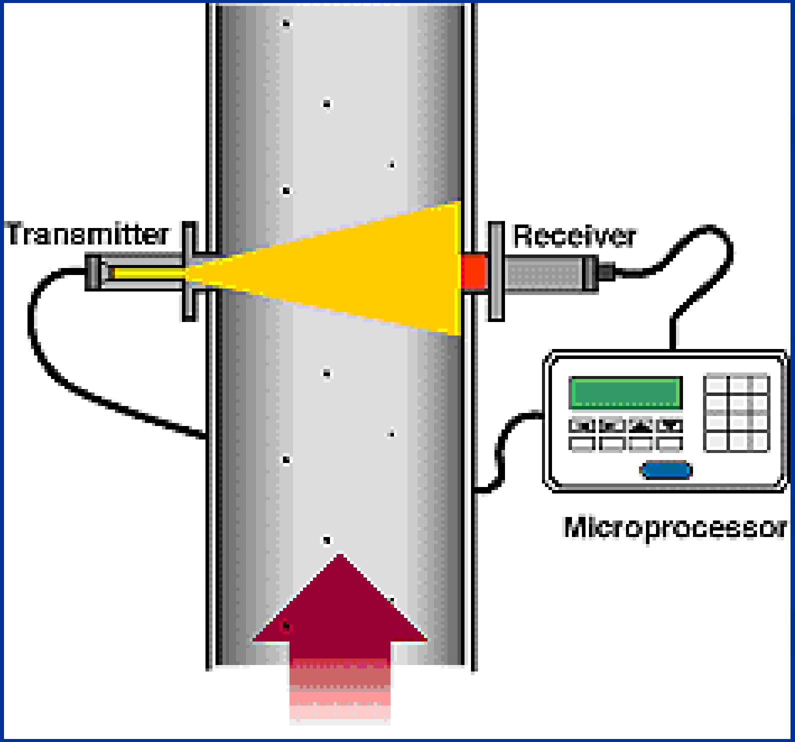
U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 320 and 321 FTIR



U.S. EPA APTI

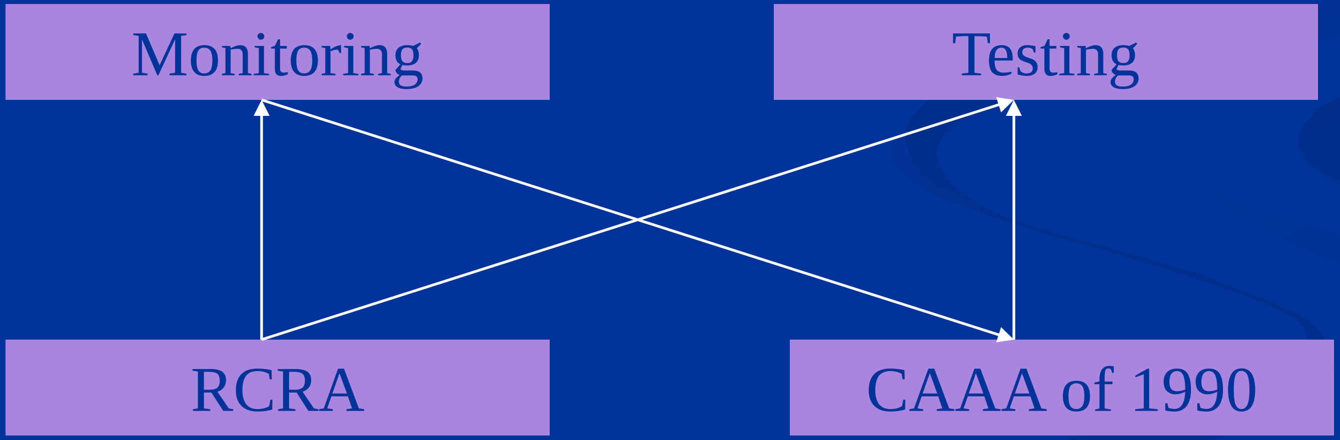
Compliance Test and Source Test Observation

CEMs for Hg, PM, Multi-metals, and HCl



Why is EPA Requiring Development of New CEMS?

- Control of hazardous air pollutants (HAPs) through the MACT program!



Monitoring

Testing

RCRA

CAAA of 1990

Emission Standards for Existing Incinerators

Dioxin/Furan	0.20 ng/dscm (TEQ)
Particulate Matter	69 mg/dscm (0.30 gr/dscf)
Mercury	50 ug/dscm
Metals (Cd,Pb)	270 ug/dscm
Metals (As, Be, Cr, Sb)	210 ug/dscm
$HCl + Cl_2$	$280 ppm_v$
CO	$100\ ppm_v$
HC	$12\ ppm_v$

Implications of MACT Standards

- Combustion system upgrade
- Air pollution control upgrade
- Continuous emission monitoring
- Permitting
- Testing
- Operational

CAAA of 1990 MACT

Monitoring	Process	Temperature, pressure, flow feed constituents
	Process or CEM CEM	HCl, Metals PM, Hg, CO, O_2, THC
Testing	Confirmation Test (Normal Operations)	1/18 or 30 Months
	Comprehensive Performance Test	1/3 or 5 Years

Monitoring Hierarchy (Three Tiered Approach)

- Tier 1: CEM for HAPs
- Tier 2: CEM for HAP Surrogate/Sum Operating Limits
- Tier 3: Feedstream and Operating Permit Limits With Periodic Testing

What Are the Drivers To Use CEMS?

- CEM Emphasis in Draft MACT Regulations
  - Hg, PM, THC, CEMS Required
  - Metal, HCl, and Cl_2 CEMS Optional
  - No VOC, SVOC CEMS Proposed
- CEMS Provide Stakeholder and Regulatory Assurance
- CEM Data Can Be Used For System Optimization
- CEM Technologies Are New and Changing…

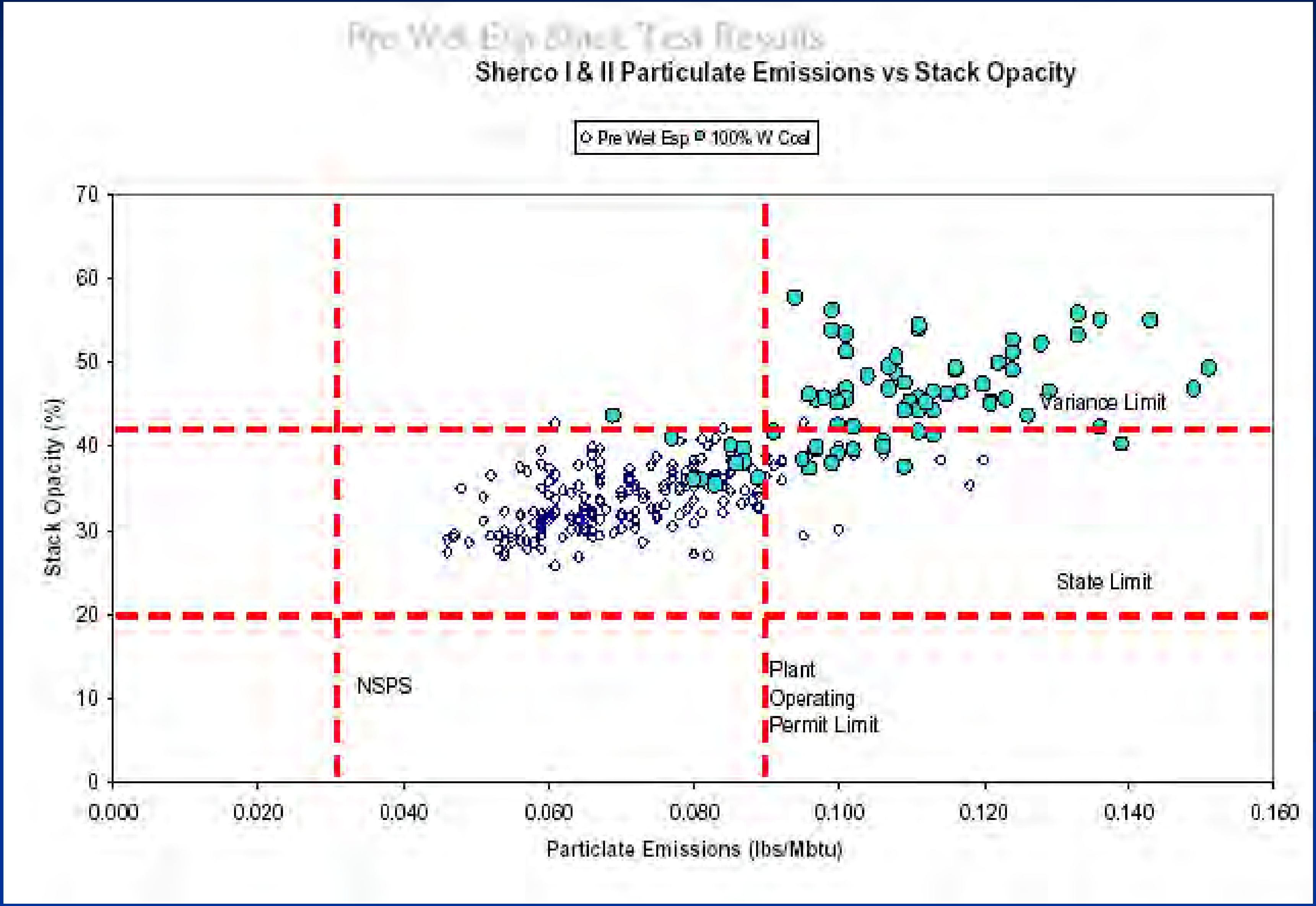
Use of CEMS

HAP	CEM Available
HCl/Cl_2	Yes
PM	Yes
Hg	Yes?
SVM (Pb, Cd)	Yes??
LVM (Sb, As, Be, Cr)	Yes??
Dioxin/Furan	No
Other Toxic Organics (PIC's)	CO/THC-Yes

Why are PM CEMs Important?

- Opacity correlates poorly to PM emissions
  - No less than 14 NSPS have opacity monitoring
  - All States have opacity monitoring
  - Many MACT require COMS as PM surrogate
  - PM CEMs can address the shortfalls of COMS
- Title V CAM plans
- Wet stack PM monitoring
- Utility & Industrial Boiler MACT
- HWC & Portland Cement MACT
- New coal-fired power plant permits
- Fine PM Transport Rule

Opacity vs PM Emission Conc.



Historical Perspective

- 1964 – German Federal Law for Citizens
  - Continuous "dust" monitoring of industrial plants
  - No "dust" monitors were yet available
  - Started monitor development and field study
- 1974 – German Federal Law of Env. Protection (new plants)
- 1983 – German power plants
- 1990 – German waste incinerator
- 1990's – UK requires "dust" monitoring

Historical Perspective (B)

- 1970's U.S. EPA does several correlation studies
- 1975 – EPA Promulgates PS-1 for COMS
- 1976-77 – University of Windsor field study
    - 2 opacity monitors
    - 1 light scatter monitor
    - 1 charge transfer monitor
    - 1 beta gauge monitor
- 1980 – Last EPA funded study on PM mass concentration monitor

Historical Perspective (C)

- 1995 – EPA OSWER begins looking at PM CEMs for HWC MACT
  - 3 field evaluations
  - Proposed PS-11 in April 1996

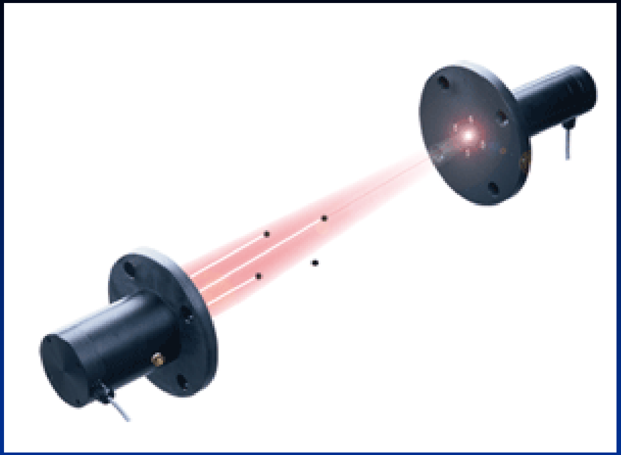
- 1997 – EPA OSWER NODA
  - Second proposed PS-11 in December 1997

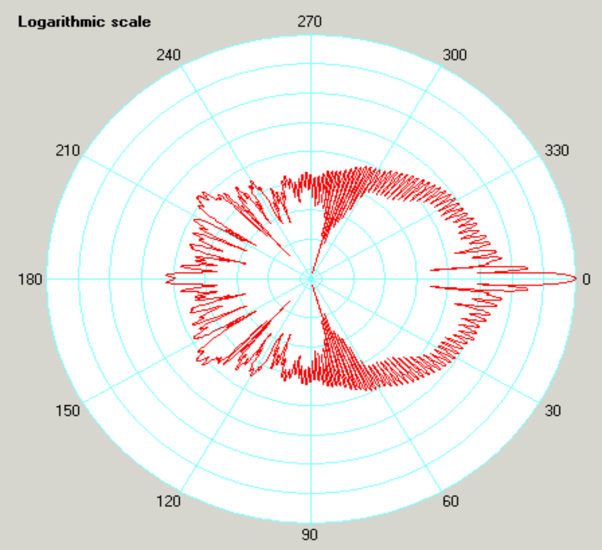
Historical Perspective (D)

- 1999 – EPA OAQPS EMC does field study

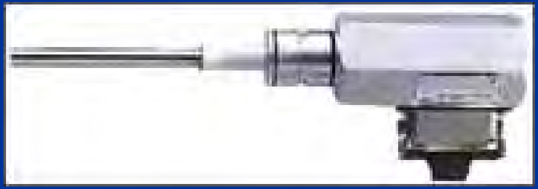
- 1999 – Tampa Electric Consent Decree – 1 PM CEM for 2 year demonstration – installed Feb. 2002
- 2001 – EPA reproposes PS-11 in December
- 2003 – Dominion Energy and WE Energy Consent Decrees – 19 boilers will have PM CEM; final PS-11 soon

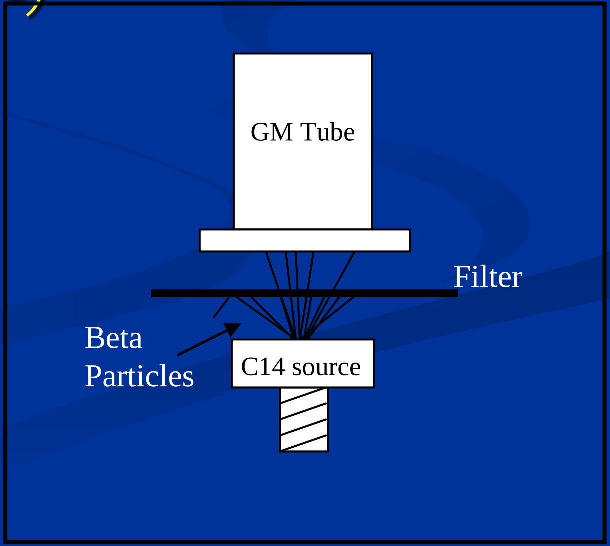
Types of PM CEM





- Light scatter
  - Forward, side, backward
- Beta Gauge
- Probe Electrification (charge transfer)
- Light Extinction (opacity)
- Optical Scintillation





GM Tube

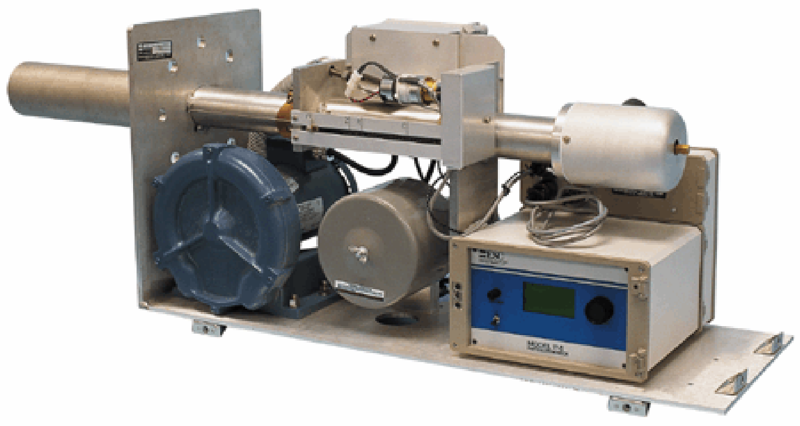
Filter

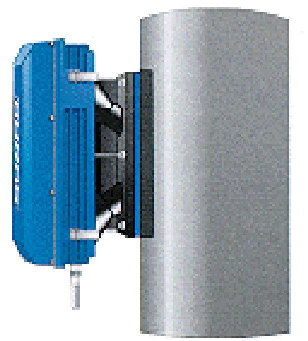
Beta Particles

C14 source

Typical Light Scatter PM CEMs

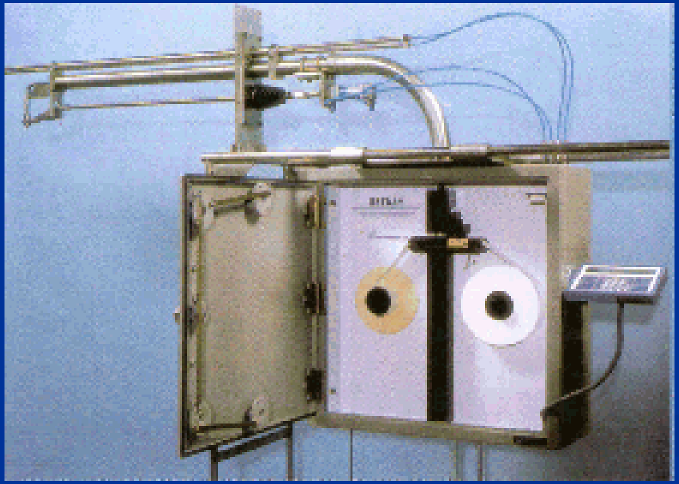
- Sigrist KTNR & CTNR
- Durag DR-300-40
- ESC P5
- Sick RM210, FW 100, FWE 200
- Grimm Technology 6300
- Teledyne ML 300L





Beta Attenuation PM CEMs

- MSI BetaGuard PM
- Durag F904K
- Environment S.A. Beta 5M

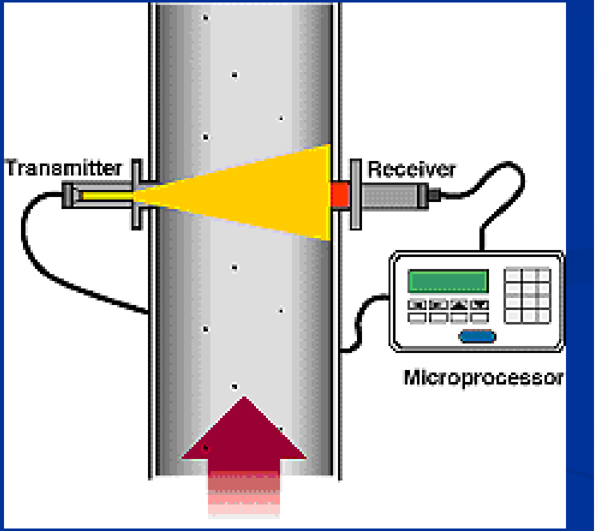


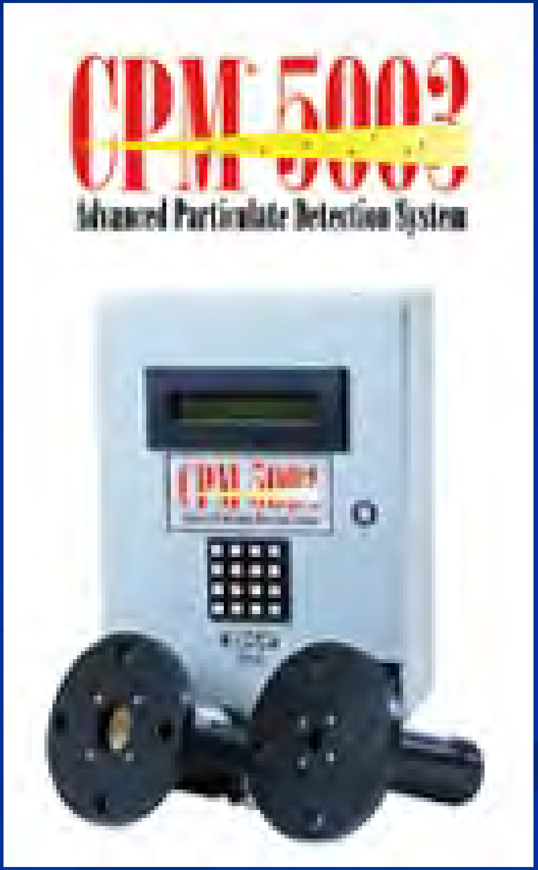
Probe Electrification

- PCME DustAlert
- Auburn Triboguard
- Codel StakGard
- DataTest 201LP
- FilterSense ProFLOW

Optical Scintillation

- BHA CPM 5000
- PCME Scintilla SC600





Recent Opacity CEMs

- Land Combustion 4500
- Durag DR-280 and 290
- KVB Enertec MIP
- ML/USI 560

- Rosemount OPM 2000R
- Phoenix OPAC 20/20
- Sick OMD41
- TECO 440
- DataTest 1000

Light Scatter Adv./Disadv.

- Easy to install
- Low maintenance
- Sensitive to low PM concentration
- Not restricted to visible light spectrum
- Low price $10-15,000
- Effective after FF or multi-stage APC

- Measures secondary properties of PM
- Adversely affected by
  - Particle size, density, shape change
- IR light better than visible light
- Measures liquid drops as PM; can't be used after a scrubber
- Must correlate output to RM measurements

Beta Gauge Adv./Disadv.

- Direct measure of PM concentration
- Not affected by particle characteristic changes – use at multi-fuel fired boilers
- Designed to work in wet stack applications – use after scrubber
- Lower cost of ownership

- More difficult to install
- Sample extraction and transport must be done properly
- Expensive $50-75,000

Probe Electrification Adv./Disadv.

- Simple to install
- Sensitive to low PM concentration
- Inexpensive <$5,000
- Effective as bag leak detectors

- Adversely affected by
  - Particle charge (don’t use after an ESP)
  - Particle size and velocity changes
- Measures liquid drops as PM; can’t be used after a scrubber
- Difficult to correlate to mass emissions

Opacity Adv./Disadv.

- 10,000+ already installed
- Measures opacity

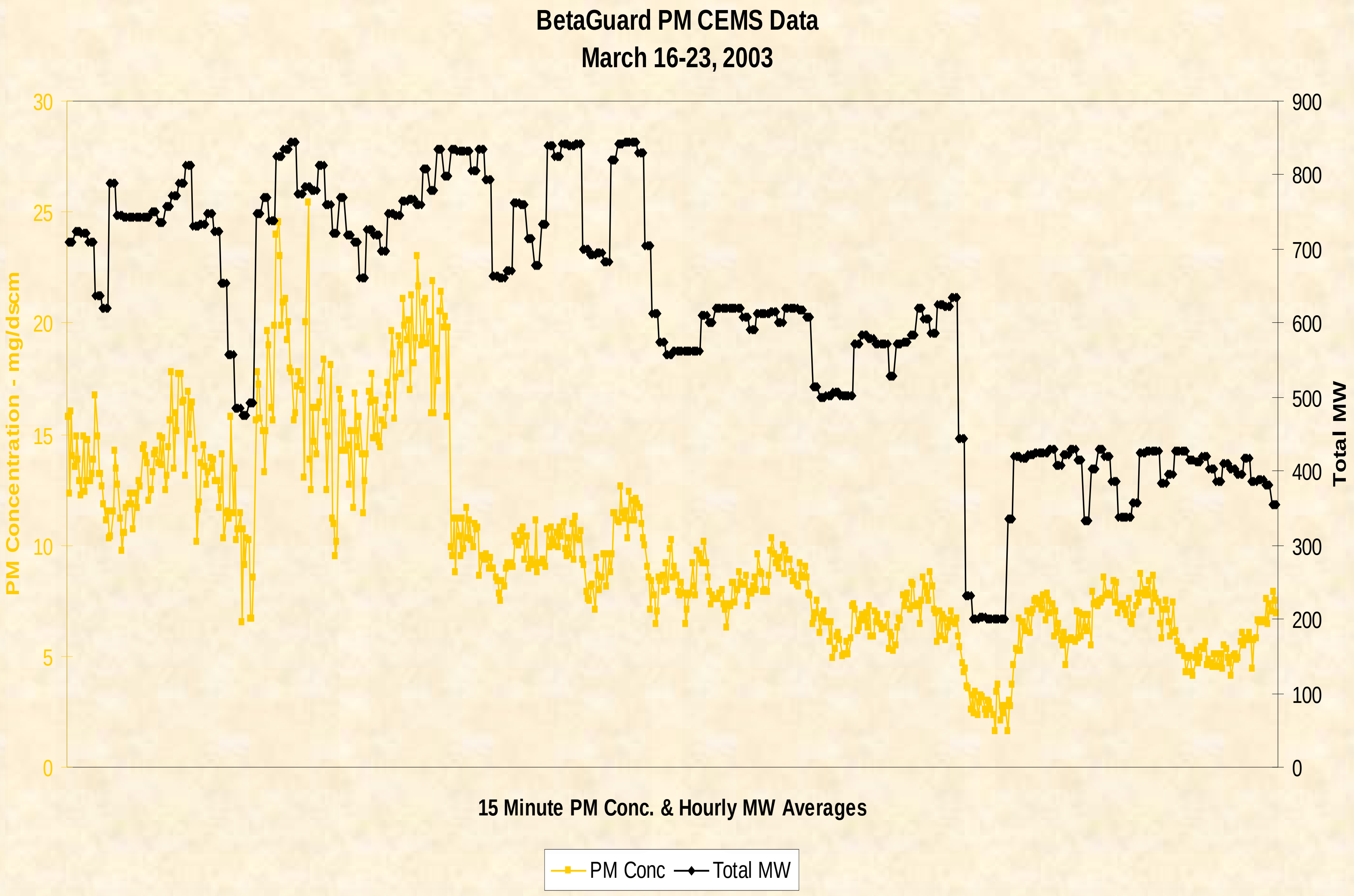
- Measures attenuation of light
- Adversely affected by
  - Particle size, shape, density changes
- Restricted to 500-600nm by PS-1
- Measures liquid drops as PM
- Not sensitive to low PM concentration <20mg/m3
- Cost more than a light scatter PM CEM
- Correlation to mass conc. not linear

Optical Scintillation Adv./Disadv.

- Easy to install
- Low maintenance
- Not affected by dust buildup on windows or misalignment
- Low price $10,000

- Not sensitive to low PM concentration
- Doesn't detect particles $< \sim 2\mu m$
- Adversely affected by particle density change
- Measures liquid drops as PM
- Must correlate output to RM measurements

BetaGuard PM Data



CEMS For PM

- Monitors Are Commercially Available
- Several Monitors Have Been Certified by TUV (German “Technical Inspection Agency,”)
- They Are Used For Compliance in Germany
- Conclusion: Monitoring Appears Feasible With Current Available Instruments

CEMS For Total Mercury

- One Monitor Is Commercially Available And Nearing TUV Certification
- Several Other Monitors Are Under Development
- Conclusion: Compliance Monitoring for Total Mercury Appears To Be Feasible

CEMS For HCl

- Several Monitors Are Commercial Available
- Several Have TUV Certification, But Not For Cl_2
- Conclusion: Compliance Monitoring Appears To Be Feasible With Currently Available Instruments

CEMS For Cl_2

- At Least One Monitor Is Commercial Available
- This Monitor Has TUV Certification
- Conclusion: Compliance Monitoring Appears To Be Feasible With Currently Available Instrument

CEMS For Multi-Metals

- Several Technologies Are Under Development, One Is Commercially Available
- Several Prototypes Have Been Field Tested By EPA/DOE
- <u>Conclusion:</u> Compliance Monitoring Appears To Be Feasible. Performance on Integrated, Manufactured Instruments Is Unknown

CEMS For Organic Compounds

- One Mass Spectrometer Based Monitor Is Commercially Available
- Several Others Are Under Development and Are Close To being Available
- Need Field Testing To Evaluate
- Several Instruments Were Field Tested By EPA/DOE
- <u>Conclusion:</u> Compliance Monitoring Appears To Be Feasible For VOCs, maybe For Some SVOCs

PM CEMS

- Opacity Monitors
- Optical Attenuation
- Forward/Back Light Scattering
- 90^o Light Scattering
- Triboelectric Effects
- Beta Transmissivity
- Acoustic Energy Monitors
- Tapered Oscillation Element Microbalance

PM CEMS Beta Attenuation Vendors

- Durag F-904K Beta Attenuation
- Environment SA 5M Beta Attenuation
- MSICEMS BetaGuard Beta Attenuation

PM CEMS Light Scatter (Extractive/In-Situ) Vendors

- Sigrist KTNR and CTNR (Extractive)
- Durag DR-300-40 (In-Situ)
- ESC P5 (In-Situ)
- Sick RM210 and FW 100/200 (In-Situ)
- Grimm Technologies 6300 (In-Situ)
- Monitor Labs 300L (In-Situ)

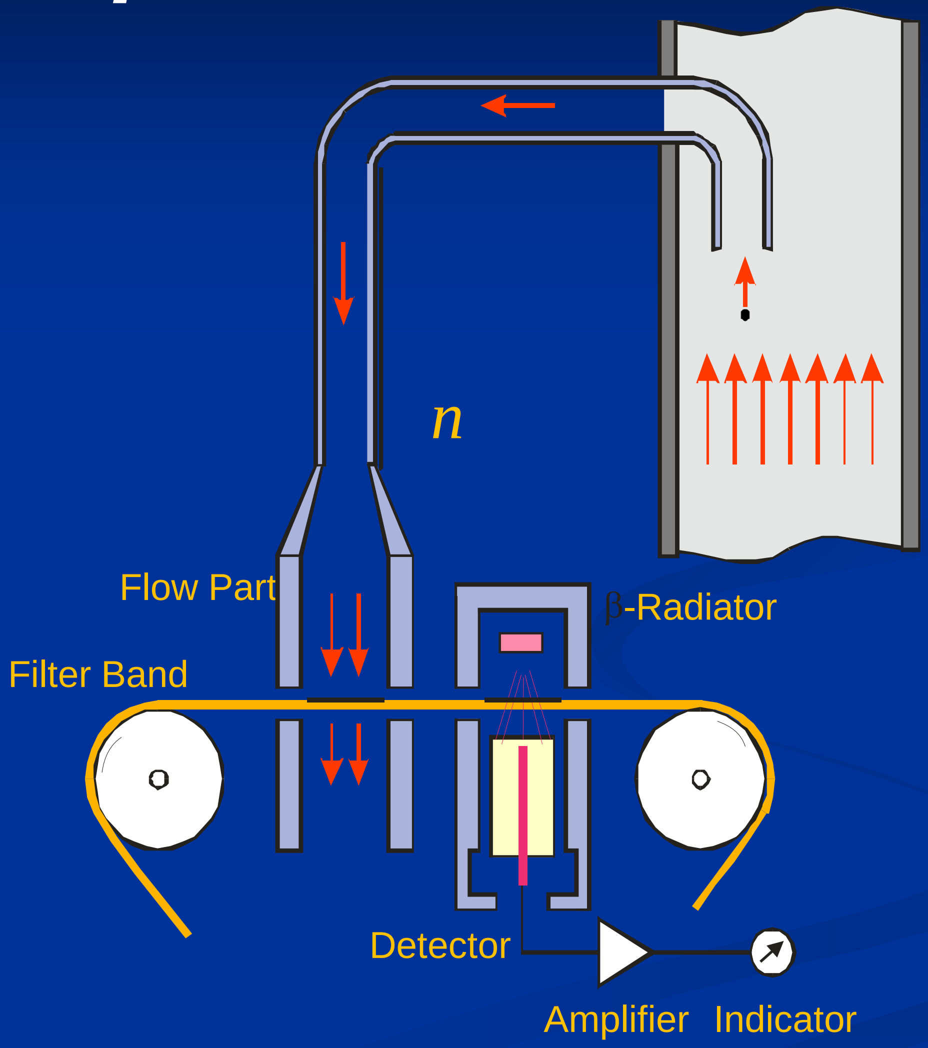
PM CEMS Scintillation Vendors

- BHA Group CPM 5000
- PCME Scintilla SC 600

PM CEMS Other Vendors

- Insitec Tess In-Situ/Extractive Laser Light Extinction-Scatter
- PCME Dust Alert 90 Electrostatic Induction
- Auburn International TriboGuard III Triboelectric
- Codel Stakgard Triboelectric

β-Ray-System


n
Flow Part
β-Radiator
Filter Band
Detector
Amplifier
Indicator

Type: β-Ray

Method: Extractive/Dynamic/Isokinetic

Measurement Value: mg/m^3 Dust Concentration

Calibration in mg/m^3 possible: yes (VDI 2066) / required

Dependent Values: V/V$_0$ Isokinetic Measurement required

Isokinetic Measurement: Required

Wet Stack Application: Yes (additional Condensor and Dryer required)

Approvals: TÜV / no EPA (opacity required)

Advantages / Disadvantages: No direct online values
- only integrated values available
- measurement cycle depends on dust level (stack applications 30 ... 60 min)
- short maintenance cycles (3 - 5 days)
- high maintenance costs
- large investment

Dependent Values: V/V_0 Isokinetic Measurement required

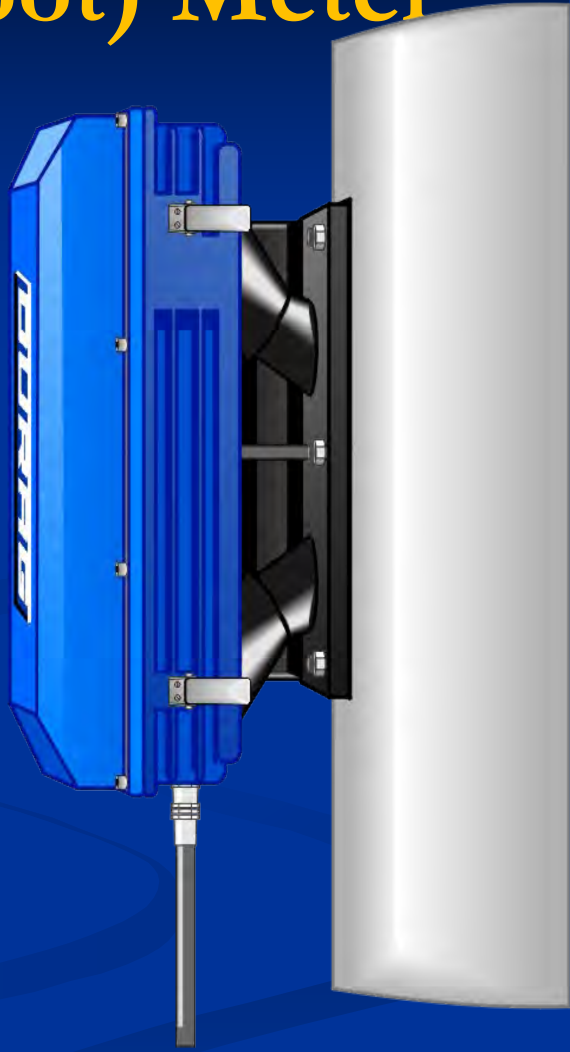
Isokinetic Measurement: Required

Wet Stack Application: Yes (additional Condensor and Dryer required)

Advantages / Disadvantages: No direct online values
- only integrated values available
- measurement cycle depends on dust level (stack applications 30 ... 60 min)
- short maintenance cycles (3 - 5 days)
- high maintenance costs
- large investment

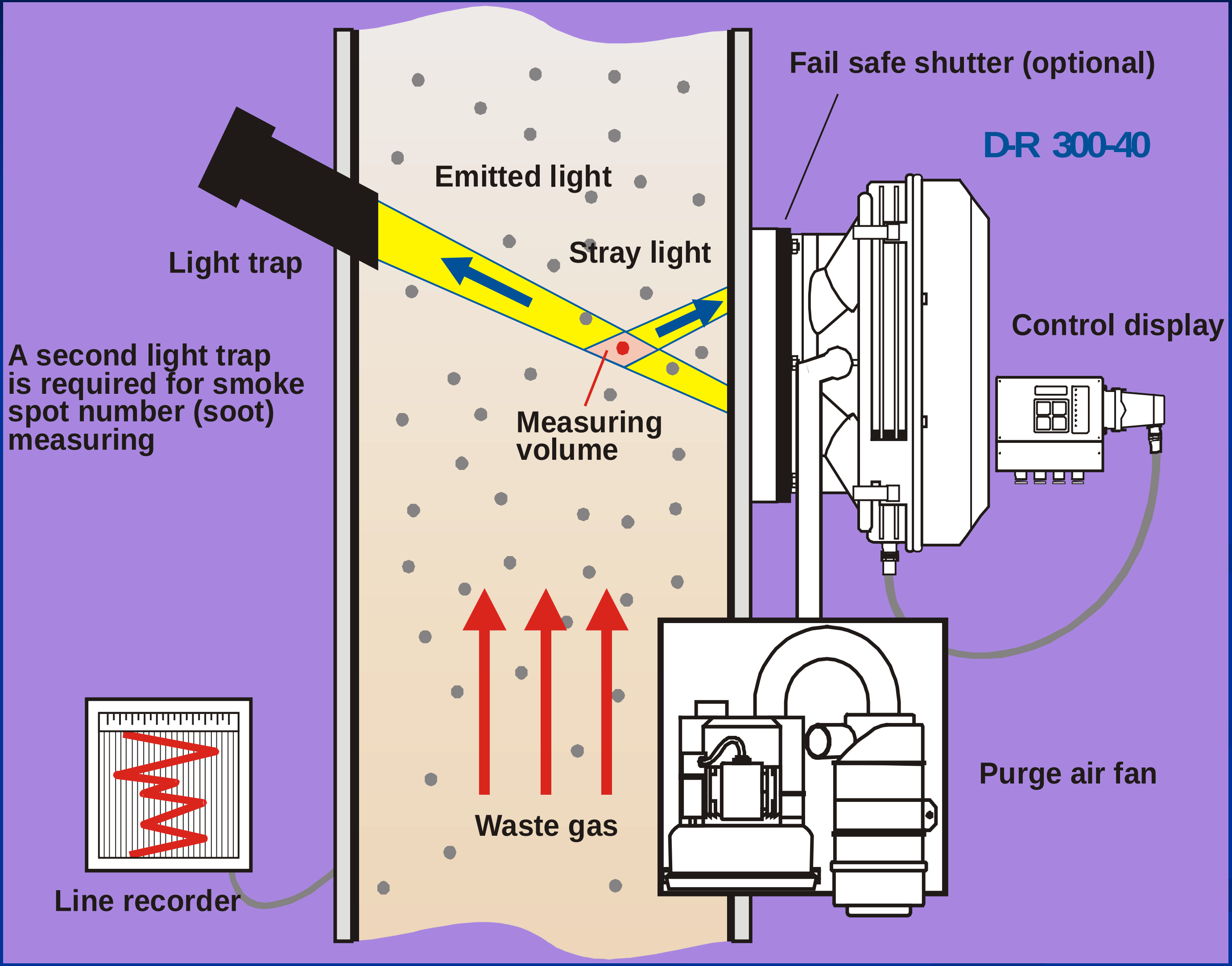
Investment Approx. US$ 60,000.- (100,000.- for wet stacks)

D-R 300 Dust Concentration and Smoke Spot Number (Soot) Meter

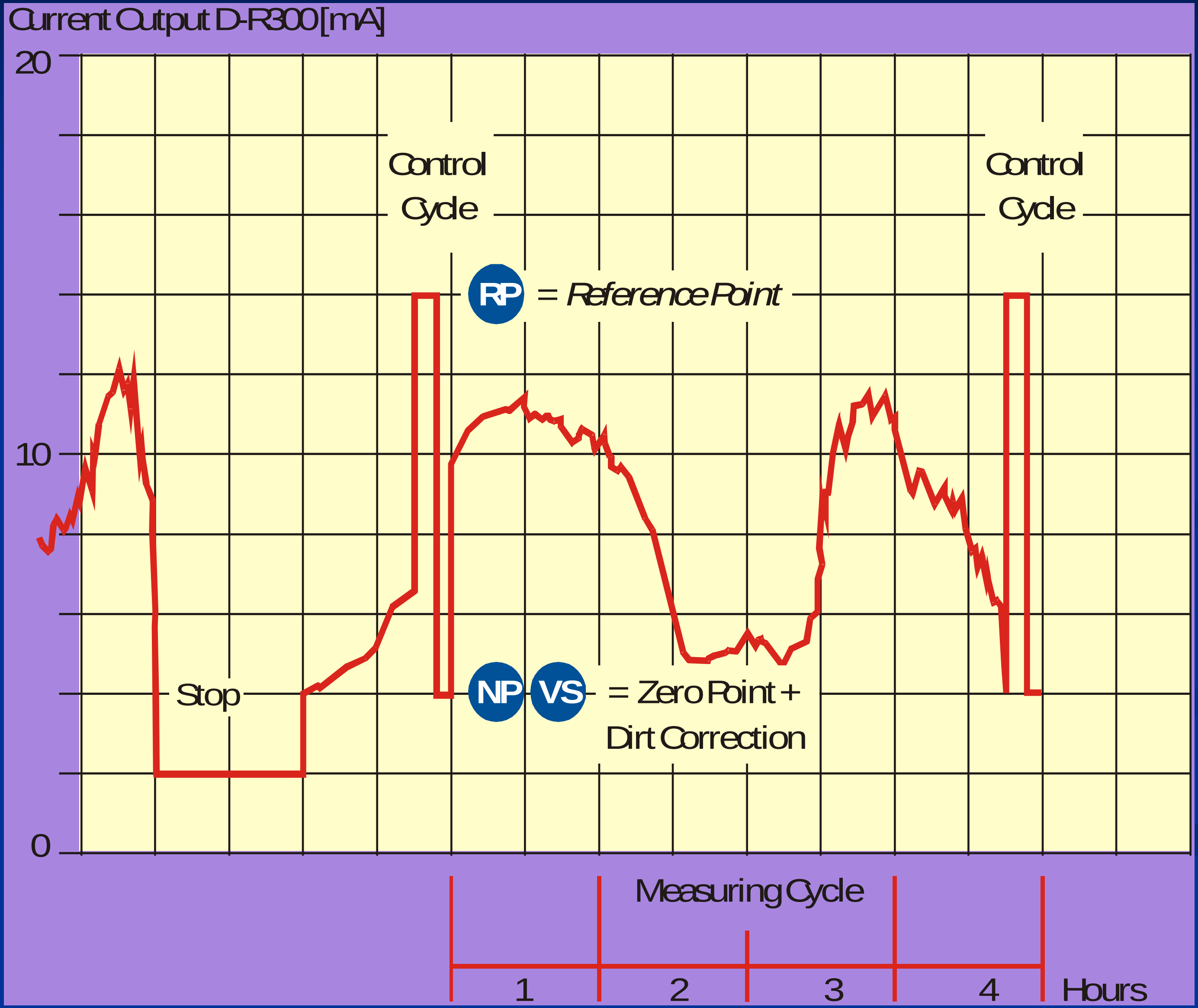


- In-situ measuring directly in the flue gas flow
- Digital evaluation of the measuring signals
- High-performance microprocessor technique and software
- Automatic system tests and correction of measuring values
- Autocalibration in 4-h-cycles
- Optics and electronics in a hermetically sealed housing
- Maintenance-friendly due to optimal purge air fan in front of the heated boundary surfaces
- Direct access to all parameters by way of the control display
- Simple adjustment without special devices
- Automatic cut-off, 250 seconds delay
- Automatic range selection according to 17. BImSchV

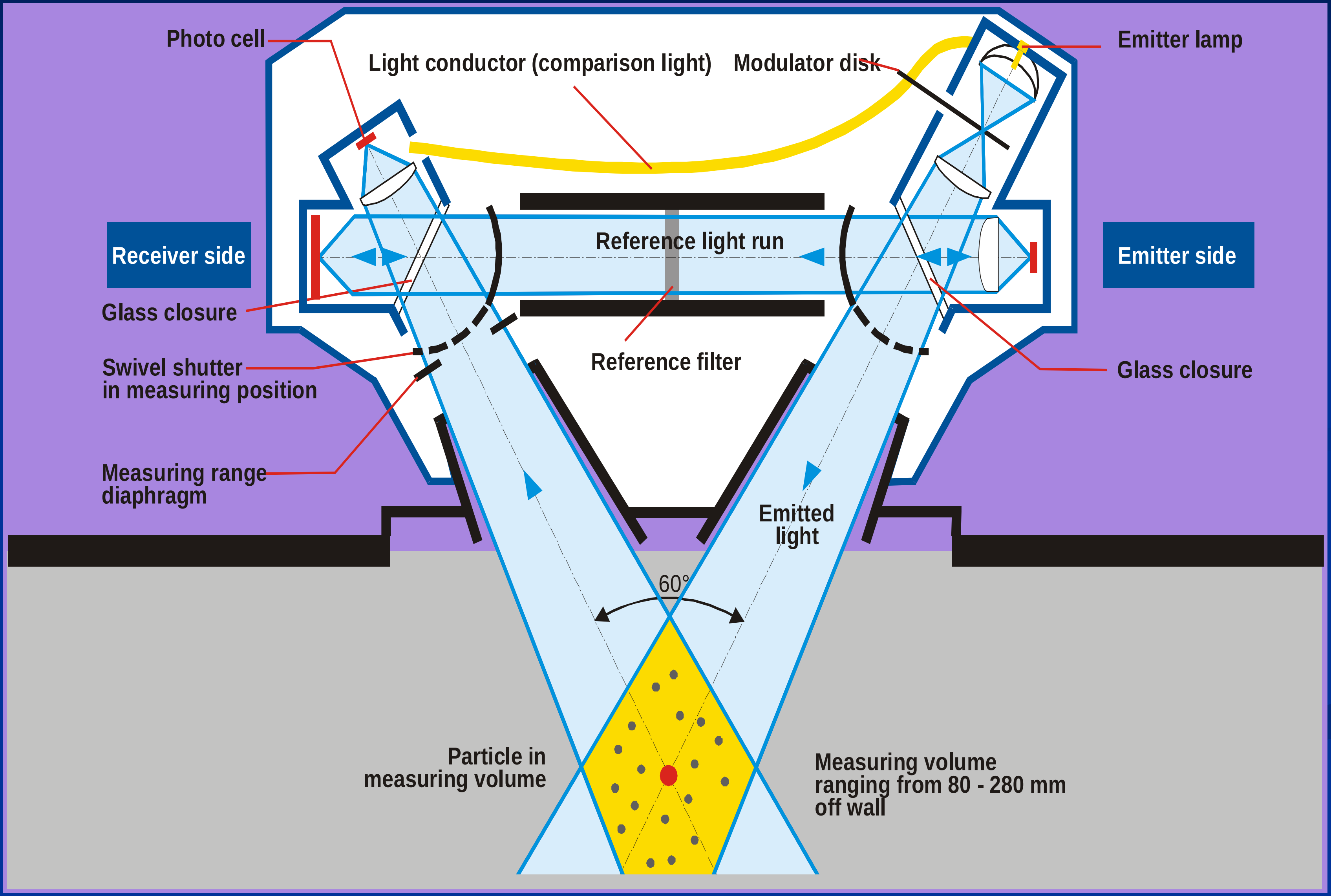
D-R 300 System Components



Measuring and Control Cycle of the D-R 300-40



D-R 300 Optics Diagram



PM Instruments Demonstrated

Rollins	LaFarge	Dupont
Sick Optic	Sick Optic	Durag
BHA	ESC	Sigrest
Environment USA		ESC
		Environment USA

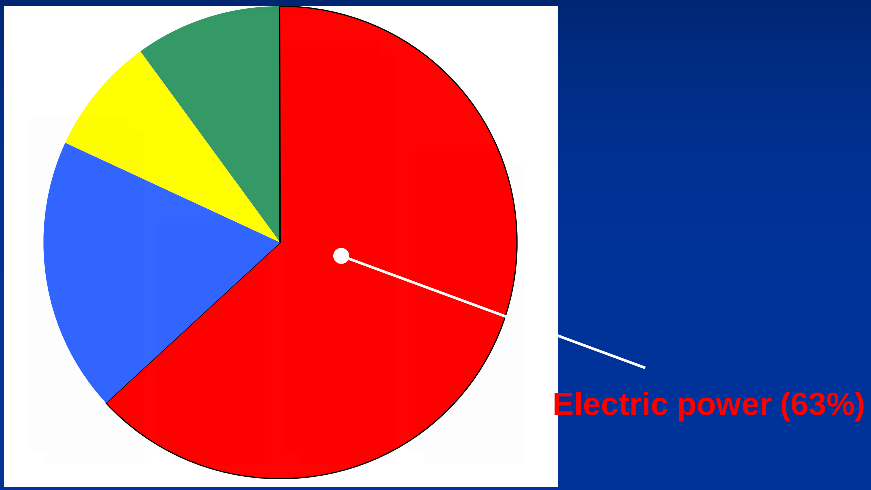
PM CEM User Assessment

- 11 Units Available, Several Have Long-term Application
- $15K-$45 K Unit Cost
- Demonstrations and Certification in Europe
- However, Calibration Concerns

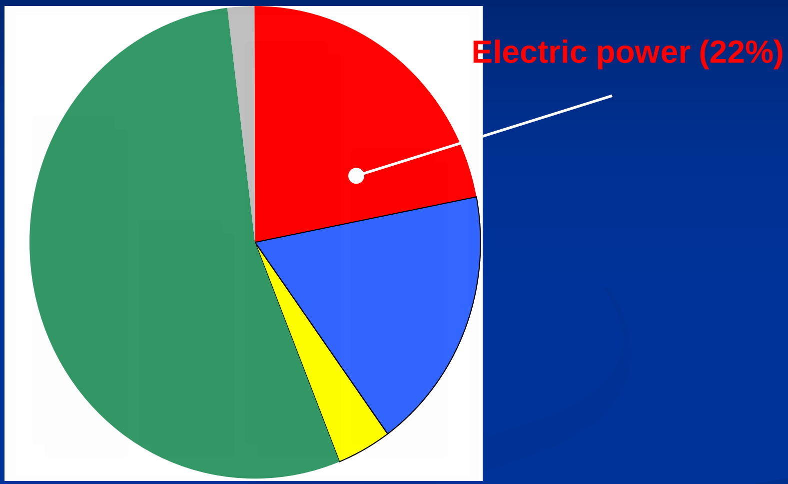
Reducing Power Plant Air Toxics Emissions: Addressing Mercury under Section 112 of the Clean Air Act

Power Sector Emissions

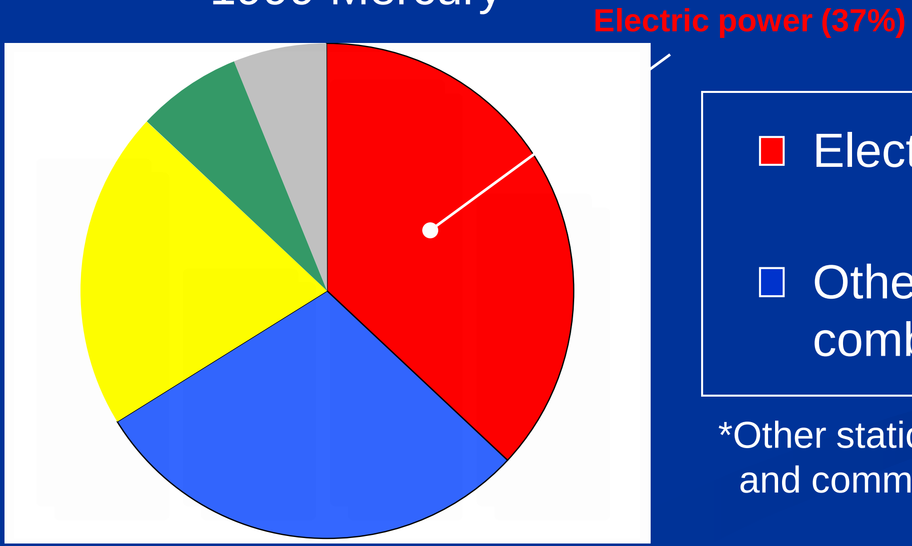
2000 Sulfur Dioxide



2000 Nitrogen Oxides



1999 Mercury



🟥 Electric power

🟦 Other stationary combustion *

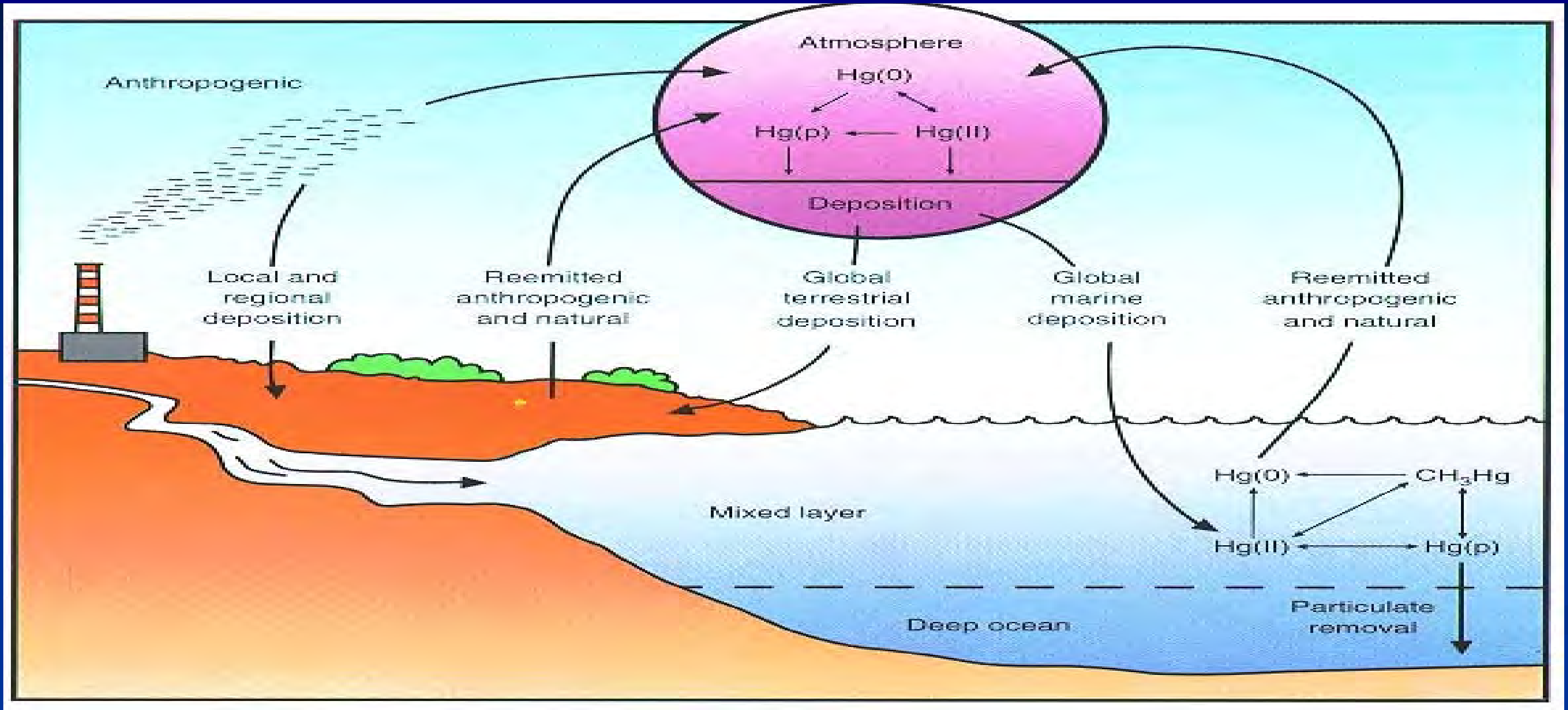
🟨 Industrial Processing

🟩 Transportation

⬜ Miscellaneous

*Other stationary combustion includes residential and commercial sources

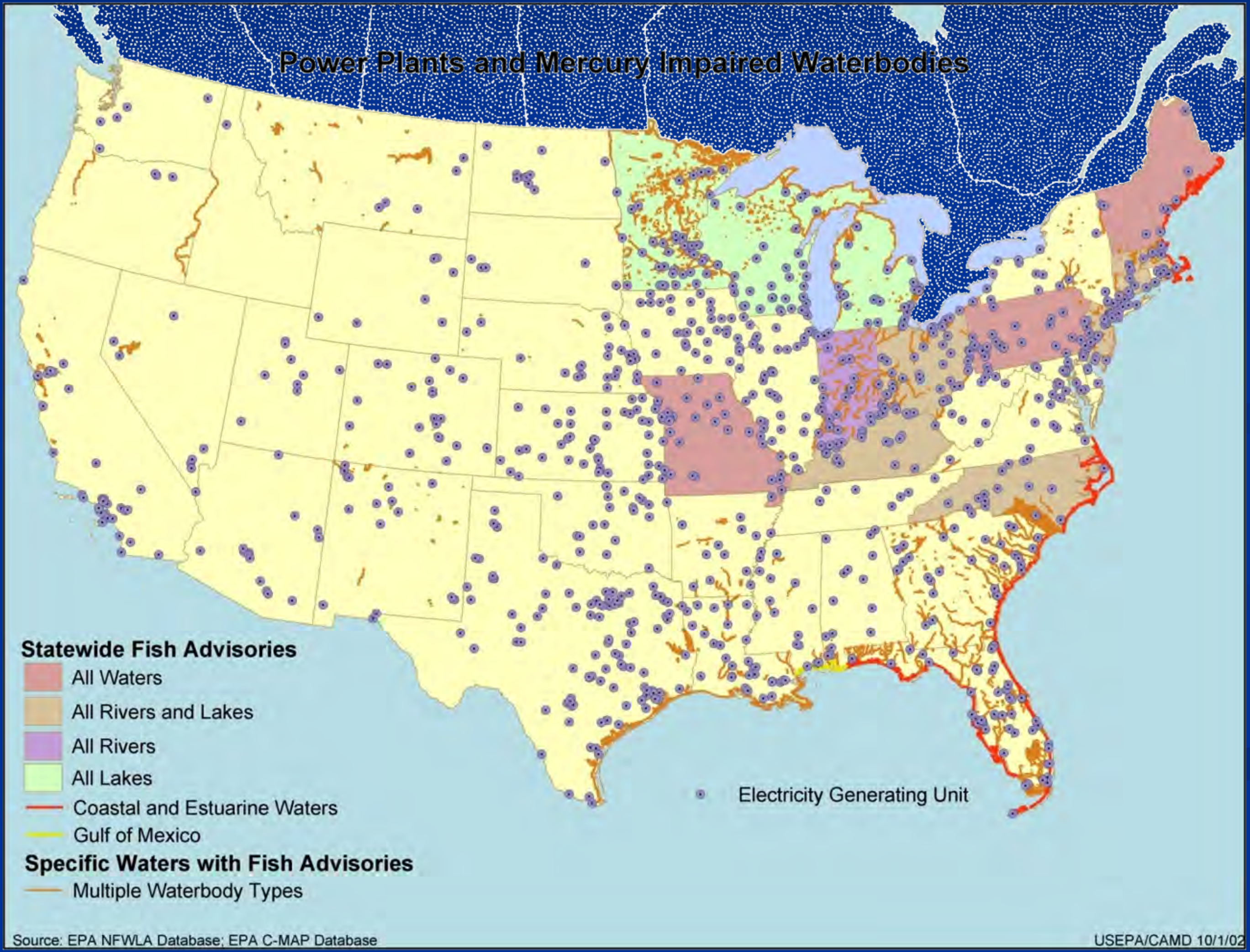
Mercury Deposition is a Nationwide Issue



- In 1999, coal-fired power plants, the largest source of mercury in the US, emitted 48 tons of mercury (approximately 40% of total)
- EPA estimates that 60% of the mercury falling on the U.S. is coming from current U.S. man-made sources
- Mercury is transported regionally and globally, and reducing deposition in the U.S. to acceptable levels will require action by other countries to reduce their emissions
- As U.S. mercury emissions are reduced, mercury emitted in other countries becomes an increasingly large percentage of our domestic problem
- Mercury emissions from the rapidly developing Pacific Rim economies, which are dependant on coal for much of their new electric generating capacity, magnifies the U.S. domestic problem

Challenges: Mercury Deposition Impacts

- Fish consumption is the primary route of exposure to mercury
- 44 States currently have fish advisories due to mercury contamination.



Source: EPA NFWLA Database; EPA C-MAP Database

Overview of Section 112 MACT Standards

- Regulation of source category pollutant emissions, not air quality
  - Different set of pollutants – 188 distinct Hazardous Air Pollutants (HAPs) - - or ‘air toxics’
  - No ambient standards.
  - EPA sets the emissions limits on sources, not states.
    - Nearing the end of the current program phase: Maximum Achievable Control Technology (MACT)
    - Starting the next phase – Residual Risk standards
  - Clean Air Act is quite prescriptive on EPA deadlines, criteria for setting emissions limits, and source compliance deadlines
- Litigation is frequent

Clean Air Act Section 112 - Governs All MACT Rules

- “Emission control achieved in practice by the best controlled sources” establishes ‘floor’ for new sources

- Average of the top performing 12 percent for existing sources defines the floor emission limit
  - Cost cannot be considered in establishing floor.   Can be considered in evaluating whether controls beyond the floor are appropriate

- Allows for subcategories

- Emissions standard applicable to each source
  - Requires compliance within 3 years, with possible 1-year extension

- Section 112 does not allow trading between facilities to meet the standard
  - Averaging among units at a given facility can be considered

Key Studies Leading to Determination of Whether Utility MACT Regulation was Necessary and Appropriate

- **1990 Amendments required**
  - Study of hazards to public health of HAP emissions from electric utility steam generating units
  - Determination on whether regulation necessary and appropriate
  - Study to have been done by November 1993

- **1990 Amendments also required**
  - Study of mercury emissions from all sources

- **Initiated data collection for mercury**
  - 1999 Information Collection Request (ICR)
  - 112(n)(1)(A) determination delayed until ICR completed

- **National Academy of Science (NAS) report on methylmercury**
  - Mandated by Congress
  - Released in July 2000
    - Confirmed EPA’s RfD for methylmercury (0.1 µg/kg/day)

Summary of Utility MACT Determination

- **EPA announced findings on 12/20/2000**
  - Regulation appropriate and necessary for oil- and coal-fired boilers
  - Regulation not necessary for gas-fired boilers
  - Based on
    - Public health concerns - especially mercury from coal-fired plants
      - Fish advisories
      - Neuro-developmental effects to children exposed in utero
      - Cardiovascular concerns
    - Level of mercury emissions from coal-fired power plants
    - Information that mercury from power plants can be controlled
    - Concerns of nickel from oil-fired plants
  - Determination on health and environmental concerns regarding other HAP was uncertain

Control Technologies for Power Plant Mercury Emissions

- From 1999 data, approximately 1/3 of the mercury in coal was being captured as a ‘co-benefit’ of SO_2 or NO_x control – not intentionally as mercury control
  - Capture by existing equipment ranges from 0 to >95%
  - Capture dependent on coal type
  - Capture dependent on installed air pollution control device

- Activated carbon injection - ACI - (and other new technologies) and optimization of existing technologies could greatly enhance mercury capture and control
  - Full-scale demonstrations completed that quantify removal rates for ACI for bituminous and subbituminous coals
    - Test durations range from a few hours to less than 2 weeks
    - Intermittent removals up to 90% demonstrated; continuous removals averaged approximately 80%
  - No full-scale ACI facility in operation

Other Utility HAP Issues

- Other hazardous air pollutants from coal-fired units
  - Acid gases (e.g., hydrogen chloride, hydrogen fluoride)
  - Trace metals (e.g., arsenic, chromium, lead)
  - Organics (e.g., dioxins)
- Nickel and other hazardous air pollutants (primarily trace metals) from oil-fired units

Public Outreach/Participation

- Public meeting in June 2000 to gain input on what regulatory determination should be
- Stakeholder meetings in March 2001 to determine best format for stakeholder involvement
  - Decided on Working Group under CAAAC
    - Formed for a period of 1 year
    - Presented Final Report to CAAAC on October 30, 2002
    - 31 members
      - Six State/Local/(Tribal) Agency representatives
      - Eight Environmental Group representatives
      - Seventeen industry representatives
  - No consensus reached on issues…but did have good discussions of the issues
  - Materials relating to Working Group (and MACT) posted on Internet

Issues for Utility MACT

- How should we subcategorize the initial source category?
- What should the floor levels be?
  - Variability Issue - How should hourly test data be used to set an achievable longer-term standard?
- What other HAP should be regulated?
- Should the rule go “beyond-the-floor”?
- What should the rule look like?
  - Input- vs. Output-based
  - Emission limit vs. Percent reduction
- How should compliance be determined?
- Same issues for oil-fired units

Summary

- Under settlement agreement, MACT rule must be proposed on or before December 15, 2003
    - Promulgation: December 15, 2004
    - Compliance: December 17, 2007
- Public comment period will follow publication in the Federal Register

- Public Hearings will undoubtedly be requested
  - Single hearing?
  - Multiple hearings in different parts of the country?

Source Monitoring for Hg

- Mercury Emitted In Different Forms
  - Elemental Hg^o
  - HgO
  - $HgCl_2$
  - $(CH_3)_2Hg$
  - CH_3HgCl

Source Monitoring for Mercury

- Five EPA Time-Integrated Test Methods
  - FRM 29/SW-846, Method 0060
  - FRM 101 (Hg in Air Streams)
  - FRM 101A (Hg in Sewage Sludge Incinerators/NESHAP)
  - FRM 102 (Hg in H_2 Streams)
- One Ontario Hydro Method

CEMS For Hg Monitoring

- Elemental Hg
- Non-Elemental Hg (Typically Mercuric Chloride)
- Total Gaseous Mercury
  - Measurement of Elemental Hg and Conversion of Non-Elemental Hg to Elemental Hg
  - CEMS Sensitivity down to 1 ug/m^3 (0.1 ppb$_v$)

Summary of Testing

Test No.	Total Hg	Elemental Hg	Speciated Hg
1	20.3	18.7	1.6
2	23.2	1.0	22.2
3	16.1	3.1	13.0
4	21.9	2.5	19.4
5	16.0	6.4	9.6
6	18.8	7.3	11.5

Mercury CEMS

- **Durag/Verewa Total Mercury Monitor (http://durag.com)**
  - Isokinetic Sampling
  - Treatment of Gas Stream
  - Elemental Hg by UV Photometry
- **ADA Technologies (http://ada.communityisoft.com)**
  - Nonisokinetic Sampling
  - Filter/Thermal Converter
  - Elemental Hg by UV Photometry
- Opsis SE (http://opsis.se)
  - In-Situ Measurement
  - UV Absorption
- PSI Monitor (http://psicorp.com)
  - Dilution Gas
  - Dielectric Barrier Discharge
  - Spectrometer As The Detection Principle

Total Mercury CEM HM 1400 TR, TUV

Maintenance cycle: 3 Month

Measuring range : 0-45 to 0-2000 µg/Nm³

Lowest detection limit: 0,5 µg/Nm³

Sample treatment : Thermocatalytic

Signal output : 4-20 mA, µg / Nm³ dry

Controller : Omron PLC

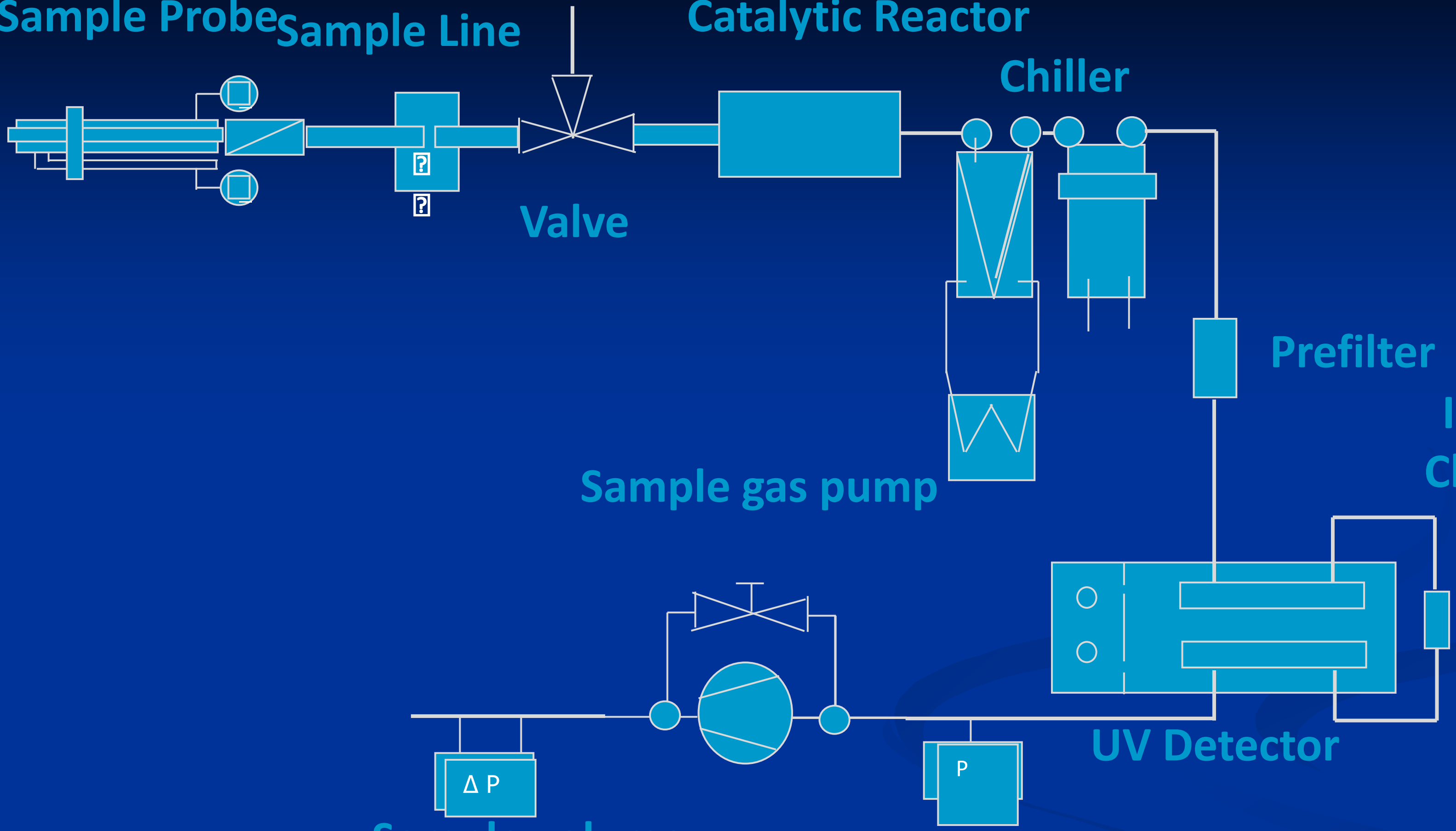
Remote control : via DMS 500 or DMS 285

Failure control: Memory stored

Interference : None

Detector : Dual Beam Photometer

Sample probe : M & C, SP 2000



Sample Probe

Sample Line

Catalytic Reactor

Chiller

Valve

Prefilter

Iodine Charcoal

Sample gas pump

UV Detector

Sample volume control

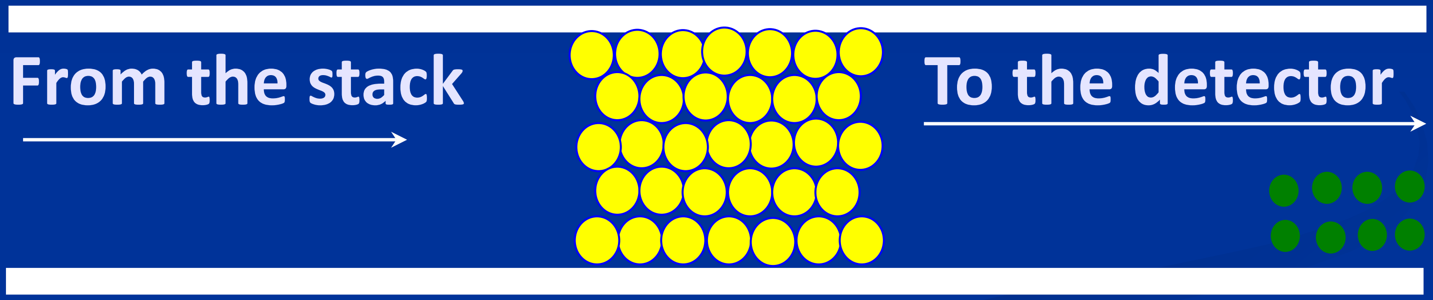
Transmitter

Thermocatalytic Reactor

Function of the thermocatalytic Reactor

- Fixing acid stack compounds like HCl, SO_2
- Chemical reduction of ionic Mercury Compounds

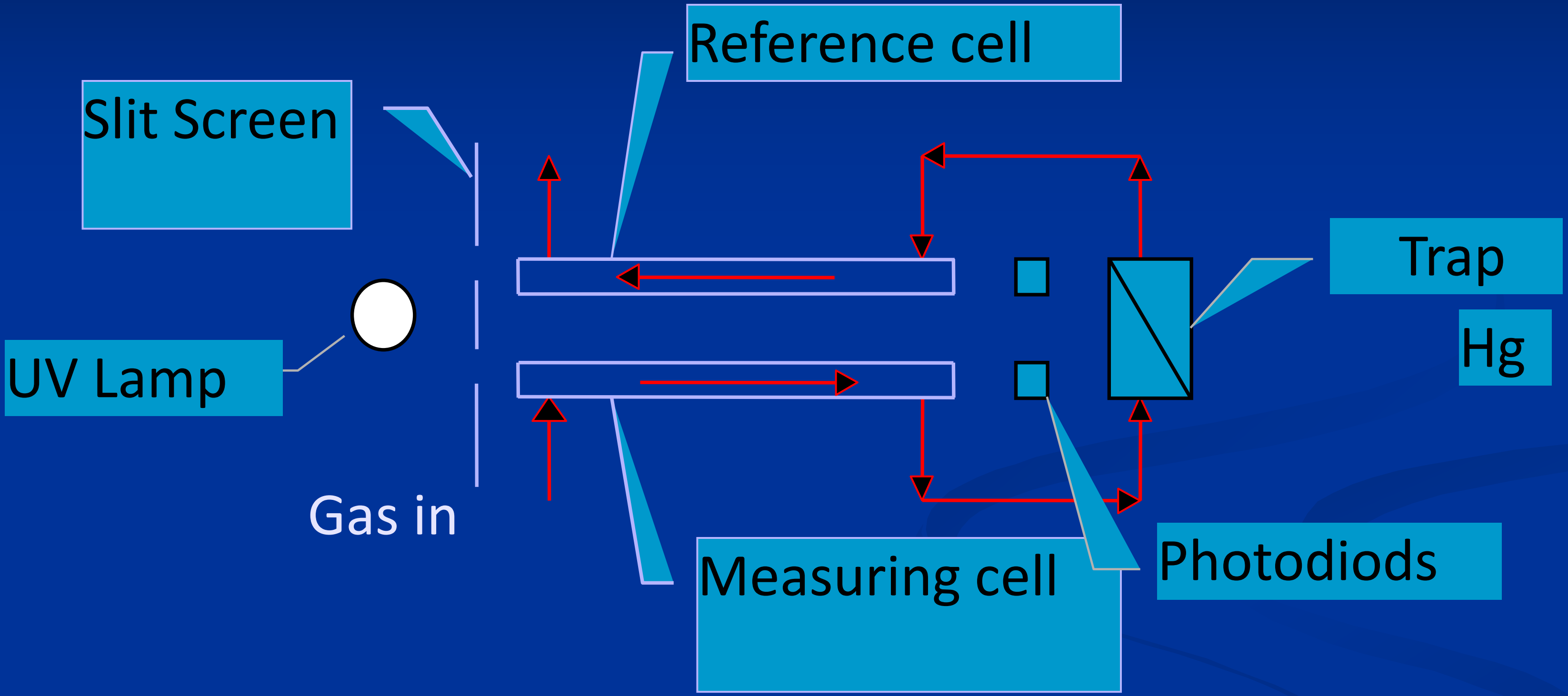
The way how the reactor works



- ● SO_2
- ● HCl
- ● NOx

- ● Hg^{n+}, ionic Mercury
- ● Hg^0, elemental Mercury

The dual beam UV detector


Reference cell
Slit Screen
Trap
Hg
UV Lamp
Gas in
Measuring cell
Photodiods

The Portable Version

Frontview

Rear View

Project Overview

- Mercury CEMS extended period evaluation
- Coal-fired power plants
- Phase I (August 2001-March 2002)
- Phase II (Sept-Dec 2002)
- Phase III (May - July 2003)

Phase III Test Design

- Installation & calibration of CEMS
- Total vapor phase Hg (no speciation)
- Initial RA test series
- Long-term operations (3 months)
- Final RA test series

Test Conditions

- 600 MW coal-fired power plant (2 yr old)
- Powder River Basin coal
- NH_3 injection, SCR, spray dryer, fabric filter
- 2-6 ug/m^3 mercury (expected)
- 1-10 ug/m^3 mercury (observed)
- 35-50 ppm SO_2

CEMS Selection

- Focus on COTS, dry systems
- Chosen by availability, cost, experience
- 4 dry-catalyst CEMS, 1 paper tape/XRF
- Reference method: Ontario-Hydro

Systems Evaluated

System	Sample line	Sample conditioning	Sample concentration	Analysis
Nippon DM-6	ambient	catalyst at stack	No	AAS
Durag HM-1400TR	heated	catalyst in unit	No	AAS
Genesis Quicksilver SkyMonitor	heated	catalyst in unit	No	AAS
OPSIS Hg 200	ambient	dilution probe & catalyst at stack	gold trap	AAS
Cooper X_{act}	heated	none	filter tape	XRF
EPRI QSEM	na	na	in-stack charcoal trap	off-site

Nippon DM-6

Opsis Hg 200

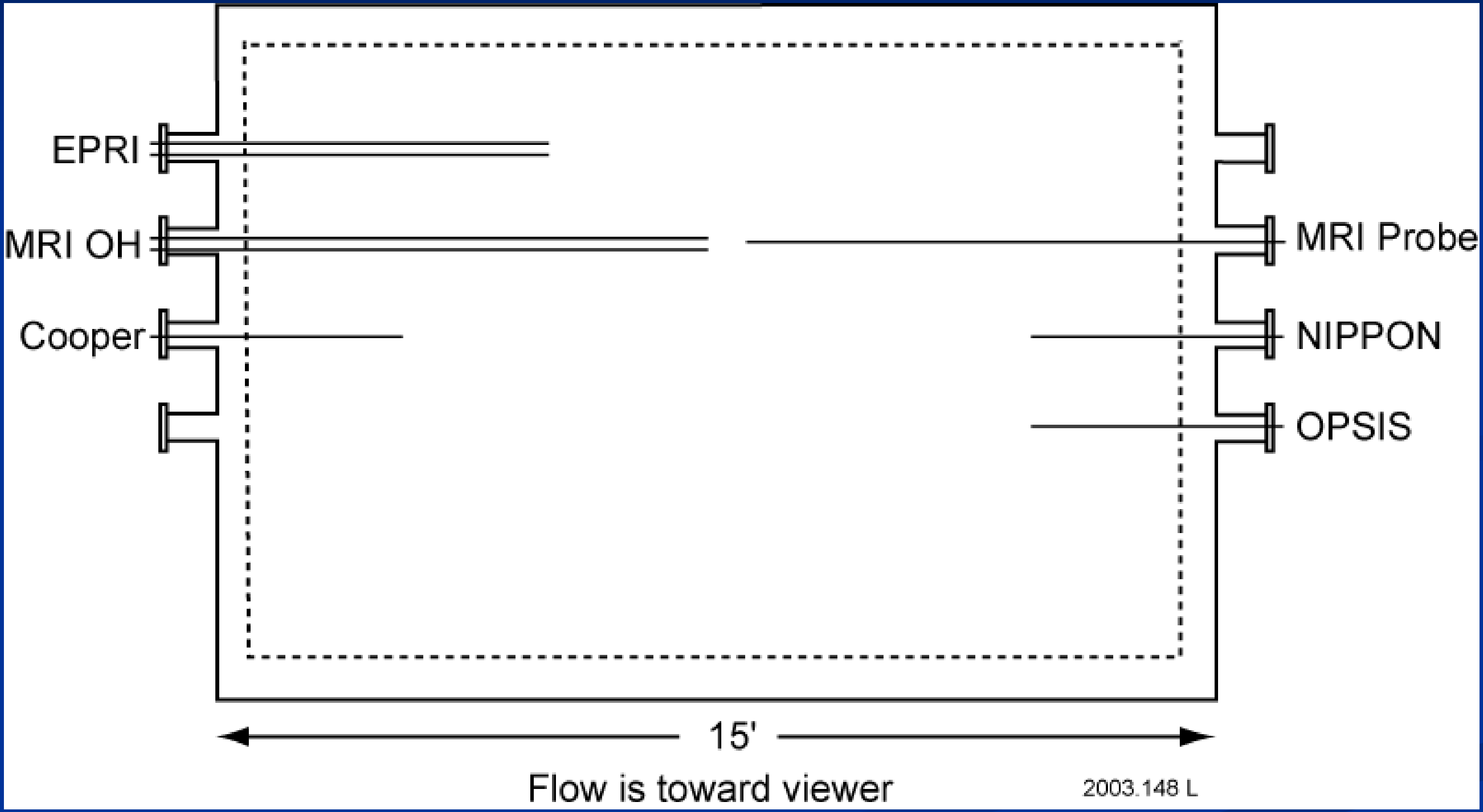
Durag HM-1400TR

Genesis Quicksilver

Cooper X_{act}

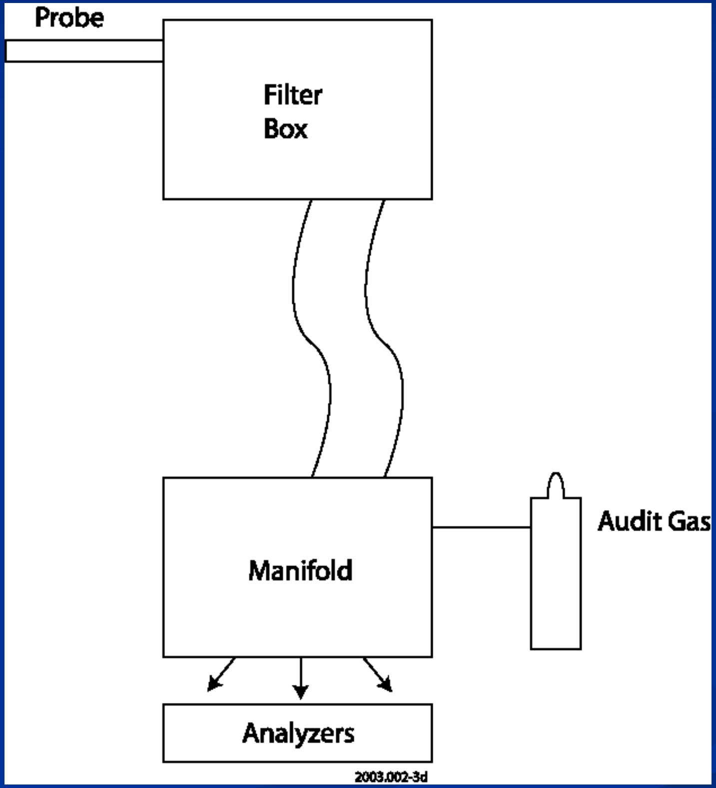
EPRI QSEM

Sampling Configuration



MRI Sampling System Configuration

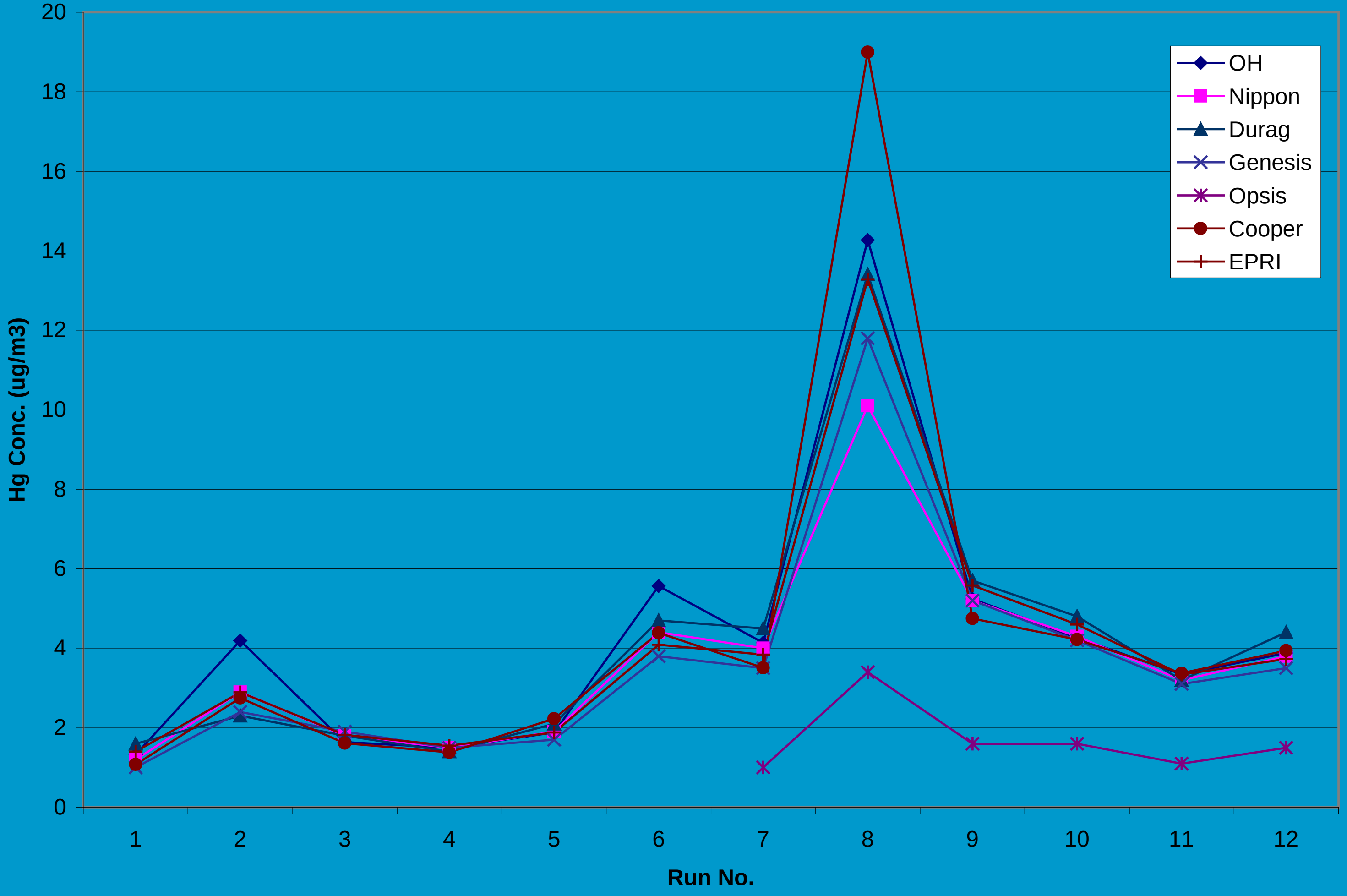
- Heated probe, filter
- Heated sample line
- Heated manifold
- Teflon PFA
- 360°F (300°F probe)
- Flowrate 5-10 lpm
- Connected to Durag, Genesis, Cooper X_{act} (Nippon, OPSIS on own separate lines)



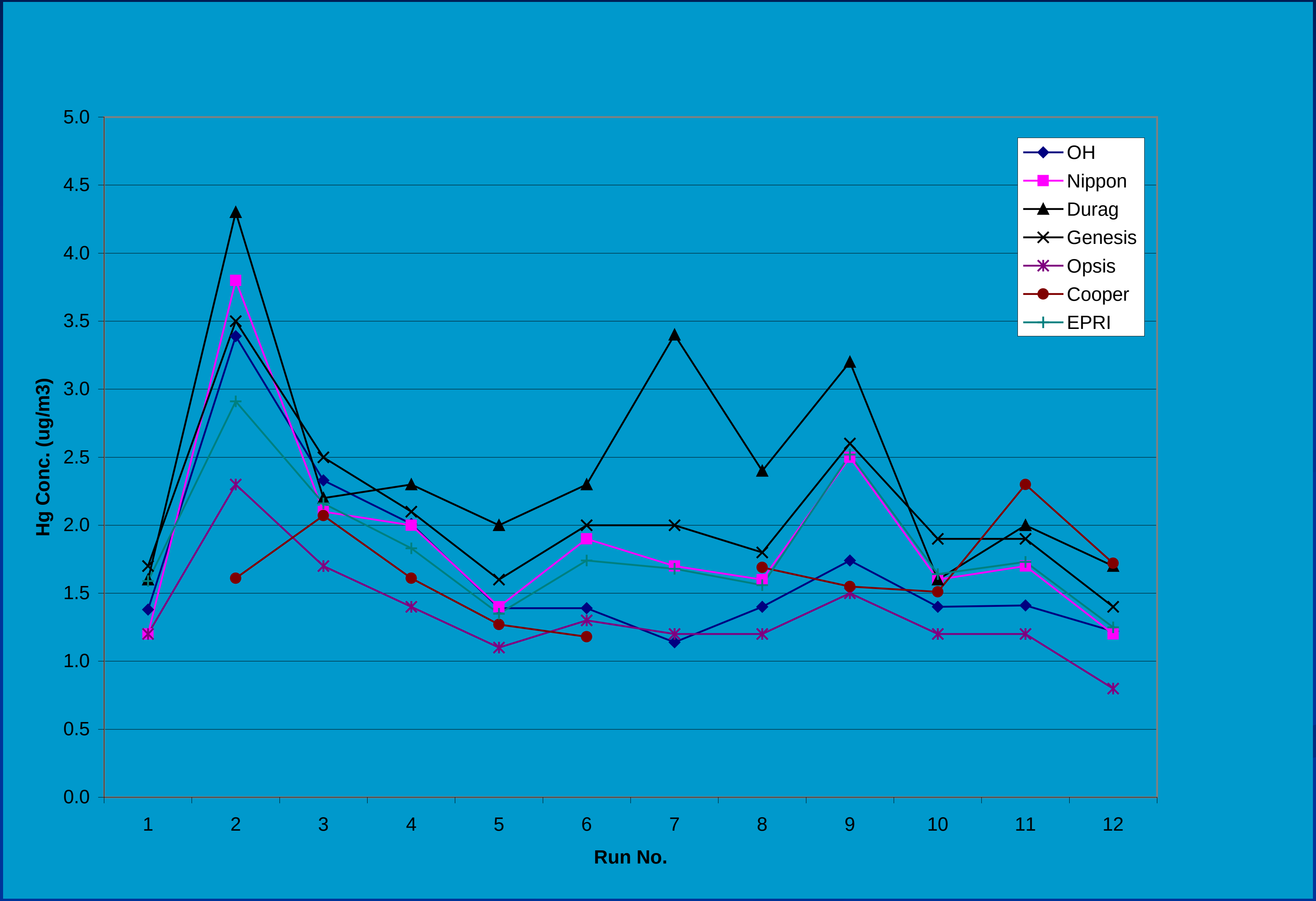
Audit Gas Checks

- Elemental Hg standard
- Performed during RATA, long-term phase, diagnostics
- During RATA at beginning/end of each day
- Gas value ~8 ug/m3
- Oak Ridge Phase II ETV gases available for linearity checks (6 and 19 ug/m3)

Initial RA Test Results



Final RA Test Results



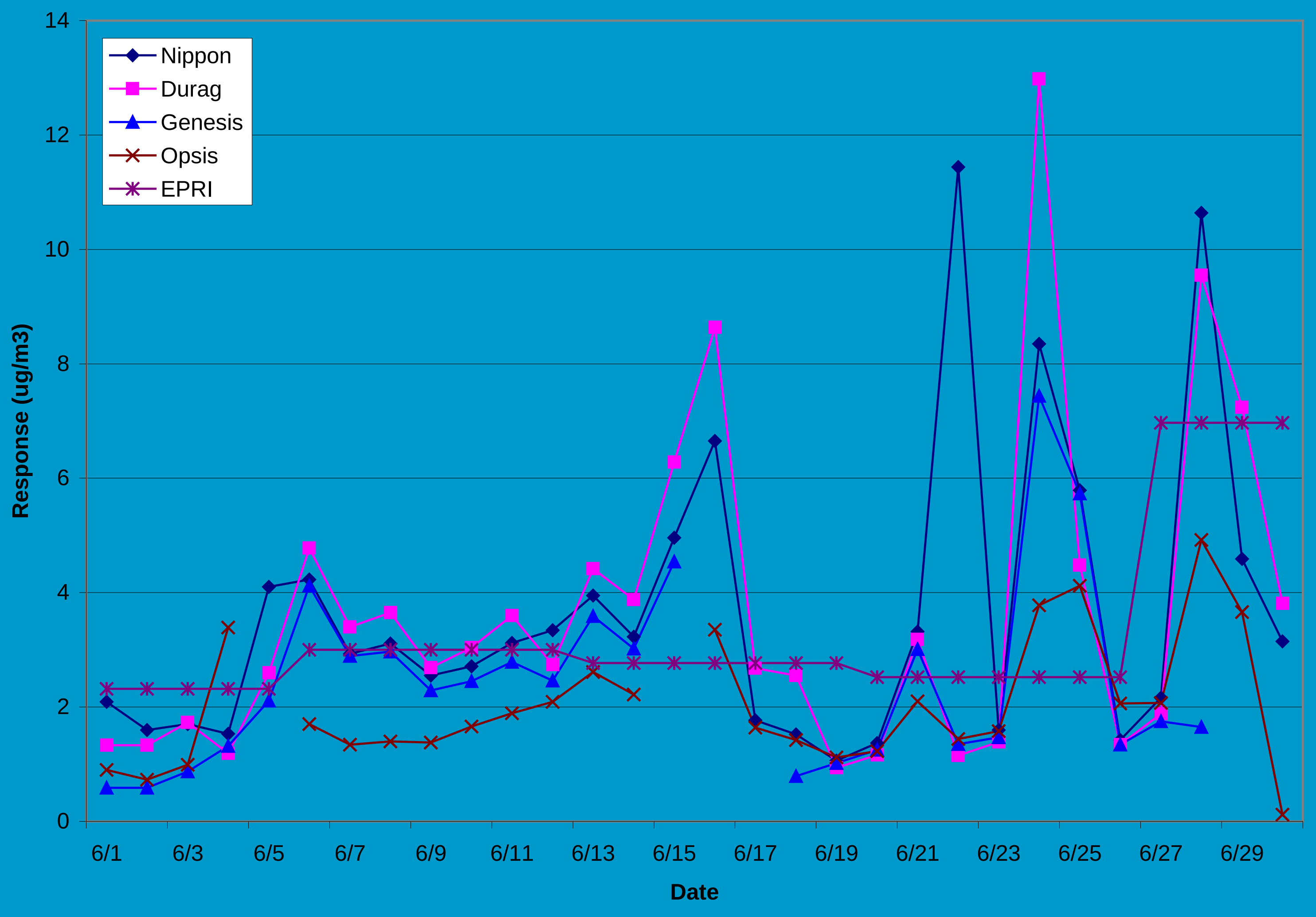
Relative Accuracy Results

	Initial RA (best nine)	Final RA (best nine)
Dry CEMS		
Nippon	4%	14%
Durag	15%	41%
Genesis	13%	22%
Opsis	NA	22%
Cooper (CEM)	NA	25%
Cooper (sampler)	12%	NA
Integrated Sampler		
EPRI QSEM	9%	12%

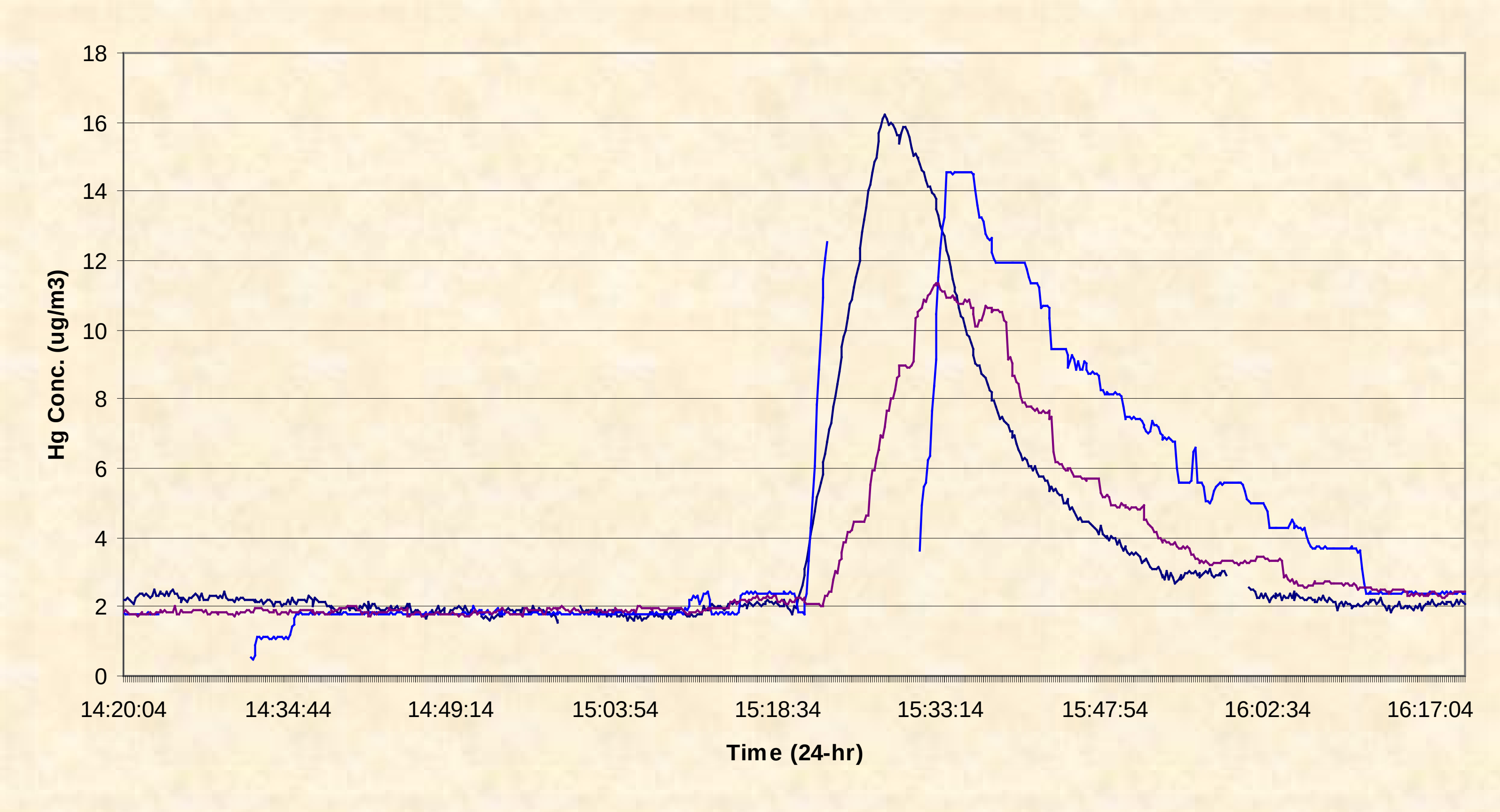
Long-term CEMS Operations

- Integrity of filter, sample line and manifold (i.e., no bias or losses)
- 4 CEMS operated during long-term monitoring phase
- Practical maintenance knowledge gained by CEMS vendors

CEMS Daily Averages - June



‘Transients’ in Hg Concentration



Summary Observations

Low SO_2 & NO_x, Newer Power Plant (PRB coal)

- Hg CEMS performance can meet 20% RA criteria of draft PS-12
- Hg CEMS operation/maintenance problems improved compared to Phase II, but…
- Continued development of individual Hg CEMS at various (high SO_2) power plants
- Transient emissions observed during study
- Duplicate Ontario Hydro trains valuable for increased precision at low Hg concentration

CEMS For Hg Conclusions

- Mercury Detectable at Less than 1 ug/m^3
- Mercury species can be converted to elemental mercury and measured using an elemental mercury analyzer
- Accurate and reproducible calibration sources are available; Elemental Hg is preferred and sufficient
- Successful field tests of analyzer on gas streams with mercurty concentrations > 1 ug/m^3

Source Monitoring for HCl/Cl_2

- Four EPA Time-Integrated Test Methods
  - FRM 26 (Constant Sampling Rate)
  - FRM 26A (Isokinetic)
  - SW-846, Method 0050 (Isokinetic)
  - SW-846, Method 0051 (Constant Sampling Rate)

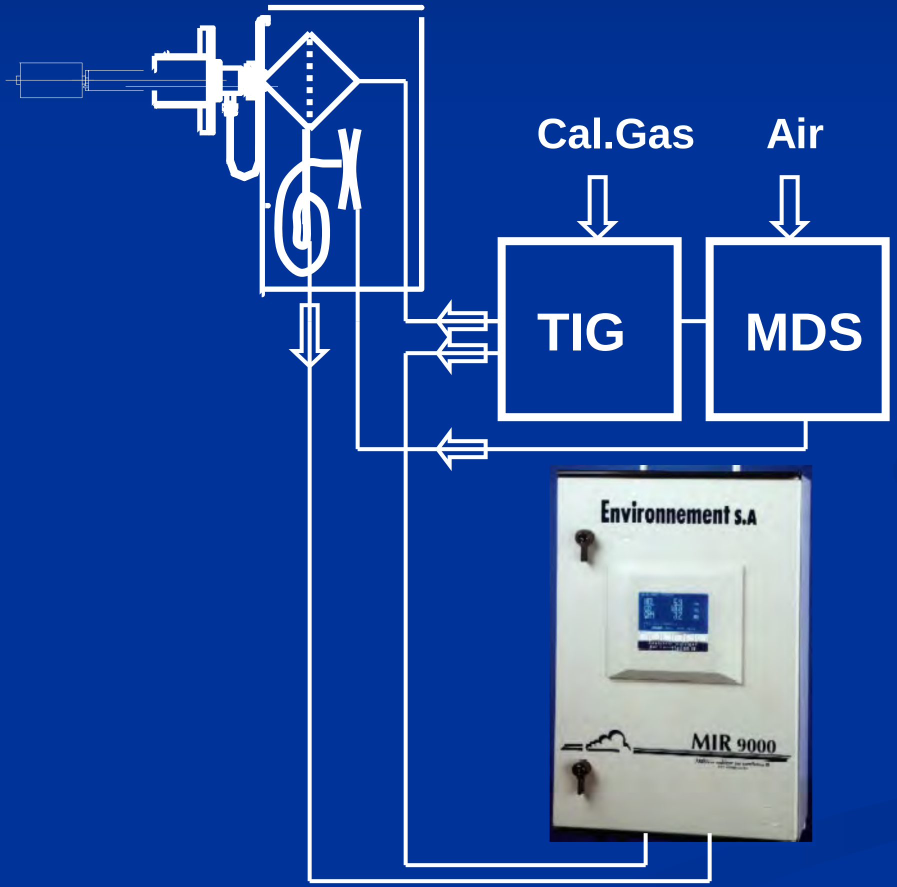
Acid Gas CEMS Monitoring Technologies

- Infrared Spectroscopy/Gas Filter Correlation (IR/GFC)
- Ion-Selective Electrode (ISE)
- Ion Mobility Spectroscopy(IMS)
- Ultraviolet Spectroscopy (UV)
- Colormetric Spectroscopy (CS)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Mass Spectroscopy (MS)

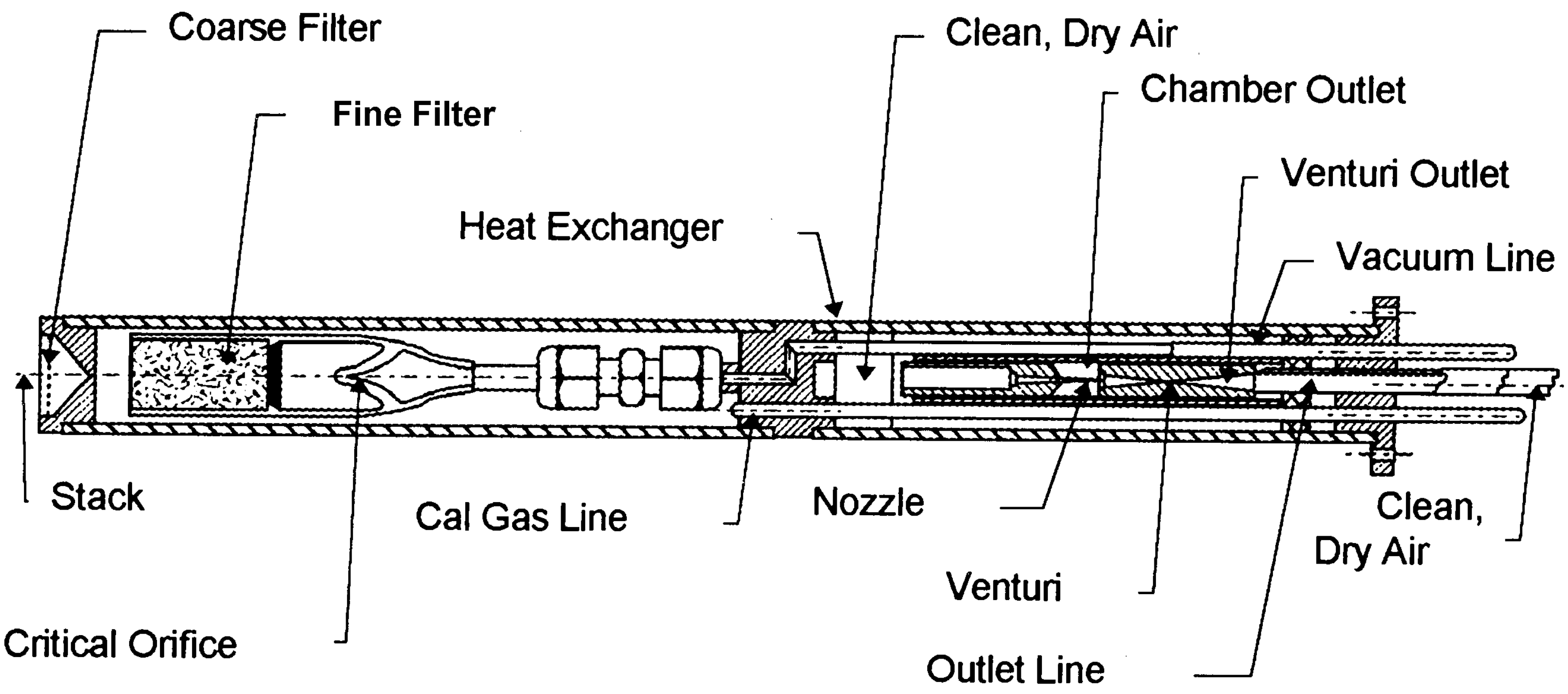
Acid Gas CEMS Vendors (IR/GFC)

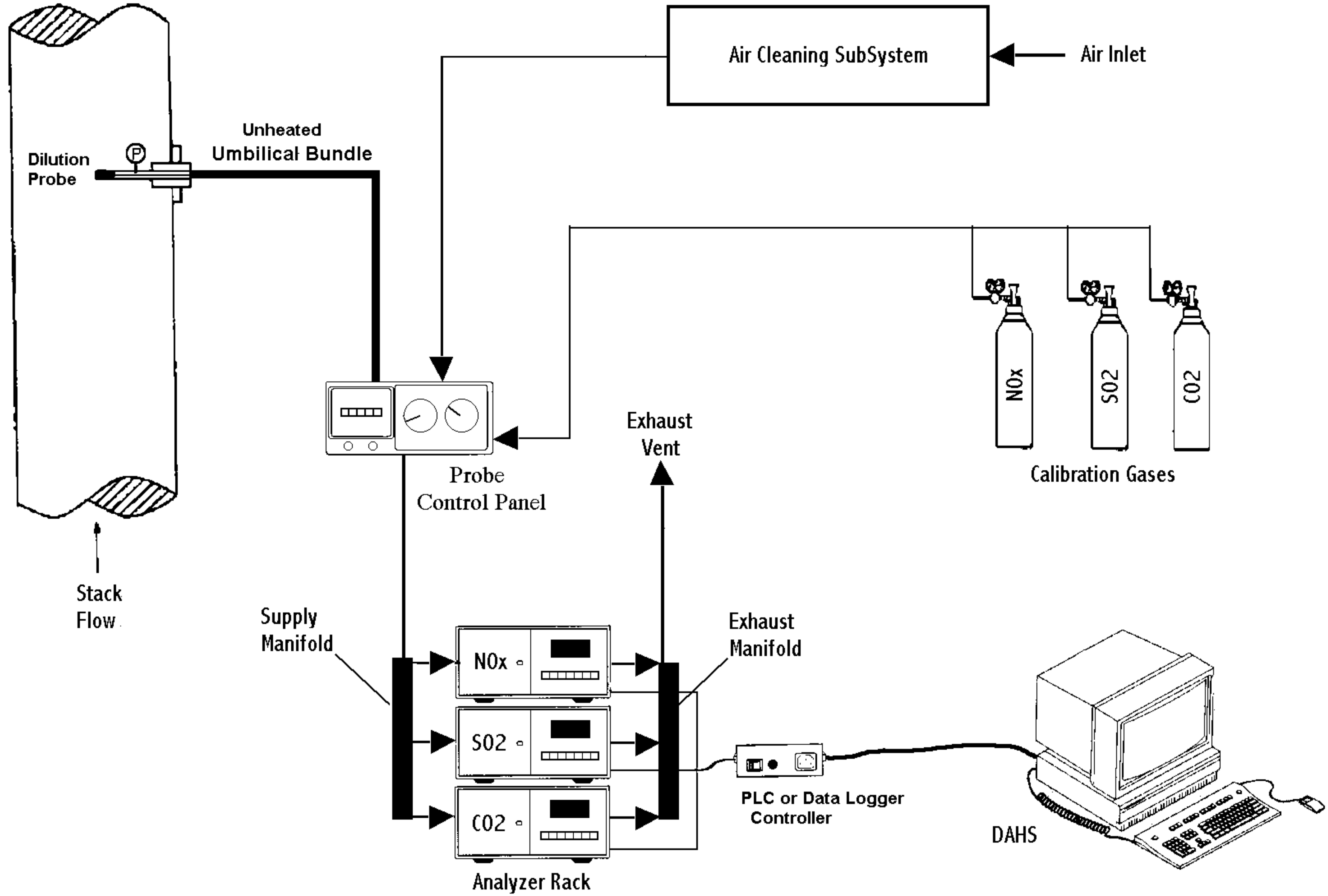
- Altech Environment USA (Environment SA)
  - Extractive/In-Situ/IR/GFC
- Air Instruments and Measurements (AIM)
  - Extractive/In-Situ/IR/GFC
- Thermo Environmental
  - In-Situ/Dilution Probe/IR/GFC

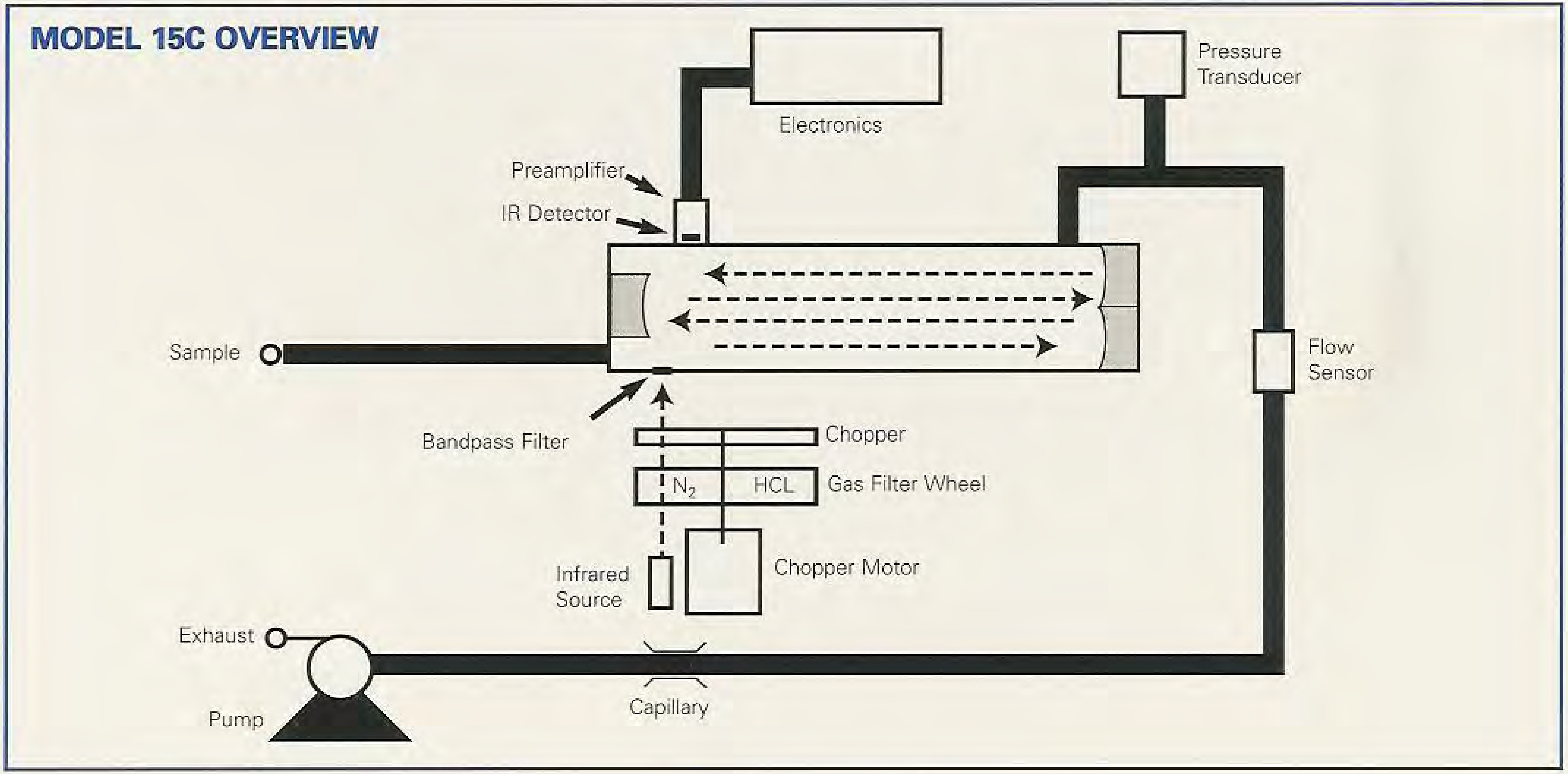
Environment SA
MIR 9000
Ext/IR/GFC



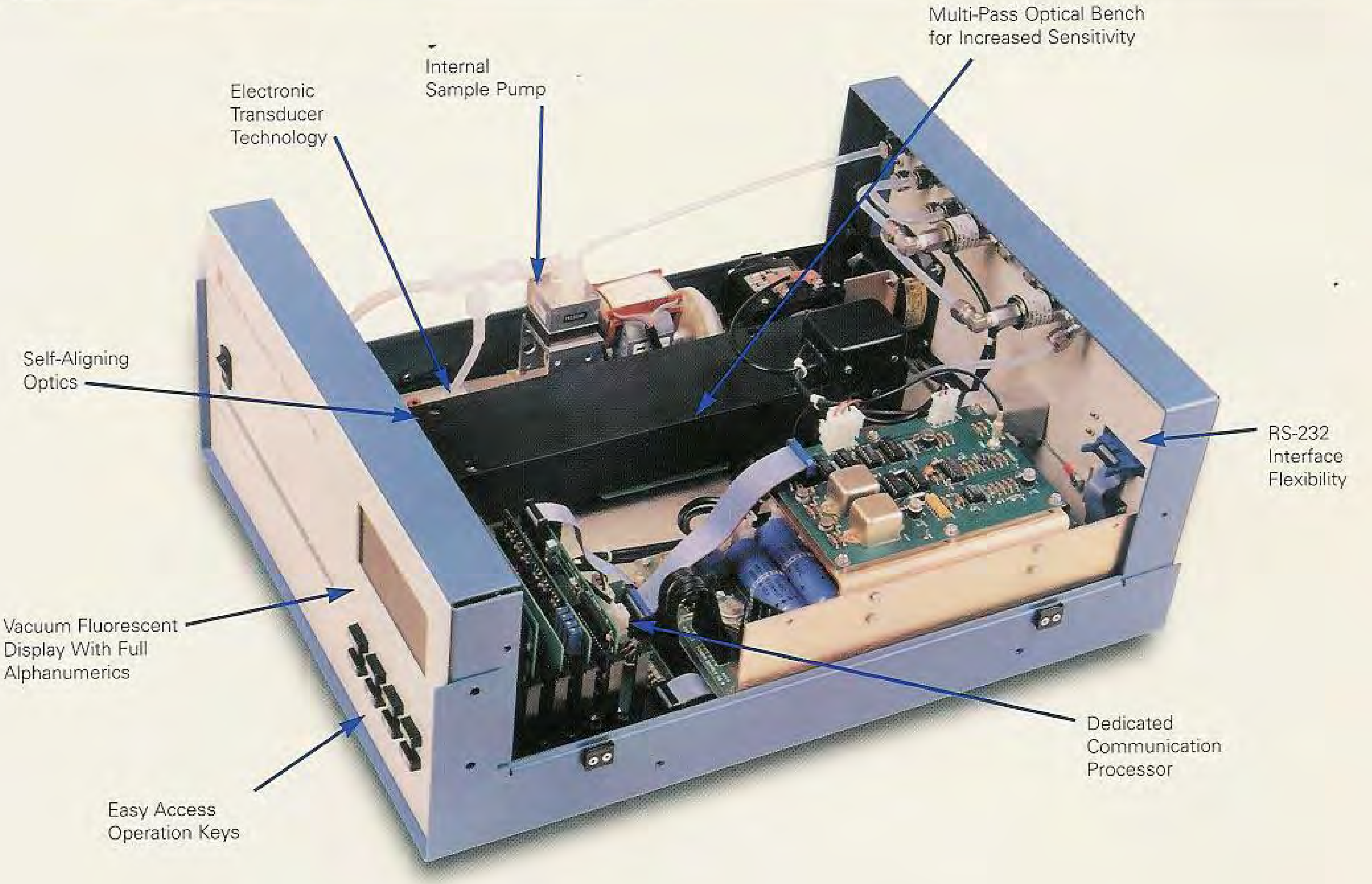
- High temp probe
- Perm. sampling
- Rem. control cable:
- Auto. Cal.
- Air dryer
- MIR9000 (IR/GFC)
- SO_2, NO, NO_2, CO, CO_2, HCl, HF


Coarse Filter
Fine Filter
Heat Exchanger
Clean, Dry Air
Chamber Outlet
Venturi Outlet
Vacuum Line
Stack
Cal Gas Line
Nozzle
Clean, Dry Air
Venturi
Critical Orifice
Outlet Line


Air Cleaning SubSystem
Air Inlet
Unheated
Umbilical Bundle
Dilution
Probe
Probe
Control Panel
NOx
SO2
CO2
Calibration Gases
Exhaust
Vent
Stack
Flow
Supply
Manifold
Exhaust
Manifold
NOx
SO2
CO2
Analyzer Rack
PLC or Data Logger
Controller
DAHS


MODEL 15C OVERVIEW
Electronics
Pressure Transducer
Preamplifier
IR Detector
Sample
Flow Sensor
Bandpass Filter
Chopper
N_2
HCL
Gas Filter Wheel
Infrared Source
Chopper Motor
Exhaust
Pump
Capillary

KEY DESIGN FEATURES



ADVANCED TECHNOLOGY **Model 15 Gas Filter Correlation HCl Analyzer**

Acid Gas CEMS Vendors (Ion Selective Electrode Based)

- TessCom
  - Extractive/Potentiometry
- Bran & Luebbe
  - Extractive/Potentiometry

Acid Gas CEMS Vendors (Ion Mobility Spectroscopy)

- Environmental Technologies Group, Inc. (ETG)
  - Dilution Probe/Ion Mobility Spectroscopy

Acid Gas CEMS Vendors (UV/FTIR Spectroscopy Based)

- Opsis DOAS System
  - In-Situ System (Cl_2, HCl, HF etc.)
- Enviroplan
  - Dilution Probe/FTIR
- Rosemount
  - Extractive Probe/FTIR
- Thermo Environmental
  - Dilution Probe/Gas Filter Correlation

Multi-Metals (MM) CEMS

- Each Multi-Metal CEMS Has Five Major Components
    - 1. Energy Source
    - 2. Stack Interface
    - 3. Light Measurement System
    - 4. Data Acquisition And Analysis System
    - 5. Calibration Method

Multi-Metal CEM Summary

Technology	Type	Vendor	Status
Laser Spark Spectrometry	In-Situ With Analysis 4 Min.	Sandia National Lab	Laboratory and Demo At Source Completed
Microwave Plasma Torch Spectrometry	Extractive With Continuous ICP Analysis	MIT	Prototype Underway with DOE Testing
On-Line ICP Spectrometry	Extractive With Continuous ICP Analysis	Thermo Jarrell Ash	Testing Over 2-Years

Current Detection Limits ($\mu g/m^3$)

Element	Method 29 (Front Half)	Method 29 (Back Half)	Extractive ICP
Sb	3.8	1.9	1.7
As	5.4	3.2	2
Be	0.035	0.029	0.06

Current Detection Limits ($\mu g/m^3$)

Element	Method 29 (Front Half)	Method 29 (Back Half)	Extractive ICP
Cd	0.5	0.25	0.21
Cr	0.85	0.4	0.15
Pb	5.0	2.5	0.47

Current Detection Limits (μg/m^3)

Element	Method 29 (Front Half)	Method 29 (Back Half)	Extractive ICP
Mn	0.25	0.1	0.10
Hg	0.3	1.5	-
Ni	1.8	0.9	0.30

General Technology Evaluation

- Most technologies need further development and quantitative field validation
- Suitability testing and certification procedures could improve user confidence
- QA/QC specification may need modification

Conclusions

- Technology advancements are encouraging to developers and the EPA
- Strong support from Government sponsors (DOE/EPA)
- User concerns need to be addressed to improve confidence
- Process control applications could lead regulatory compliance assurance
- CEMs could provide valuable data and help negotiations with regulators