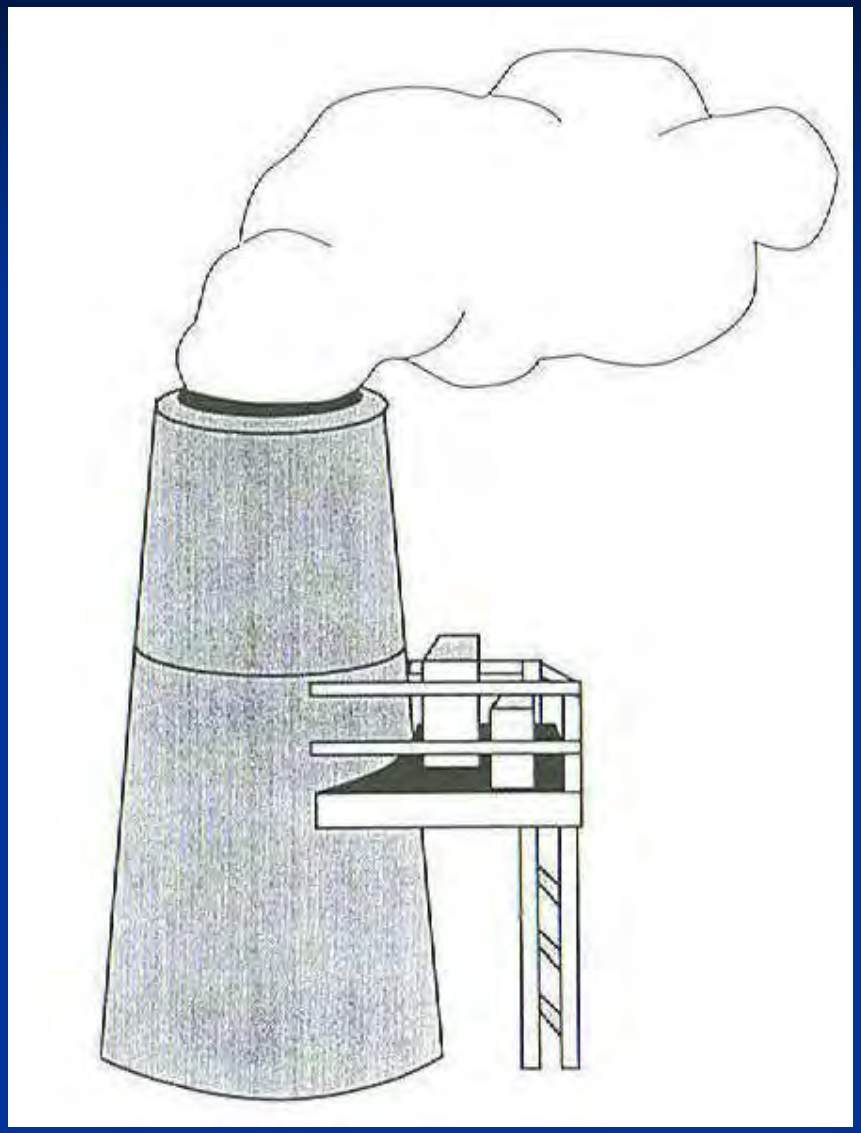
U.S. EPA APTI Compliance Test and Source Test Observation

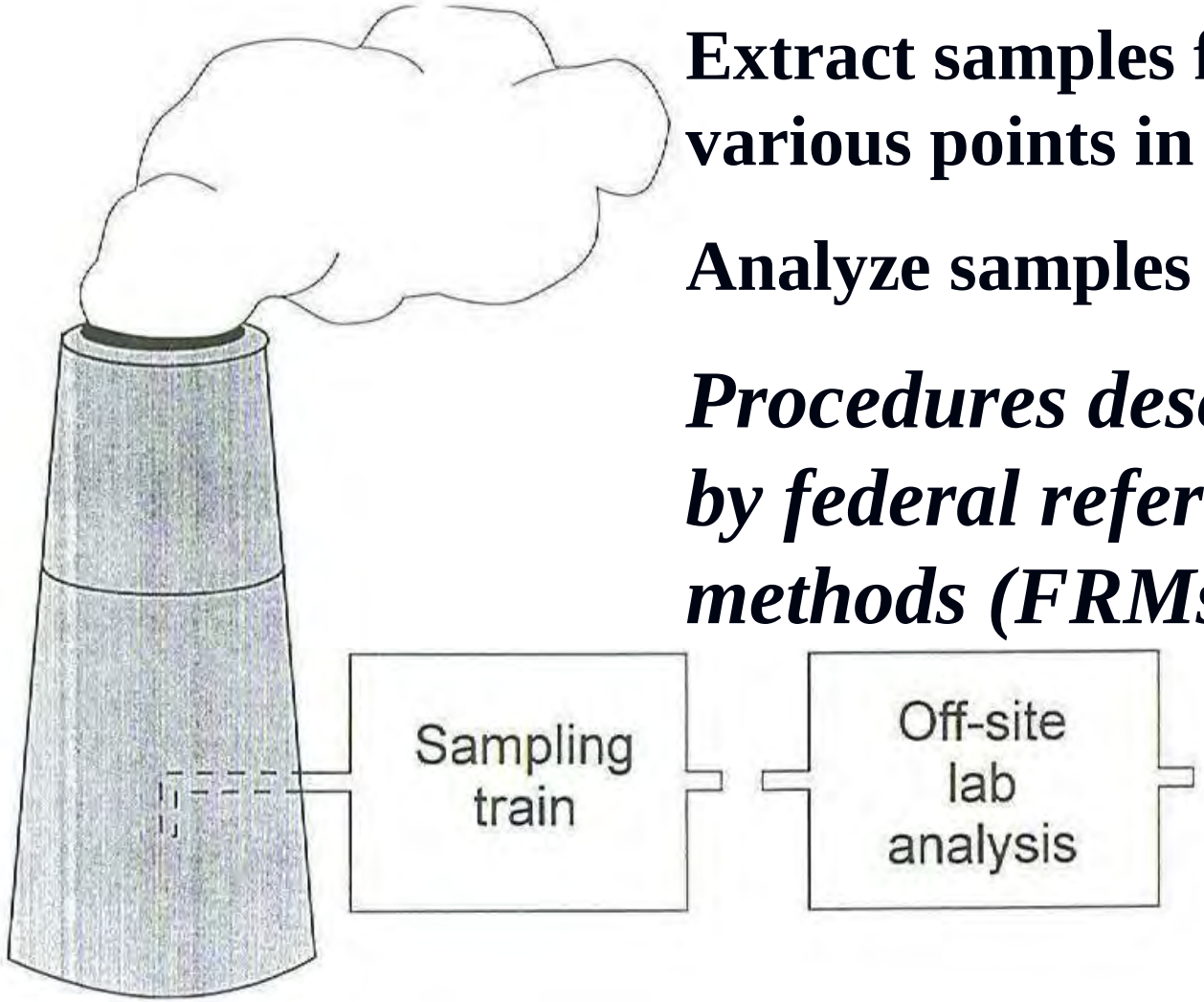
APTI Course #468 Introduction





Measurement of Source Pollutant Emissions

Manual Sampling



Extract samples from various points in stack.

Analyze samples in lab.

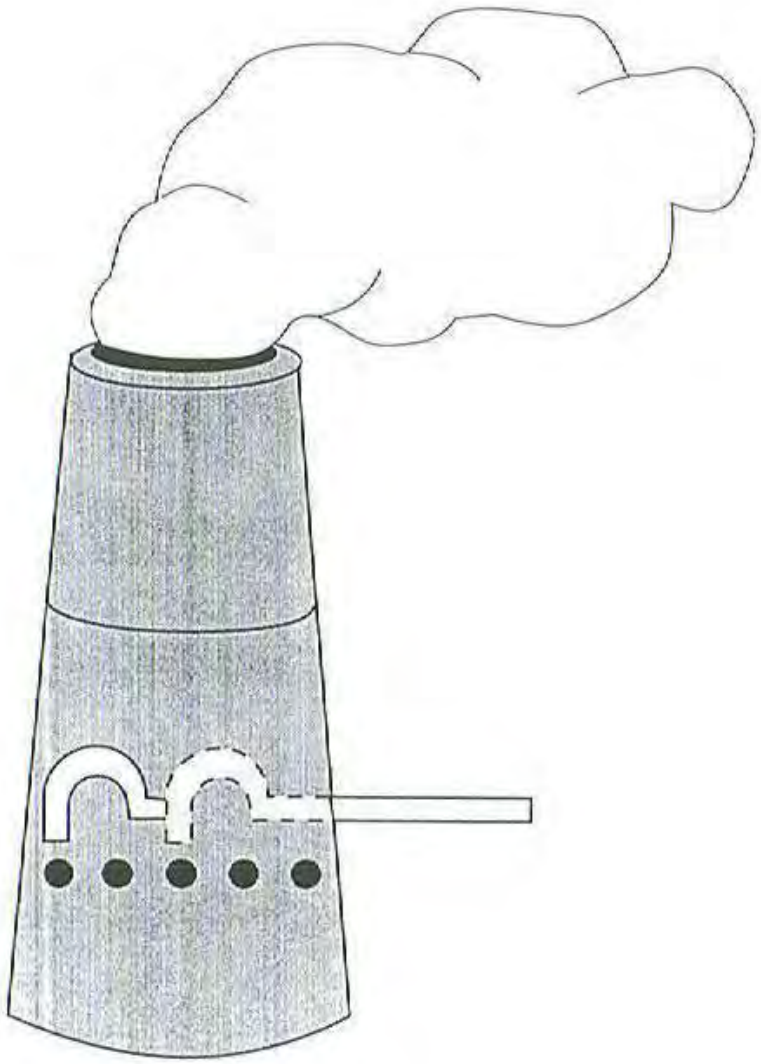
Procedures described by federal reference methods (FRMs)

Methods for Measuring Emissions

- **Manual Sampling**
- **Continuous Monitoring**
- **Remote Sensing**

EPA Manual Federal Reference Methods (FRMs)

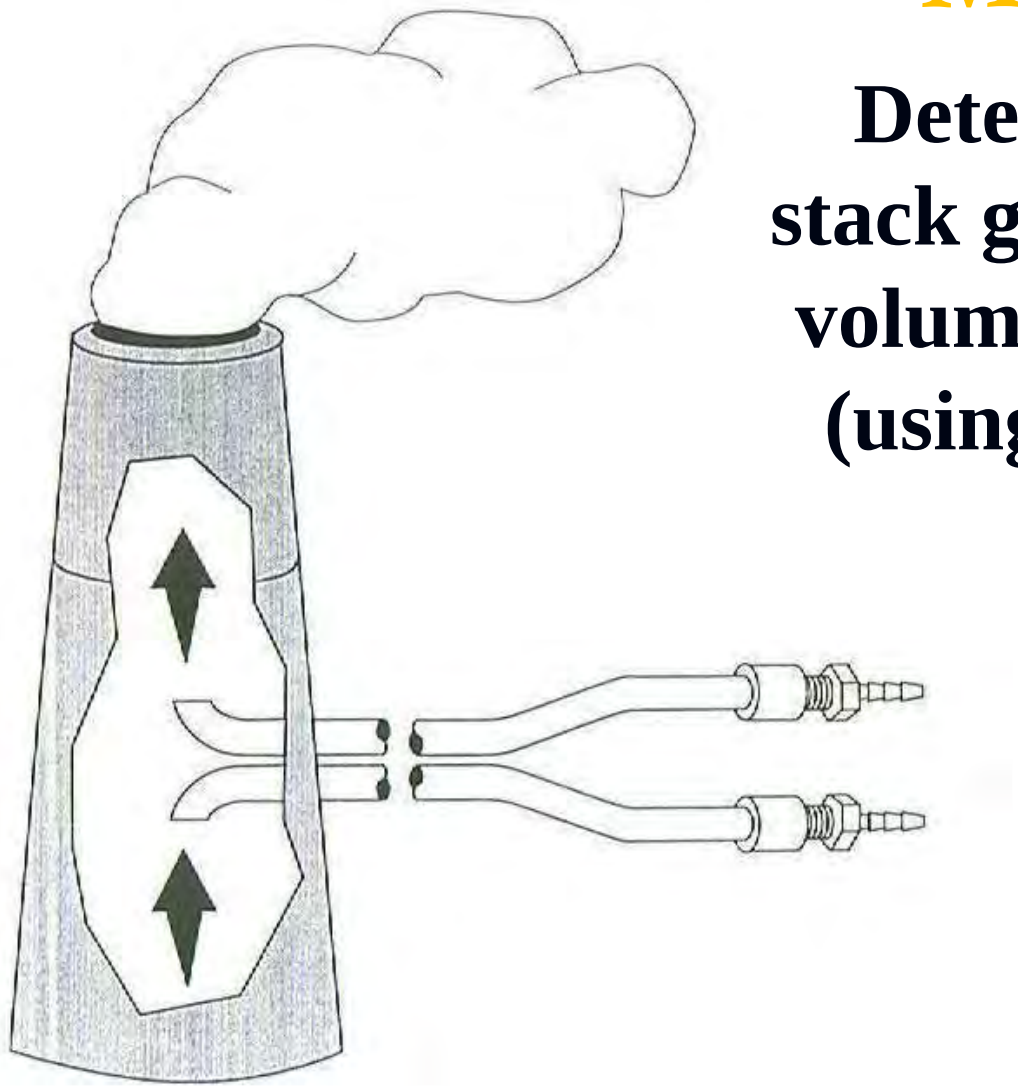
- Used for source compliance testing
- Describe actual testing procedure
- Found in Code of Federal Regulations



Method 1

Selection of sampling traverse points

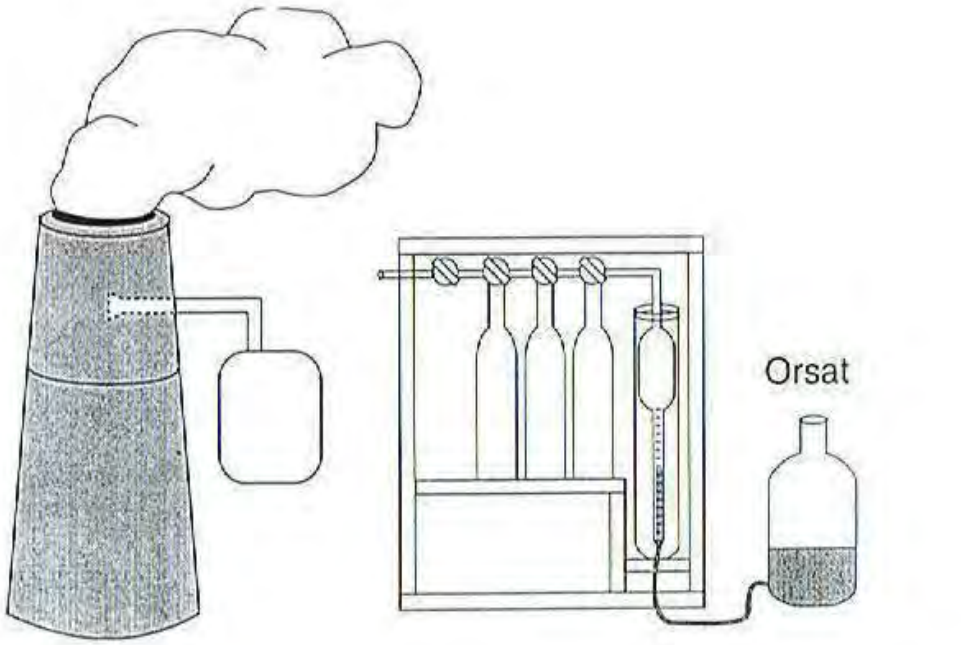
Method 2

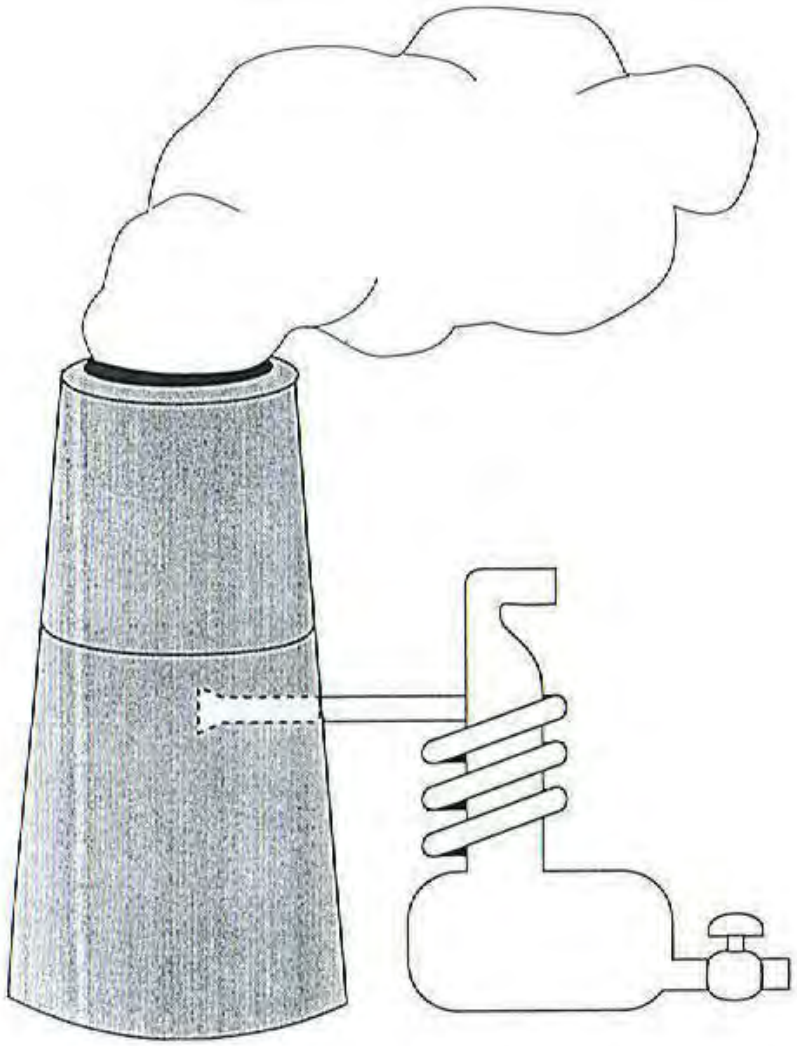


Determination of stack gas velocity and volumetric flow rate (using Type S pitot tube)

Method 3

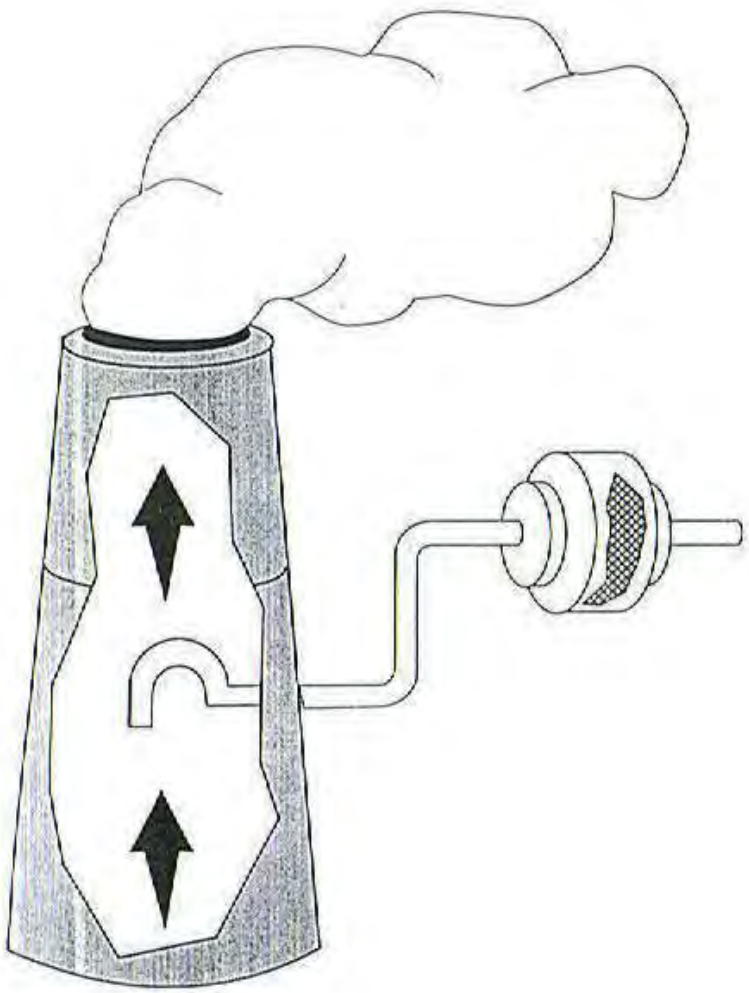
Determination of the dry molecular weight of flue gas (using Orsat apparatus measuring %O_2, %CO_2, and %CO)





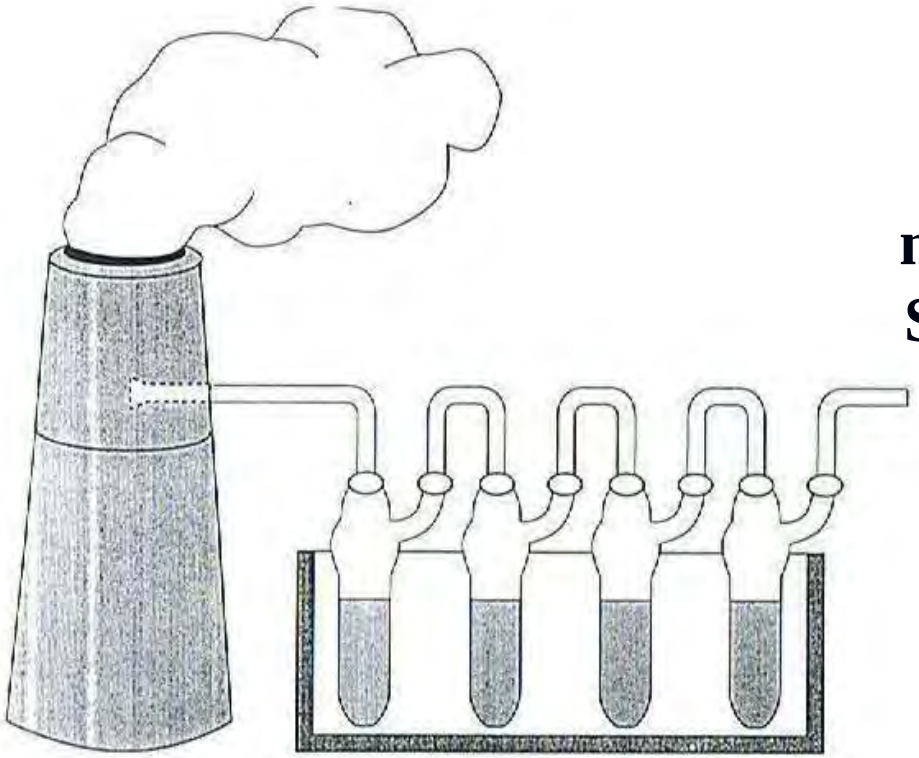
Method 4

Determination of moisture content of stack gas (by condensation method)



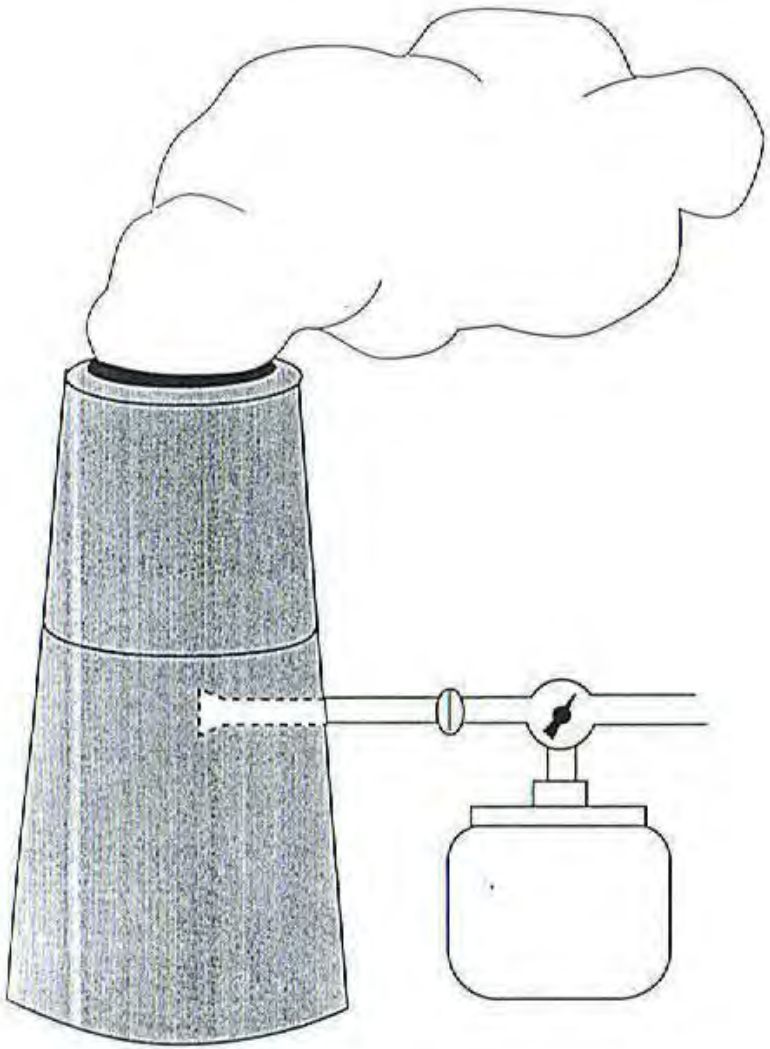
Method 5

Sampling method for particulate matter (isokinetic collection of particles on a filter)



Method 6

Sampling and analytic method for determining SO_2 emissions (barium-thorin titration)

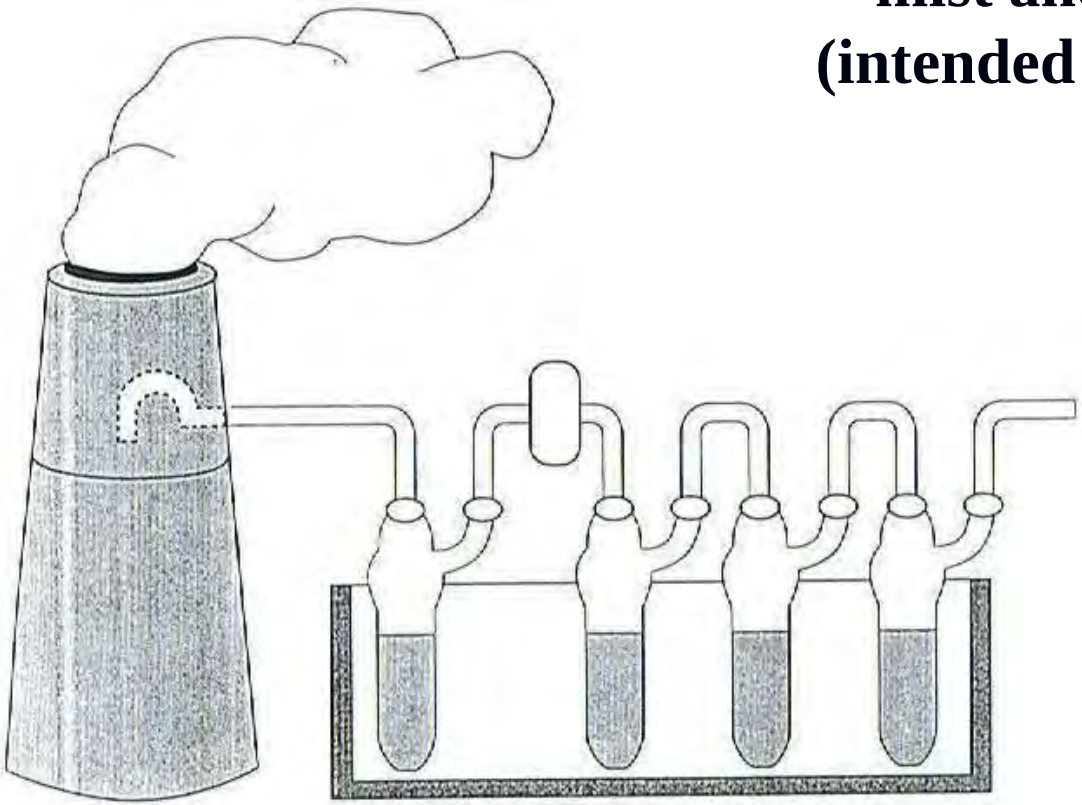


Method 7

Determination of NO_X emissions (colorimetric phenoldisulfonic acid method)

Method 8

Determination of H_2SO_4 mist and SO_2 emissions (intended for H_2SO_4 plants)



FRM 10	Determination of CO
FRM 11	Determination of flourides
FRM 12	Determination of inorganic lead emissions
FRM 13, 14	Determination of H_2S
FRM 15	Determination of H_2O, COS, CS_2
FRM 16	Determination of total reduced sulfur
FRM 17	Determination of particulates (in-stack filtration method)

FRM 23	Determination of dioxin/furans
FRM 26	Determination of HCl/Cl_2
FRM 29	Determination of multi-metals
FRM 201/201A	Determination of PM-10
FRM 316	Determination of formaldehyde
FRM 202	Determination of condensables
SW-846 Methods	Determination of volatiles, semi-volatiles etc.

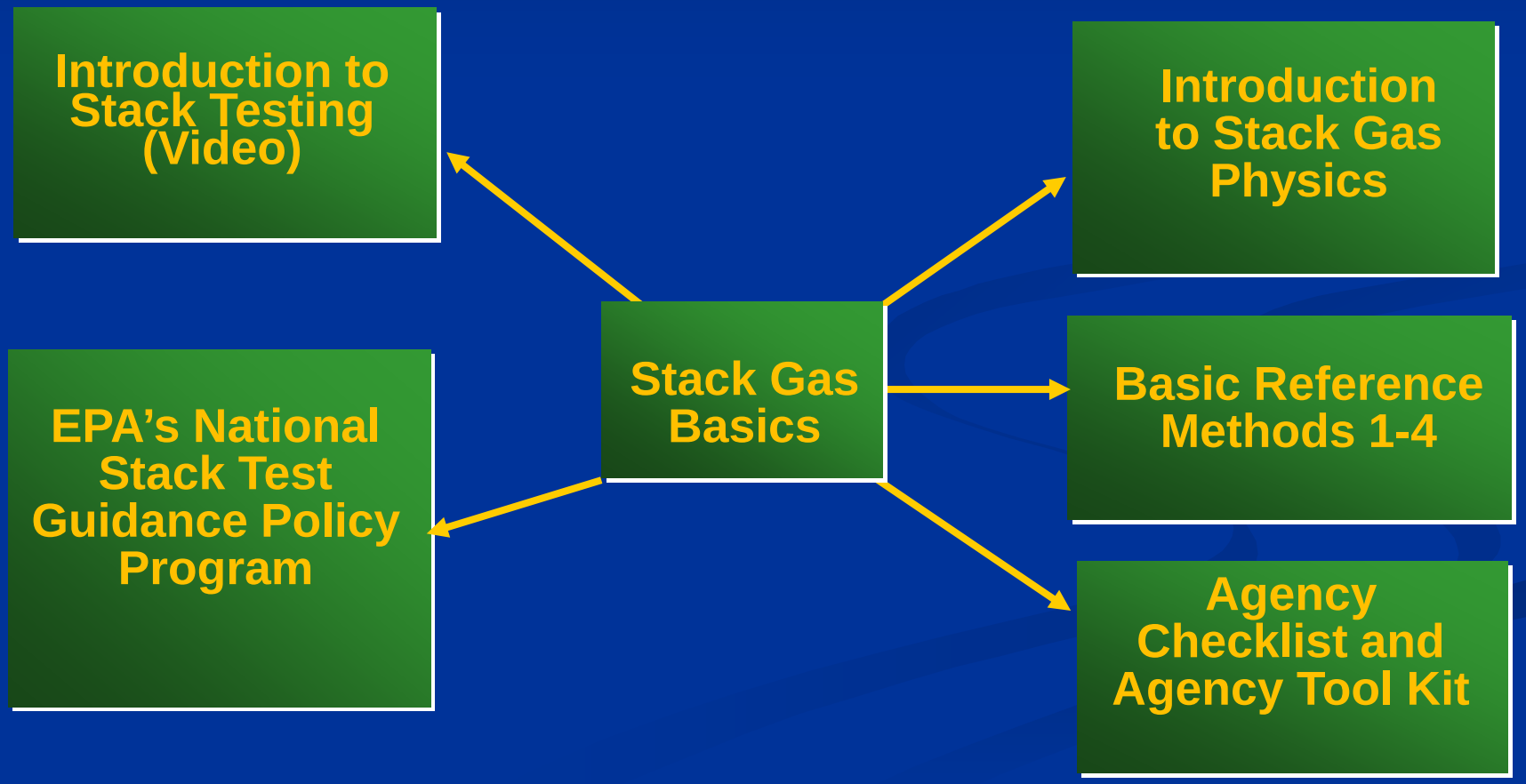
Objectives

- Instruct on a vast number of methods found in EPA's Federal Register methods (FRMs) and SW-846 test methodology
- Instruct Agency personnel in the proper observation and measurement techniques for quantifying particulate and gaseous stack emissions

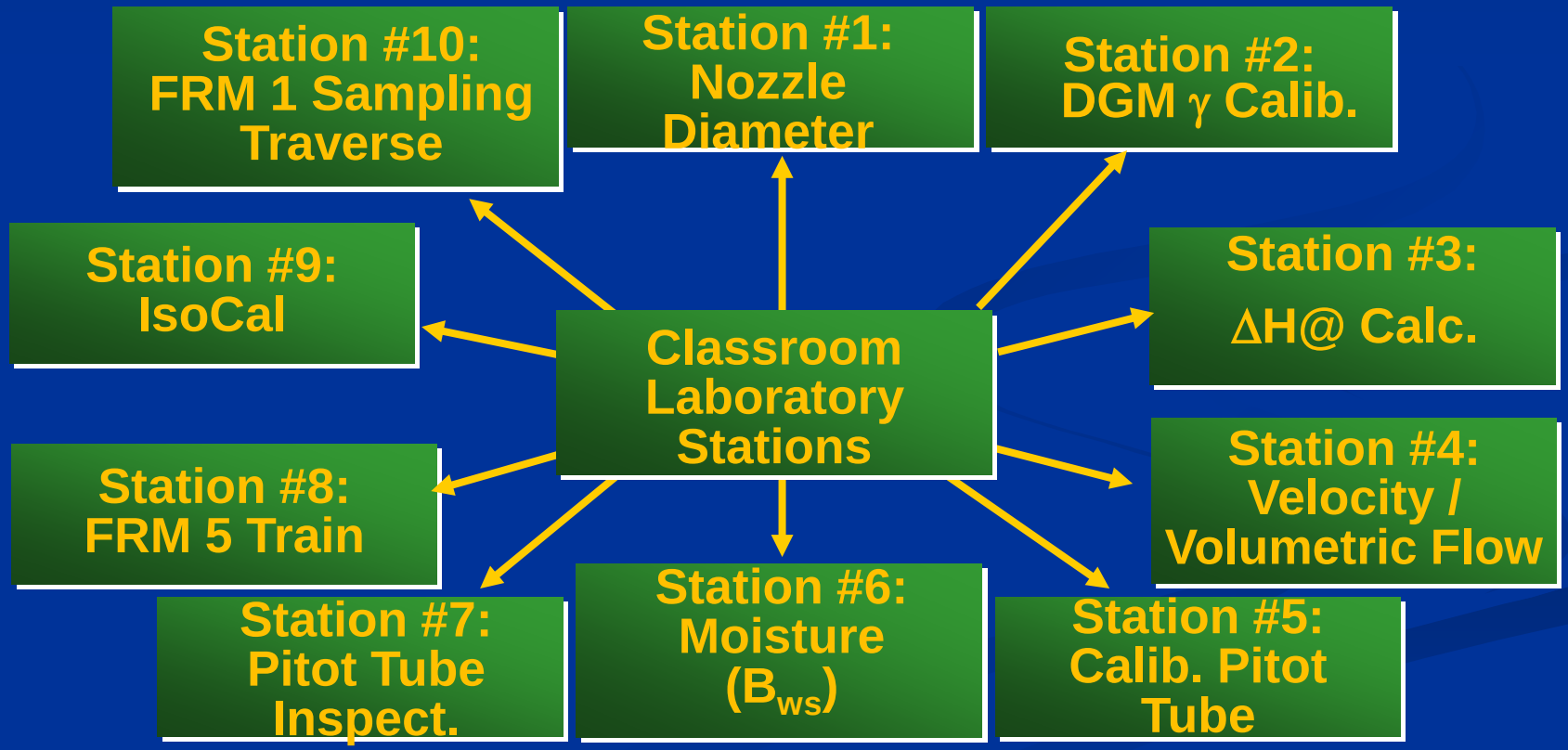
Objectives

- Focus on groups of compounds
  - Volatile Organic Compounds (VOCs)
  - Hydrogen Halides and Halogens
  - Particulate Matter (Total and Speciated) and Condensibles
  - Inorganic-base Compounds (Lead and Metals)
- Update changes associated with FRMs 1-5

What We Will Cover



What We Will Cover



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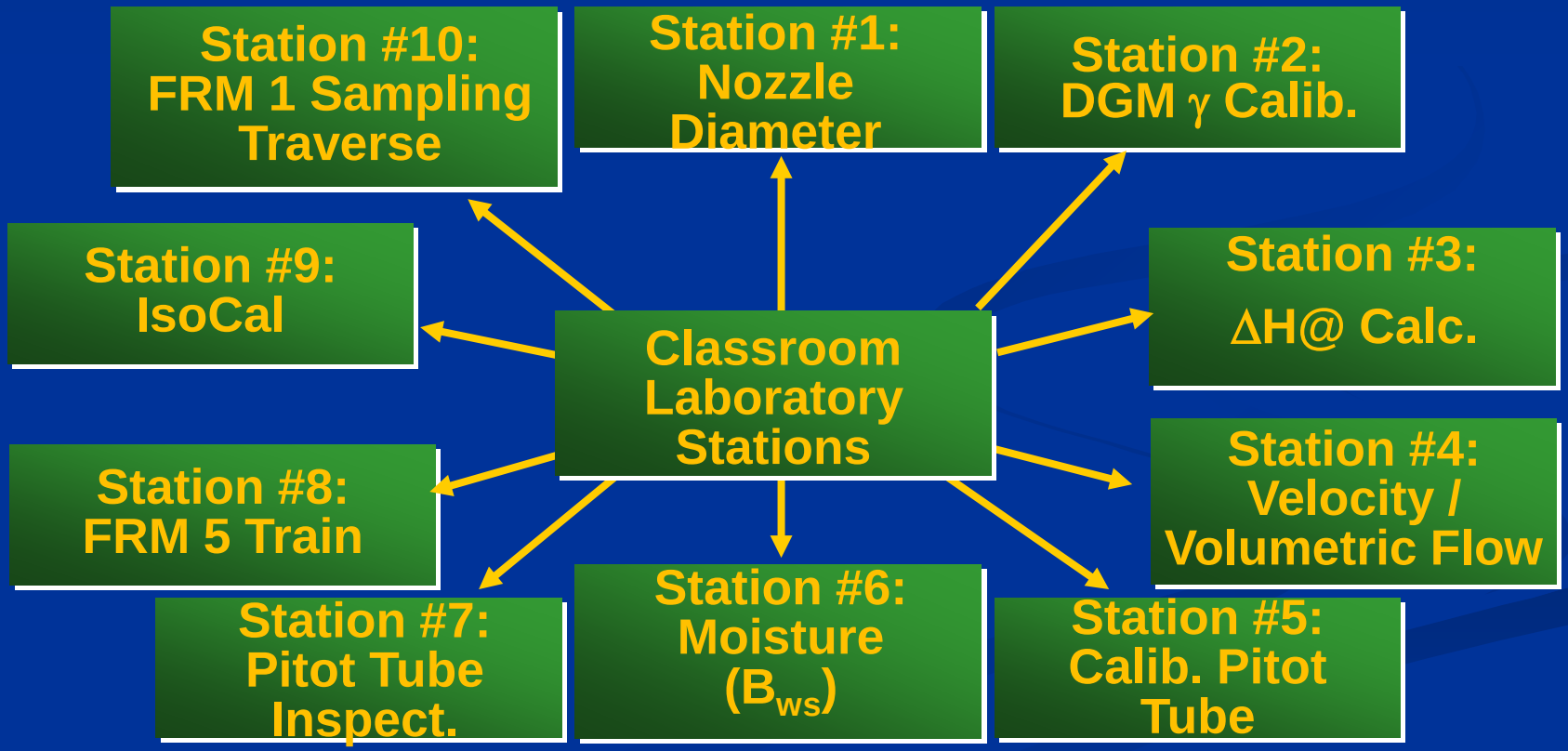

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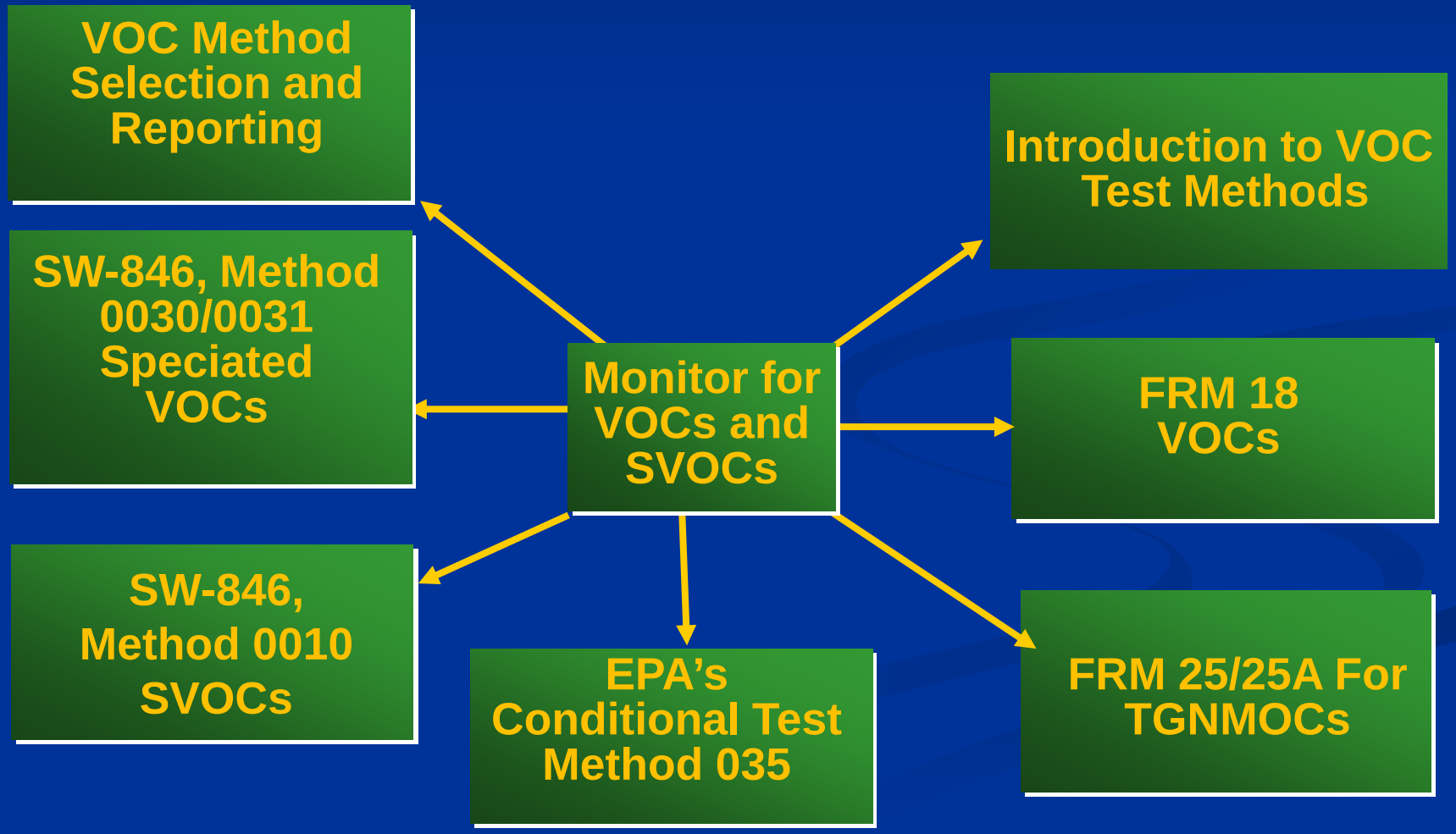

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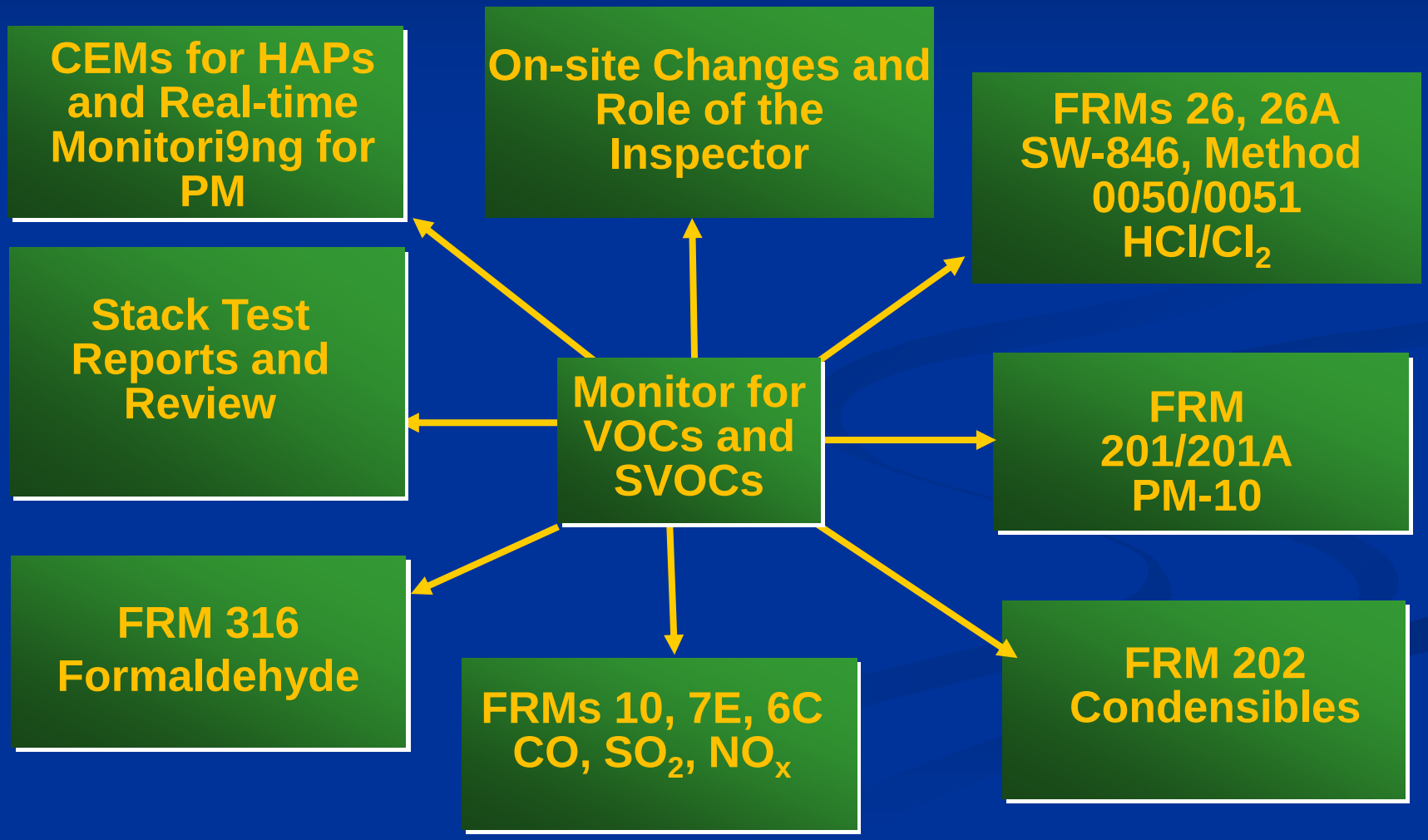

Course Materials

- **Course #468 Student Workbook (Updated 2012):** The Course #468 Student Workbook contains the course agenda, agency inspector observer checklist, and copies of selected slides from each of the lecture presentations

Course Materials

- **Course #468 Federal Reference Method 5 Operational Manual (Updated 2012):** The Course #468 Federal Reference Method 5 Operation Manual is a document describing specifically the construction and operation of Federal Reference Method 5 stack testing sampling train

Course Materials

- **Course #468 Student Laboratory Station Workbook (Updated 2012):** The Course #468 Student Laboratory Station Workbook contains the laboratory exercises for the ten (10) source simulator classroom stations involving FRMs 1 through 5.

Course Materials

- **Course #468 Resource Flash Drive (Updated 2012):** The Course #468 Resource Flash Drive includes over seventy (70) entries involving various papers and documentation associated with stack testing which are important for Agency inspectors to have in their reference library.

Role of the Inspector?

Regulatory Science vs. Measurement Science

“Procedure-Based” vs.
“Performance-Based” Methods?








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Historical Questions?

- How do we define particulate matter?
- How do we define VOCs?
- Do stack testing firms need to be certified or individual testers need to be certified?
- How do we deal with onsite changes to Federal Reference Methods (FRMs)?

Historical Questions?

- How do we define “condensible particulate matter (CPMs)?”
- Should our state stack observation program be documented?
- How many test should be required when sampling batch processes?
- What guidelines are available for onsite rejection of a “compliance test?”

Historical Questions?

- How do we report VOC emissions? As "C," as "propane," as "VOCs?"
- What requirements must be met inorder to allow a method specified under one set of regulations (i.e., incinerator) to be used for a different set of regulations (i.e., HON rule)?

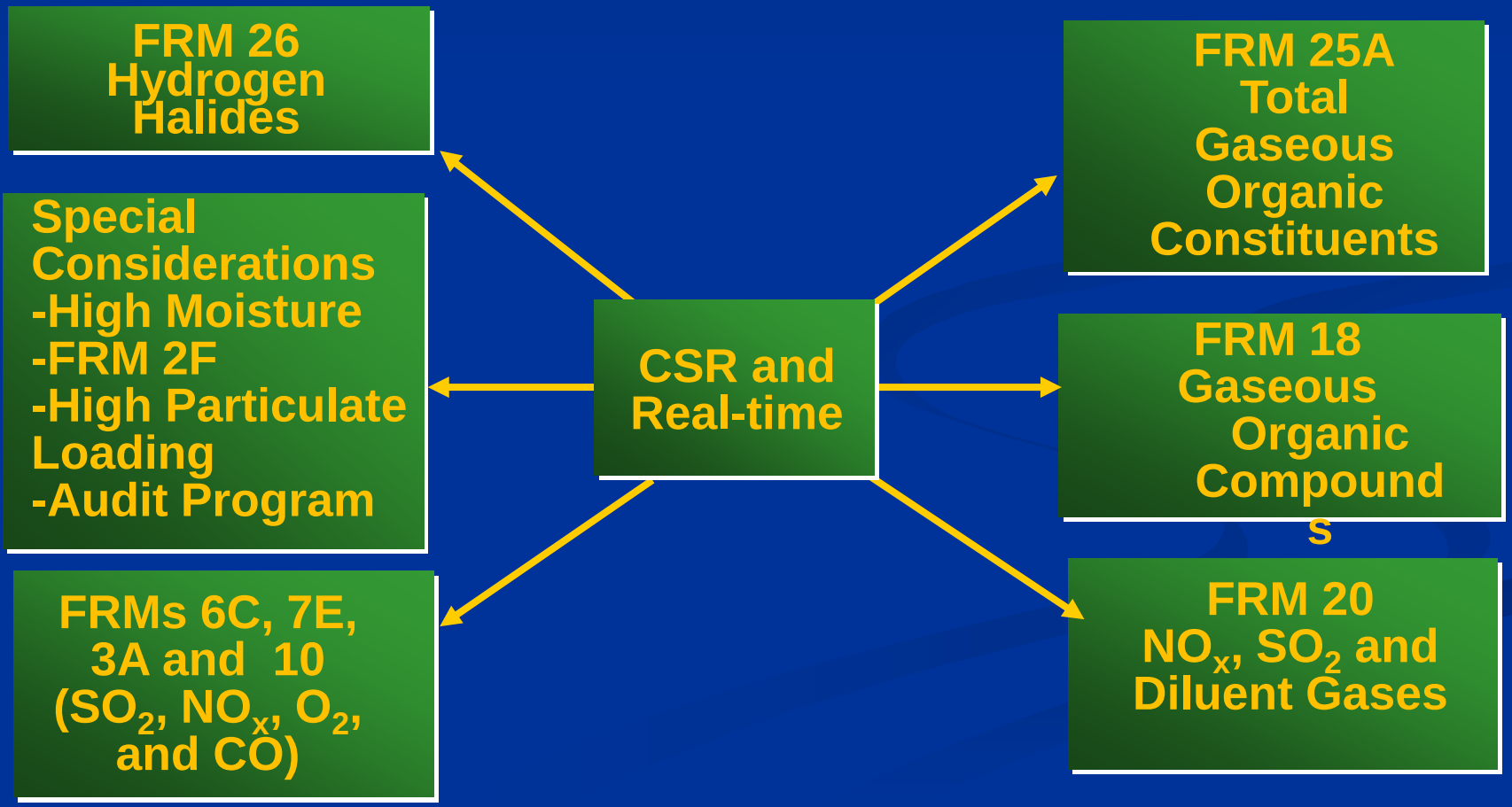
Historical Questions?

- During compliance testing, what guidelines are available for allowing a "procedure-based method" to become a "performance-based method?"
- Are there guidelines available to determines if a source test observation has been performed correctly?

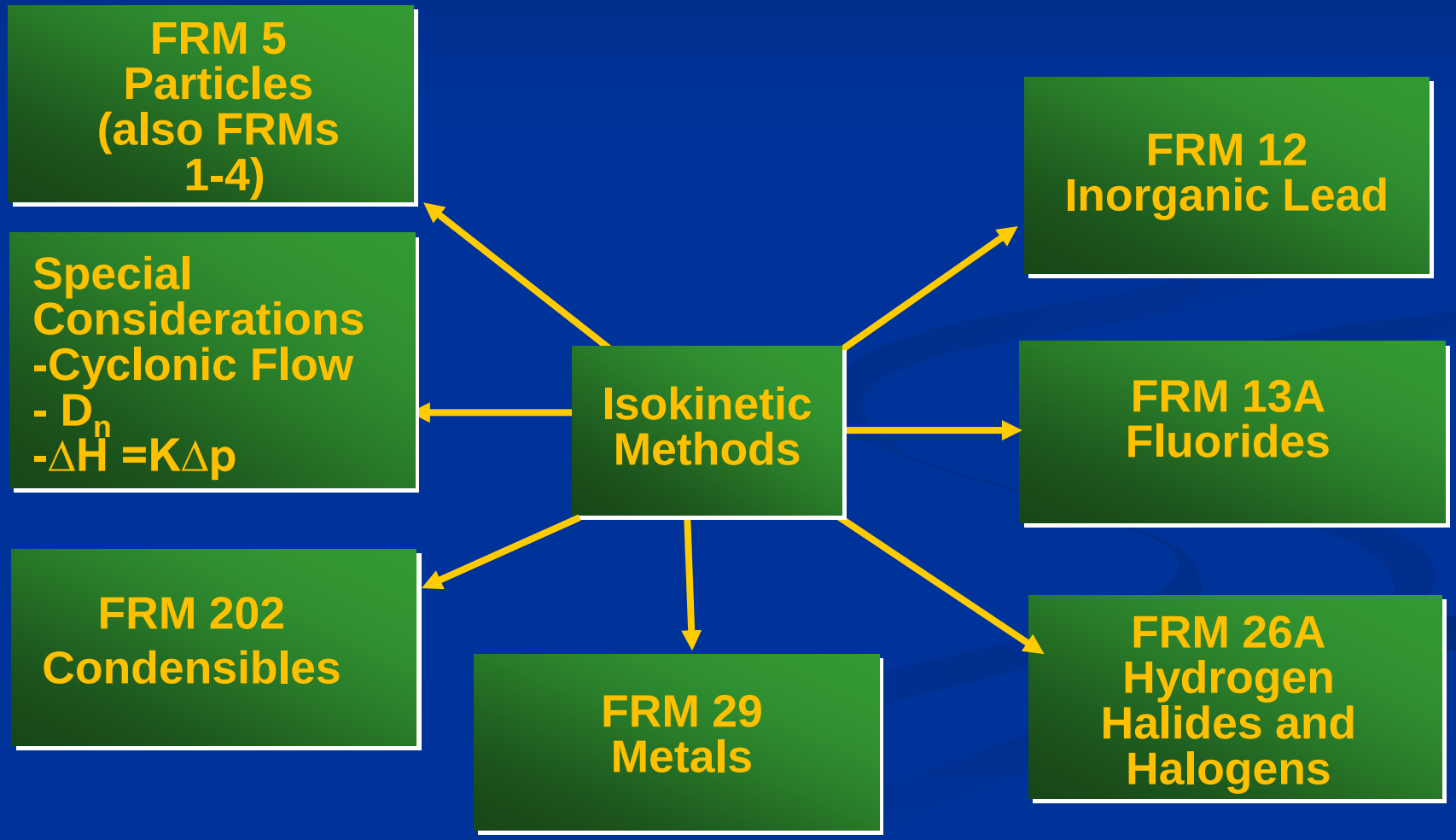
Historical Questions?

- As an Agency inspector, what guidelines are available to help me make correct decisions between "Regulatory Science" and "Measurement Science?"
- How do we implement good non-EPA programs that haven't been certified by the Agency into a State Agency program that can't be any more strict than the EPA program?

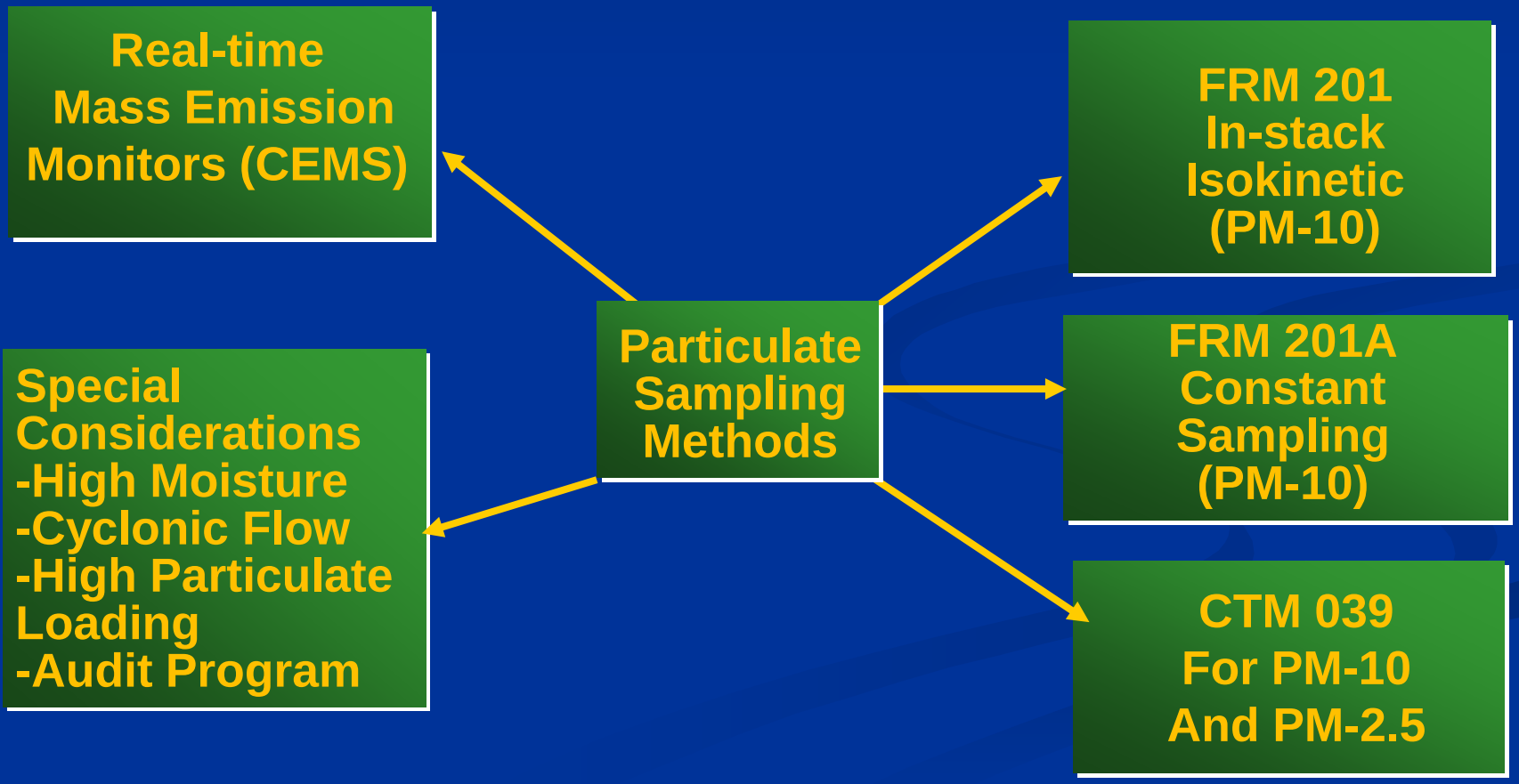
Constant Sampling Rate (CSR) and Real-time Methods



Isokinetic Sampling Rate Methods



Particulate Sampling Methods



Stack Test Methods

Why Develop Stack Test Methods and What is the Driving Force In The United States?

Objective of Stack Testing

- The objective of performing a stack test is to determine the pollutant mass rate (pmr) or emission rate (E) of pollutant being emitted to determine whether compliance limits are being met

Measurement Units

Concentration	c (ppm, gr/dscf)
Stack gas flow rate	Q (dscm)
Pollutant mass rate	pmr (lb/hr)
Mass emission rate	E (lb/10^6 Btu)
Process weight rate	E (lb/lbs product produced)

POLLUTANT MASS RATE

$$\overline{PMR_s} = \bar{c}_s Q_s$$

$\bar{Q}_s$ $\bar{C}_s$

$A_s \bar{v}_s$ $v_s = v_n$ $\frac{m_n}{V_m}$

for

Isokinetic Conditions

$$v_s = K_p C_p \sqrt{\frac{T_s \Delta p}{M_s P_s}}$$

Obtain C_p, T_s, Δp

M_s P_s

Obtain $\Delta H_@$, D_n

B_{ws}, B_{wm},

P_m, T_m

What is the Driving Force?

- New Source Performance Standards (NSPS-1970)
- National Emission Standards for Hazardous Air Pollutants (NESHAP-1977)
- Prevention of Significant Deterioration (PSD-1977)

What is the Driving Force?

- Resource Conservation and Recovery Act (RCRA-1978)
- Boiler and Industrial Furnace (BIF-1990)
- Clean Air Act Amendments (CAAA-1990)
  - Maximum Achievable Control Technology (MACT)
  - Title III Hazardous Air Pollutants (HAPs) list of 188

Why Have Title III Hazardous Air Pollutants?

- Section 112 of CAA established standards for only seven hazardous air pollutants to date
  - Asbestos, mercury, beryllium, vinyl chloride, benzene, radionuclides, arsenic

Why Have Title III Hazardous Air Pollutants?

- Additional controls needed for large number of toxic substances not covered in Section 112

Title III
Hazardous Air Pollutants

- Title III
  - Establishes a list of 188 designated substances to be regulated
  - Requires sources to apply maximum achievable control technology (MACT)

Title III
Hazardous Air Pollutants

- Provides that EPA may require additional controls after MACT to 10^{-6} residual risk levels at the property line (Driving detection limits lower)
- Establishes a program associated with accidental releases

Title III
Hazardous Air Pollutants

- Requires MACT for all major sources > 10 tons/year or 25 tons/year for combination of toxics
- Requires emission reductions of 75 to 90% below current levels through MACT controls

Title III
Hazardous Air Pollutants

- Impact on Industry
  - Application of maximum achievable control technology (MACT)
  - Standards are technology-based
  - May have to control after MACT to 10^{-6} risk level at property line

Example of MACT Standards

- Subpart FFFF (Misc. Organic Chemical Production and Processes [MON])
- Subpart DDDDD (Industrial, Commercial and Institutional Boilers and Process Heaters)
- Hazardous Organic NESHAP (HON) Rule: Regulates SOCMI
  - 370 Facilities
  - 111 of the 188 Title III HAPs

Where Do We Find the Test Methods?

- Federal Test Methods- Methods are those (Federal Reference Methods and others) specified in the applicable standards as the test methods used to demonstrate compliance with emission limits or quantitate emissions in meeting regulatory initiatives

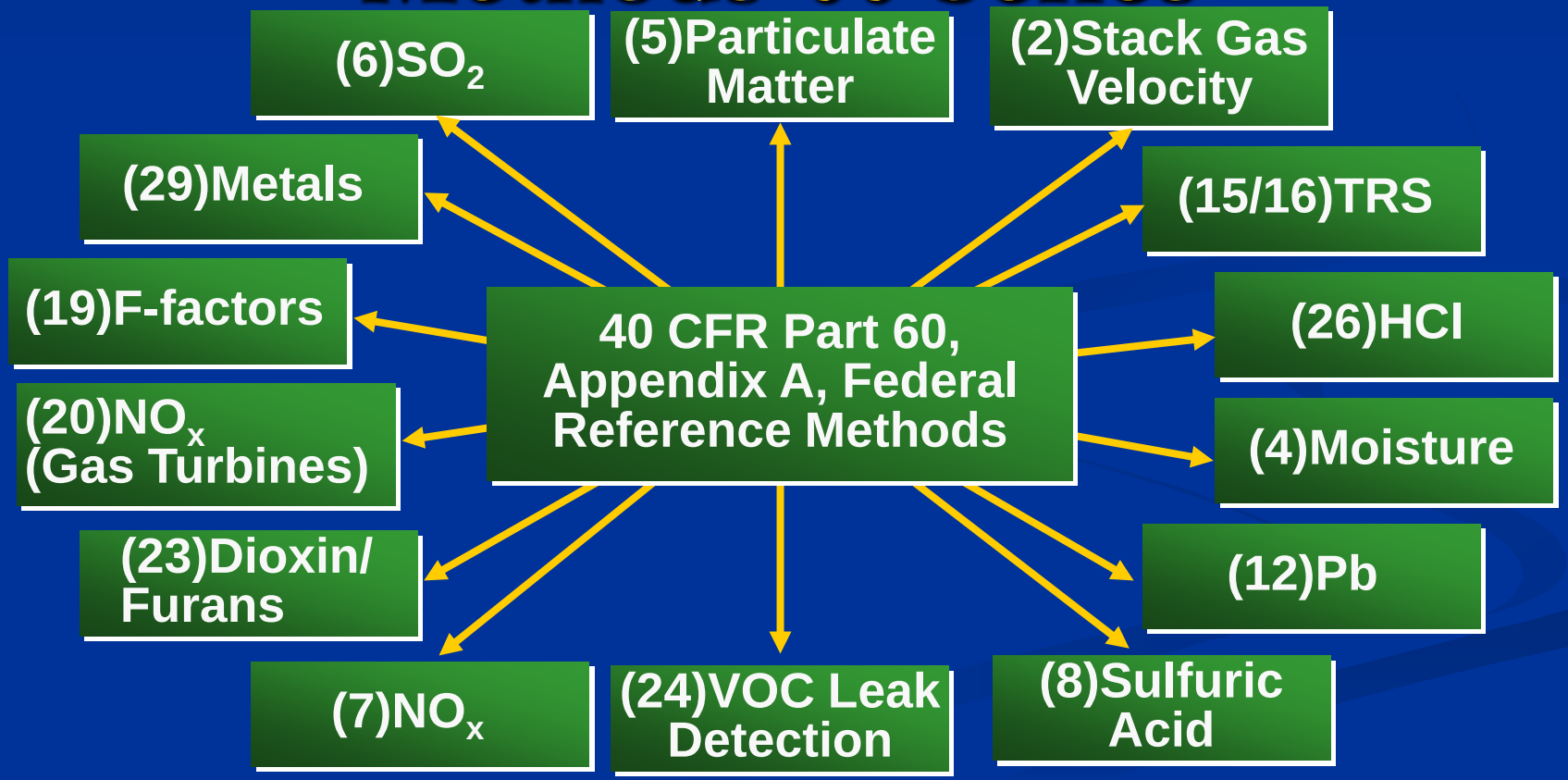
Where Do We Find the Test Methods?

www.epa.gov/ttn/emc/tmethods.html

Regulations

- 40 CFR Part 60, Appendix A Standards of Performance for New Stationary Sources (i.e., NSPS), Federal Reference Methods (00 Series)

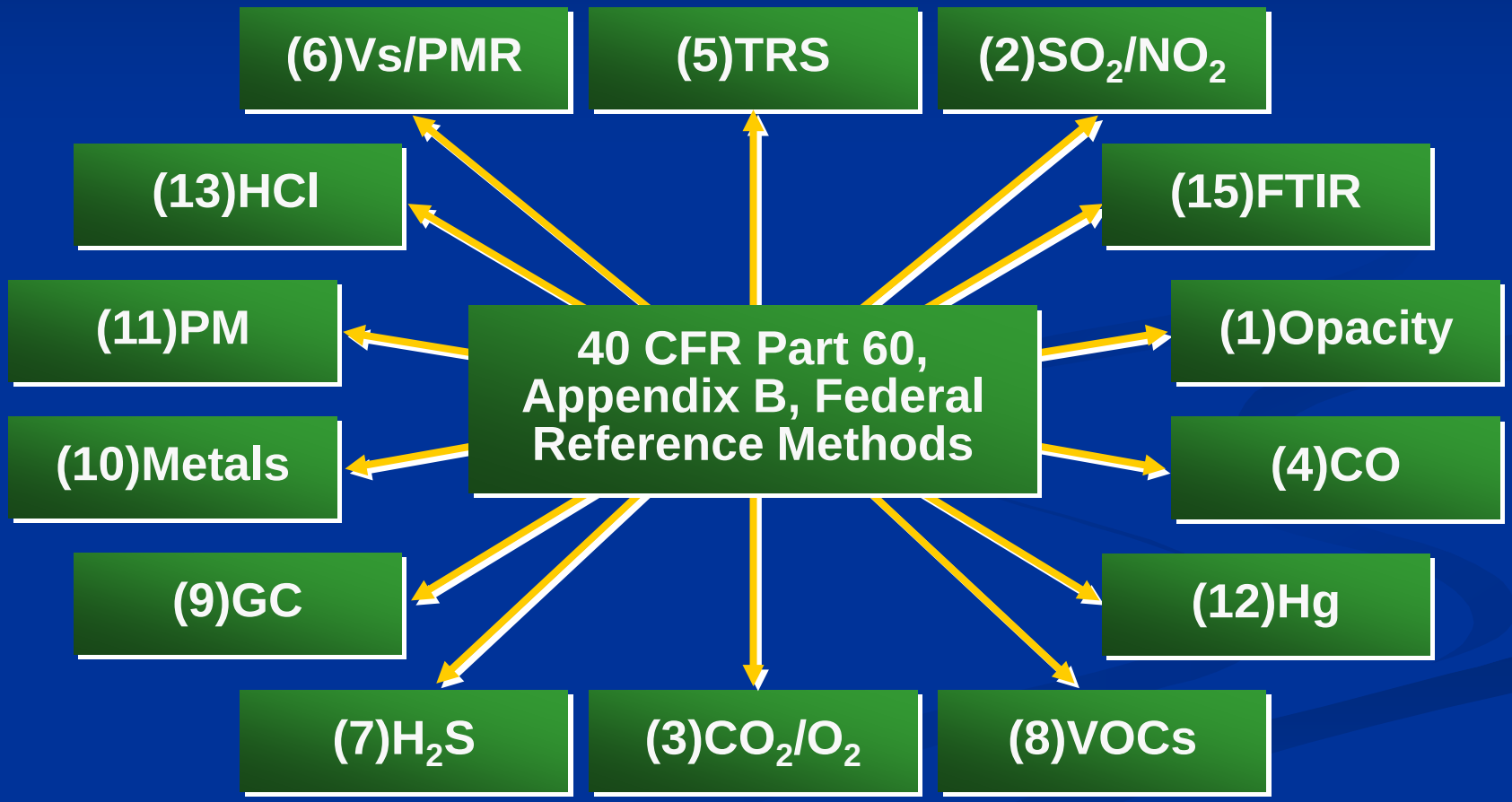
New Source Performance Standard (NSPS) Reference Methods-00 Series



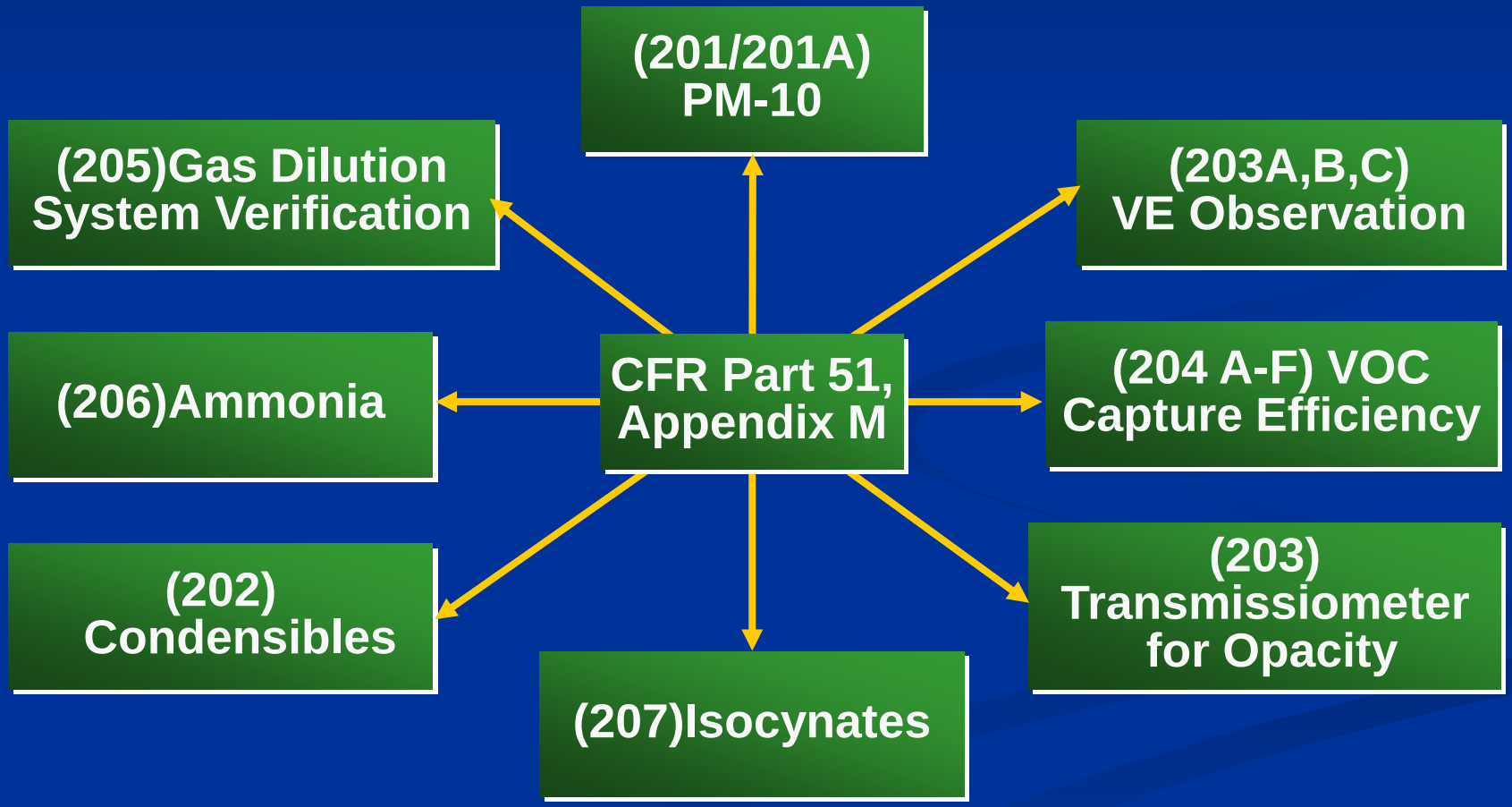
Regulations

- 40 CFR Part 60, Appendix B
  Performance Specification Test (PST) Methods (00 Series)
- 40 CFR Part 51, Appendix M
  State Implementation Plan (SIP) Methods (200 Series)

Performance Specification Test (PSTs)-00 Series



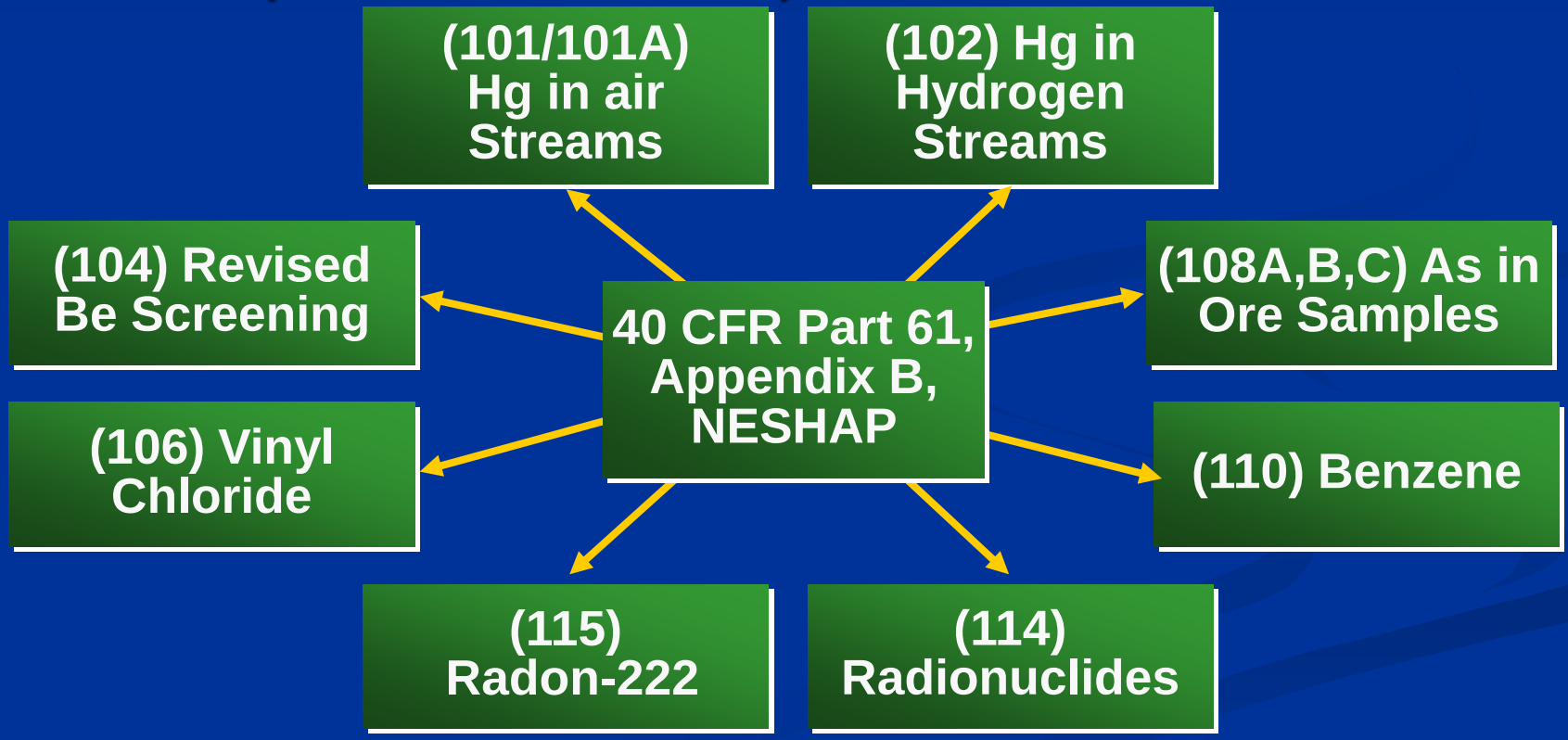
State Implementation Plan (SIP)- 200 Series



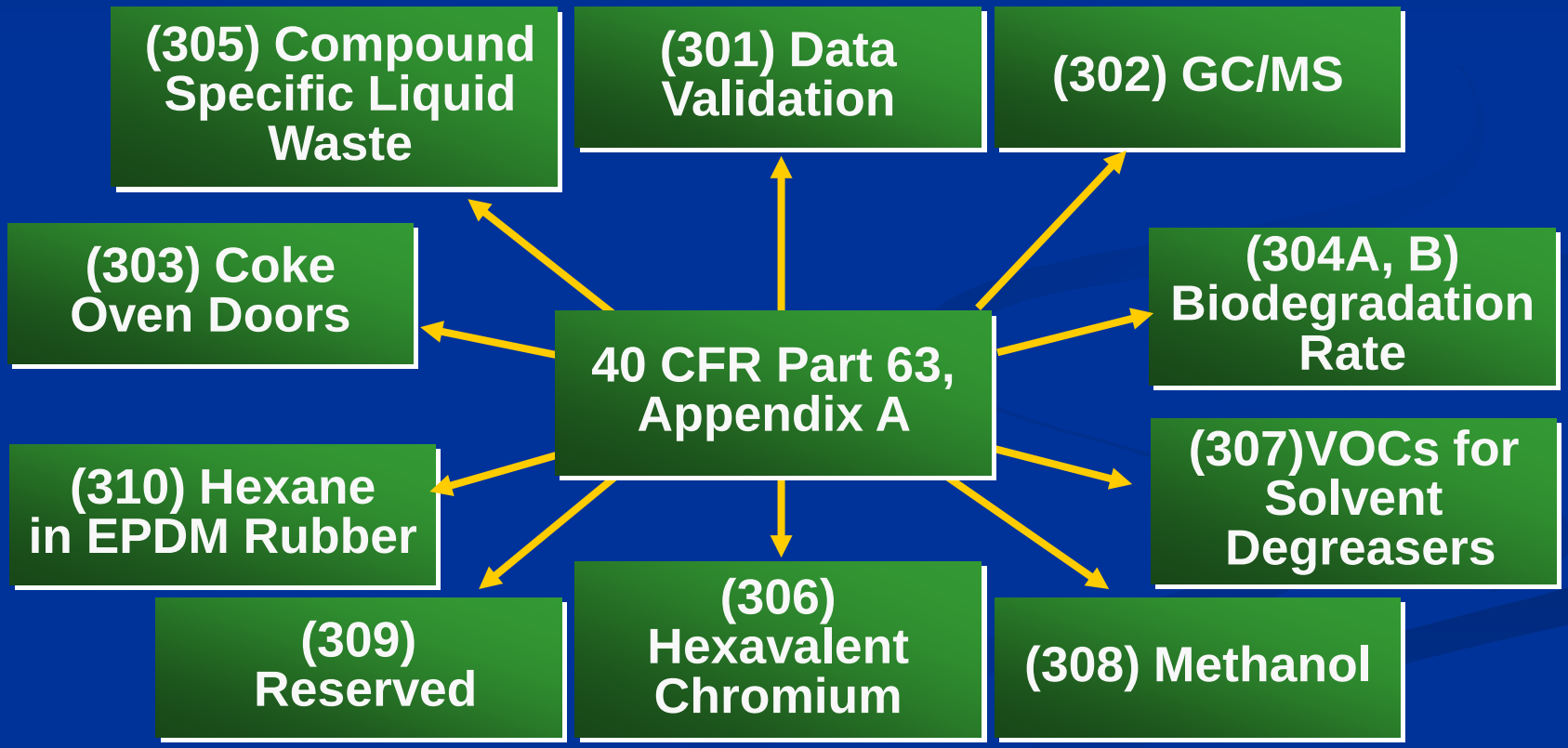
Clean Air Act and It's Amendments

- 40 CFR Part 61
  National Emission Standards for Hazardous Air Pollutants (NESHAP)(100 Series, Appendix B)
- 40 CFR Part 63
  Maximum Achievable Control Technology (MACT) Methods (300 Series, Appendix A)

National Emission Standards For Hazardous Air Pollutants (NESHAPs)- 100 Series



Maximum Achievable Control Technology (MACT)-300 Series



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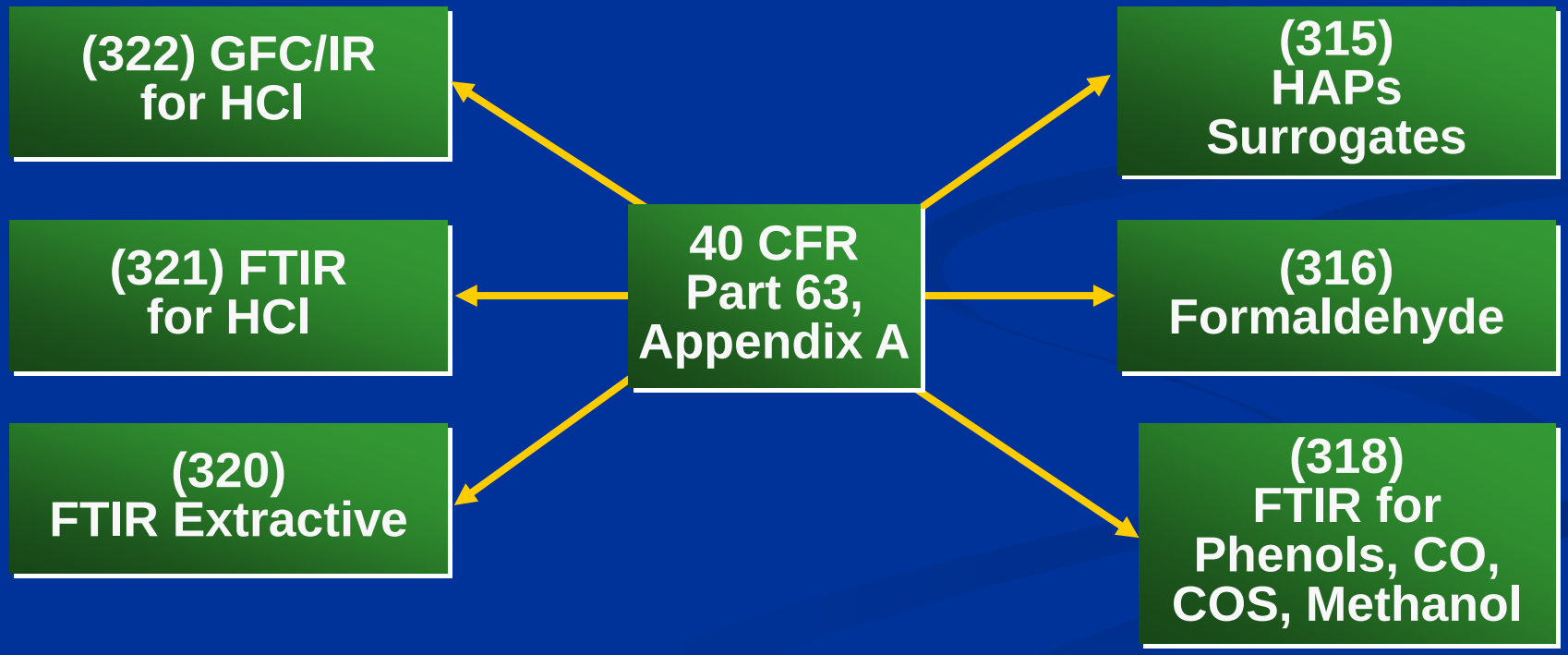


Categories of Stack Test Methods by EPA

www.epa.gov/ttn/emc/tmethods.html

- Category A: Methods proposed or promulgated in Federal Register
  - Compliance Methods for 40 CFR Parts 60, 61, and 63
- Category B: Source category " Approved Alternative"
  - Compliance Methods for specific applications with approval from EPA

Categories

- Category C:
  "Other Methods" which have not yet been subject to the Federal rulemaking process. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the Emission Measurement Center staff and have been found to be potentially useful to the emission measurement community.

Categories

- Category D: "Historic Conditional Methods." These HCMs have been evaluated by the Agency and may be applicable to one or more categories of stationary sources. The EPA confidence in a method included in this category is based upon review of various technical information including, but not limited to, field and laboratory validation studies.

Example Category Stack Test Methods

- Category A (FRMs):
  FRMs 1-29, FRM 100s,
  200s, and 300s
- Category B (Approved Alternatives):
  ALT-007 (use of dilution probe in Methods 6C, 7B, 3A, 10 and 20)

Example Category Stack Test Methods

- Category C (Other Methods): Particulate (PM Screening) Method; Test method for Isocynates; Optical Remote Monitoring, Metal CEMS, HCN

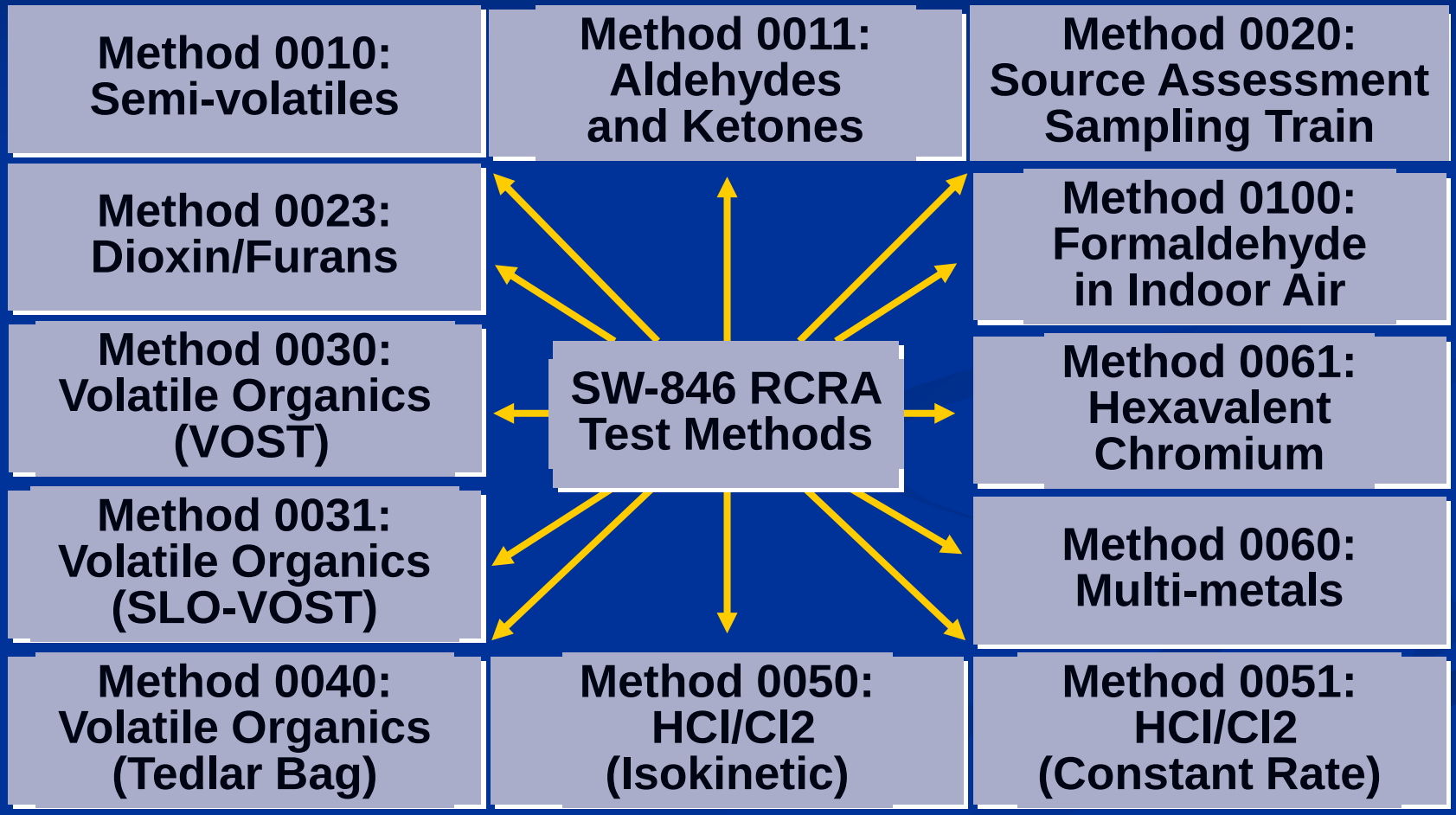
Example Category Stack Test Methods

- Category D (Historical Conditional Methods): Determination of oxides of nitrogen from stationary sources (UV Instrumental Analyzer), PM Screening Methods, Halogenated Organics

Resource Conservation And Recovery Act (RCRA)

- SW-846 is the compendium of analytical and test methods used in determining regulatory compliance under RCRA
  - (http://www.epa.gov/sw-846)

SW-846 Stack Test Methods



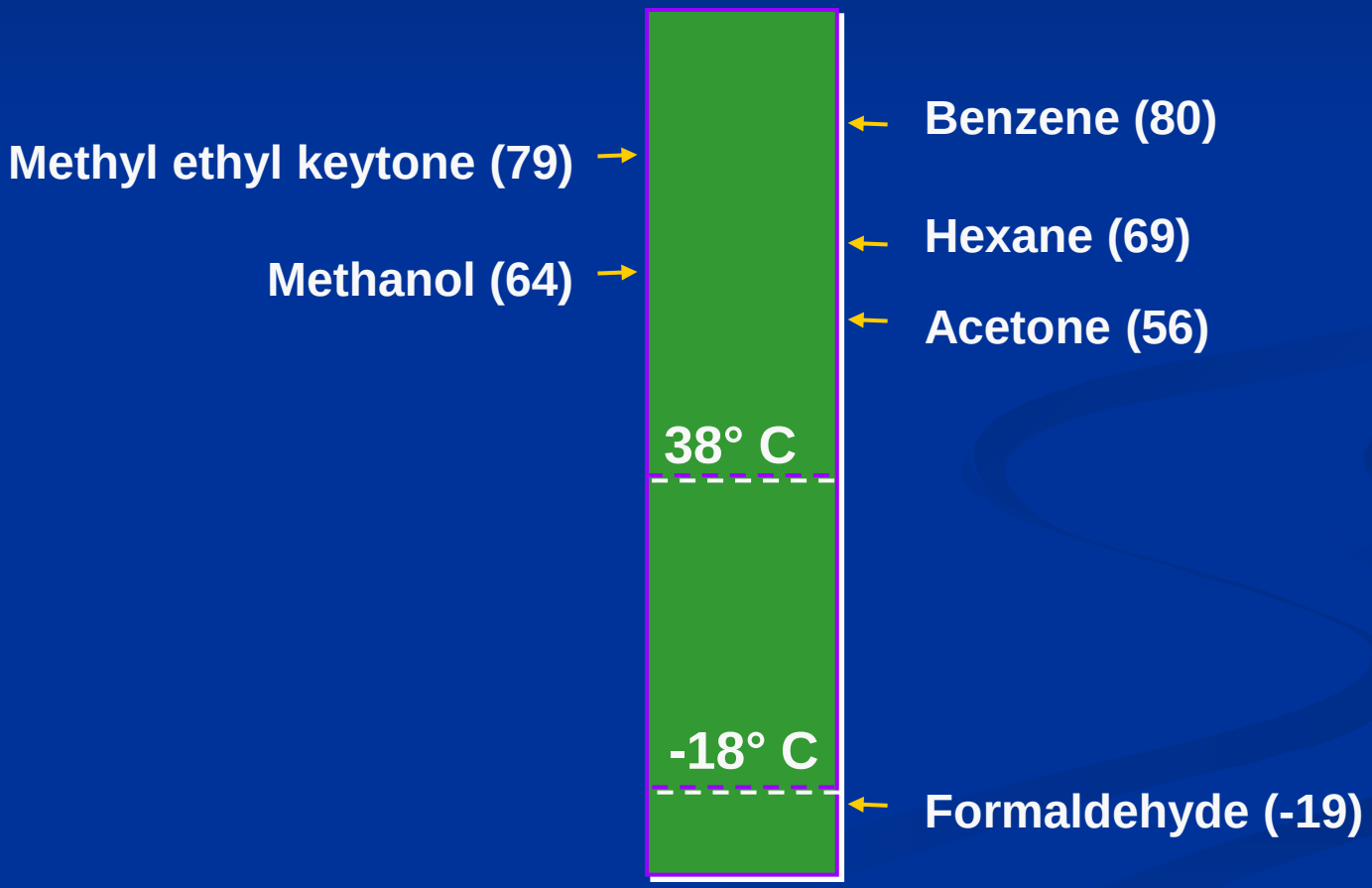
How Do We Define HAPs

- CAAA of 1990, Title III now contains a list of 188 HAPs containing both organic and inorganic analytes
- Defining the 188 HAPs according to
  - Vapor Pressure (in mm Hg at 25°C)
  - Boiling Point Temperature (°C)

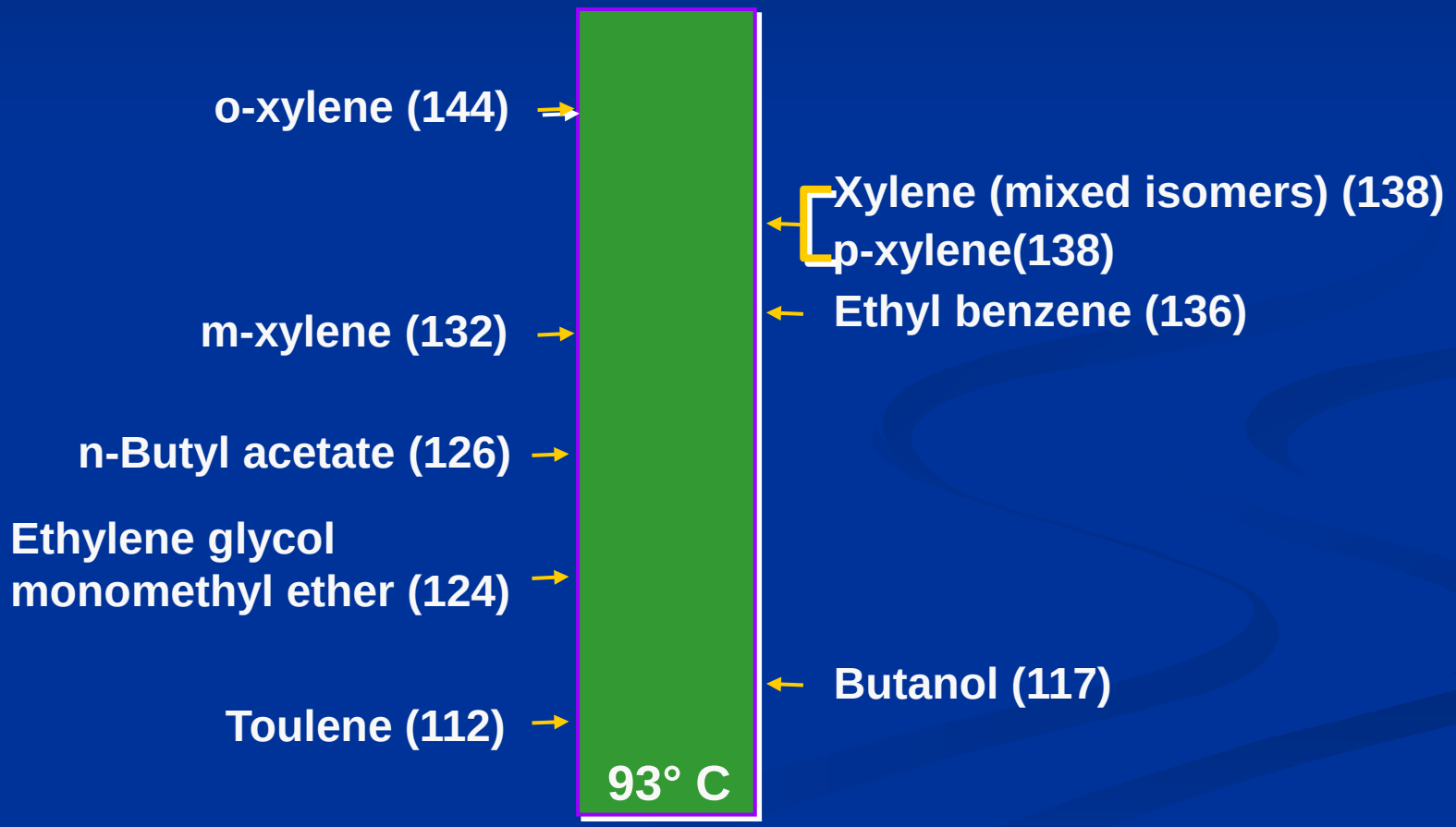
General Classification of VOCs

Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	> 10^{-1}	< 200°C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	200 - 500°C
Particles (NV)	< 10^{-7}	> 500°C

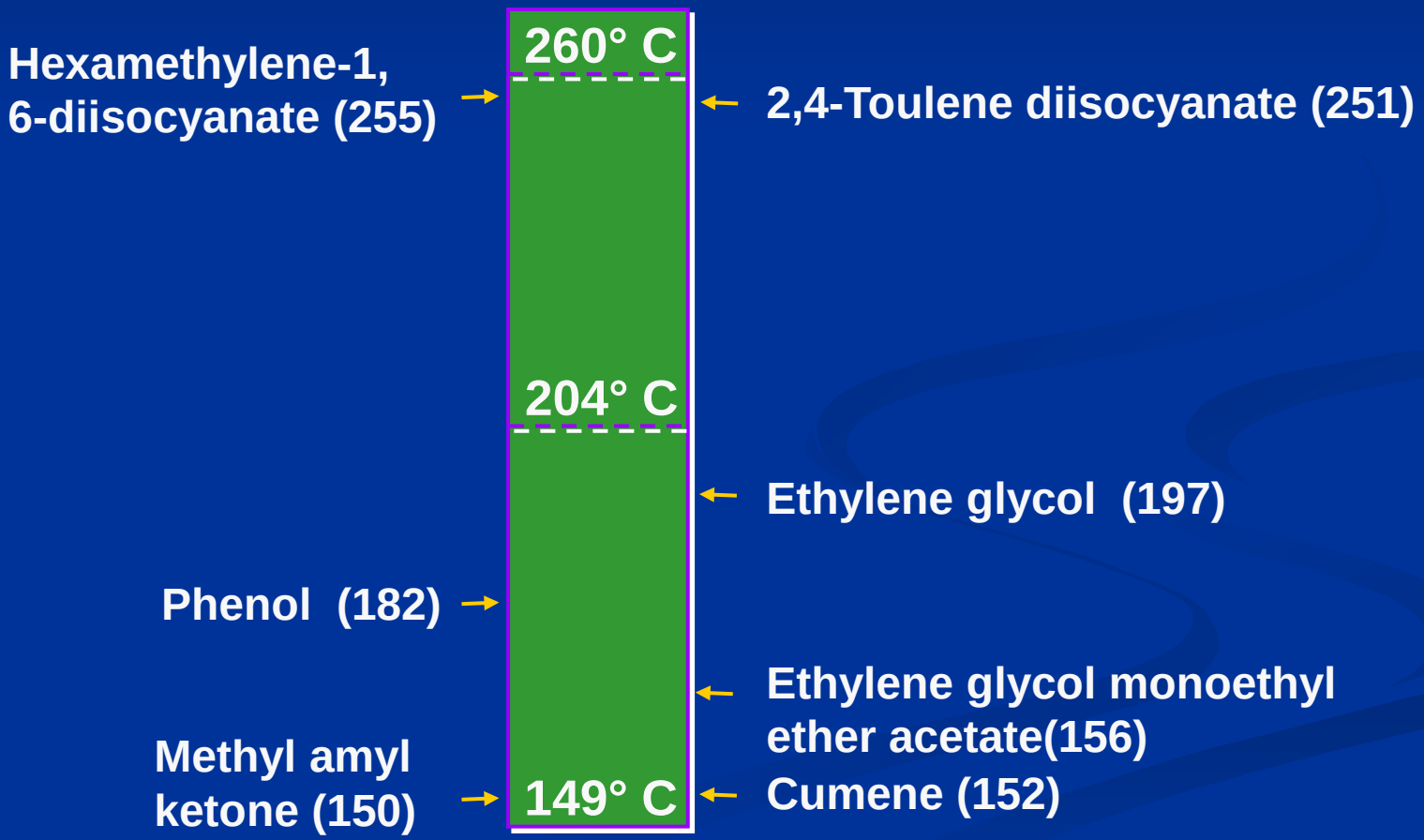
Boiling Points of Volatile Organic Compounds



Boiling Points of Volatile Organic Compounds



Boiling Points of Semi-volatile Organic Compounds



General Classification of HAPs

Volatility Class	Number of HAPs in Class
Volatiles (VV/V)	104
Semi-volatiles (SV)	65
Non-Volatile (NV) Particles	17
Total HAPs	**186**

Example of HAPs in Each Volatility Class

VP (0.1- 380 mm Hg)
BP (< 200°C)

VOLATILE

Benzene	76 mm Hg	80.1°C
Xylene, ortho	5 mm Hg	144.4°C
Hydrazine	16 mm Hg	113°C
Hydrochloric acid	23 mm Hg	110°C

Example of HAPs in Each Volatility Class

VP (10^{-7} to 10^{-1} mm Hg)
BP (200 to 500°C)

SEMI-VOLATILE (65 HAPs)

Benzidine	10^{-5} mm Hg	402°C
Captan	10^{-6} mm Hg	479°C
Phosphorus	10^{-2} mm Hg	280°C
Mercury Compounds	10^{-3} mm Hg	356°C

Example of HAPs in Each Volatility Class

VP (< 10^{-7} mm Hg)
BP (>500°C)

NON-VOLATILE [Particles] (17 HAPs)

3,3'-Dimethoxybenzidine	10^{-13} mm Hg	458°C
Antimony	Very Low	656°C
Coronene	10^{-13} mm Hg	525°C

General Classification of VOCs

Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	> 10^{-1}	< 200°C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	200 - 500°C
Particles (NV)	< 10^{-7}	> 500°C

Compliance Test and Source Test Observation

EPA's National Stack Testing Guidance






'94 6 18


'94 5 20


'94 6 19

Purpose/Goals

- Recognize importance of stack testing as a primary method for determining whether facility has ability to comply with CAA and continues to be in compliance with emission limits
- Improve uniformity in how tests are conducted, evaluated, and reported
- Improve coordination with states/locals
- Enhance oversight

Major Issues Addressed By Guidance

- Time Frame
- Waivers
- Notification
- Observation
- Representative Testing Conditions
- Stoppages
- Postponements
- Test Reports

Where We Are

- Interim Guidance: February 2, 2004
- Final Guidance: September 30, 2005
- Subsequent rulemaking to allow for extensions in testing deadlines in Force Majeure events
  - Parts 60, 61, 63 of General Provisions amended May 16, 2007
  - Consolidated Federal Air Rule (GP Part 65) amended August 27, 2007
- Draft Guidance Revision: November 2008

Definition

- Definition and "Scope of Guidance" sections clarify guidance applies only to tests conducted for compliance purposes under NSPS, NESHAP, and MACT programs:

  Any Performance Testing Conducted for the Purposes of Determining and Demonstrating Compliance with the Applicable Standards of 40 CFR Parts 60, 61, and 63 Using Promulgated Test Methods, Other Test Methods or Procedures Cited in the Applicable Subpart(s), or Alternative Test Methods Approved by the Administrator Under §§60.8, 61.13, or 63.7. It Does Not Include Visible Emission Observation Testing.

Compliance Monitoring Strategy (CMS)

- Provides national consistency in developing stationary source CAA compliance monitoring programs while allowing states/locals flexibility to address local air pollution/compliance problems
- States/locals submit CMS plans biennially to Regions
- Enter compliance evaluation results in AFS
- Sources covered are Title V majors and synthetic minors that emit or have potential to emit emissions at or above 80 percent of Title V major source threshold (SM80s)

CMS

- Agency should conduct, or require facility to conduct, a stack test:

  - Whenever the Agency deems appropriate

  - Where there is no other means for determining compliance with emission limits

- Report date and results of all stack tests in AFS, and adjust HPV status, if necessary

High Priority Violations Policy (HPV)

- Designed to prioritize violations for federal, state, and local agency enforcement efforts
- Covers definition/identification of HPVs, timely and appropriate enforcement response, penalties, and reporting in AFS
- Applies to any major source, any synthetic minor source and any source, major or minor, upon mutual agreement between EPA and state/local at their discretion

HPV Policy

- HPV status is triggered by failure of a stack test
- Violations of emission limits for pollutants for which facility is not designated as a "major source" may not rise to HPV status, but still must be addressed
- If fail test, facility must:
  - Document failure
  - Submit report
  - Resolve conditions
  - Test again

Time Frame

- Current regulations do not provide for extensions of test deadlines, except in the event of a force majeure
  - Violation of requirement to stack test
  - Violation of requirement to demonstrate compliance with underlying standard
- Failure to conduct test established in permit or enforcement document
  - Violation of permit or enforcement document
  - May be a violation of underlying requirement
- Concern that only way to grant additional time to test is through formal enforcement action regardless of circumstances

Time Frame (Cont.)

- Guidance takes into account inability to meet regulatory testing deadlines due to circumstances beyond facilities' control
- Currently, four scenarios for how delegated agencies should respond to facilities not testing by deadline
  - Scenarios range from "Force Majeure events" beyond control of facility to those instances where the facility knowingly and willfully violates test requirement
    - Prior to Force Majeure rule, delegated agency was to use enforcement discretion by issuing letter (versus a formal AO) acknowledging circumstances and establishing new test date

Force Majeure Event

- Force Majeure rules for Parts 60, 61, and 63 of The General Provisions and Part 65 (Consolidated Federal Air Rule):
  - Allow an extension of the deadline by which source owners or operators are required to conduct an initial or subsequent test required by applicable regulations in the event of a Force Majeure
  - Under such circumstances, no violation and thus no need to use enforcement discretion to extend deadline
  - Guidance is being updated consistent with the Rules

Waivers For Identical Units

- Text includes pertinent regulatory references
- Criteria for determining when stack tests for identical units may be waived
- Concept that margin of compliance may not have to be significant where the emissions variability of identical units is low

Notification

- Sufficiency of both the timing and content of the notification is discussed
- Text clarifies that notification is not necessary if test is outside scope of guidance, unless potential for applicable limits to be exceeded
- Clarifying language on submitting site-specific test plans and the contents of such plans

Observation

- No requirement that agency be present for tests. However, whenever possible, delegated agencies should observe
- If agency unable to observe test, review of test protocol even more important
- If timely notification and opportunity to observe not provided, results may be rejected

Representative Testing Conditions

- Guidance reinforces Agency position that the CAA requires continuous compliance with emissions limits except where explicitly excused
- Tests should be performed under those representative conditions that:
  - Represent the range of combined process and control measure conditions under which the facility expects to operate (regardless of the frequency of the conditions)
  - Are likely to most challenge the emissions control measures of the facility with regard to meeting the applicable emission standards, but without creating an unsafe condition

Soot-Blowing

- Guidance consistent with and relies upon past Agency position for including soot-blowing
- Emissions from soot-blowing cannot be discarded as the result of an upset condition
- Erroneous to stop soot-blowing for the purpose of conducting a stack test

Stoppages/Postponements

- No regulatory provision allows stoppage, except for force majeure event
- Depending on circumstances, facility may be in violation of requirement to conduct test, underlying requirement, or both
  - If in jeopardy of failing test, violation of both
  - Currently, Guidance states that if facility is forced to stop due to a force majeure event, agency should evaluate circumstances to determine appropriate enforcement response, if needed
- Guidance is being updated consistent with rulemaking
- Postponements should be treated similar to stoppages
  - If fail to complete test within required time, violation of requirement to test

Test Reports

- Information necessary to adequately document results
- At a minimum, test submittal:
  - NSPS: Within 180 days after initial startup date or within 60 days after reaching maximum production rate
  - NESHAP: Within 31 days after test completed
  - MACT: Within 60 days after test completed

Data Reporting

- Minimum Data Requirements (MDRs) for reporting air compliance monitoring and enforcement activity
- Stack test data reported into national air data system (AFS)
- Test date reported with compliance determination from results
  - Compliance status updated, as appropriate
  - High Priority Violator (HPV): failing test for pollutant for which facility is major
  - Test date is to be reported within 60 days of event
- Test results reported as pass, fail, or pending
  - Tests may be reported as pending for up to 120 days from test date
- Reporting of stack test pollutant
  - Mandatory for federal reporters
  - Optional for state reporters

Reported Tests

- State reporting of tests conducted
  - FY 2008: 13,642*
  - FY 2007: 15,476
  - FY 2006: 14,292
- EPA reporting of tests conducted
  - FY 2008: 16*
  - FY 2007: 55
  - FY 2006: 77
- Most tests reported as pass or fail within 120 days

Reported Tests

- Reported test failures
  - FY 2008: 619*
  - FY 2007: 809
- Among states, variation in number of failures vs. total tests conducted*
  - FL: 1235 tests – 8 failures: AL: 1976 tests – 23 failures
  - GA: 862 tests – 40 failures; NJ: 105 tests – 33 failures; IA: 426 tests – 73 failures
- For sources that failed, data issue concerning compliance status. For FY '07:
  - 48% listed "in violation"; 20% listed as HPV

---

*States/EPA have until 12/1 to report FY '08 data

Additional Information

- Robert Lischinsky

  lischinsky.robert@epa.gov

  202-564-2628
- Internet Address:

  http://www.epa.gov/Compliance/resources/policies/

  monitoring/caa/stacktesting.pdf

Compliance Test and Source Test Observation

EPA's Compliance Monitoring Strategy (CMS)




'94 5 20

CMS's Full Compliance Evaluation

- A Full Compliance Evaluation is a comprehensive evaluation of the compliance status of a facility
  - A review of all required reports, and to the extent necessary, the underlying records. This includes all monitored data reported to the regulatory agency (e.g., CEM and continuous parameter monitoringreports, malfunction reports, excess emission reports). It also includes a review of Title V self-certifications, semi-annual monitoring and periodic monitoring reports, and any other reports

CMS's Full Compliance Evaluation

- An assessment of control device and process operating conditions as appropriate.
- A visible emission observation as needed.
- A review of facility records and operating logs.
- An assessment of process parameters such as feed rates, raw material compositions, and process rates.

CMS's Full Compliance Evaluation

- An assessment of control equipment performance parameters(e.g., water flow rates, pressure drop, temperature, and electrostatic precipitator power levels).
- A stack test where there is no other means for determining compliance with the emission limits.

CMS's Partial Compliance Evaluation

- A Partial Compliance Evaluation is a documented compliance assessment focusing on a subset of regulated pollutants, regulatory requirements, or emission units at a given facility. A Partial Compliance Evaluation should be more comprehensive than a cursory review of individual reports. It may be conducted solely for the purpose of evaluating a specific aspect of a facility, or combined over the course of a year (or up to three years at mega-sites) to satisfy the requirements of a Full Compliance Evaluation.

CMS's Investigation Evaluation

- An Investigation can be distinguished from the other two categories in that generally it is limited to a portion of a facility, is more resource intensive, and involves a more in-depth assessment of a particular issue. It usually is based on information discovered during a Full Compliance Evaluation, or as the result of a targeted industry, regulatory or statutory initiative.

Frequency of Evaluations

- A Full Compliance Evaluation should be conducted, at a minimum, once every two years at all Title V major sources except those classified as mega-sites and once every five years at synthetic minor sources that have the potential to emit 80% of Title V sources threshold. For mega-sites, a Full Compliance Evaluation should be conducted, at a minimum, once every three years.

Frequency of Evaluations

- An on-site visit should be conducted, at a minimum, once every five years at all Title V major sources to ensure a compliance presence in the field, verify record reviews, observe modifications or new construction, and identify any major permit deviations.

Elements of the CMS Plan

- CMS plans should be submitted biennially, consistent with the current EPA two-year MOA planning process.
- The content of CMS plans will vary depending upon whether States/locals develop and negotiate alternatives to the minimum frequencies.

Elements of CMS Plan

- In those instances where States/locals meet the recommended minimum frequencies and do not develop and negotiate alternative approaches, the plan should include the following elements:
  - A facility-specific list (including the AFS identification numbers) of all Title V major sources.
  - A facility-specific list (including the AFS identification numbers) of all synthetic minor sources and a list of those facilities covered by the policy.

Elements of CMS Plan

- A description of how a State/local will address any identified program deficiencies in its compliance monitoring program.

- In those instances where the States/locals propose alternatives to the recommended minimum frequencies, States/locals should provide a more detailed plan.
- If can't meet two year commitments, notify the Region and revise their CMS plan accordingly.

Compliance Monitoring Report

- General information--date, compliance monitoring category (i.e., FullCompliance Evaluation, Partial Compliance Evaluation, or Investigation),and official submitting the report.
- Facility information--facility name, location, mailing address, facilitycontact and phone number, Title V designation and mega-site designation

Compliance Monitoring Report

- Applicable requirements--all applicable requirements including regulatory requirements and permit conditions.
- Inventory and description of regulated emission units and processes.
- Information on previous enforcement actions.

Compliance Monitoring Report

- Compliance monitoring activities--processes and emission units evaluated; on-site observations; whether compliance assistance was provided and if so, nature of assistance; any action taken by facility to come back into compliance during on-site visit.
- Findings and recommendations relayed to the facility during the compliance evaluation.

High Priority Violators

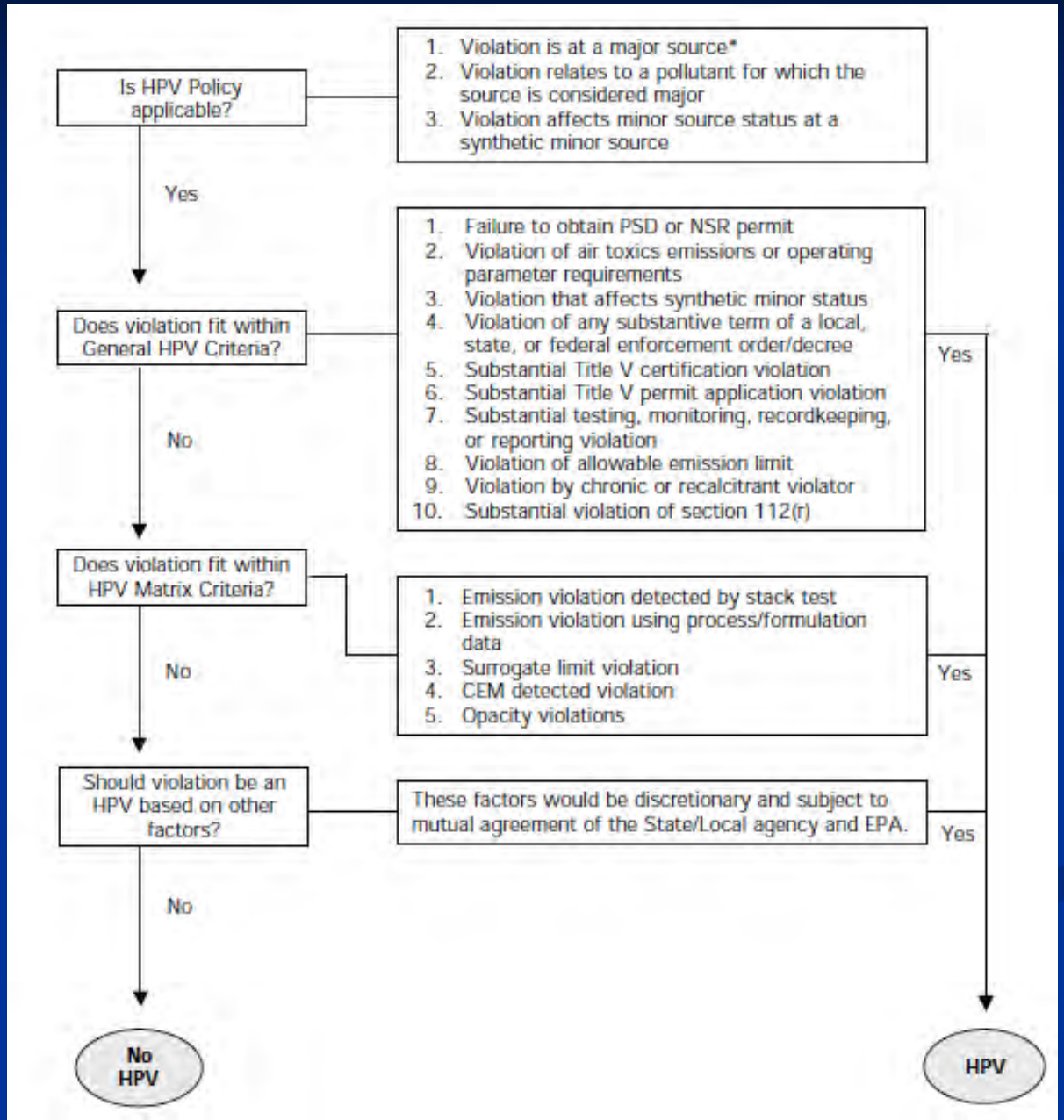
- December 22, 1998 Memo
  - This memo eliminates use of the terms "Significant Violator" and "Significant Violation" and substitutes the term "High Priority Violation" (HPV) in describing violations.
  - EPA expects that all violations of air pollution regulations, whether meeting the HPV criteria or not, will be addressed by States, local agencies, or EPA. EPA

High Priority Violators

- Agency High Priority Violation activities shall be designed to identify and to expeditiously return to compliance those violating sources that the agency believes are environmentally most important, namely the HPVs.
- In accordance with the revised Policy Framework for State/EPA Enforcement Agreements issued by the Deputy Administrator on August 25, 1986 (and its three addenda), this national policy serves as the framework for State specific agreements reflecting the parties' mutual expectations.

HVP Applicability Determination

(See Resource CD, Session 1: EPA's HPV Workbook)



Definition of High Priority Violations

- Failure to obtain a PSD permit (and/or to install BACT), an NSR permit (and/or to install LAER or obtain offsets) and/or a permit for a major modification of either.
- Violation of an air toxics requirement (i.e., NESHAP, MACT) that either results in excess emissions or violates operating parameter restrictions.

Definition of High Priority Violations

- Violation by a synthetic minor of an emission limit or permit condition that affects the source's PSD, NSR or Title V status.
- Violation of any substantive term of any local, state or federal order, consent decree or administrative order.
- Substantial violation of the source's Title V certification obligations, e.g., failure to submit a certification.

Definition of High Priority Violations

- Substantial violation of the source's obligation to submit a Title V permit application.
- Violations that involve testing, monitoring, record keeping or reporting that substantially interfere with enforcement or determining the source's compliance with applicable emission limits.

Definition of High Priority Violations

- A violation of an allowable emission limit detected during a reference method stack test.
- Clean Air Act (CAA).violations by chronic or recalcitrant violators.
- Substantial violation of Clean Air Act Section 112® requirements (for permitting authorities that are not implementing agencies under Section 112(r) program, limited to source's failure to submit Section 112(r) risk management plan).

HPV Determination Using Matrix

Matrix Criterion 1:	Violation of allowable emissions limitation, detected by stack testing
Matrix Criterion 2:	Violation of applicable emissions limitation, detected by coatings analysis, fuel samples, other process materials sampling, or raw/process materials usage reports
Matrix Criterion 3:	Violation of parameter limits where parameter is a direct surrogate for an emissions limitation, detected by continuous/periodic parameter monitoring
Matrix Criterion 4:	Exceedance of applicable non-opacity standard, detected by CEMS
Matrix Criterion 5:	Exceedance of applicable opacity standard (detected by COMS or by VE)

Violations and Method of Detection

- Violation of Allowable Emissions Limitations
  - Reference Method Stack Testing or
  - Coatings Analysis, Fuel Samples or Other Process Material Sampling
- Violation of Parameter Emissions Limitations
- Continuous/Periodic Parameter Monitoring

Violations and Method of Detection

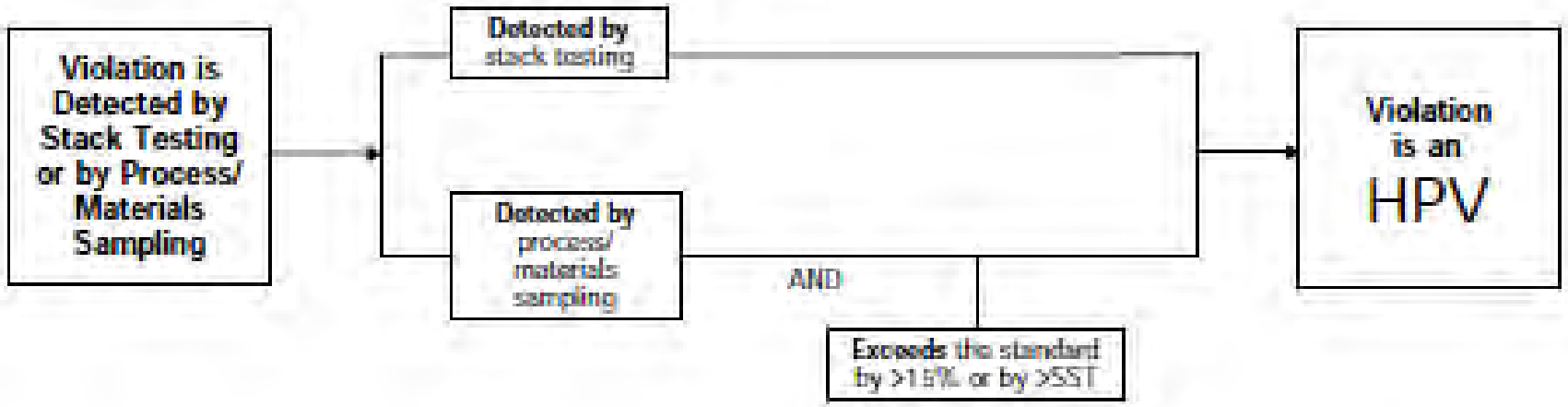
- Violation of Applicable Standards (non-opacity)
  - Continuous Emissions Monitoring (where the CEM is certified under federal performance specifications)
- Violation of Applicable Standards (opacity)
  - Continuous Opacity Monitoring or
  - Method 9 Visual Emissions Readings

Standards For Violation

- Standards For Violations (See Resource CD, Session 1: EPA's High Violations Policy)

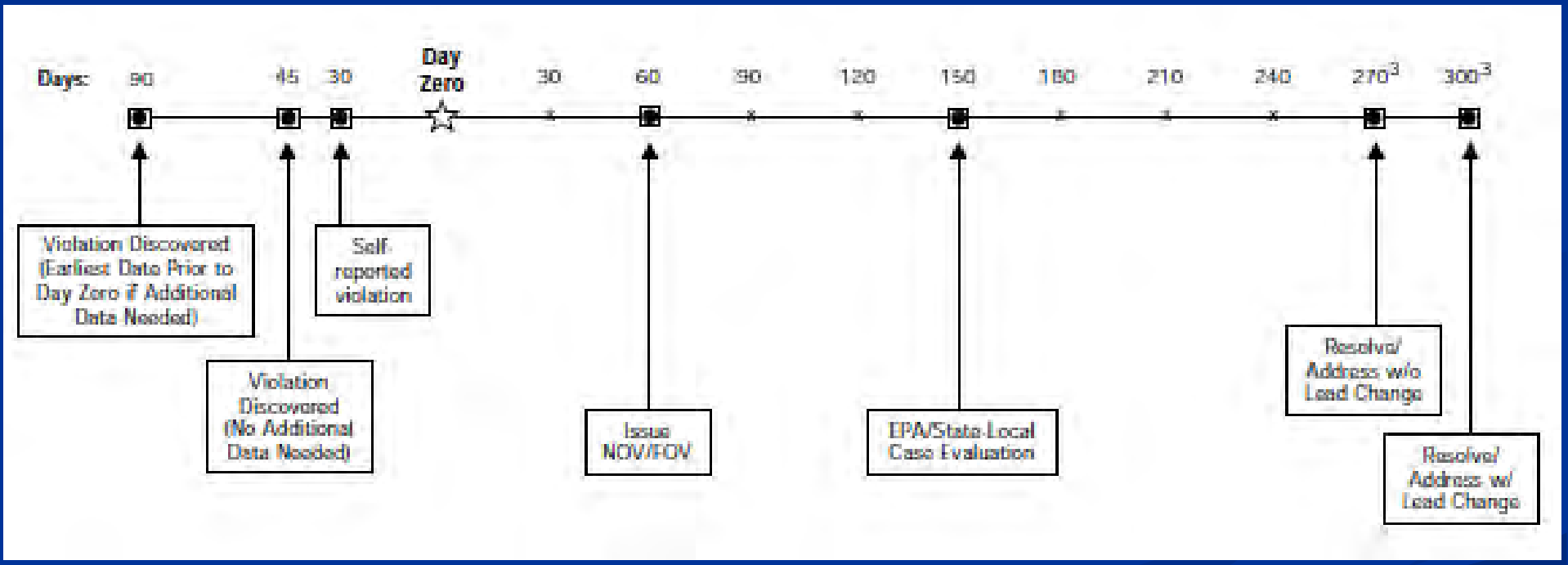
VIOLATION	DETECTION METHOD	STANDARD	SUPPLEM. THRESHOLD	% EXCESS REF. LIMITS
Allowable Emission Limits	Stack Test	Any Applicable Requirement		Any Violation of Standard
	Coating Analysis, Fuel Samples, Other Process Material Sampling	Any Applicable Requirement	CO 23 lb/hr NOx 9 lb/hr SO2 9 lb/hr VOC 9 lb/hr	> 15% of Applicable Emission Limits

Logic Flow For Stack Testing Violation



(See Resource CD, Session 1: EPA's HPV Workbook for Examples)

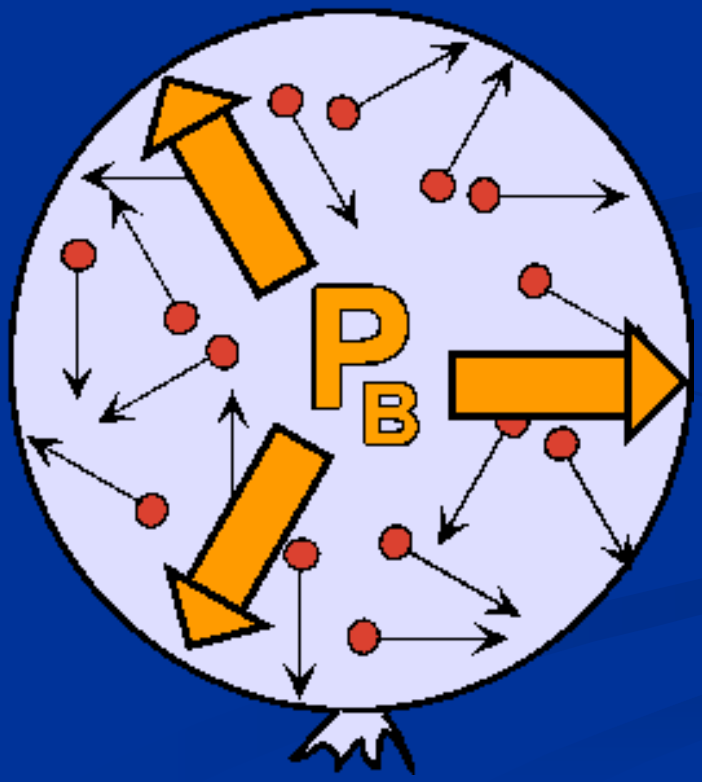
Timely and Appropriate Enforceable Timeline



(See Resource CD, Session 1: EPA's HPV Workbook for Examples)

Compliance Test and Source Test Observation

Properties of Gases



Properties of Gases

- Temperature
- Pressure
- Atomic Weight
- Molecular Weight and Moles
- Avogrado's Number
- Ideal Gas Law
- Moving Gases

Temperature

Degrees Fahrenheit: °F

Degrees Centigrade: °C

$°C = 5/9\ (°F - 32)$

$°F = 9/5\ (°C) + 32$

Absolute Temperature

Degrees Rankine: R

Degrees Kelvin: K

$R = °F + 459.49$

$K = °C + 273.16$

Absolute Pressure, P

$P = P_b + p_g$

P_b = Barometric pressure

P_g = Gauge pressure



Units of Pressure

in. Hg	atmospheres
mmHg	torr
in. H_2O	pascals

1 Atmosphere =

29.92 in. Hg

39.90 ft H_2O

14.70 lbs/in.^{2}

760 mmHg

1 torr

EPA Standard Pressure and Temperature

P_{std} = 29.92 in. Hg

T_{std} = 20° C or 68° F

for source testing

Atomic Weight

A number that indicates how heavy (on the average) an atom is compared to an atom of another element

(Assign **carbon** atomic wt = 12)

Molecular Weight, M

The sum of the atomic weights of all the atoms in a molecule

MW of CO

12 + 16 = 28

n = number of moles

1 mole =

The molecular weight of a compound expressed in lbs (lb-mole) or in grams (g-mole)

1 mole of CO = 28 grams

1 gram-mole =

6.023×10^{23} molecules
(Avogrados's Number)

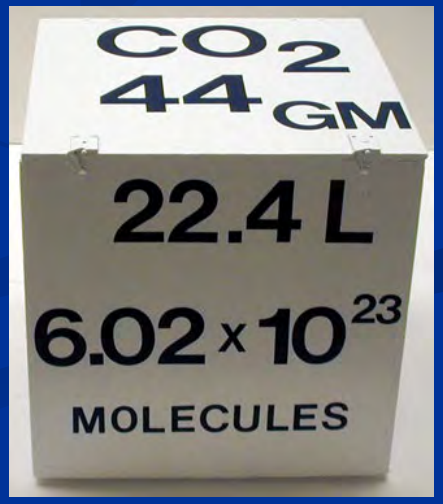
1 mole = Avogrado's Number worth of molecules

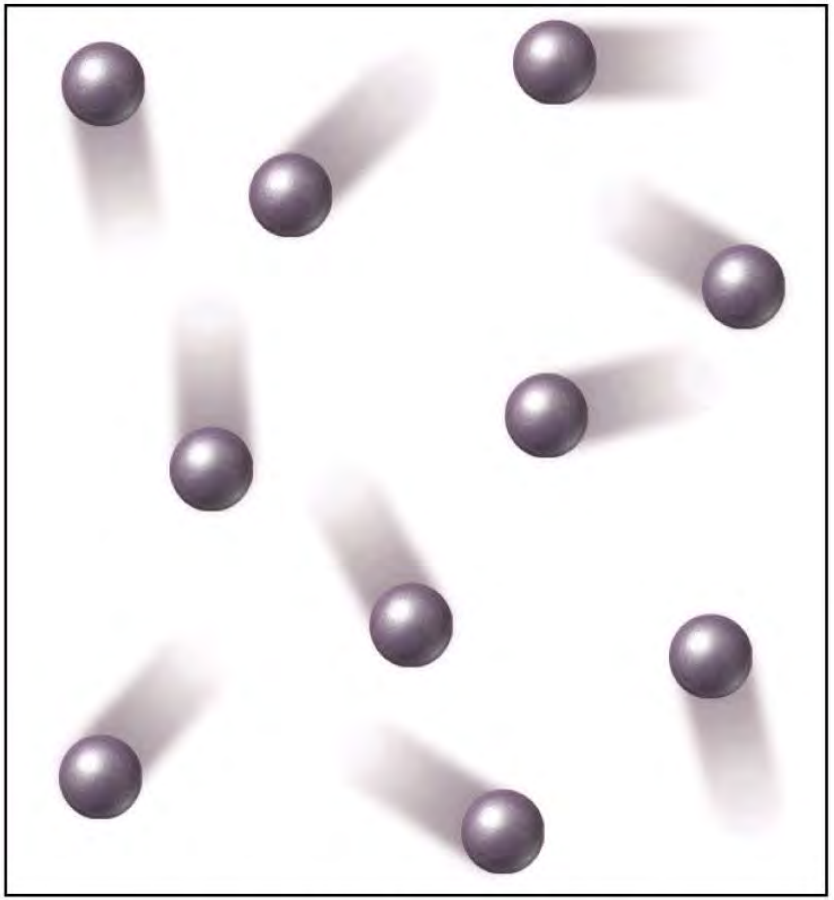
(6.023×10^{23})

Occupies

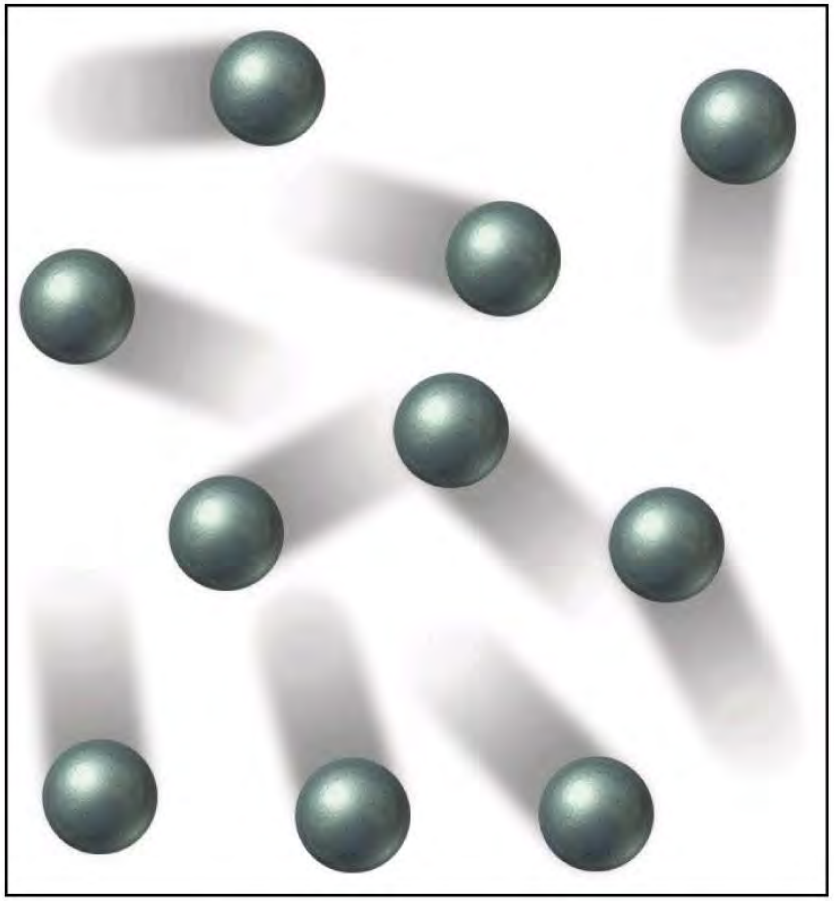
22.4 L

At O° C and 1 atmosphere





1 mol helium at STP
Volume = 22.4 L
Mass = 4.00 g

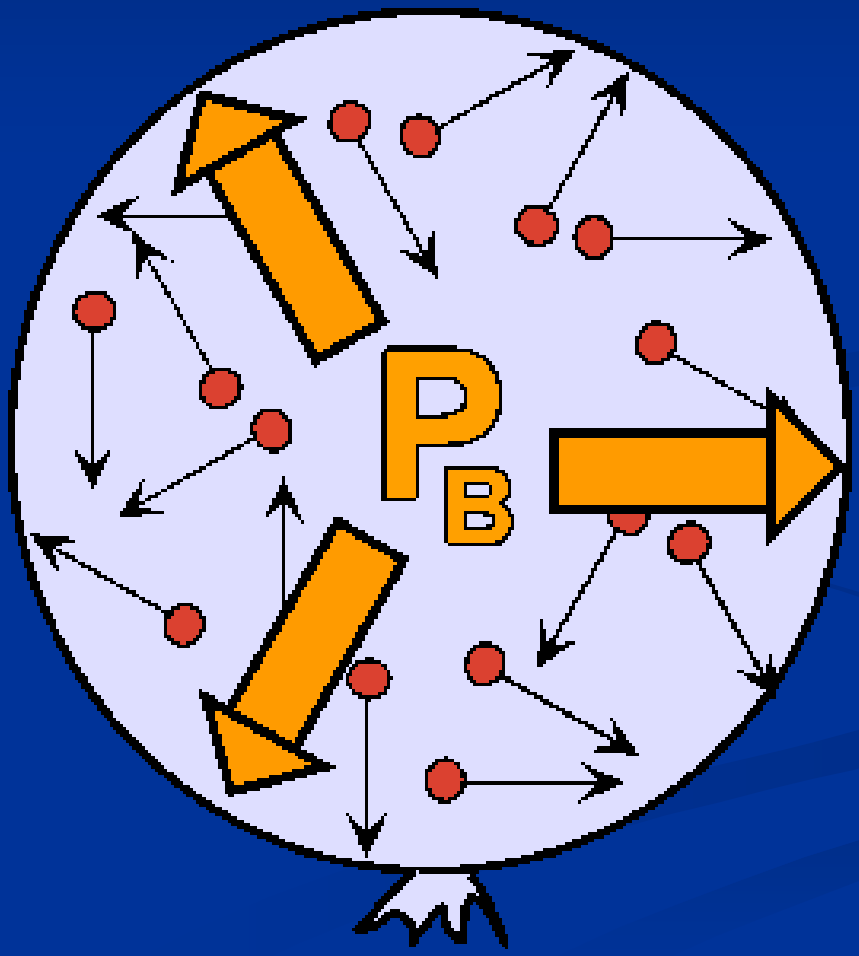


1 mol xenon at STP
Volume = 22.4 L
Mass = 131.3 g

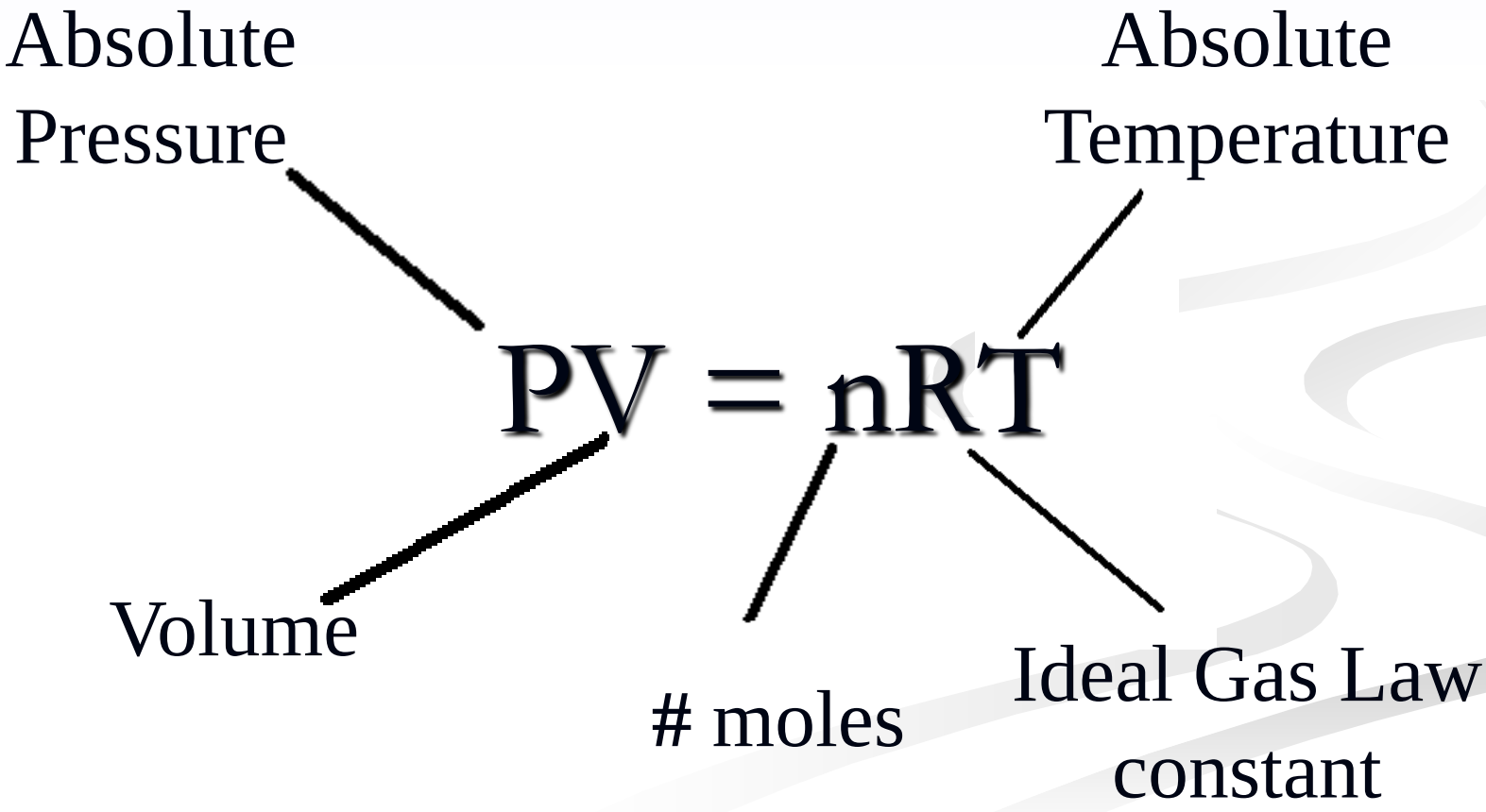
Given a mass, m, of a compound, the number of moles is calculated by:

$$n = \frac{m}{M}$$

The Ideal Gas Law



The Ideal Gas Law



R

The gas law constant is dependent on units used for EPA reference methods in English units:

$$R = 21.83 \frac{(\text{in. Hg})\,(\text{ft}^3)}{(\text{lb-mole})\,(^\circ\text{R})}$$

Correcting Volume to Standard Conditions

$$V_{s\ stack} = nR \frac{T_s}{P_s}$$

$$V_{s\ std} = nR \frac{T_{std}}{P_{std}}$$

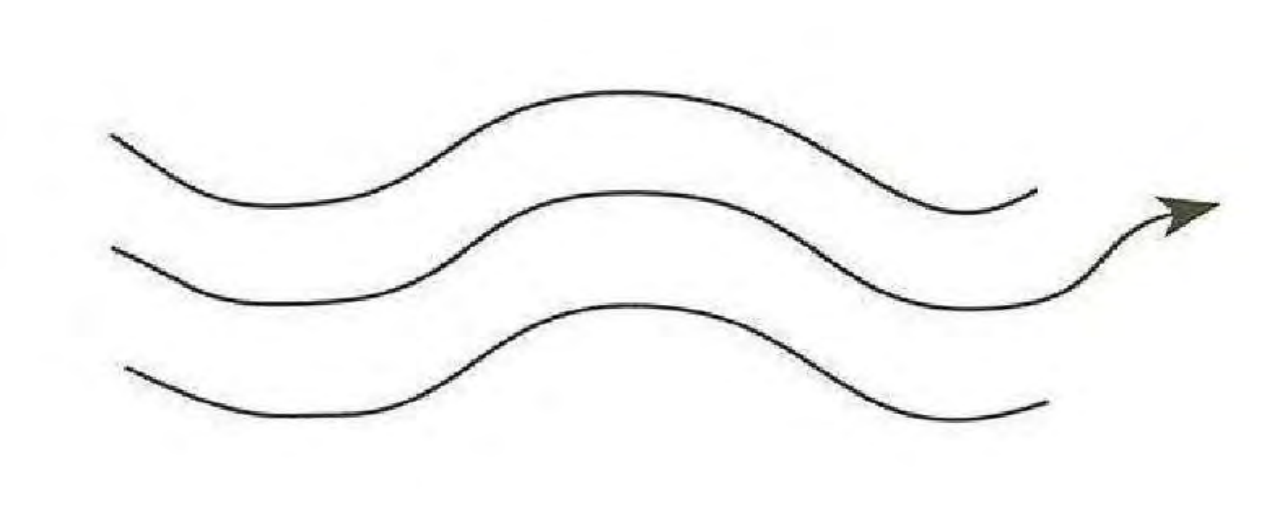
Dividing top by bottom gives

$$V_{std} = V_s \frac{T_{std}\, P_s}{P_{std}\, T_s}$$

Properties of Moving Gases

- Velocity
- Volumetric flow rate
- Isokinetic sampling
- Pollutant mass rate

Velocity



V_s = ft/sec or ft/hr

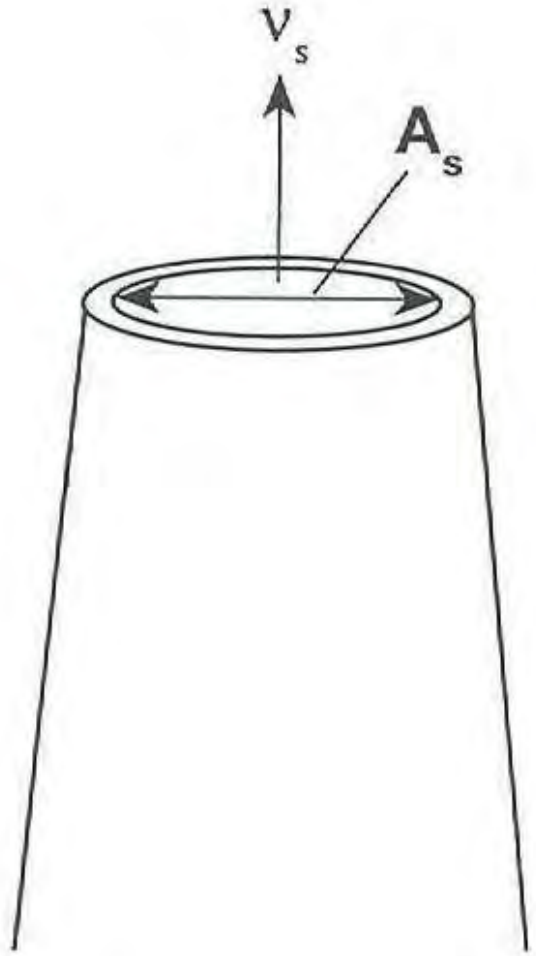
Velocity, v_s $\frac{ft}{sec}$ $\frac{ft}{hr}$

Determined by Method 2 using the Type S pitot tube

The Pitot Tube Equation

$$v_s = K_p C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}}$$

Volumetric Flow Rate



$$Q_s = v_s A_s$$

$$\frac{ft^3}{sec} = \frac{ft}{sec} \times ft^2$$

or

$$\frac{ft^3}{hr} = \frac{ft}{hr} \times ft^2$$

Isokinetic Sampling

$$\% \text{ Isokinetic} = \frac{V_n}{V_s} \times 100$$

FRM 5 Isokinetic Rate Equation

$$\%I_{int} = 100 \frac{T_s V_{m(std)} P_{std}}{T_{std} v_s \theta A_n P_s 60 (1 - B_{ws(est)})}$$

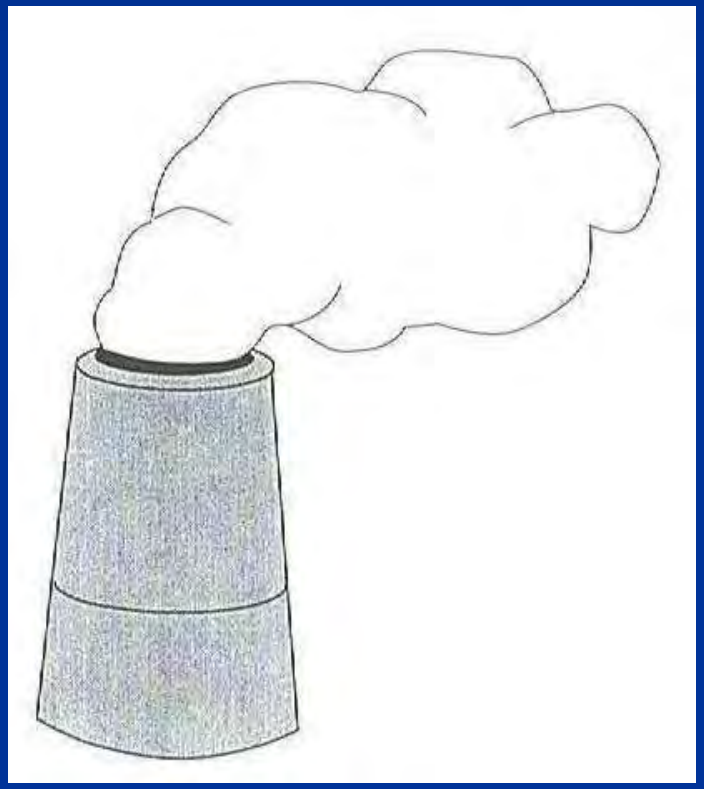
$$\%I_{final} = \frac{100\, T_{s(avg)} \left[K_3 V_{1c} + \left(\frac{V_{m(avg)}}{T_{m(avg)}} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60\, \theta\, V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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

Pollutant Mass Rate (pmr)



$$pmr = c_S Q_S$$

Where: c_S = the pollutant concentration

Concentration, c_S

$$c_S = \frac{m}{V} = \frac{\text{Quantity of pollutant (mass)}}{\text{Quantity of effluent gas (vol)}}$$

Units: g/m^3 , lbs/ft^3 , gr/ft^3, ppm

Note : 7000 grains (gr) = 1 lb

$$pmr_S = c_S Q_S$$

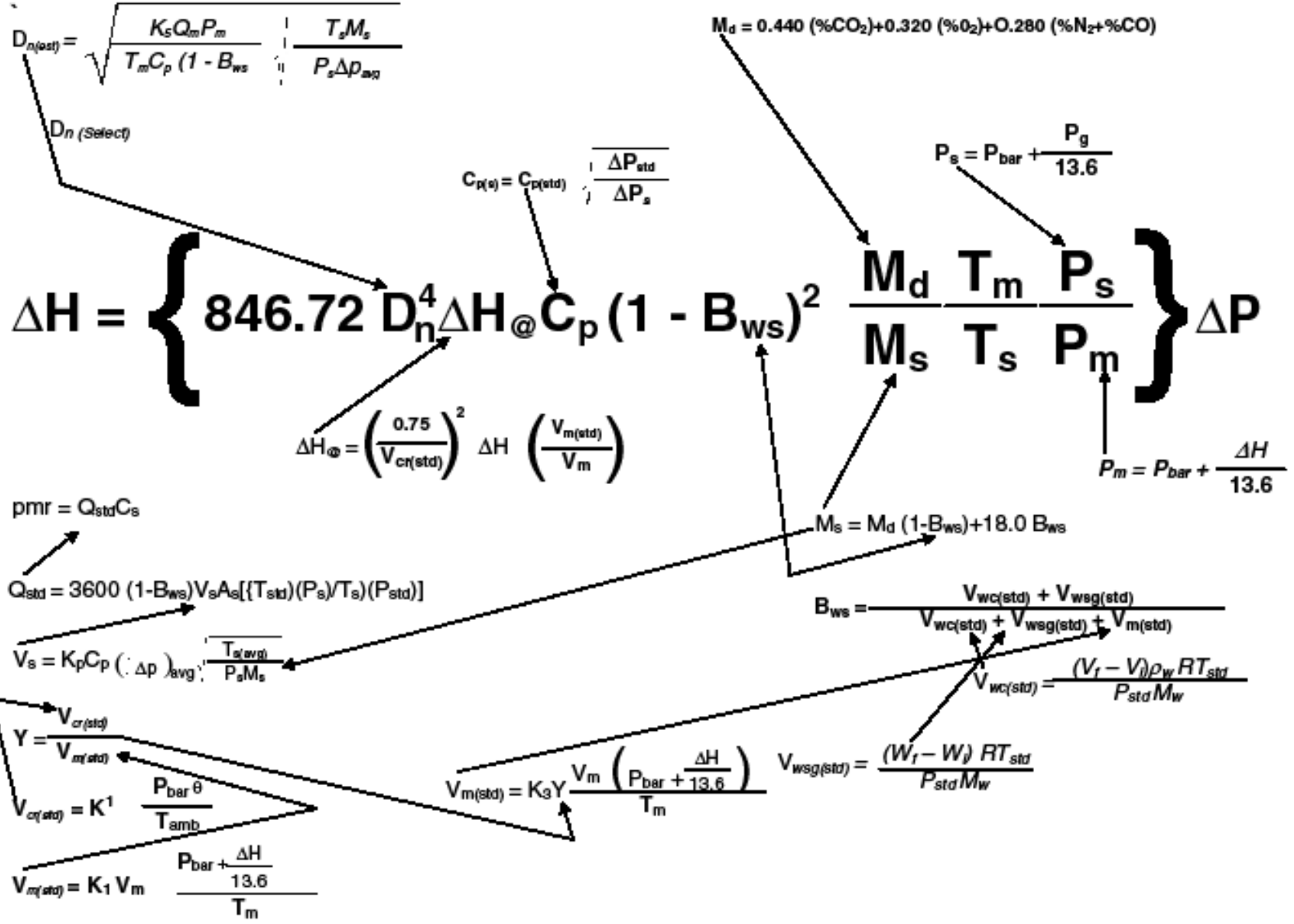
$$\frac{lbs}{hr} = \frac{lbs}{\cancel{ft^3}} \times \frac{\cancel{ft^3}}{hr}$$

Emission Rate (Combustion Sources)

$$E = \frac{pmr_s}{Q_H}\left(\frac{lbs}{10^6\ Btu}\right)$$

Where: Q_H = heat input rate in units of Btu/hr

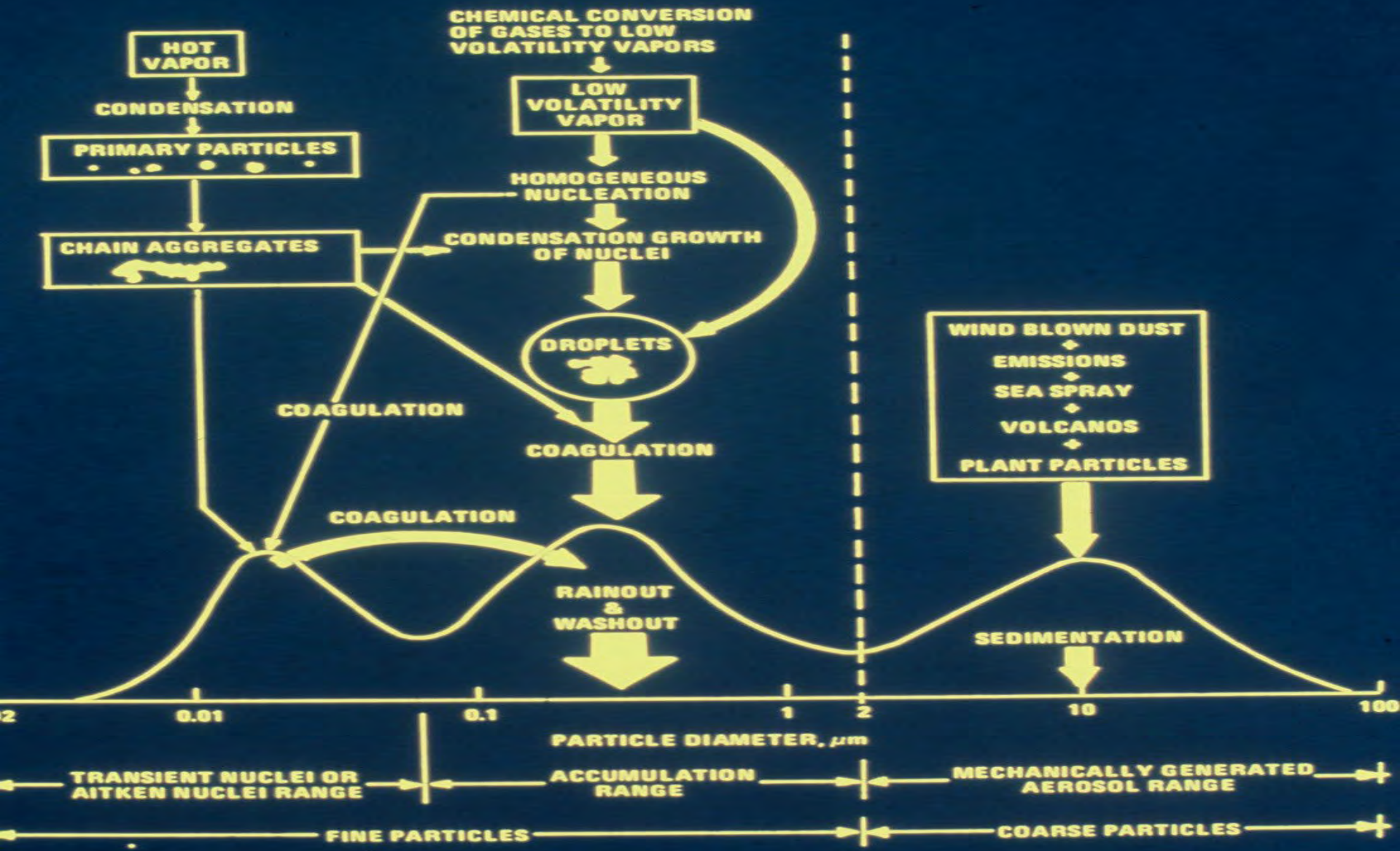
Federal Reference Method 5 Equations

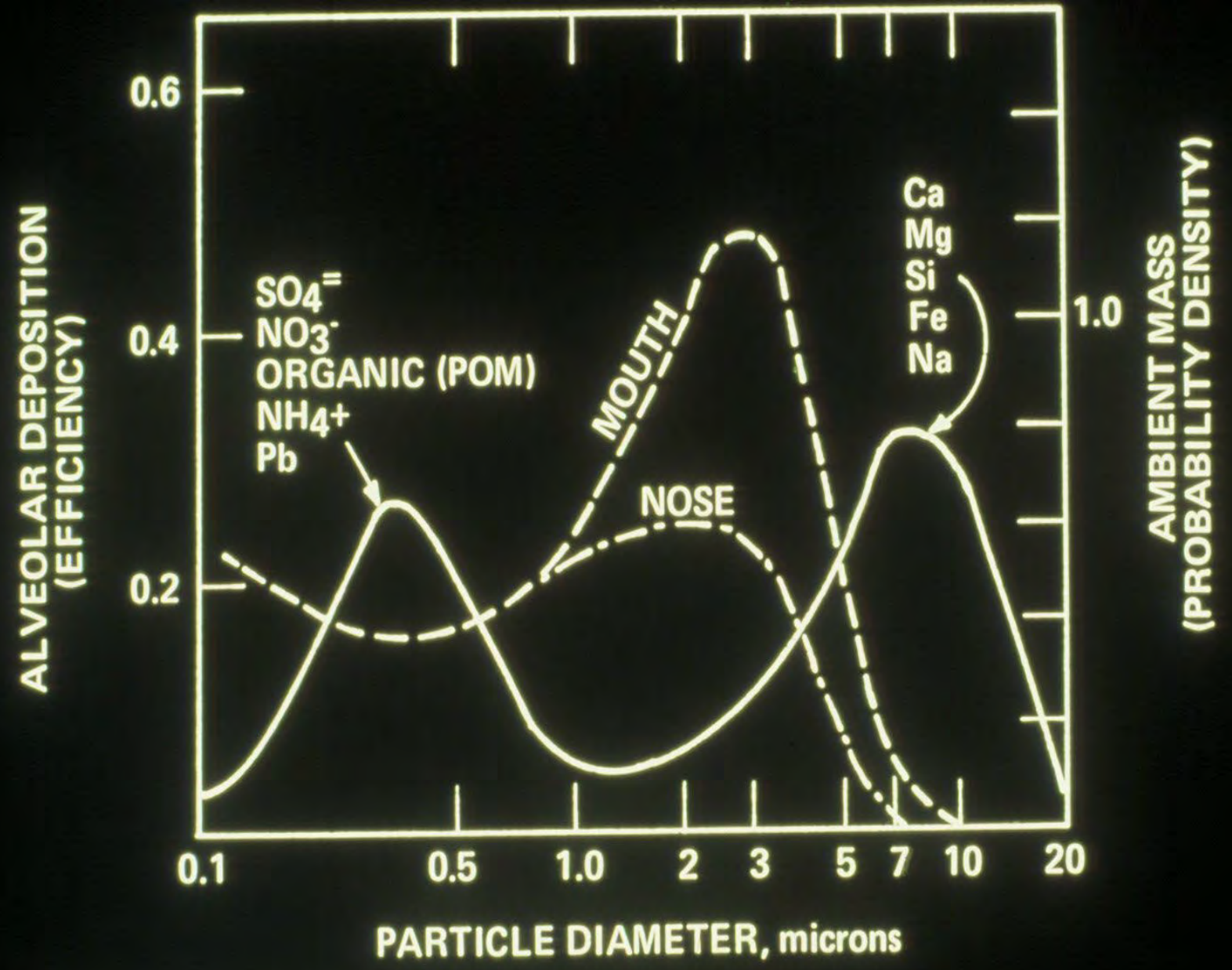


Compliance Test and Source Test Observation

Stack Test Basics

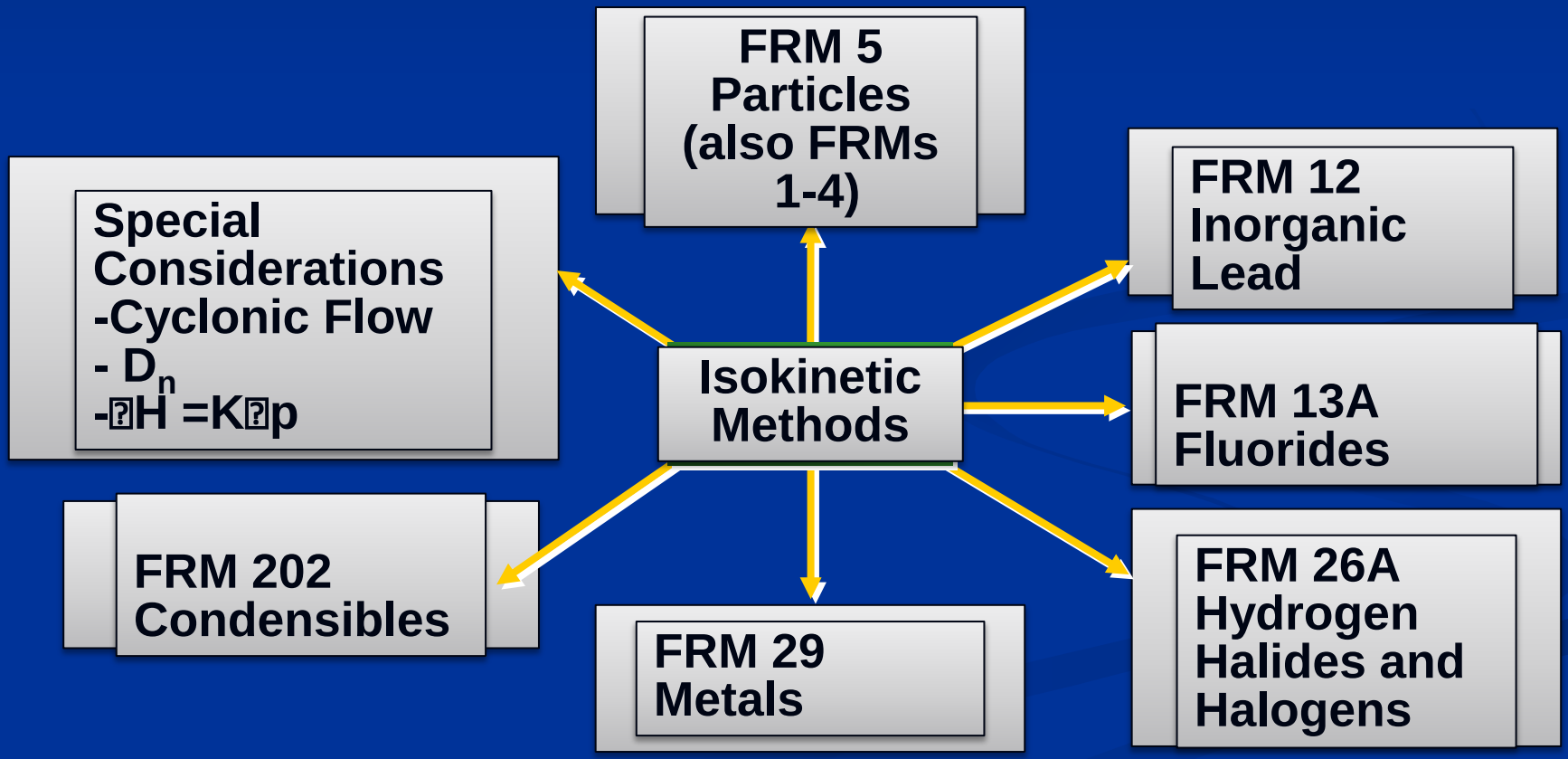



HOT VAPOR
CONDENSATION
PRIMARY PARTICLES
CHAIN AGGREGATES
CHEMICAL CONVERSION OF GASES TO LOW VOLATILITY VAPORS
LOW VOLATILITY VAPOR
HOMOGENEOUS NUCLEATION
CONDENSATION GROWTH OF NUCLEI
DROPLETS
COAGULATION
COAGULATION
COAGULATION
RAINOUT & WASHOUT
WIND BLOWN DUST
EMISSIONS
SEA SPRAY
VOLCANOS
PLANT PARTICLES
SEDIMENTATION
02
0.01
0.1
1
2
10
100
PARTICLE DIAMETER, μm
TRANSIENT NUCLEI OR AITKEN NUCLEI RANGE
ACCUMULATION RANGE
MECHANICALLY GENERATED AEROSOL RANGE
FINE PARTICLES
COARSE PARTICLES



ATMOSPHERIC PARTICLE DISTRIBUTION (——)
AND PARTICLE LUNG DEPOSITION (-----)

Isokinetic Sampling Methods

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Basic Definitions

- Source Sampling for Particulate Emissions
  - Source sampling methods are used to determine emission compliance with regulatory statutes
  - C (ppm, gr/dscf), pmr (lb/hr), E (lb/10^6 Btu or lb/lbs product produced)

POLLUTANT MASS RATE

$$\overline{PMR_s} = \bar{c}_s Q_s$$

$\bar{Q}_s$ $\bar{C}_s$

$A_s \bar{v}_s$ $v_s = v_n$ $\frac{m_n}{V_m}$

for

Isokinetic Conditions

$$v_s = K_p C_p \sqrt{\frac{T_s \Delta p}{M_s P_s}}$$

Obtain C_p, T_s, Δp

M_s P_s

Obtain $\Delta H_@$, D_n

B_{ws}, B_{wm},

P_m, T_m

How Do We Define Particulate Matter?

- TPM?
- FPM?
- FPM-I?
- TPM-PM10?
- FPM-I-PM10?
- CPM?
- MCEM?

Definition of Particulate Matter

- Total Particulate Matter (TPM): The sum of the filterable particulate (i.e., front half of the FRM 5 sampling train) and the condensable particulate matter (i.e., the back half of the FRM 5 sampling train, including water and organic soluble extractions, Method 202)

Definition of Particulate Matter

- Filterable Particulate Matter (FPM): The mass of the filterable particulate matter (i.e., front half of the FRM 5 sampling train) that is captured on the filter at a temperature of 248 F +/- 25 F

Definition of Particulate Matter

- Filterable (In-stack) Particulate Matter (FPM-I): Particulate matter as measured by FRM 17 at stack temperature and pressure
- Total Particulate Matter PM-10 (TPM-PM10): Sum of the filterable PM-10 as measured by FRM 201 and 201A and the condensable particulate matter determined by FRM 202

Definition of Particulate Matter

- Filterable (In-Stack) Particulate Matter PM-10 (FPM-I-PM10): Particulate matter with an aerodynamic diameter of < 10 micrometers as measured by FRM 201 or 201A
- Condensable Particulate Matter (CPM): Particulate matter captured in the back half of the FRM 5 sampling train, including water and organic soluble extraction components, Method 202.

Definition of Extractable Particulate Matter

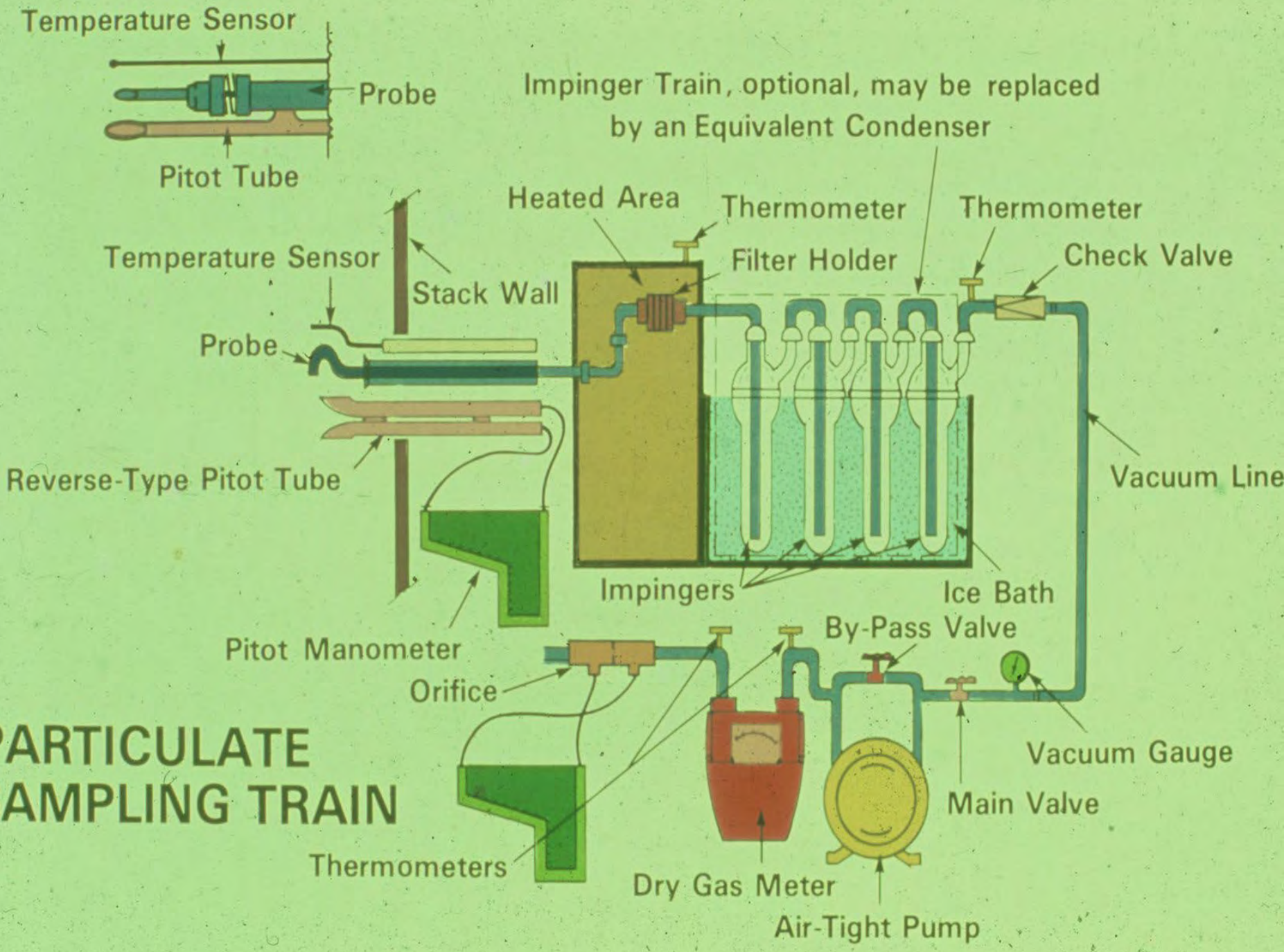
- Methylene Chloride Extractable Particulate Matter (MCEM): MCEM involves methylene chloride rinse of the probe and filter holder, extracting the condensable hydrocarbons collected in the impinger water and rises after the filter to the silica gel, all residue determined gravimetrically after evaporation of solvents (i.e., FRM 315)

Basic Definitions

- Isokinetic Source Sampling
- "Iso" as denoting equality, similarity, uniformity. "Kinetic" is defined as of, pertaining to, or due to motion
  - $\Delta H = K \Delta p$

$$\Delta H = K \Delta p$$

SIMPLIFIED ISOKINETIC RATE EQUATION



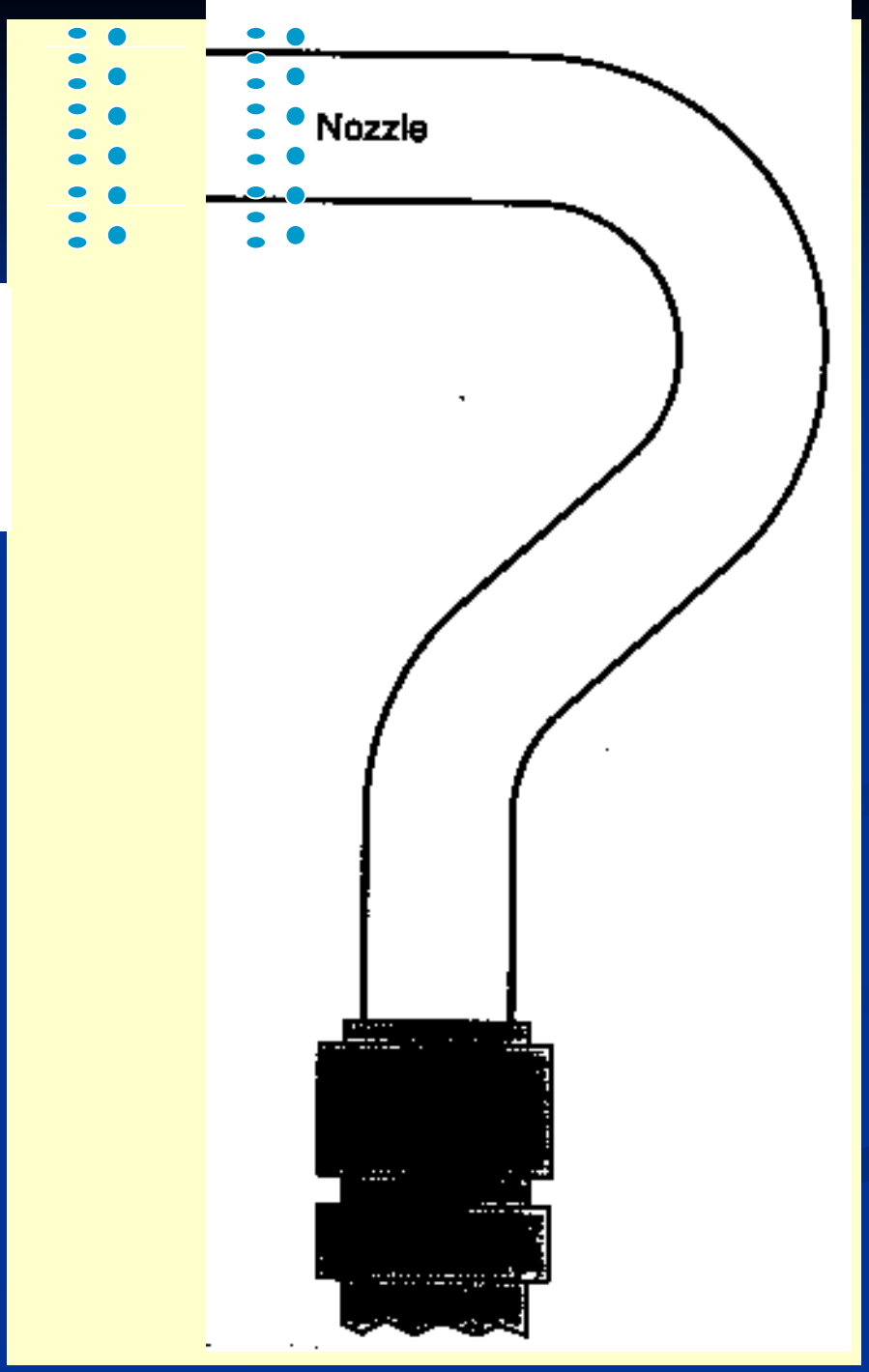
PARTICULATE SAMPLING TRAIN

Isokinetic Sampling and Bias

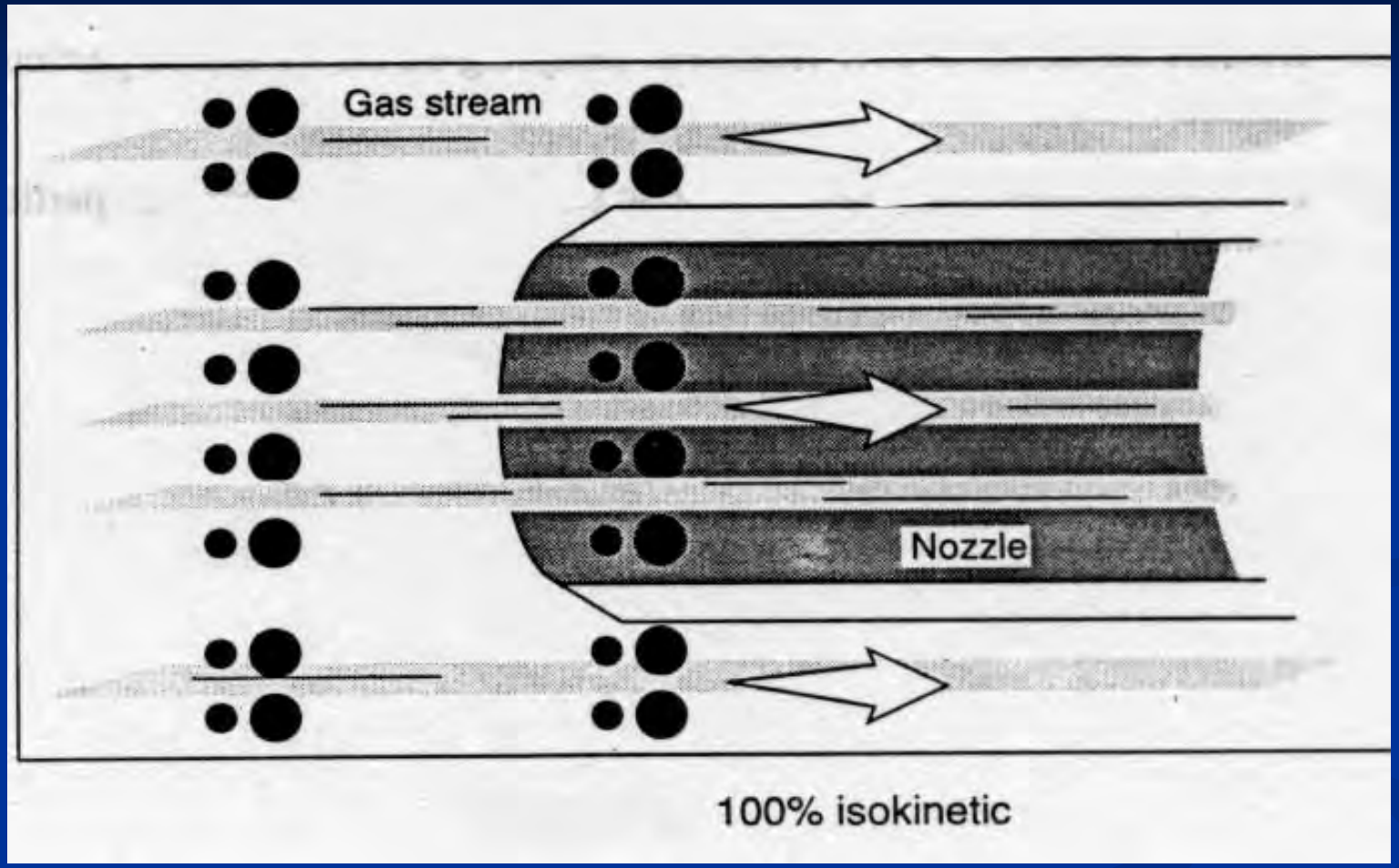
- To obtain average pollutant concentration, need parameters:
  - Quantity of mass emitted from stack
  - Total quantity of volume from stack
- Isokinetic sampling provides best approach for accurate data
- Pollutant mass rate (pmr)
  - pmr_a (Ratio-of-areas: A_n ratio A_s)
  - pmr_c (Ratio-of-conc.: m_n ratio A_n)

$V_n = V_s$

100% Isokinetic

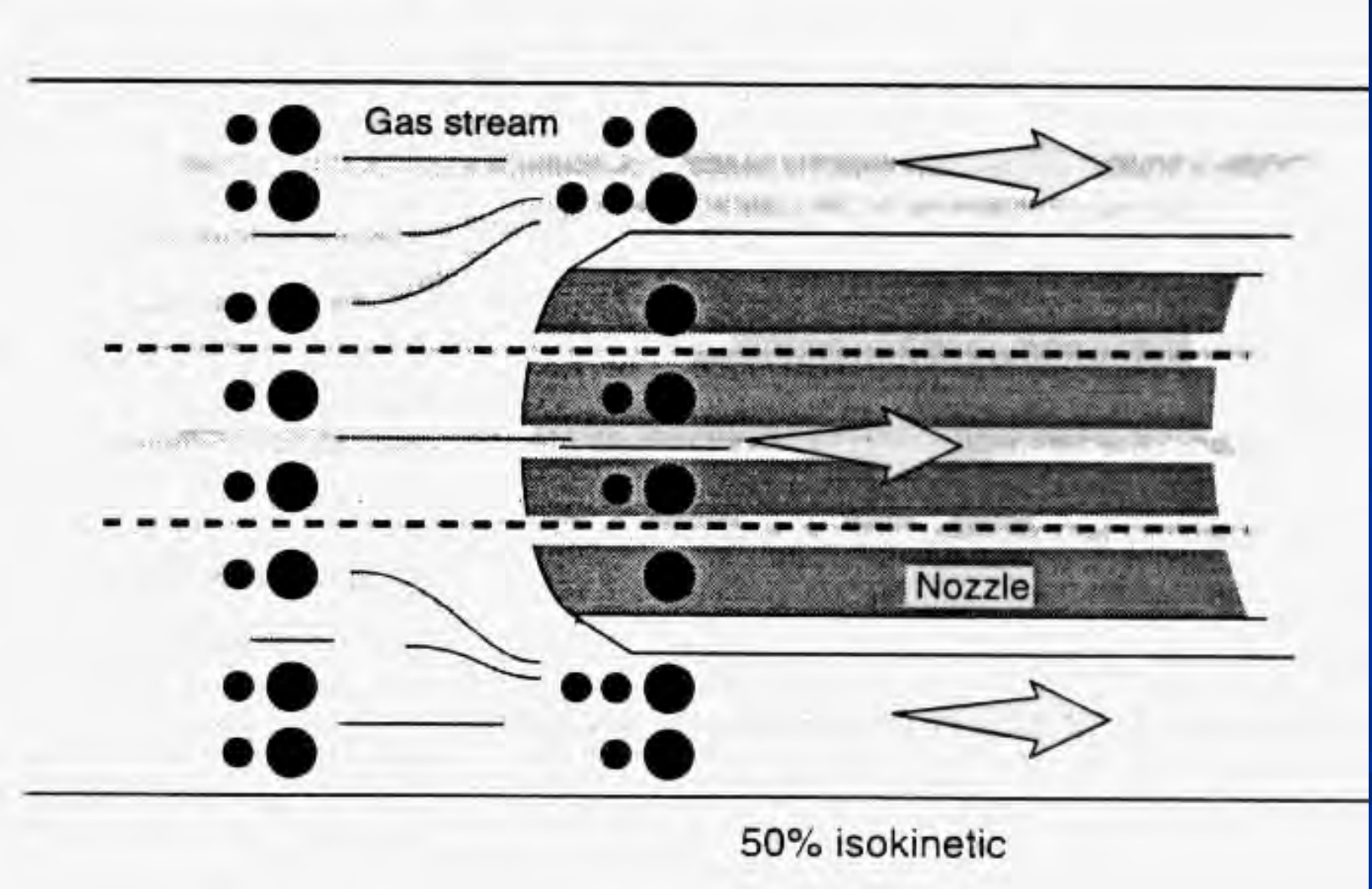


100 % Isokinetic



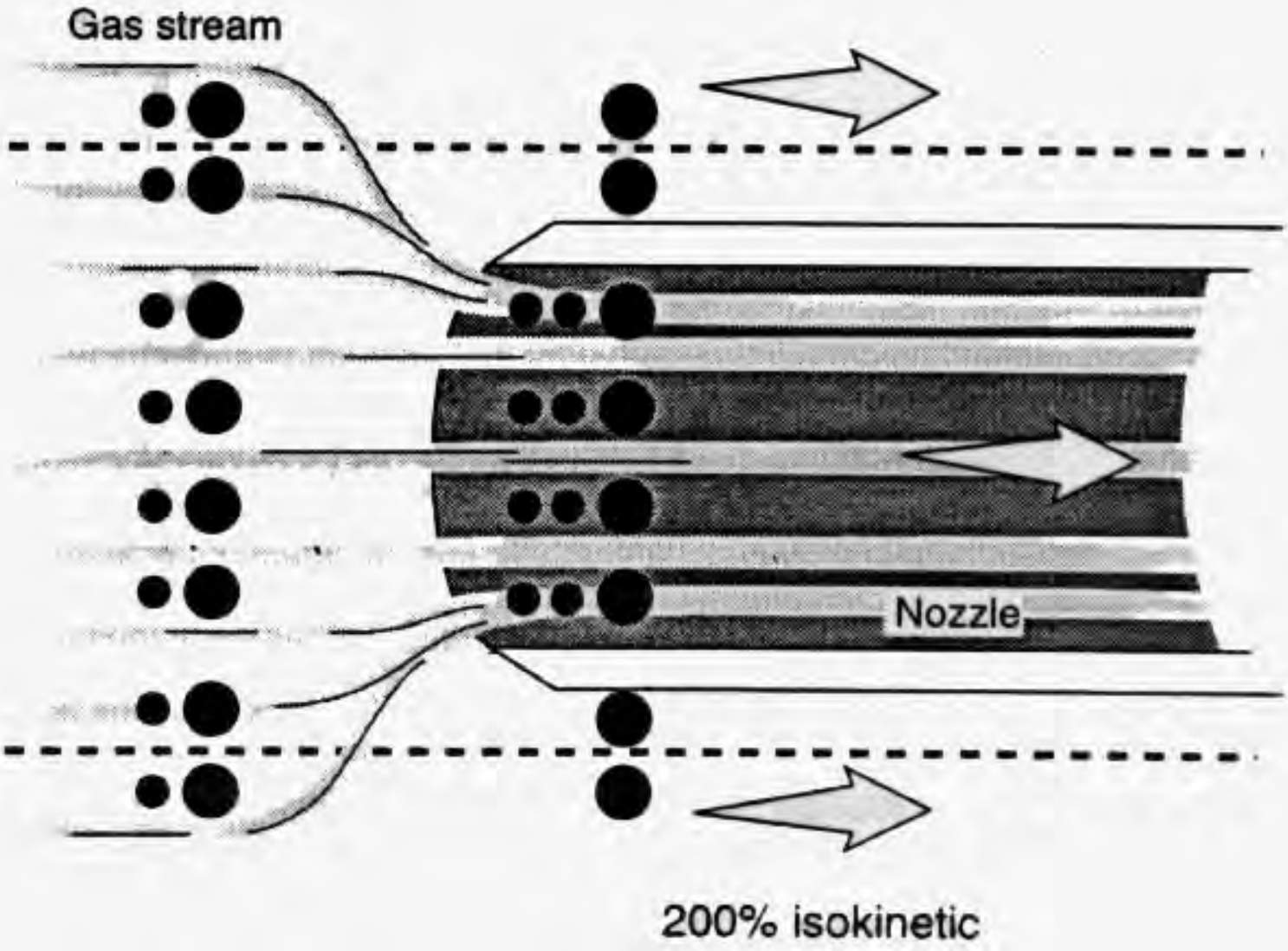
Vs=Vn

Sub-Isokinetic (50%)



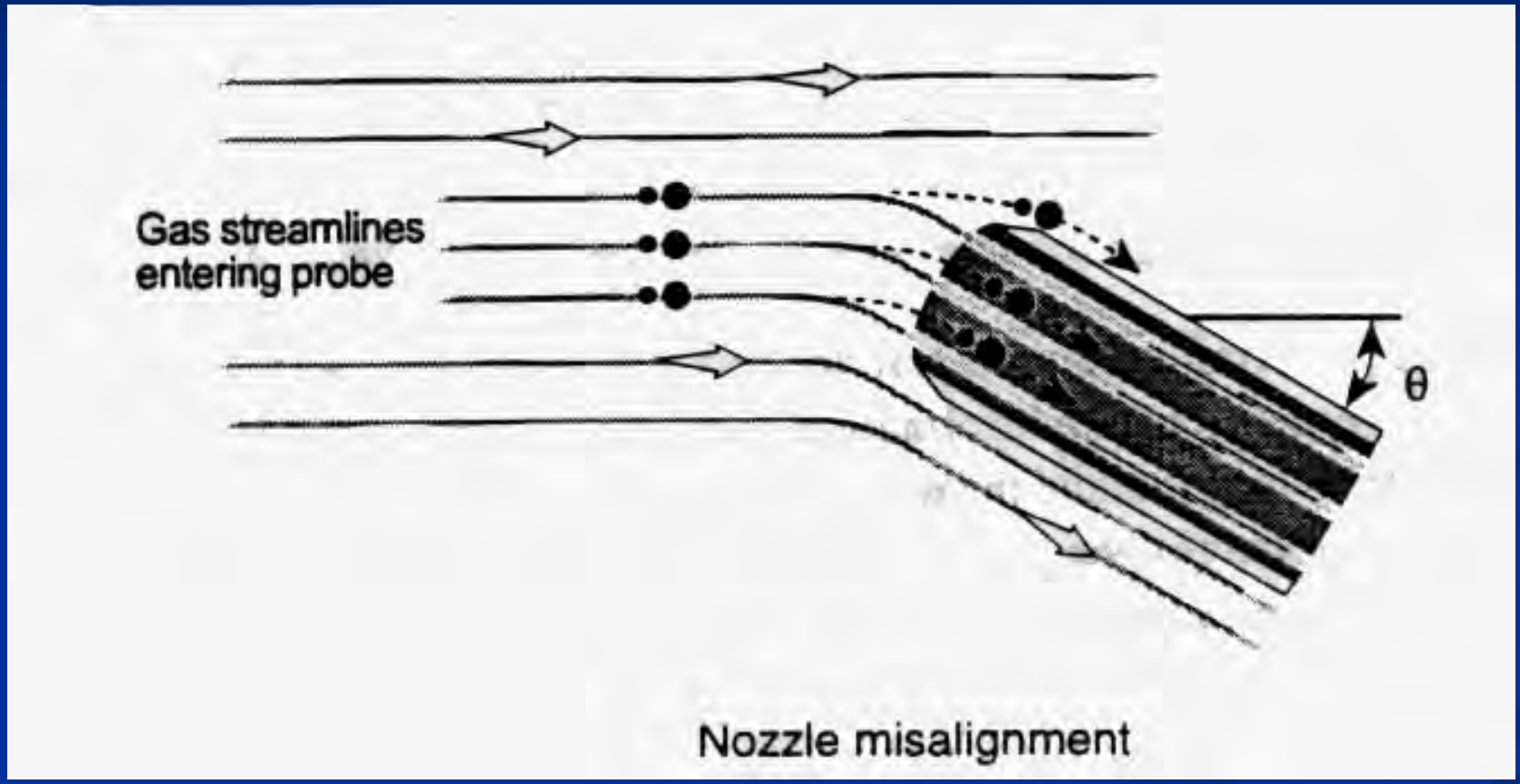
Vn=1/2Vs

Over-Isokinetic (200%)

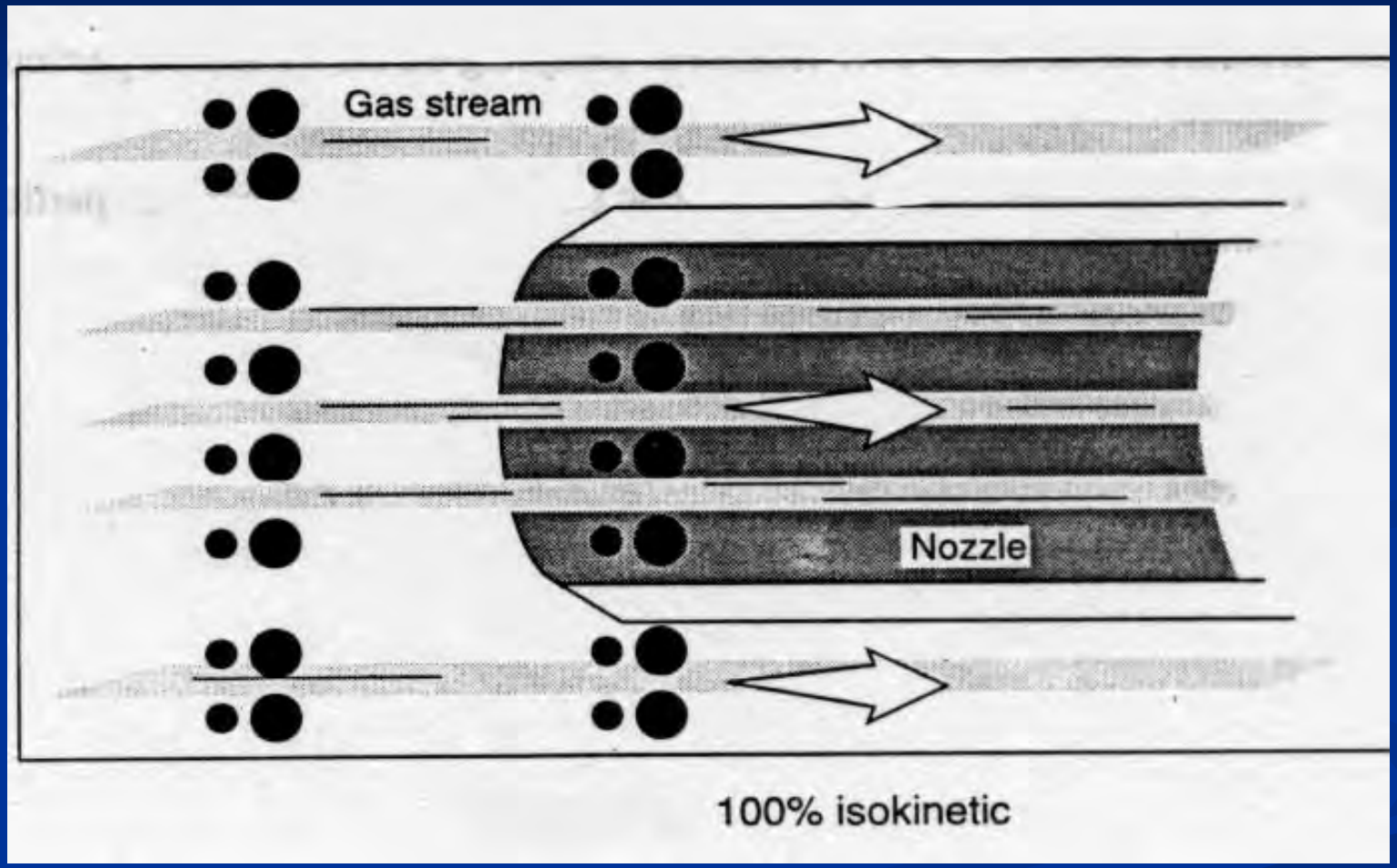


Vn=2Vs

Nozzle Misalignment



$\Delta H = K\Delta p$



Vs=Vn

Isokinetic Sampling

$$\% \text{ Isokinetic} = \frac{V_n}{V_s} \times 100$$

In Order To Take An Isokinetic Sample, We Must….

- Calculate the motion of the gas stream passing by the sampling system, and
- Recreate that motion in the sampling system

FRM 5 Isokinetic Rate Equation

$$\%I_{int} = 100 \frac{T_s V_{m(std)} P_{std}}{T_{std} v_s \theta A_n P_s 60 (1 - B_{ws(est)})}$$

$$\%I_{final} = \frac{100\, T_{s(avg)} \left[K_3 V_{1c} + \left(\frac{V_{m(avg)}}{T_{m(avg)}} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60\, \theta\, V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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

History of FRM 5

- 1970 FRM 5: Filterable PM @ 248 F
- 1982 FRM 5A: PM @ 108 F for Asphalt Roofing, Pre-collector cyclone and trichloroethane (TCE) rinse
- 1986 FRM 5B: Nonsulfuric Acid PM with Sampling and Volitilization of Filter @ 320 F
- Reserved FRM 5C: Small Ducts (Reserved)
- 1984 FRM 5D: PM @ 248 F from Positive Fabric Filters

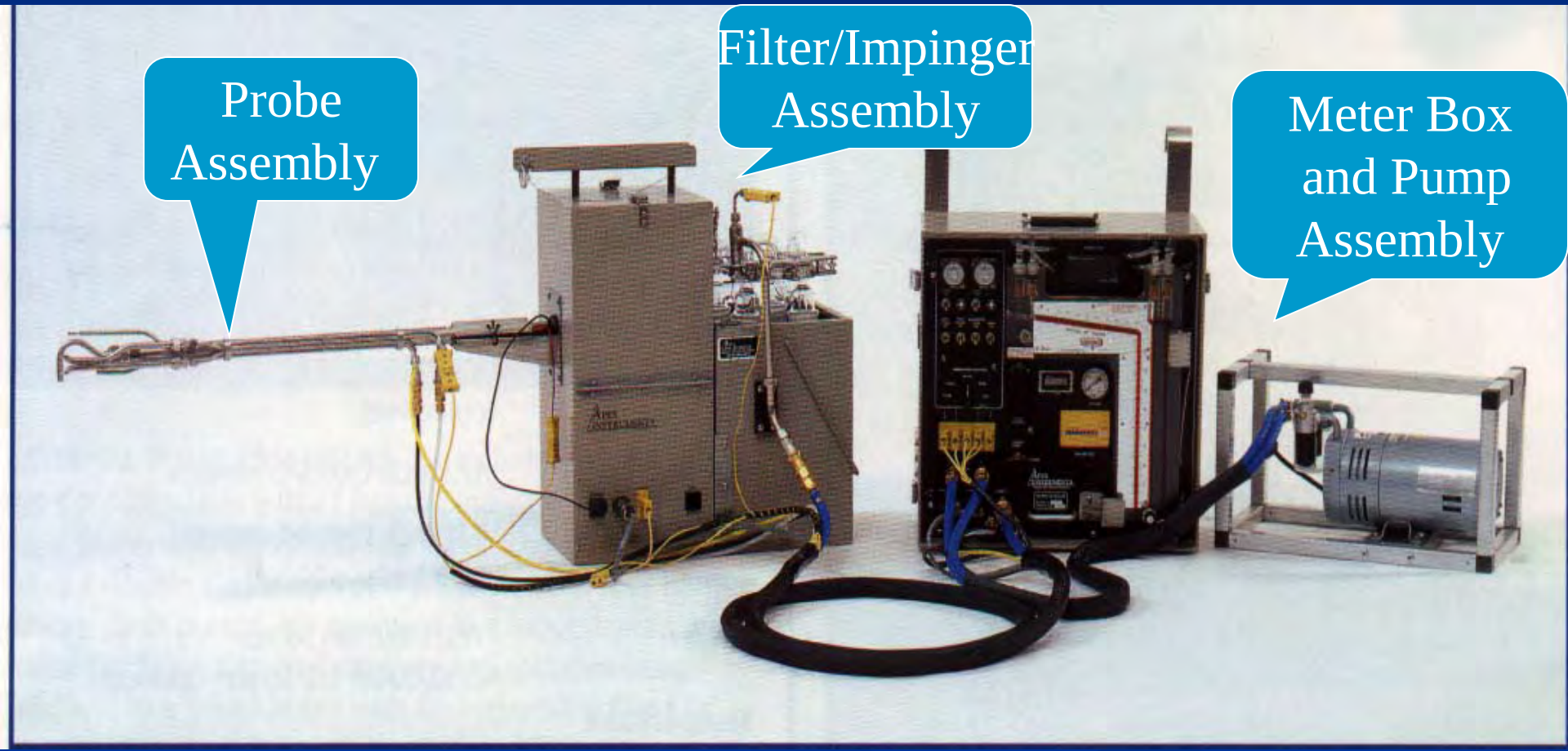
History of FRM 5

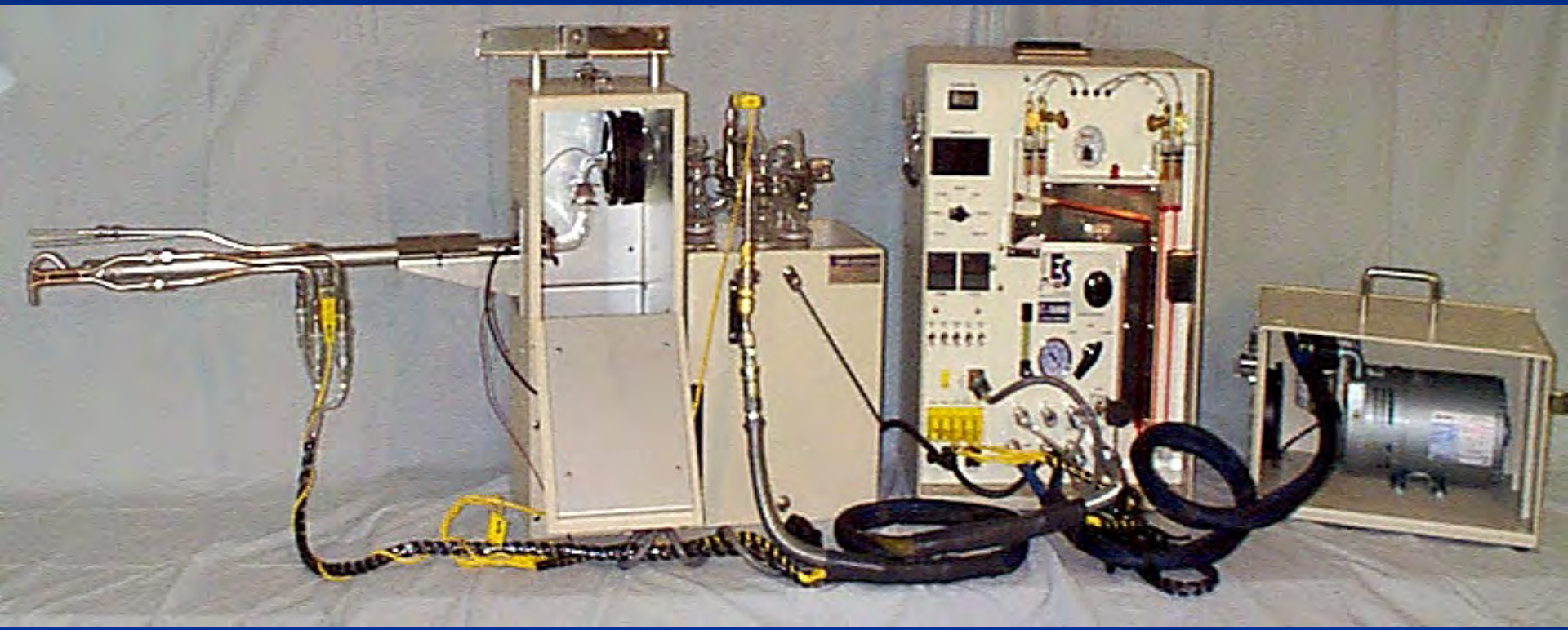
- 1985 FRM 5E: PM @ 248 F from Mineral Wool Plus Captured Condensible in 0.1 N NaOH (TOC)
  - Total Carbon @ 1740 F
  - Inorganic Carbon @ 300 F
  - $C_t = C_s + C_c$
- 1986 FRM 5F: Non-sulfuric acid PM @ 320 F with water rinse and ammonium sulfate substraction

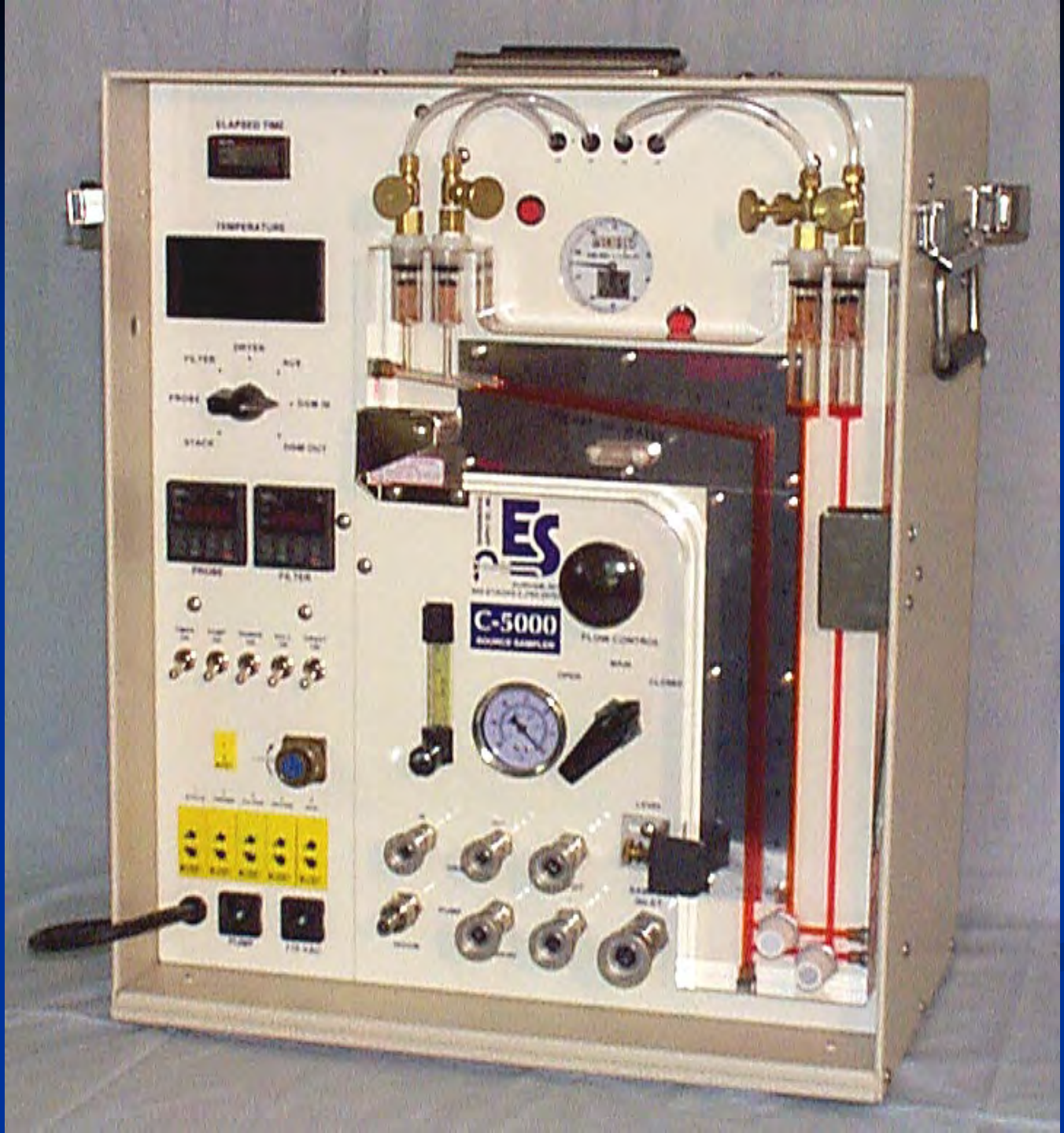
History of FRM 5

- 1988 FRM 5G: PM @ 90 F from wood stoves using a dilution tunnel with 100-mm series filters
- 1988 FRM 5H: PM from wood stoves stack with 1st filter @ 248 F, then impingers followed by 2nd filter @ 68 F
- 1999 FRM 5I: Low level (<50 mg) PM using FRM 5 sampling train with 47-mm filter @ 248 F and paired sampling trains (< 10%)

FRM 5 Sampling Train






ELAPSED TIME
TEMPERATURE
C-5000

Errors in pmr Calculations Using FRM 5

- T_s: 1.4 %
- DGM: 1.0 %
- P_s: 0.4 %
- P_m: 0.4 %
- P_b: 0.2 %
- B_{ws}: 1.0 % Affects % Iso
- Δ H: 5.0 %
- D_n: 1.0 %
- Delta $H_@$: 1.5 %

Federal Reference Methods (FRMs) 1 through 4

- Used in other reference methods
- Used to determine
  - Number of sampling points (FRM 1)
  - Stack gas velocity (FRM 2)
  - Stack gas molecular weight (FRM 3)
  - Stack gas moisture content (FRM 4)
  - Stack gas particulate matter (FRM 5)
- All have available checklist

Compliance Test and Source Test Observation

FRM 1: Sampling/Velocity Traverse Points



Code of Federal Regulations

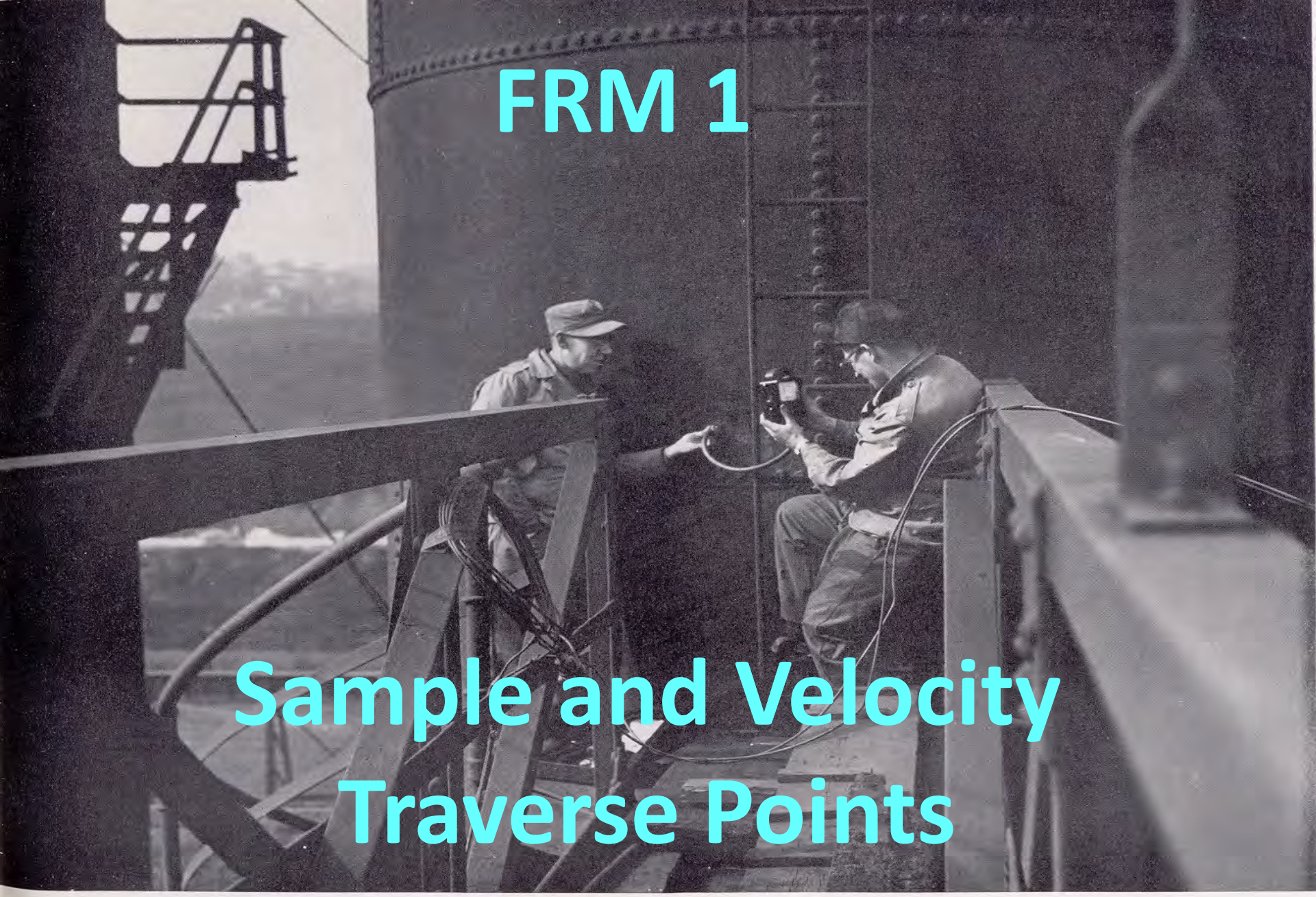
40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1 FRM 2 FRM 3 FRM 4 FRM 5 FRM 19

FRM 1

Sample and Velocity Traverse Points



Measurements of airflow in study of stack effluents.


36

FRM 1 History

- 1970 Promulgated
- 1983 Reduced Number of Traverse Points
- 1986 Alternative Procedure for Site Selection
- 1989 Method 1A, Traverse Points in Small Ducts

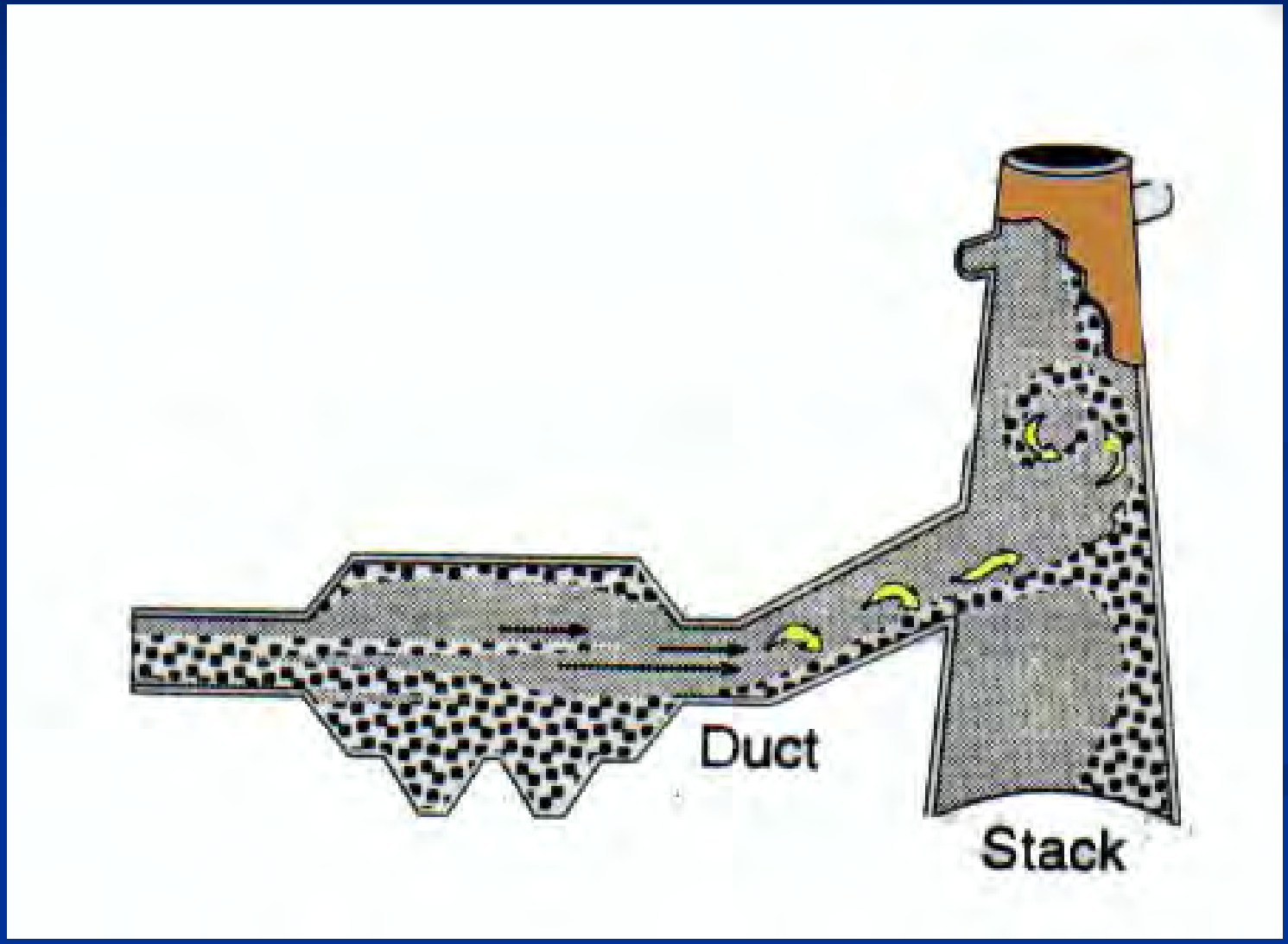
FRM 1

- Method 1 specifies both the sampling site location and the location of the sampling points to which the source tester will measure a representative sample
  - Pollutant emissions
  - Total volumetric flow rate

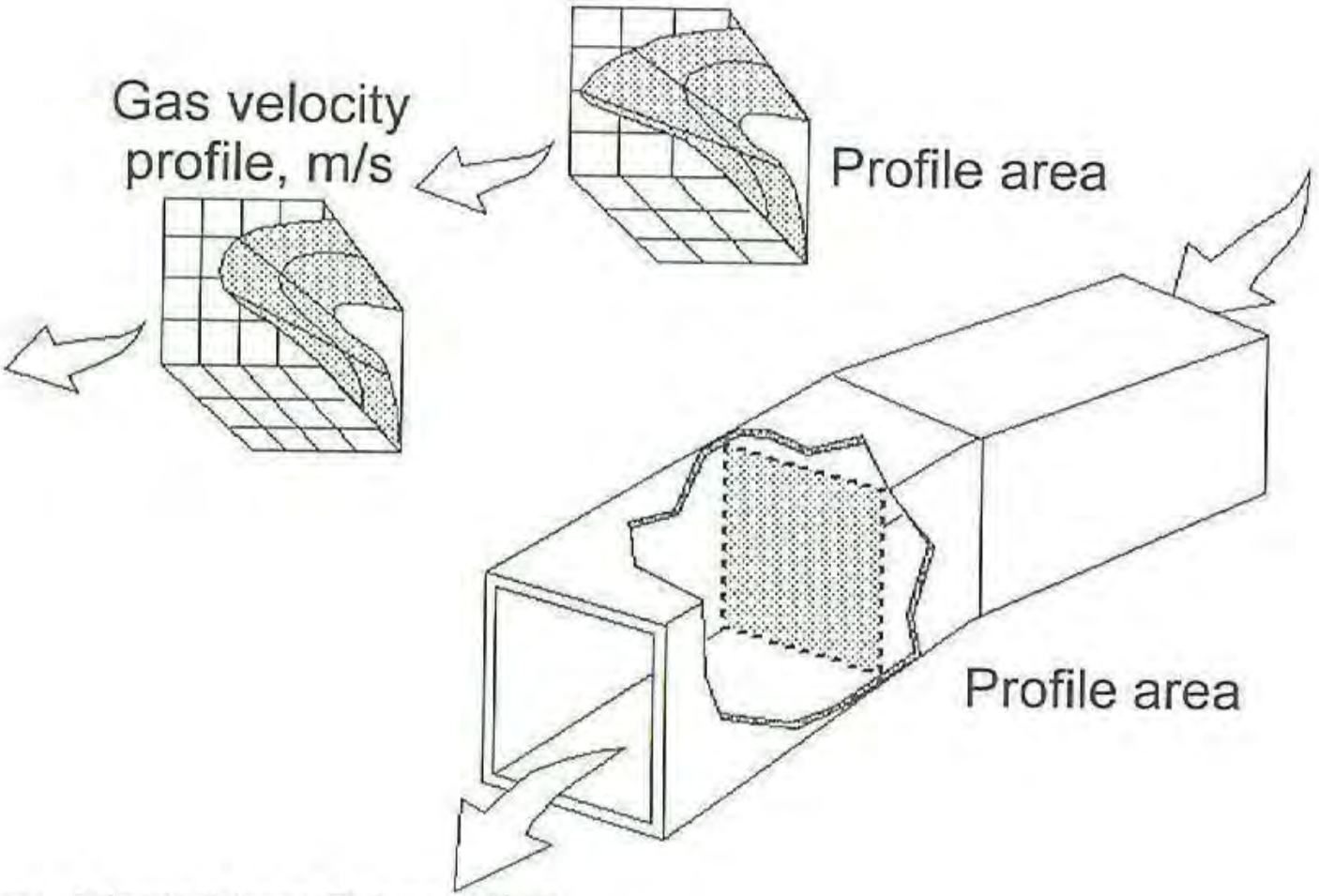
FRM 1 Basic Principle

- "…the more convoluted the ductwork, the more points will need to be tested."
- Representative measurement
- Modifications to FRM 1
  - Rectangular stacks
  - Only measuring velocity
  - Stacks smaller than 12 inches

FRM 1 Sampling Site Locations

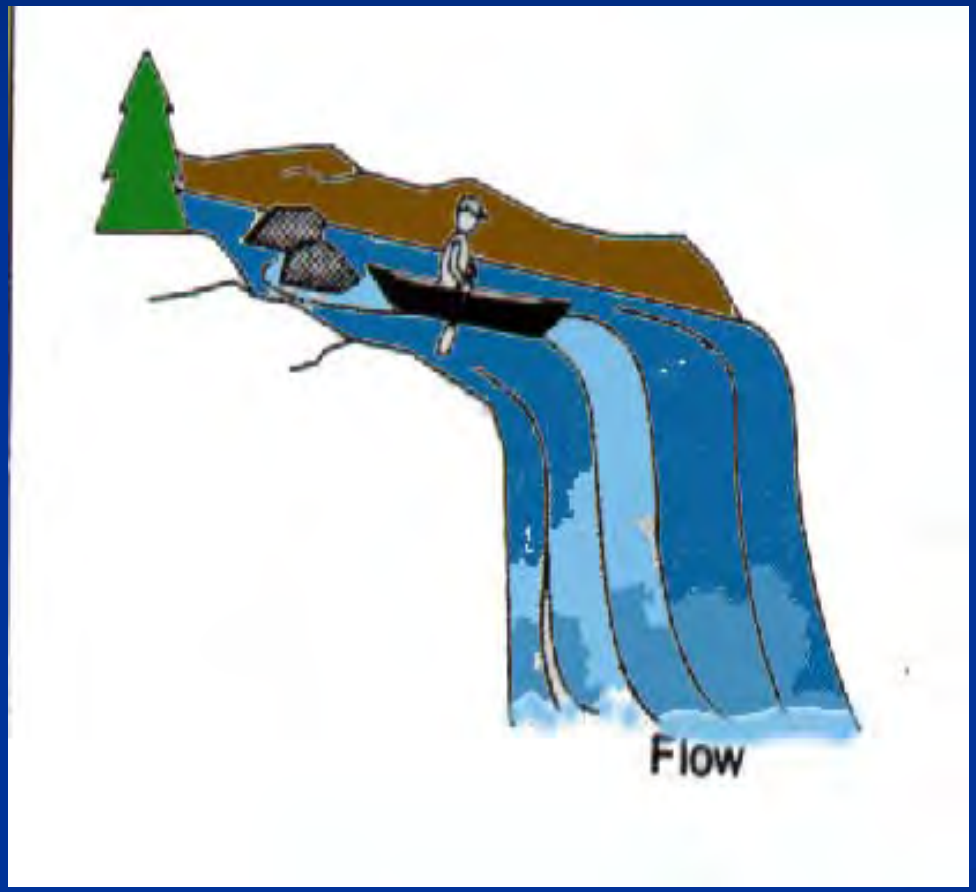


Particle mass concentration profile, mg/m^3



Source: Adapted from Buhne, 1977

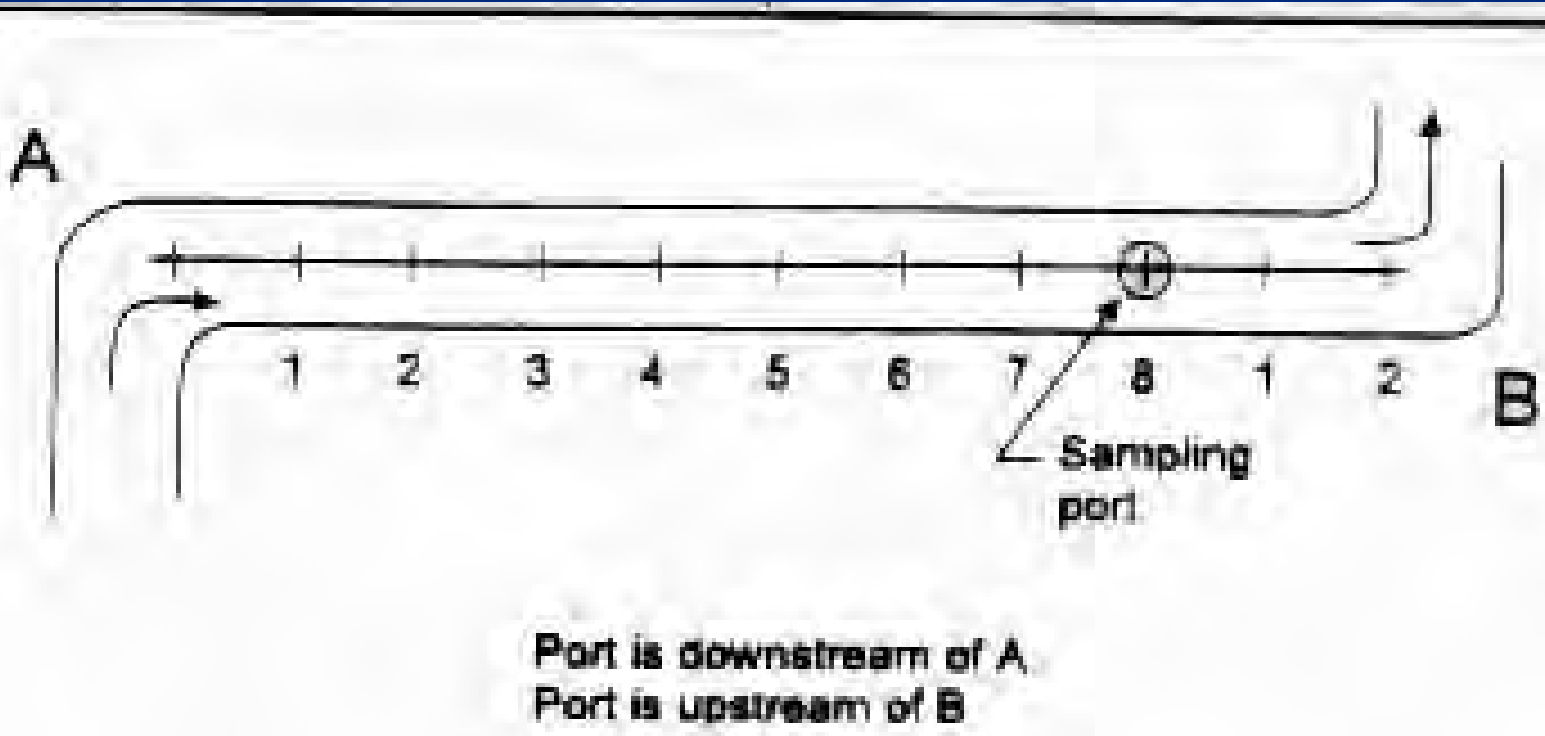
FRM 1 Siting Criteria



Boat is downstream from rocks. Rocks are upstream from boat. Boat is upstream from falls. Falls are downstream from boat.

The position of objects relative to a boat

Ideal Siting Criteria



FRM 1 Applicability

- > 12” diameter duct, stack
- Not for use in cyclonic, swirling
- Not for sample locations
  - < 2 Diameter downstream from flow disturbance
  - < 0.5 Diameter upstream from flow disturbance
  - Check “as built” drawings for external and internal interferences above and below sampling port locations

Exceptions to FRM 1 (Can't use FRM 1)

- #1: Cyclonic or swirling gas flow (>20 degrees)
- #2: Stack smaller than 0.30 m (12") in diameter or cross-section area is less than 0.71 m^2 (113 in^2), Use Method 1A

Exceptions to FRM 1 (Can't use FRM 1)

- #3: Measurement site is less than 2 duct diameters downstream or less than 0.5 diameters upstream from a flow disturbance
  (Use Alternative Procedure, Section 2.5)

FRM 1 Flow Disturbance

- Bend in duct
- Expansion or contraction in the duct
- Visible flame

Stack Extensions Required

- When stack is too short for proper port location
- Straightening vanes are needed to remove cyclonic or swirling flow
- Possible down draft from wind blowing across stack

Sampling Location

- Determine the upstream and downstream disturbances
- Measure the distance the sampling port is from those disturbances
- Divide the distance by the diameter of the stack
- Ideal location is 8 downstream and 2 upstream







FRM 1 Siting Criteria

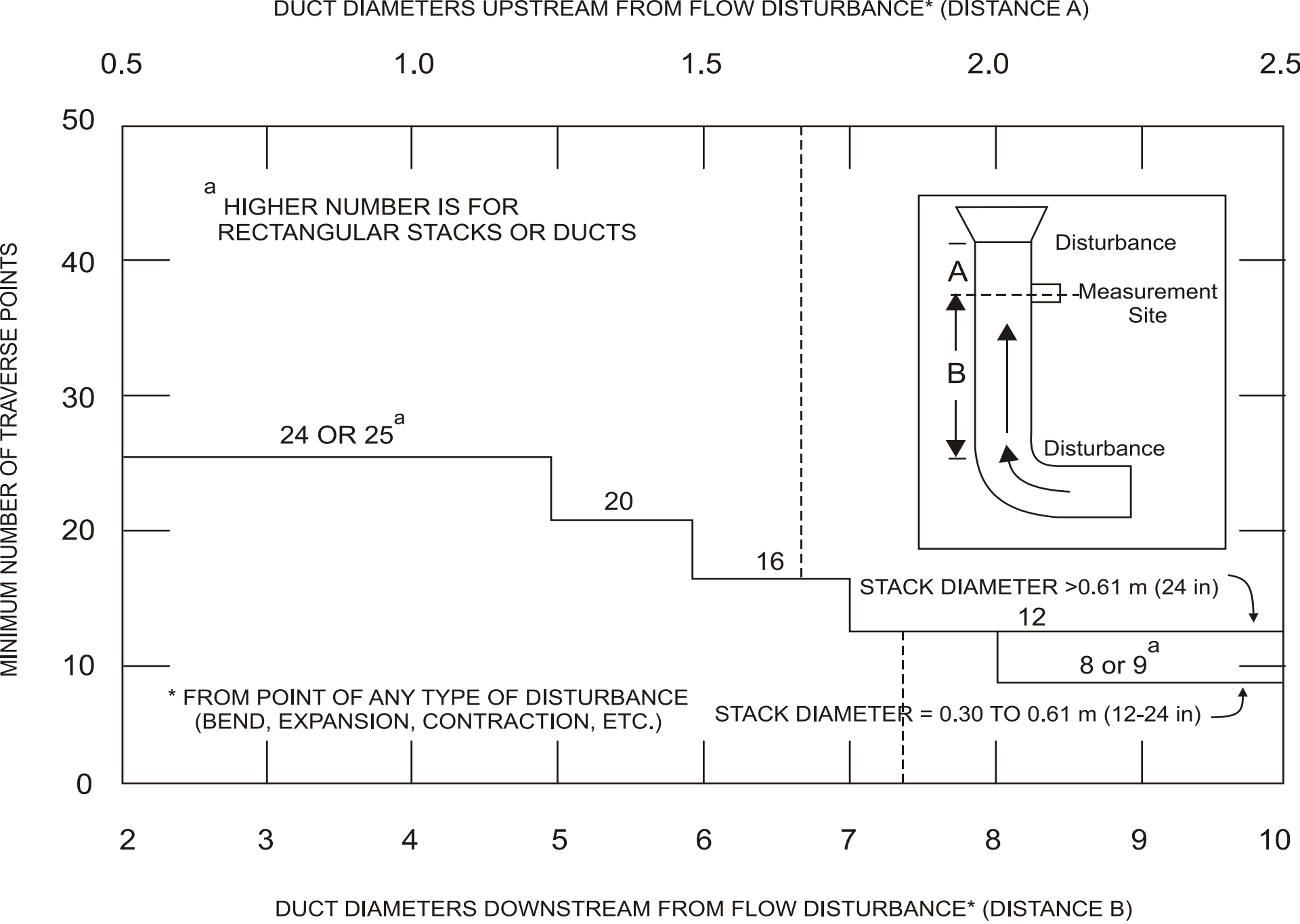
- At 8 duct diameters downstream and 2 duct diameters upstream of a flow disturbance, the siting criteria states
  - Velocity head profile is assumed to resemble laminar flow

FRM 1 Siting Criteria

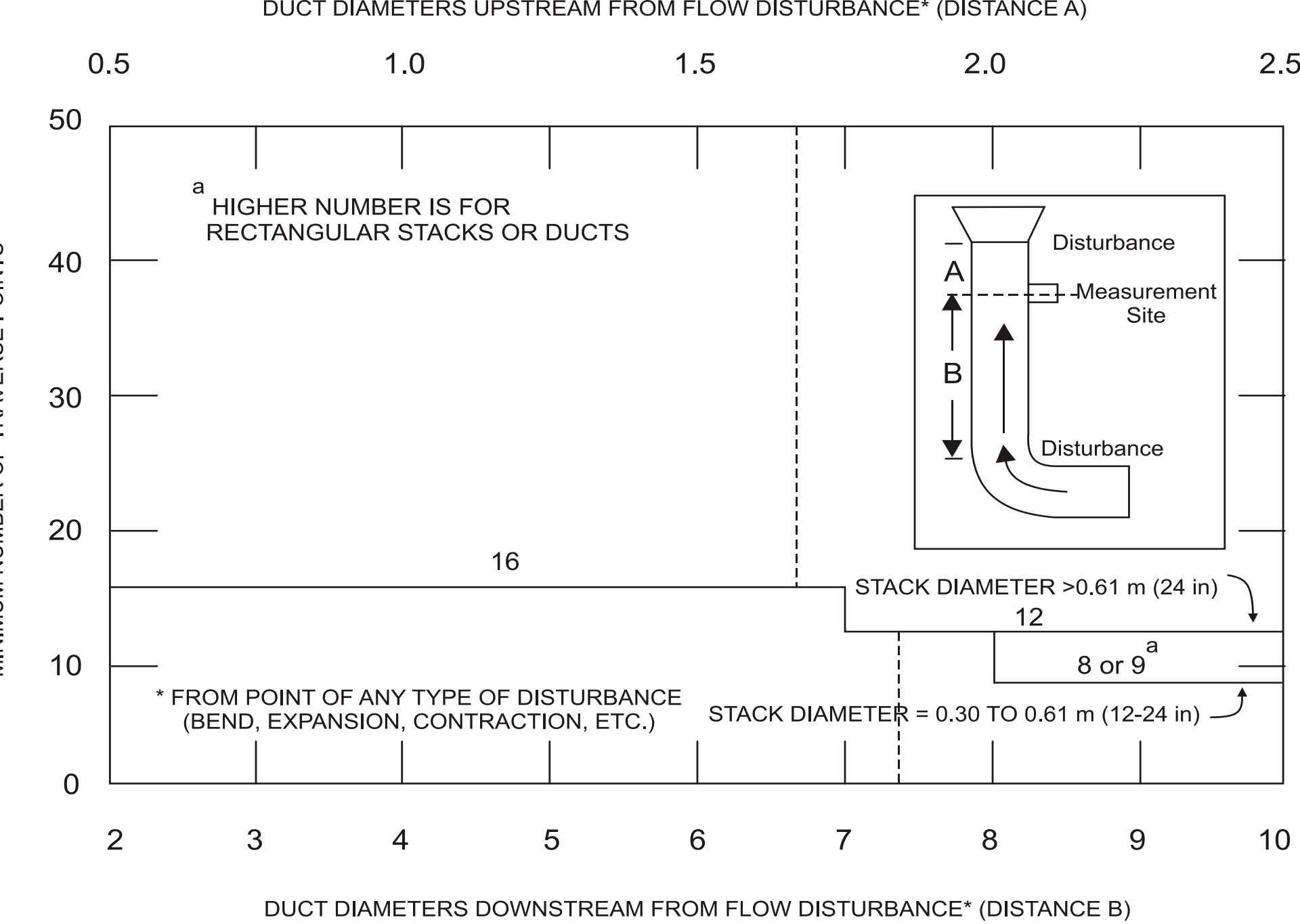
- The minimum number of sampling points can be used
  - 8 or 9 for 12-24 in. stacks
  - 12 for > 24 in. stacks

FRM 1 Siting Guidance

- Federal Register provides illustrations for minimum number of traverse points for particulate traverses and velocity traverses (Figure 1-1 in Federal Register)
- Federal Register provides location of traverse points (Figure 1-2 in Federal Register)



(Minimum number of traverse points for particulate traverses.)



(Minimum number of traverse points for non-particulate traverses.)

FRM 1 Equal Areas

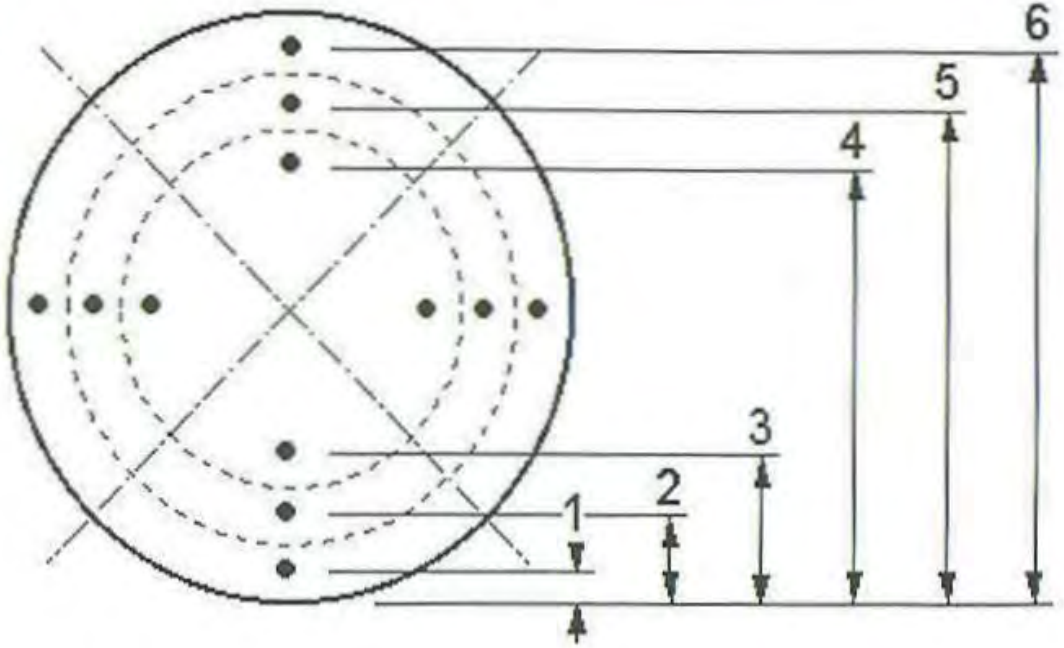
- The circular duct is divided up into four equal quadrants, each of which is divided into equal areas
- Traverse points are then located at the centroid of these areas
  - Two perpendicular diameters
  - One diameter must be in the “plain of the bend.”

Table 1 - 2 Location of Traverse Points in Circular Stacks

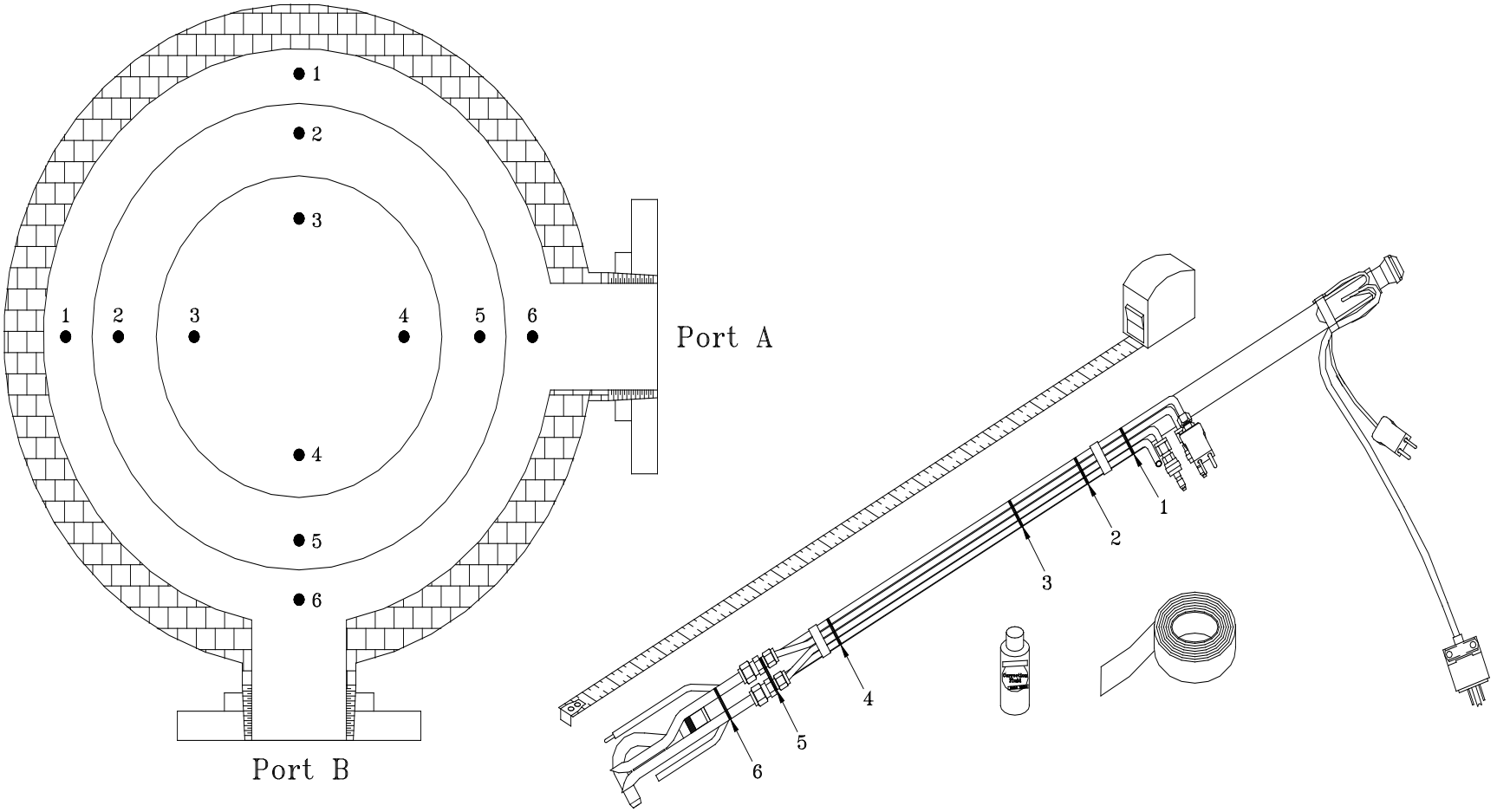
(Percent of stack diameter from inside wall to traverse point)

Traverse point on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

Traverse Point	Distance, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6



Smoke Stack Cross Section
with Traverse Points Indicated





FRM 1 Location of Traverse Points

- Percent distance of traverse point from inside wall of duct determined from Table 1-2 in Method 1
  - >24” stacks, no traverse point within 1 inch
  - <24” stacks, no traverse point within 0.5 inches



FRM 1 Rectangular Ducts

- In the case of rectangular ducts, an “equivalent diameter”, De, is used in the siting and traverse point consideration
- De = 2LW/(L + W)
- Must use balance matrix

$$D_e = \frac{2\,LW}{(L + W)}$$

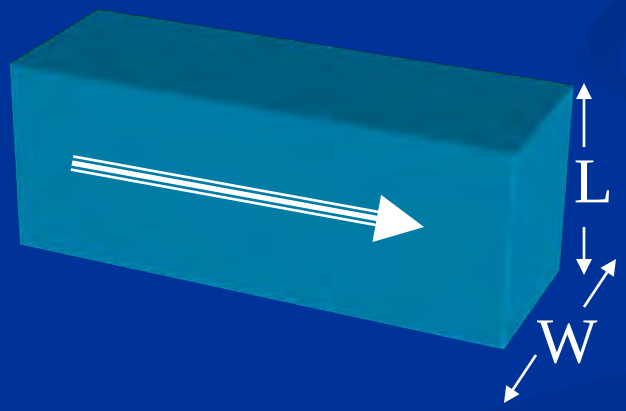
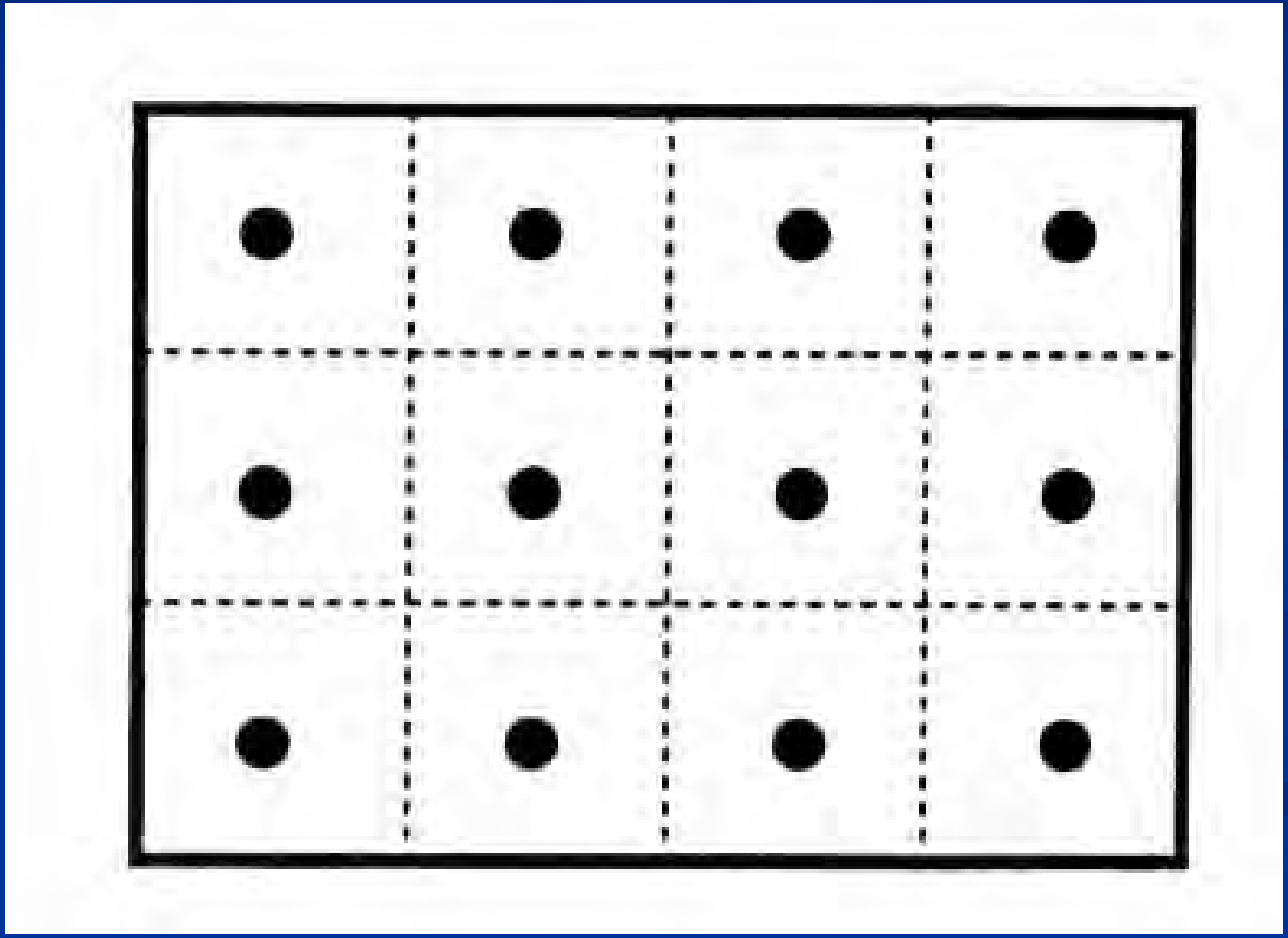


Table 1-1. Cross-Section Layout for Rectangular Stacks

Number of traverse points	Matrix layout
9	3x3
12	4x3
16	4x4
20	5x4
25	5x5
30	6x5
36	6x6
42	7x6
49	7x7

Rectangular Duct
(3 X 4)



FRM 1 Verification or Absence of Cyclonic Flow

- Cyclonic flow may exist (Section 2.4)
  - After such devices as cyclones and inertial demisters following venturi scrubbers
  - In stacks having tangential inlets or other duct configurations which tend to induce swirling

Cyclonic Flow Determination (Ducts >4in.)

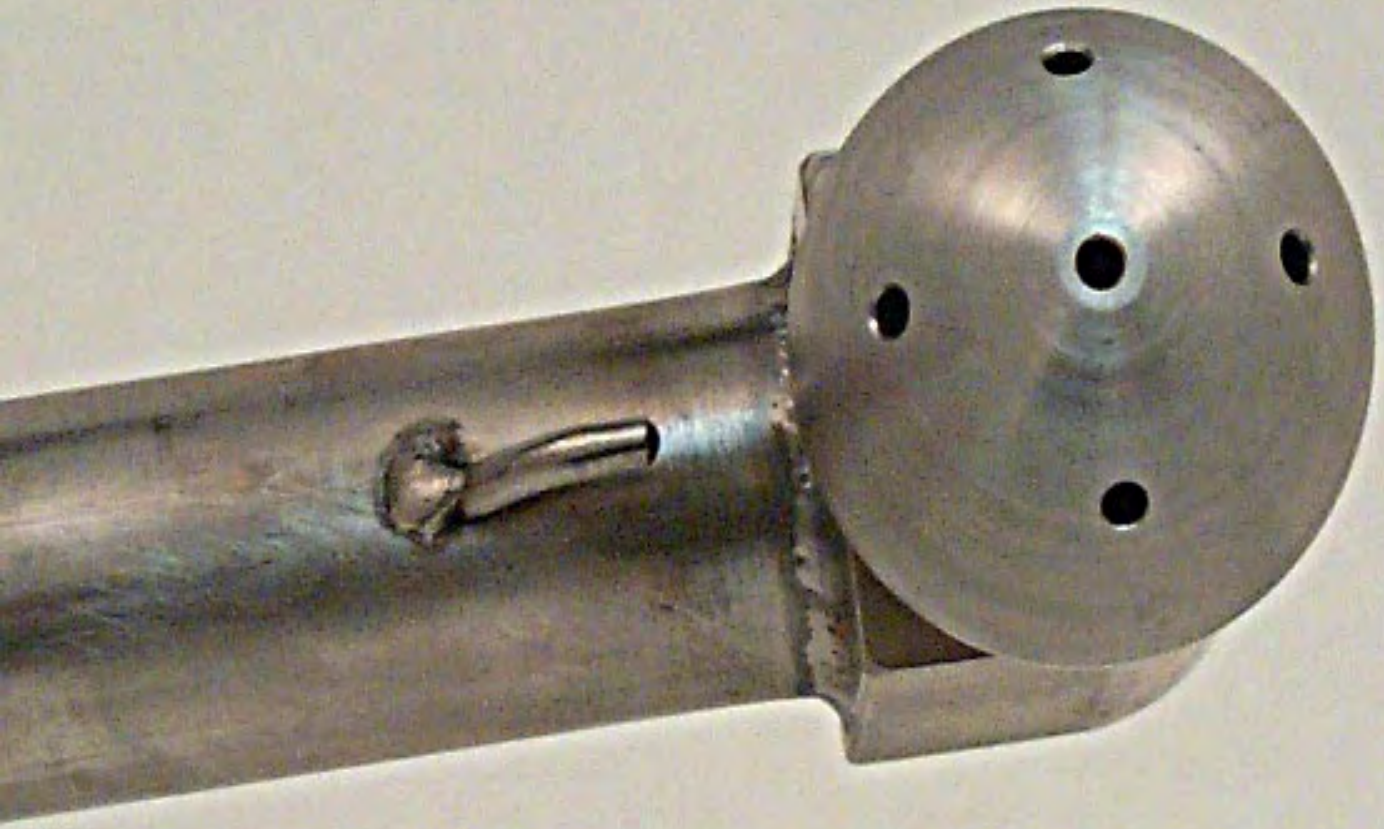
- Equipment
  - Manometer
  - Type S pitot tube/level indicator
- Procedure
  - “Null” reading; O.K.
  - Determine delta p if not “null”
  - Acceptance avg. $\Delta p < 20$ degrees

FRM 1 Alternative Measurement Site Selection Procedure

- Applies at sites < 2/0.5 siting
  - Must use “directional probe” to measure “yaw” and “pitch” angles at more than 40 traverse points
  - Calculate Resultant Angle (Ri)
    - Ri = Arccos[(cosYi)(cos Pi)]
    - If Ri < 20 degrees, then can use sample location

Method 2F Equipment

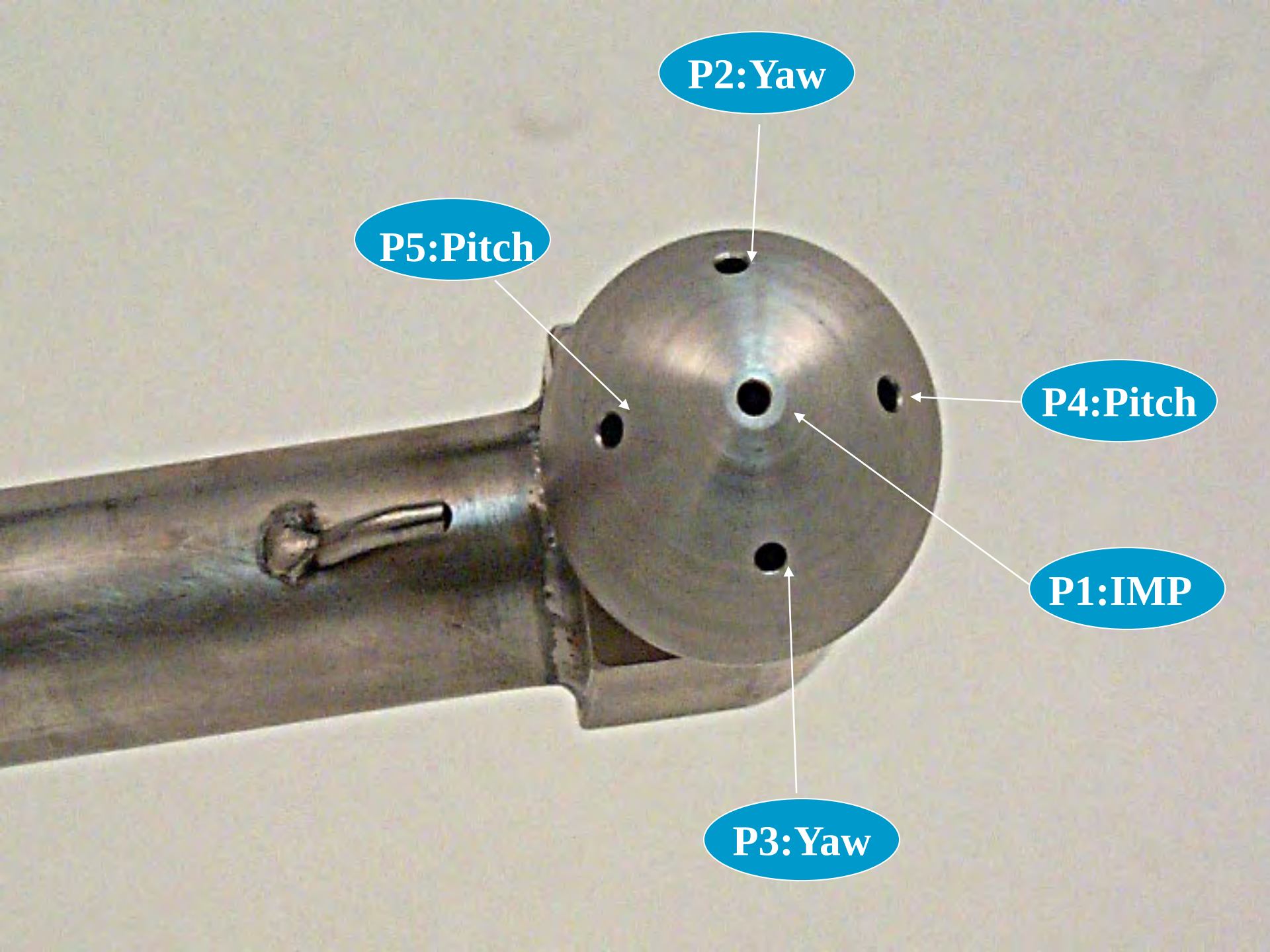
- 3D Probes
  - Spherical
    - Easy Leak Check
    - More Sensitive
    - Less Costly
  - Prism (DAT)





3-D Probe Measurements

- P1: Impact Pressure
- P2-P3: Yaw Angle
- P4-P5: Pitch Angle
- P1-P2: Total Velocity


P2:Yaw
P5:Pitch
P4:Pitch
P1:IMP
P3:Yaw

3-D Probe Measurement

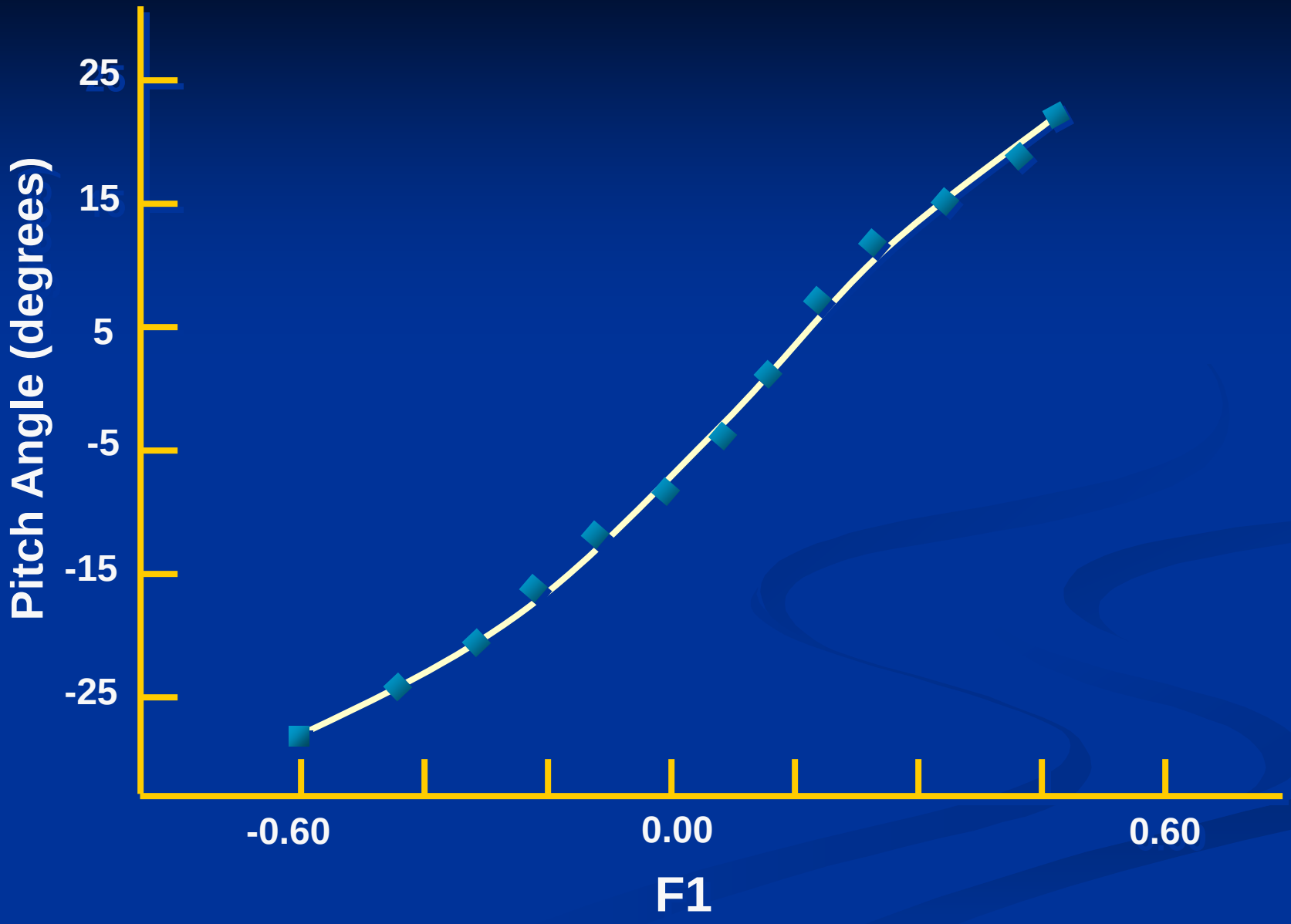
- Position probe at traverse point and verify position of “scribe line.”
- Pre leak check
- Record yaw and pitch angles at each traverse point
- Calculate resultant angle
- Post leak check

3-D Probe Measurement

- Yaw to “null”; Record gauge reading yaw angle (Yi) at traverse point.
- Record gauge reading pitch angle and determine pitch angle (Pi) from calibration curve.
- Complete for each traverse point.
- Calculate Resultant Angle (Ri)
  - Ri = Arccos[(cosYi)(cos Pi)]

Pitch Angle Curve (F1 Calibration Curve)

- F1 = (P4-P5)/(P1-P2)
- Manufacturer plots F1 vs. Pitch Angle at Qualified Wind Tunnel at Two Flow Rates (60 and 90 ft/sec)


Pitch Angle (degrees)
25
15
5
-5
-15
-25
-0.60
0.00
0.60
F1

3-D Probe Measurement For Acceptance Criteria

- Calculate Resultant Angle (Ri)
  - Ri = Arccos[(cosYi)(cos Pi)]
- Measurement location is acceptable if
  - $Ri_{avg} = \leq 20$ degrees
  - $S_d = 10$ degrees

Role of the Inspector
FRM 1 Activities

- Verify duct > 12 in. diameter for proper equipment selection
- Verify duct dimensions
- Verify upstream/downstream distances
- Check for blockage (Feel, look into duct for blockage)

Role of the Inspector
FRM 1 Activities

- Verify required number of points
- Adjust the required number of points if required (0.5 in. < 12 in.;
  1 in. > 12 in. to stack wall
- Check for cyclonic flow (average of < 20 degrees for all sampling point)
- Observe “Alternative Site Selection” verification

Major Points in FRM 1

- Limitation of method (Sec. 1.2)
- For rectangular stacks, equivalent diameter (Sec. 2.1)
- Minimum number of traverse points (Sec. 2.2.1)
- For particle sampling, one diameter in plain of bend (Sec. 2.3.1)

Major Points in FRM 1

- Relocation of traverse points (Sec. 2.3.1.1)
- Definition of cyclonic flow (Sec. 2.4)
- Verification of absence of cyclonic flow (Sec. 2.4)

Major Points in FRM 1

- Alternative Measurement Site Location (Sec. 2.5)
  - Directional flow sensor and resultant angle (Sec. 2.5.1.1)
  - Post leak check required at 3 in. water (Sec. 2.5.3.3)

Major Points in FRM 1

- Alternative Measurement Site Location (Sec. 2.5) Continued
  - Calculate resultant angle at each traverse point (Sec. 2.5.4.1)
  - Calibration of directional flow sensor (Sec. 2.5.6)

FRM 1 Inspector Tools

- Tape measure
- Field Observation Agency Checklist
- Type S pitot tube (cyclonic flow check) and level indicator
- 3-D pitot tube (alt. meas. site) and level indicator

FRM 1 Tips

- Measure the stack diameter from each sampling port and average values
- Find in-stack restrictions by using gloved hand and visual inspection of internal area
- Don’t forget to take into consideration the nipple of the stack or inner lining in calculations

FRM 1 Tips

- If measurement site location is after venturi scrubber or stack has tangential inlets, verify absence of cyclonic flow
- If stack is < 12 in., do not use this method (Use FRM 1A)
- If measurement site location < 2 D/0.5 D, don't use method

FRM 1 Tips

- Add first and last traverse points together to get internal stack diameter and compare to calculated value
- Don’t forget to add nipple diameter to calculated traverse points
- “White-out” is an excellent tool for marking probe

Dismiss Stack Test FRM 1

- Stack geometry not measured properly (Wrong number of points)
- Failure to identify cyclonic flow
- Failure to consider small ducts

Compliance Test and Source Test Observation

FRM 2: Stack Gas Velocity



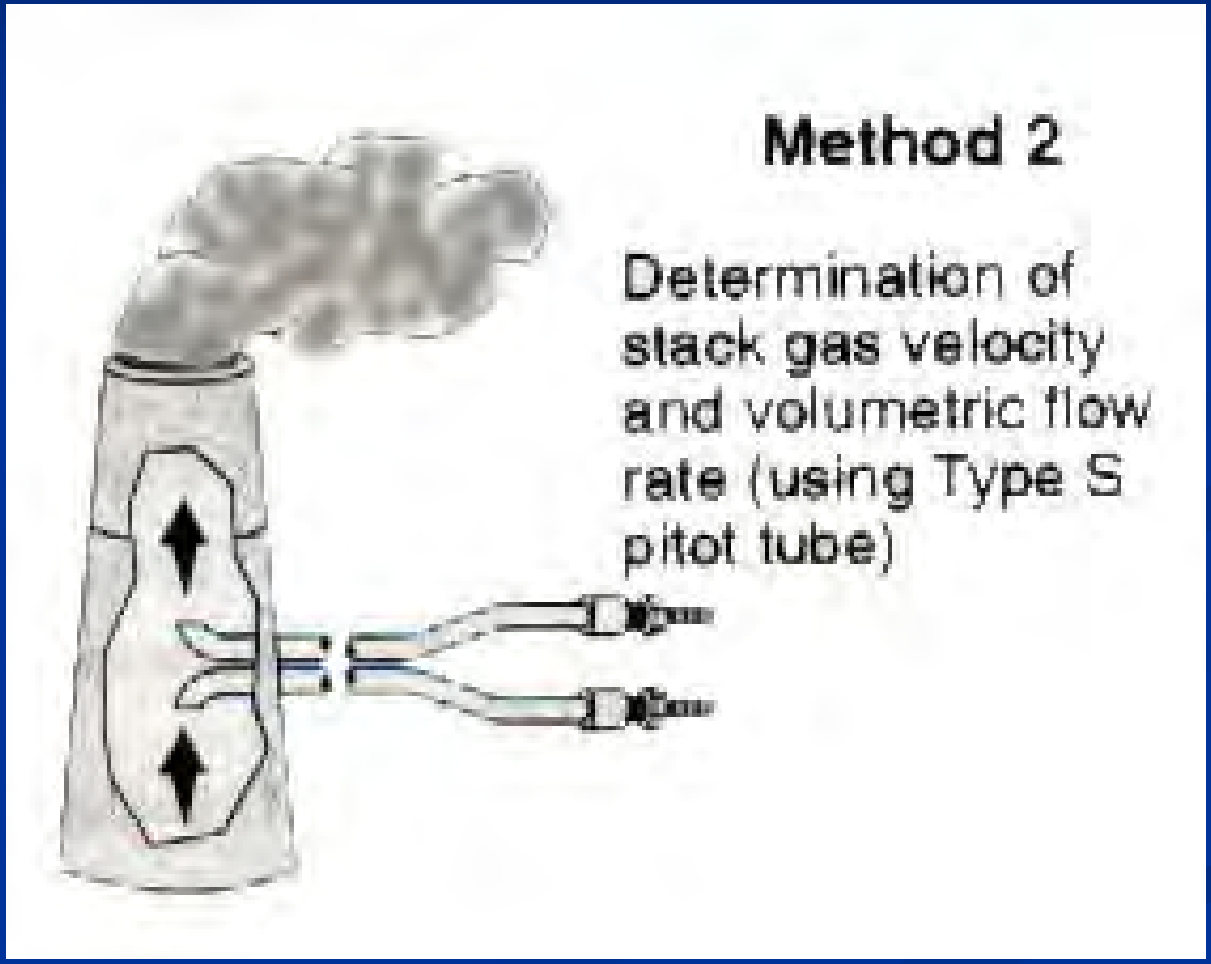
Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1 | FRM 2 | FRM 3 | FRM 4 | FRM 5 | FRM 19

FRM 2 Method


Method 2
Determination of stack gas velocity and volumetric flow rate (using Type S pitot tube)

POLLUTANT MASS RATE

$$\overline{PMR_s} = \bar{c}_s Q_s$$

$\bar{Q}_s$ $\bar{C}_s$

$A_s \bar{v}_s$ $v_s = v_n$ $\frac{m_n}{V_m}$

for

Isokinetic Conditions

$$v_s = K_p C_p \sqrt{\frac{T_s \Delta p}{M_s P_s}}$$

Obtain C_p, T_s, Δp

M_s P_s

Obtain $\Delta H_@$, D_n

B_{ws}, B_{wm},

P_m, T_m

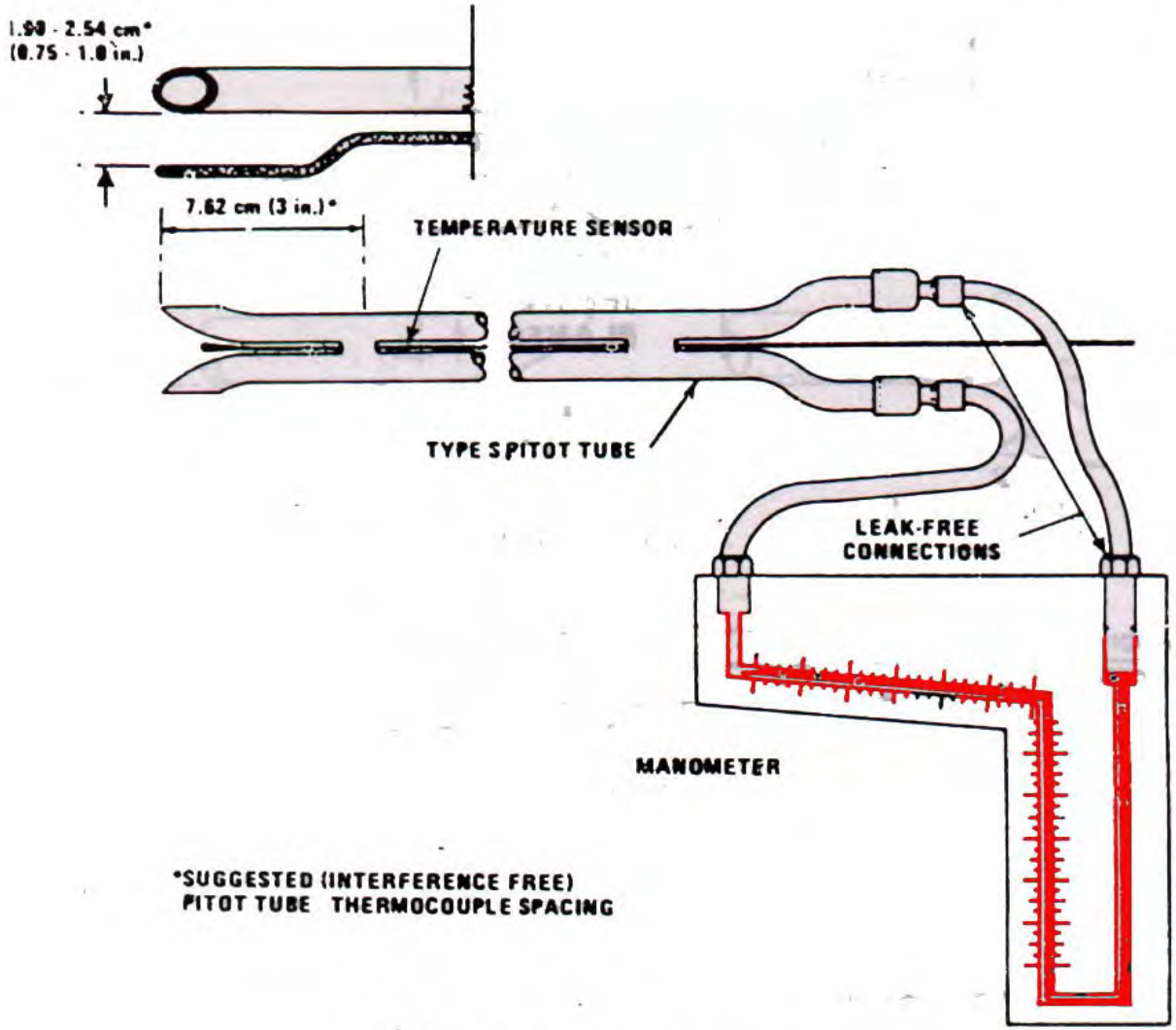


Figure 2-1. Type S pitot tube manometer assembly.



FRM 2

- This method is applicable for measurement of the average velocity of a gas stream
- The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube

FRM 2 History

- 1970 Promulgation of FRM 2
- 1983 FRM 2A in Small Ducts
- 1983 FRM 2B Stoichiometry Flow
- 1989 FRM 2C Std Pitot Small Ducts
- 1989 FRM 2D Rate Meter
- 1996 FRM 2E Landfills
- 1999 FRM 2F 3-D Yaw/Pitch Angle
- 1999 FRM 2G Type S/3-D
- 1999 FRM 2H Wall Effects

Can't Use FRM 2

- Failed siting criteria (Mininum of 2/0.5 diameters)
- Duct/stack < 12"
- Cyclonic flow exist at location
  - Install straightening vanes
  - Calculate total volume flow stoi.
  - Go to another sampling location

FRM 2 Pitot Tubes

- Each type pitot tube measures an impact and stagnation pressure and combines the measurements to obtain a velocity pressure
- Size of manometer requires:
  - $\Delta p > 0.05$ " water, then 0-10 " manometer adequate
  - $\Delta p < 0.05$ " water, then use manometer with 0.005 /division (i.e., micro-manometer)
  - $\Delta p < 0.01$ "water, then use high sensitivity transducer such as Hasting Thermo Probe

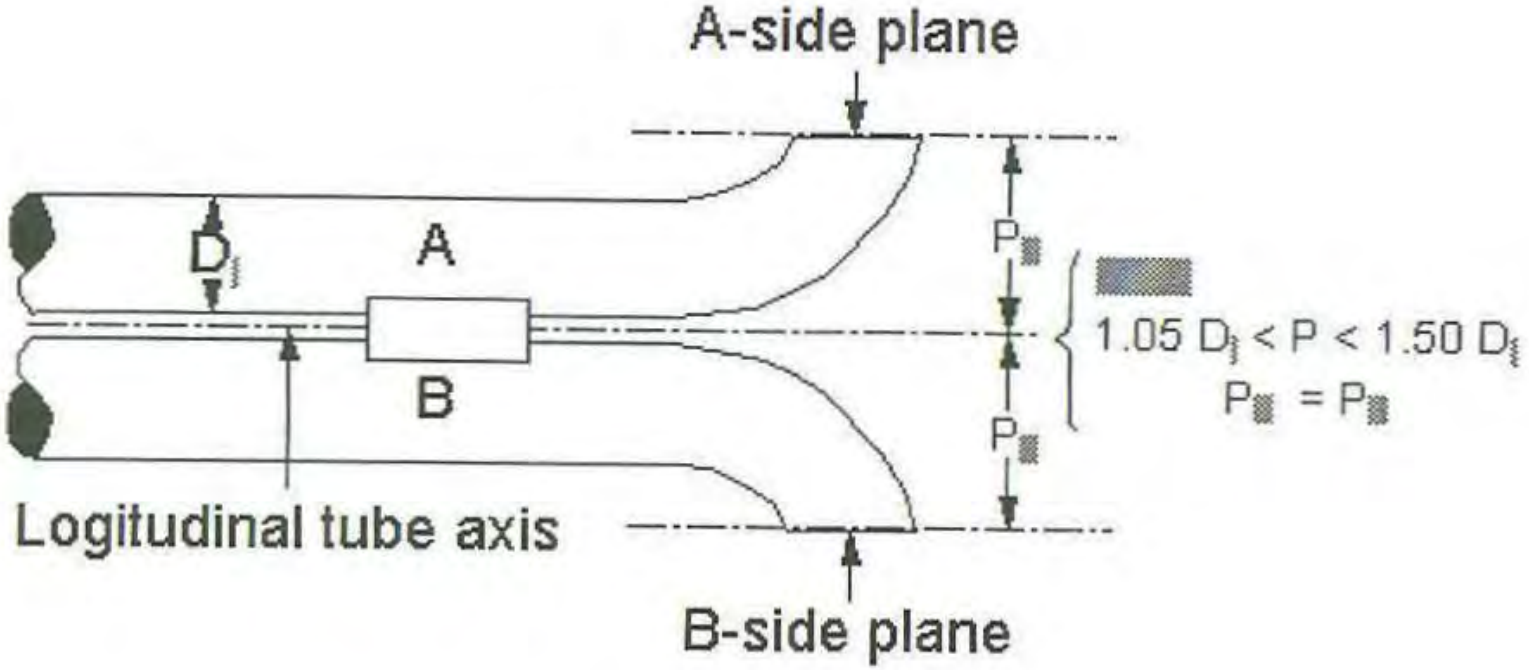
Interference-Free Component Arrangement

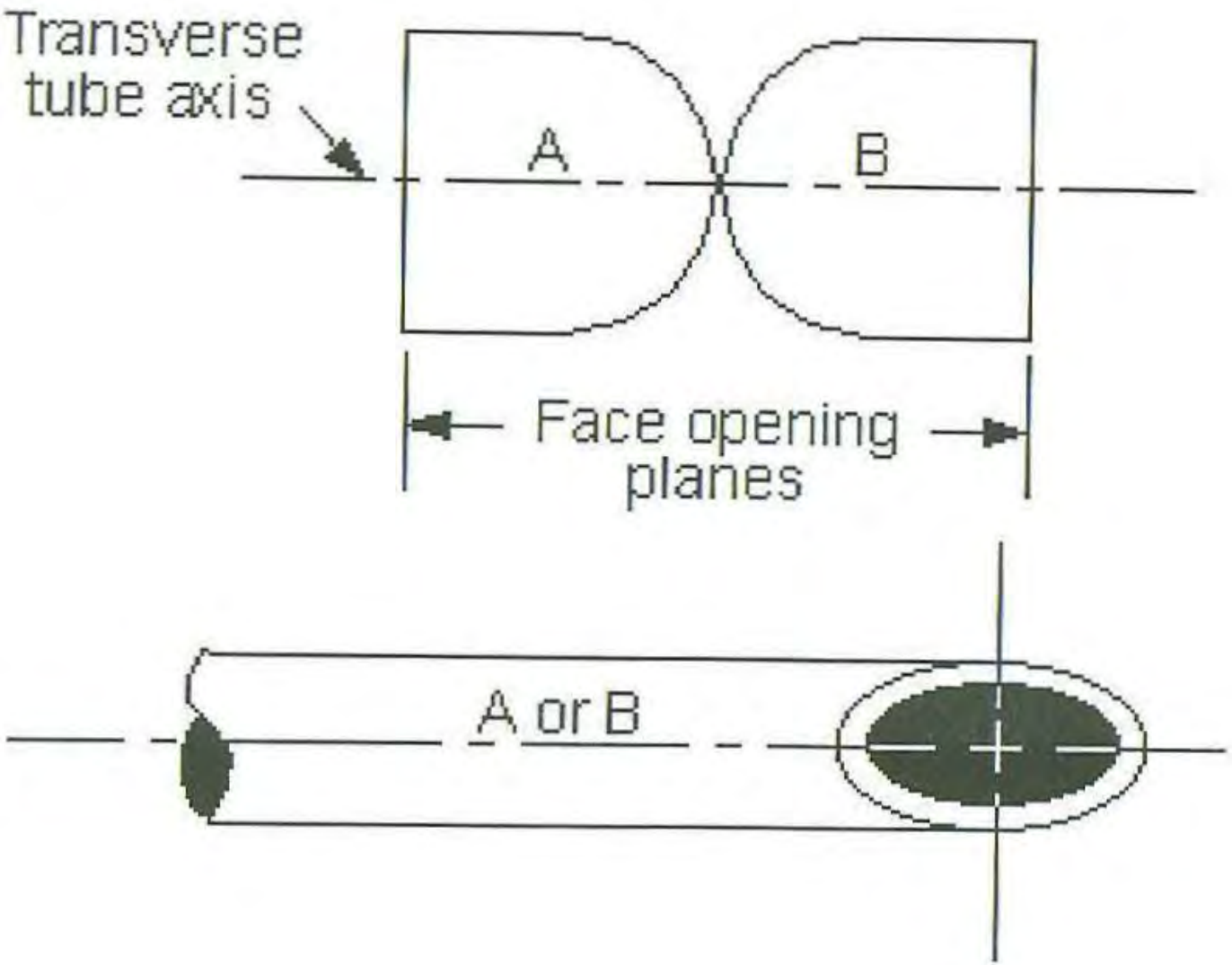
- Pitot tube distance to nozzle: >3/4 inches for ½ nozzles
- Center of nozzle and pitot tube opening aligned
- Thermocouple location to pitot tube > ¾ inch for 3 inches
- Back-recess thermo. > 2 inches
- Gas sampling assembly > 3 inches from pitot tube

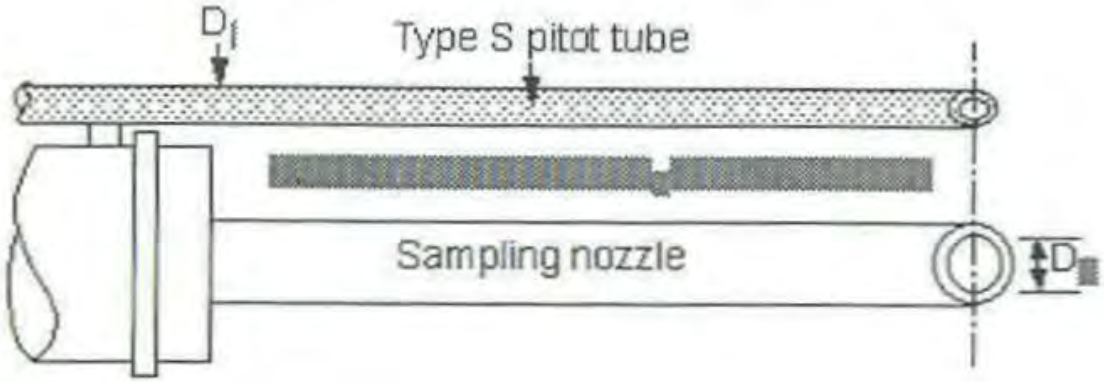
Type S Pitot Tube

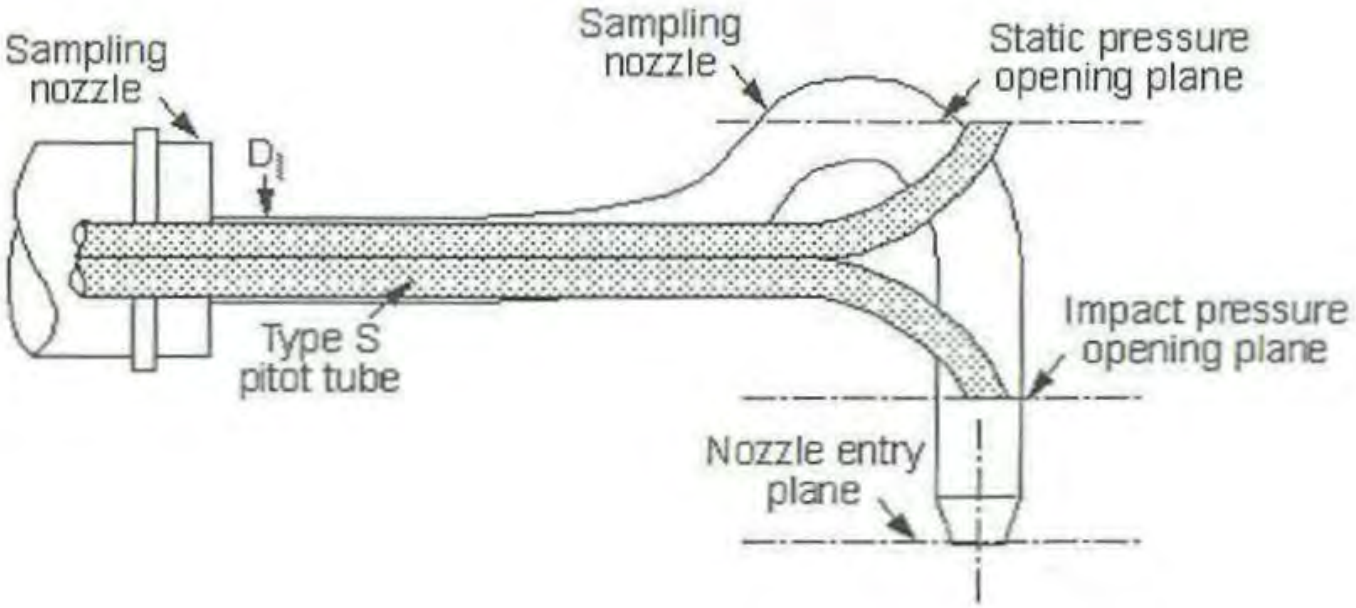
Design criteria for assigning

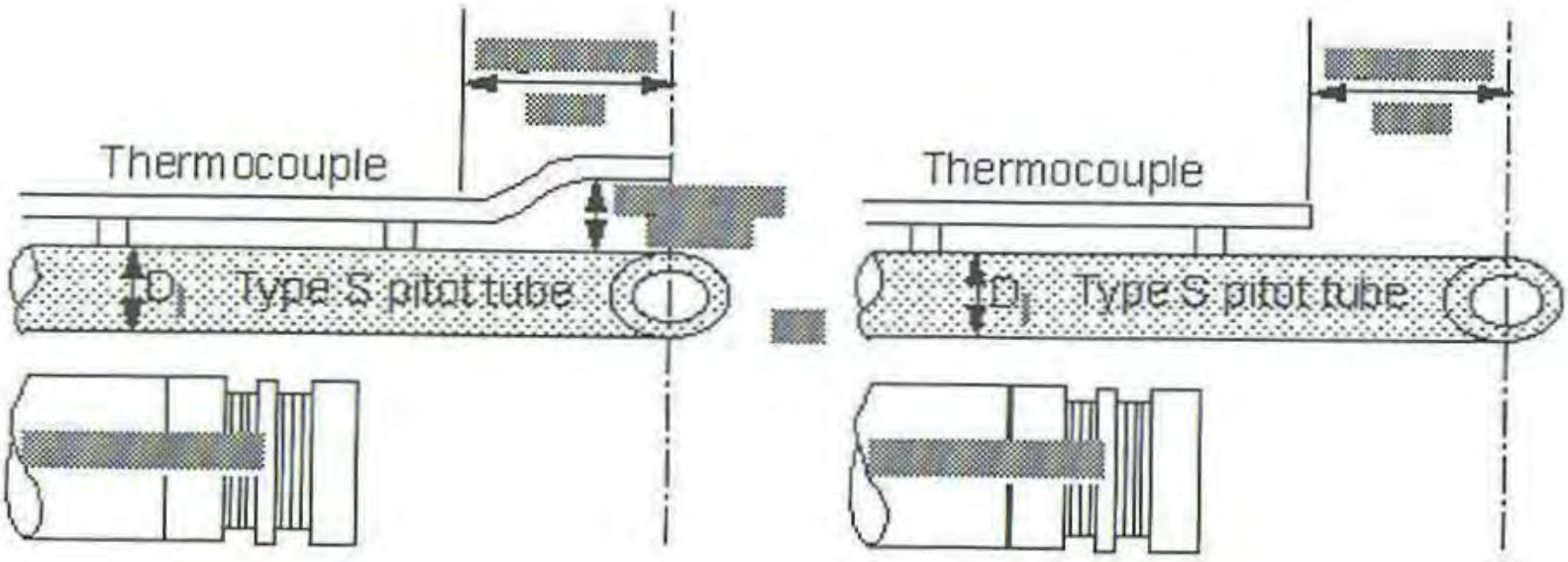
$$C_p = 0.84$$

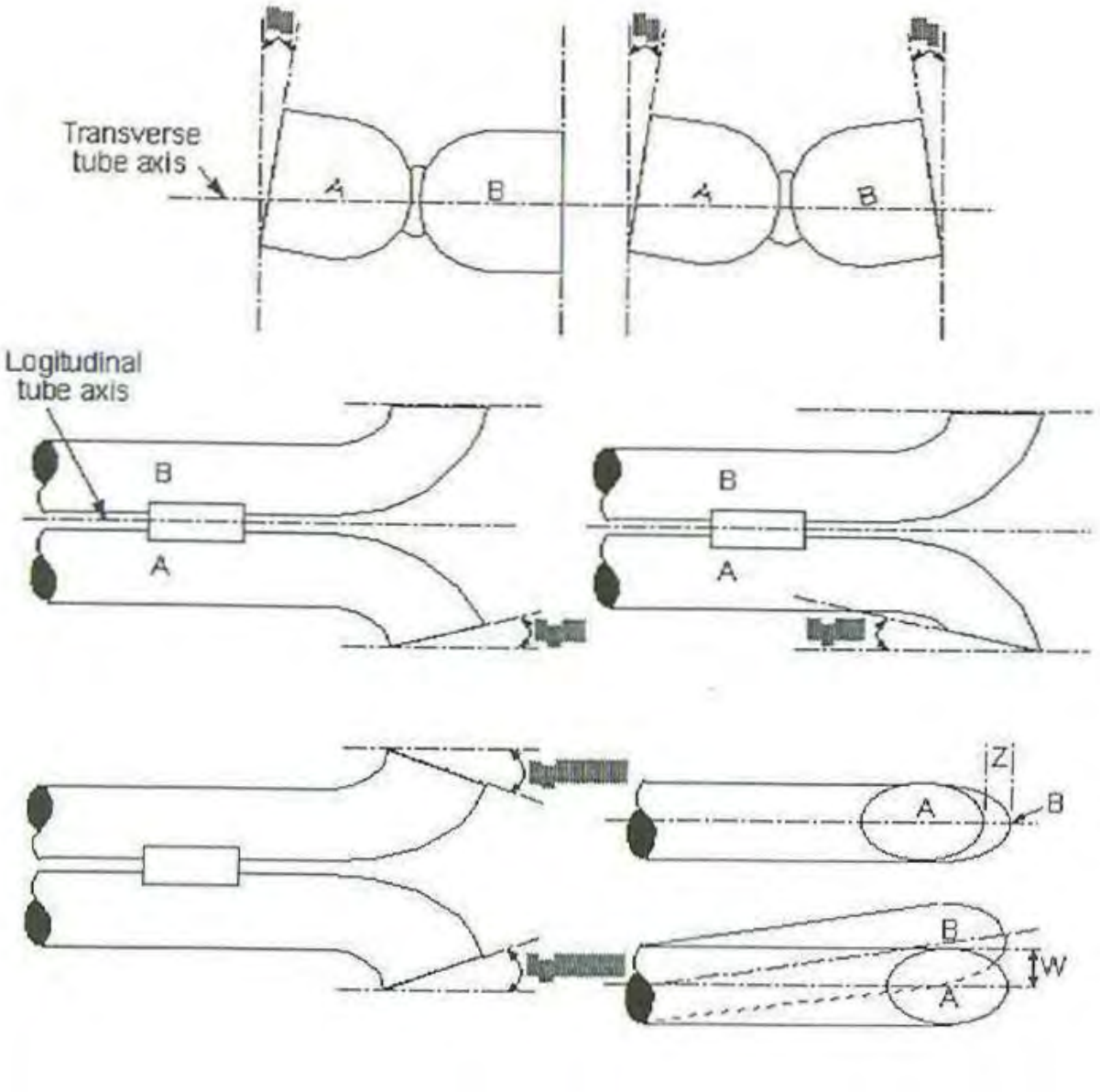

A-side plane
D
A
B
P
P
1.05 D < P < 1.50 D
P = P
Logitudinal tube axis
B-side plane


Transverse
tube axis
A
B
Face opening
planes
A or B


D_t
Type S pitot tube
Sampling nozzle
D_n


Sampling nozzle
D_n
Type S pitot tube
Sampling nozzle
Static pressure opening plane
Impact pressure opening plane
Nozzle entry plane


Thermocouple
D_1
Type S pitot tube
Thermocouple
D_1
Type S pitot tube


Transverse
tube axis
A
B
A
B
Logitudinal
tube axis
B
A
B
A
Z
A
B
B
W
A

Verification of Geometry of Type S Pitot Tube To Assign 0.84

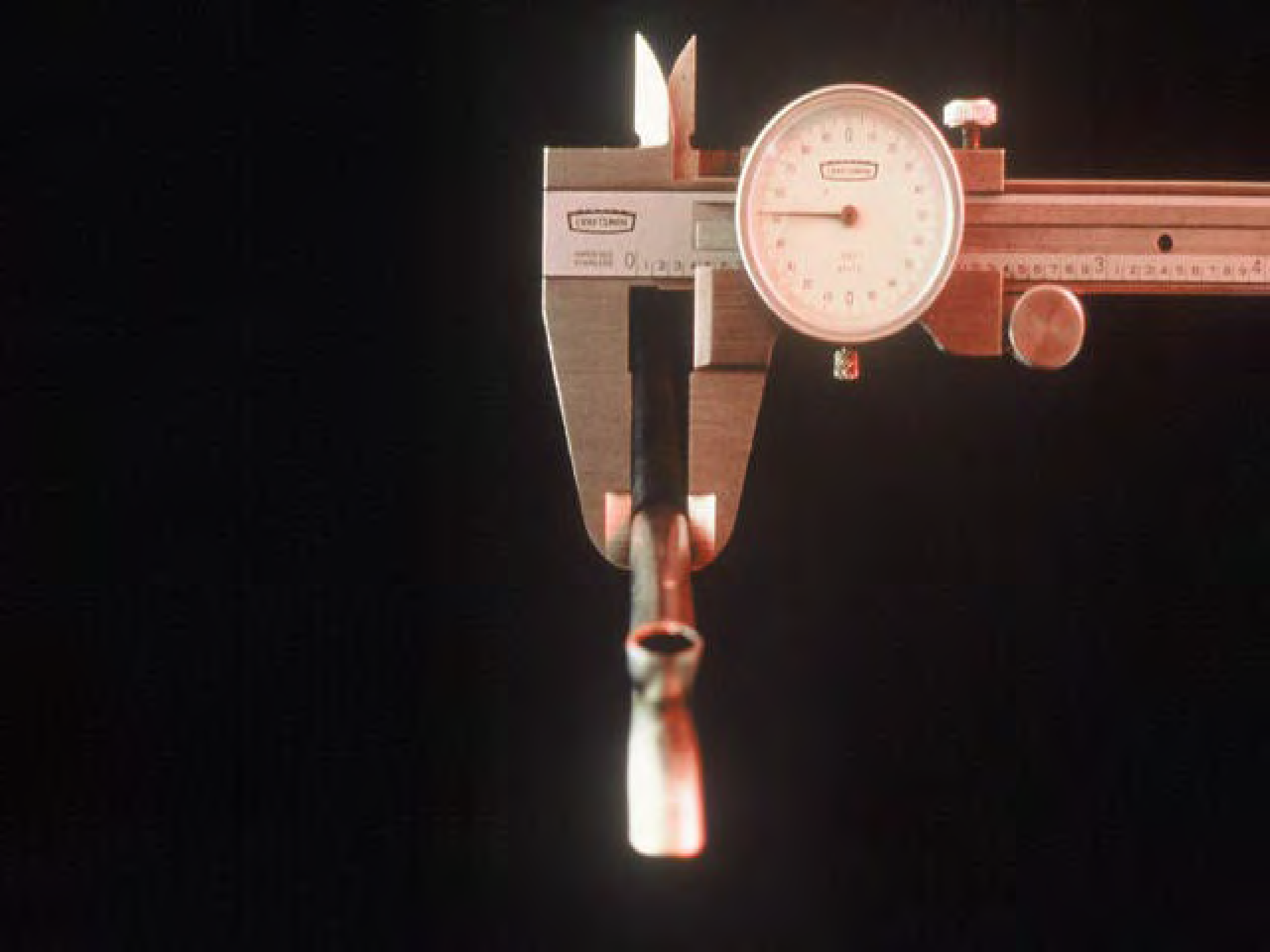
- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375





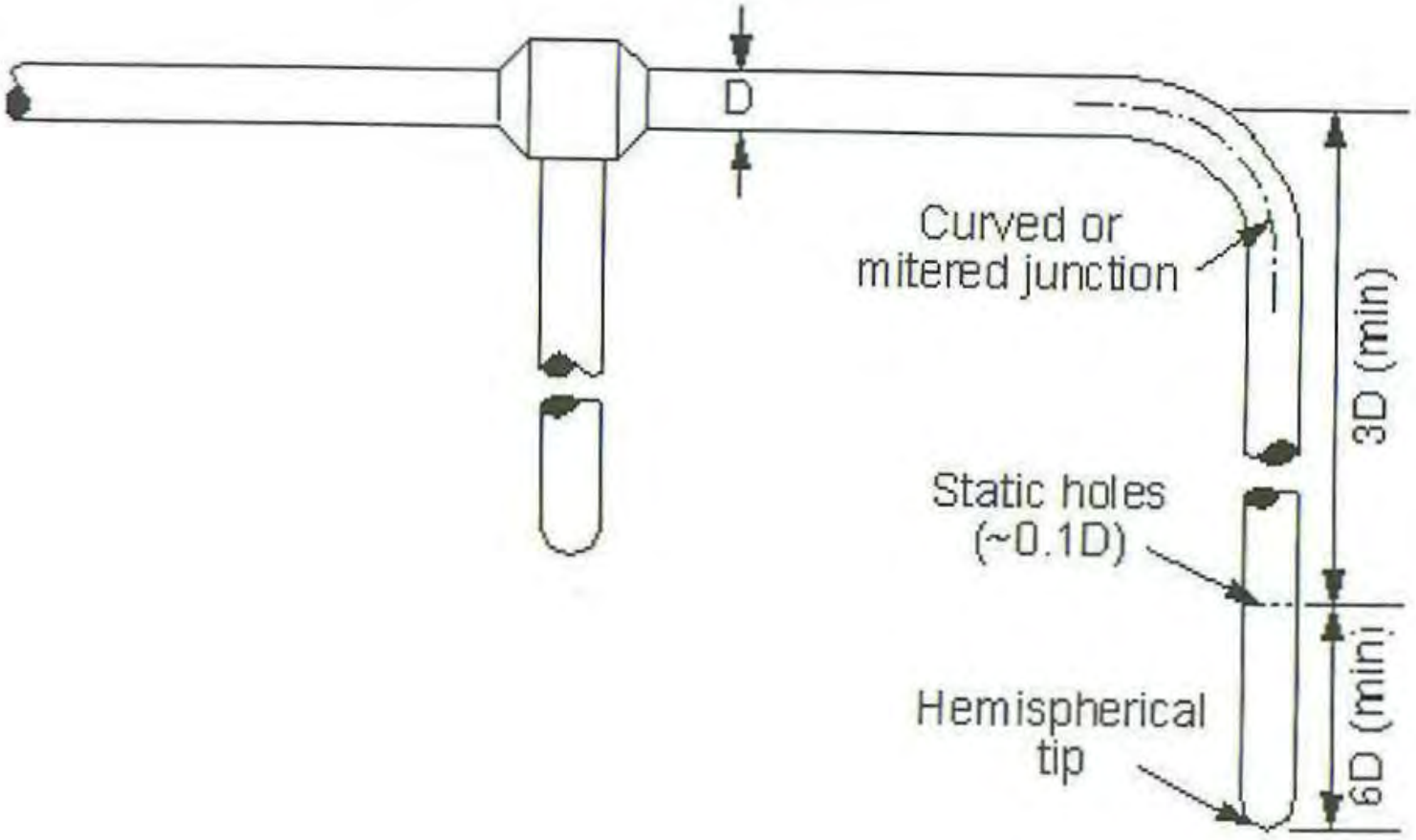

CRAFTSMAN
ANGLE FINDER
MAGNETIC BASE

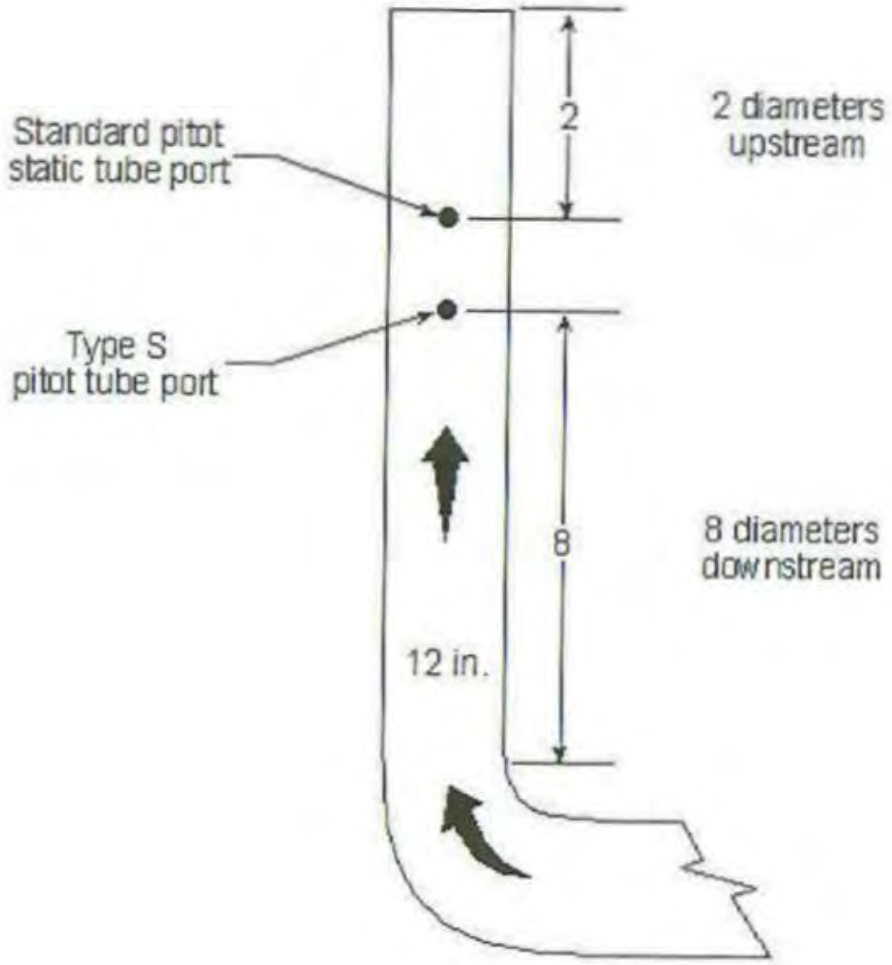

Sears
CRAFTSMAN
ANGLE FINDER
MAGNETIC BASE




CRAFTSMAN
CRAFTSMAN

Type S Pitot Tube Calibrate Using a Standard Pitot Tube and Wind Tunnel

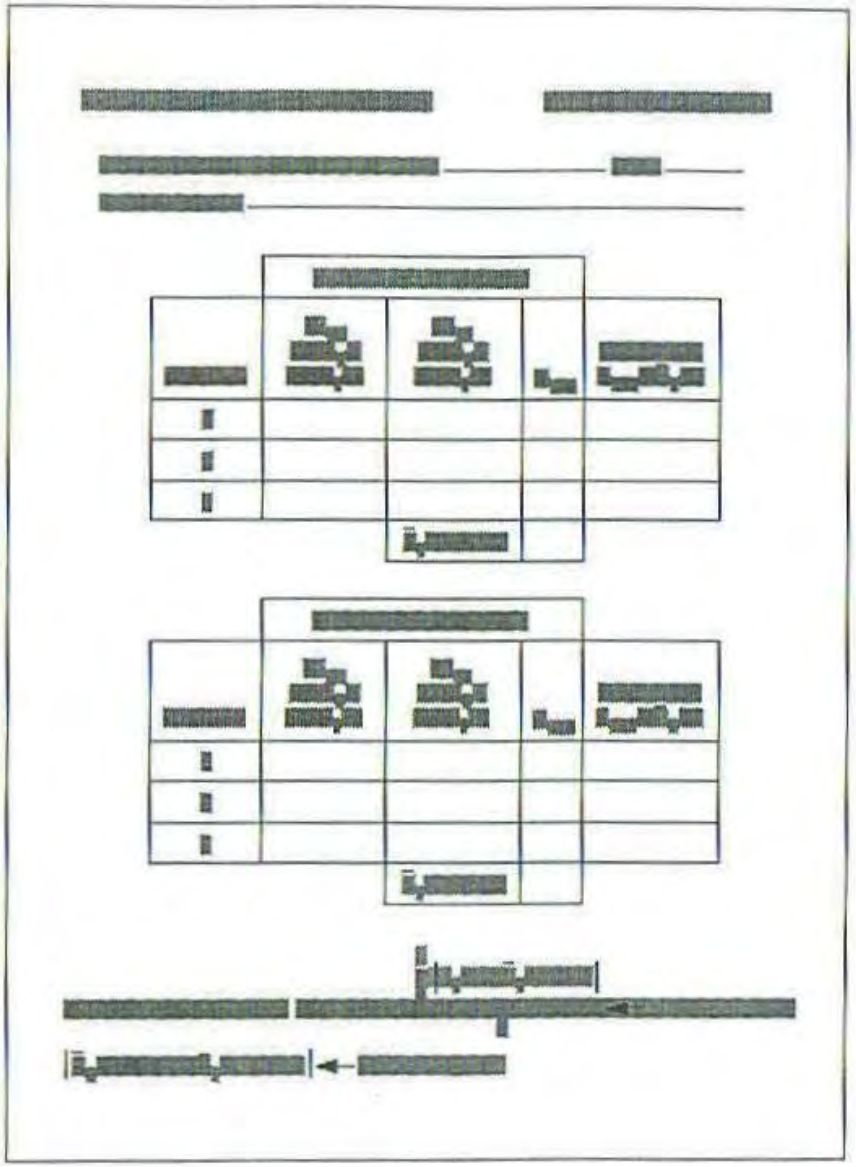

D
Curved or
mitered junction
3D (min)
Static holes
(~0.1D)
Hemispherical
tip
6D (min)


Standard pitot
static tube port
Type S
pitot tube port
2
2 diameters
upstream
8
8 diameters
downstream
12 in.

Pitot Tube Calibration Equation

$$C_{p(s)} = \left[\frac{\Delta p_{std}}{\Delta p_s} \right]^{1/2} C_{p(std)}$$

Pitot Tube Calibration Data Sheet



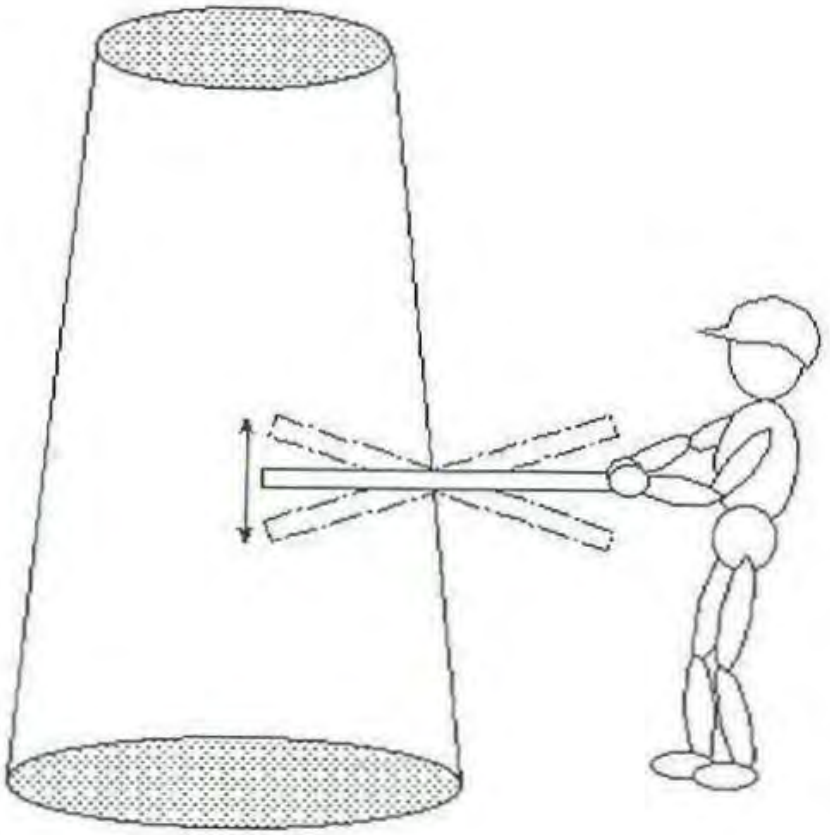
Velocity Measurement Procedures

1. Leak-check pitot tube and differential pressure gauge.
2. For circular stacks less than 10 ft in diameter, two ports are sufficient. Use four ports when stack diameter is greater than 10 ft.
3. Pitot tubes longer than 10 ft should be structurally reinforced to prevent bending of tube and misalignment errors.
4. Identify each sample port and traverse point with a letter or number.
5. Read velocity head and temperature at least twice at each point and record the average.

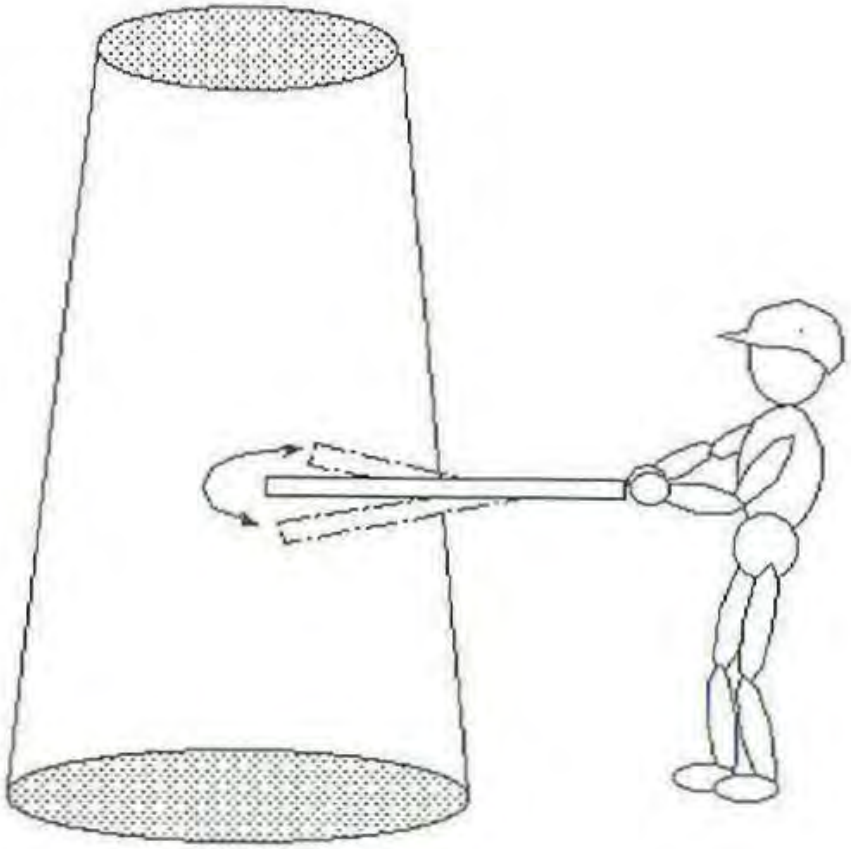
Velocity *(cont.)*

6. Care should be taken to prevent touching the pitot tube tip to the side of the stack.
7. Plug unused sampling ports and seal port being used as tightly as possible.
8. After traverse, check differential pressure gauge; repeat traverse if zero has shifted.
9. If liquid droplets are present, use a liquid trap in positive pressure leg of pitot tube.
10. A post-test leak check is required after each run of the pitot tube and velocity pressure system.

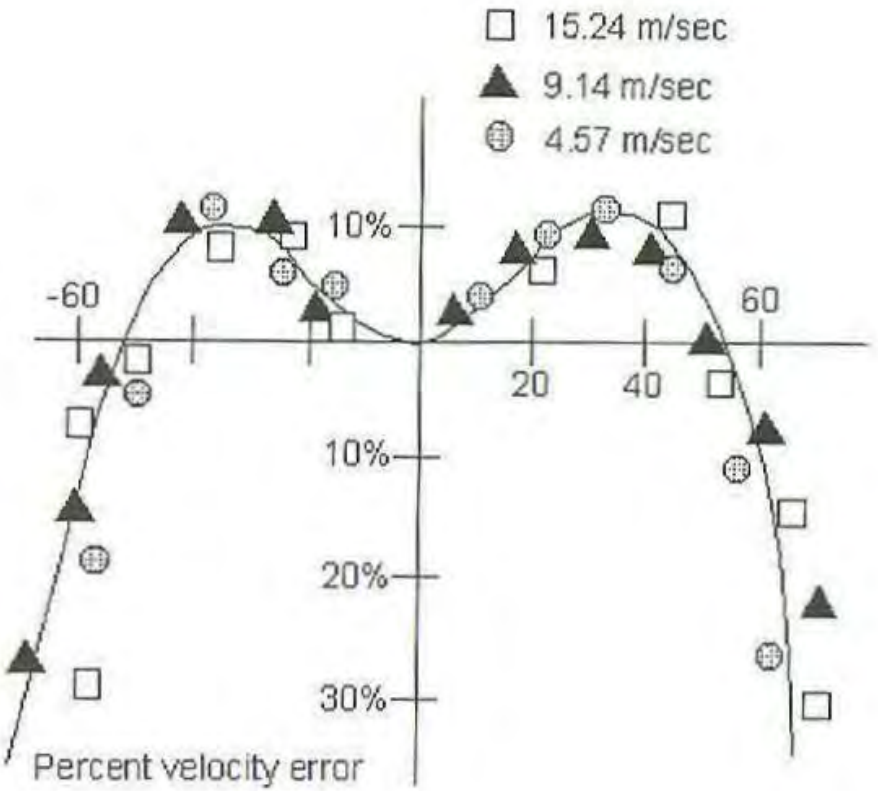
Pitch Angle



Yaw Angle



Velocity Error vs. Yaw Angle For a Type S Pitot Tube



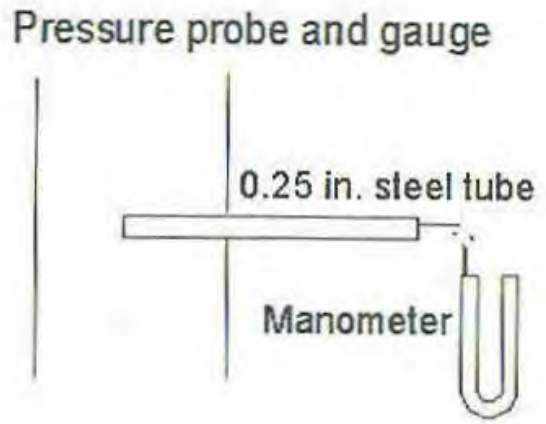
Federal Reference Method 2
Average Velocity Over Cross-Section

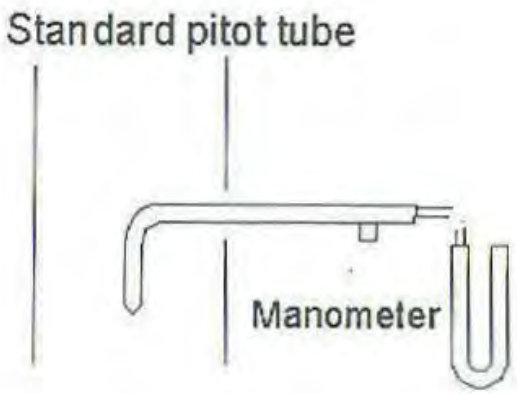
$$\bar{v}_s = K_p C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s(avg)}}{M_s P_s}}$$

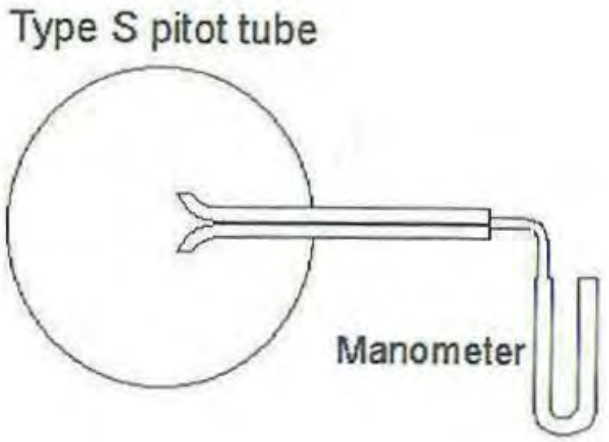
Average Stack Gas Dry Volumetric Flow Rate

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

Static Pressure Measurements







Stack Pressure (P_s)

$$P_s = P_b + \frac{P_g}{13.6}$$

Barometric Pressure

Barometric pressure during testing is obtained by:

Instrument

- Mercury, aneroid or other barometer (with required sensitivity)

Other

- Obtain barometric pressure from nearby National Weather Service station (station pressure) and adjust for elevation differences between sampling site and weather station.

Pressure Probe and Gauge

Static pressure measurement must be accurate to within 1 in. Hg (13.6 in. H_2O).

Pressure sensors typically used to measure static pressure during testing include:

- A piezometer tube and mercury or water-filled U-tube manometer
- The static tap of a pitot tube
- One leg of the Type S pitot tube

Applicability

Method 2 is applicable only at sites that:

- Meet the criteria of Method 1
- Do not contain cyclonic or non-parallel flow

Alternatives When Unacceptable Conditions Exist

(Subject to approval of the Administrator)

- Install straightening vanes.
- Calculate total volumetric flow rate stoichiometrically.
- Move to a measurement site at which flow is acceptable.
- Use procedures as described in Method 2 for cyclonic flow.

Type S Pitot Tube Inspection Data Sheet

- With the S-Type pitot tube, determine whether it meets the design specifications to be able to assign a C_p of 0.84
- C_p may be determined in conjunction with standard pitot tube
- Identification number scribed on pitot tube

FRM 2 Velocity Equation

$$v_s = K_p C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s\,(avg)}}{P_s M_s}}$$

FRM 2 Inspector Tools

- Level indicator
- Modular pitot tube
- Hand-held manometer
- Pocket barometer
- Hand-held digital thermometer and thermocouples

FRM 2 Inspector Tools

- Bull's eye level
- Field observation agency checklist
- Stack sampling nomographs for field estimations
- 3-D pitot tube

Major Points in FRM 2

- 0-10 in. manometer for > 0.05 Δp
- < 0.05 Δp, use 0.005 in. divisions
- Thermocouple and magnehelic calibration required
- Type S pitot tube: configuration, calibration, and leak check

Major Points in FRM 2

- FRM 2 not applicable at sites not meeting FRM 1 (Sec. 1.2)
- FRM 2 cannot be used in cyclonic or swirling flow (Sec. 1.2)
- Alternative guidance
  - install straightening vanes
  - calculate flow stoichiometrically
  - select another location (Sec. 1.2)

Major Points in FRM 2

- Type S pitot tube should have a known coefficient (Sec. 2.1)
- Ident. # on pitot tube (Sec. 2.1)
- Acceptable design specifications allow C_p of 0.84 (Sec. 2.1)
- Standard pitot may be used, but must demonstrate not plugged during use (Sec. 2.1)

Major Points in FRM 2

- Design specification of Type S pitot tube (Fig. 2-3)
- Manometer specifications of 0-10 in. for >0.05 Δp (Sec. 2.2)
- Provides guidance on use of more sensitive gauge (Sec. 2.2)
- Provides calibration of magnehelic gauge (Sec. 2.2)

Major Points in FRM 2

- FRM 2 provides guidance on adjustment of barometric pressure with altitude (Sec. 2.5)
- Need to take static pressure measurement only once during the test (Sec. 3.4)
- Must verify the face opening alignment, measure and record (Sec. 4.1)

Major Points in FRM 2

- Guidance with Type S pitot tube in association to probe/nozzle/ thermocouple placement (Sec. 4.1)
- Calibrate against standard pitot tube at 3,000 ft/min (Sec. 4.1.2.3)

Major Points in FRM 2

- Must leak check all pitot lines (Sec. 4.1.3.1)
- May calibrate Type S pitot tube at source (Sec. 4.1.5.1.1)

Major Points in FRM 2

- Must verify that probe sheath interference is < 2% of area of stack (Sec. 4.1.5.1.3)
- May use of C_p for Side A or B or may average (Sec. 4.1.6.1.1)

FRMs 2F, 2G, and 2H New Flow Test Methods

- Method 2F: calculates axial velocity (3-D Probes)
- Method 2G: calculates "near-axial" velocity (Type S or 3-D probes)
- Method 2H: Wall effects (Type S or 3-D probes or default wall effects adjustment factor)

Dismiss Stack Test FRM 2

- Pitot tube leak check at 3 “ water failed
- Pitot tube geometry not to specifications
- Pitot tube orientation during test not proper

Compliance Test and Source Test Observation

FRM 3: Gas Analysis Molecular Weight



FRM 3

Method 3

Determination of the dry molecular weight of flue gas (using Orsat apparatus measuring $\%O_2$, $\%CO_2$, and $\%CO$)



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1 FRM 2 FRM 3 FRM 4 FRM 5 FRM 19

Principle

A gas sample is collected by one of the following methods:

- Single-point grab sampling
- Single-point integrated sampling
- Multi-point integrated sampling

Principle

The sample is analyzed for the following components:

- Carbon dioxide (CO_2)
- Oxygen (O_2)
- Carbon monoxide (CO) (if necessary)

Applicability

For determining dry molecular weight and excess air correction factor from fossil-fuel combustion sources

Sampling Procedures

- Single-point grab
- Single-point integrated
- Multi-point integrated

Analytical Procedures

- Orsat (Method 3)
- Automated (Method 3A)

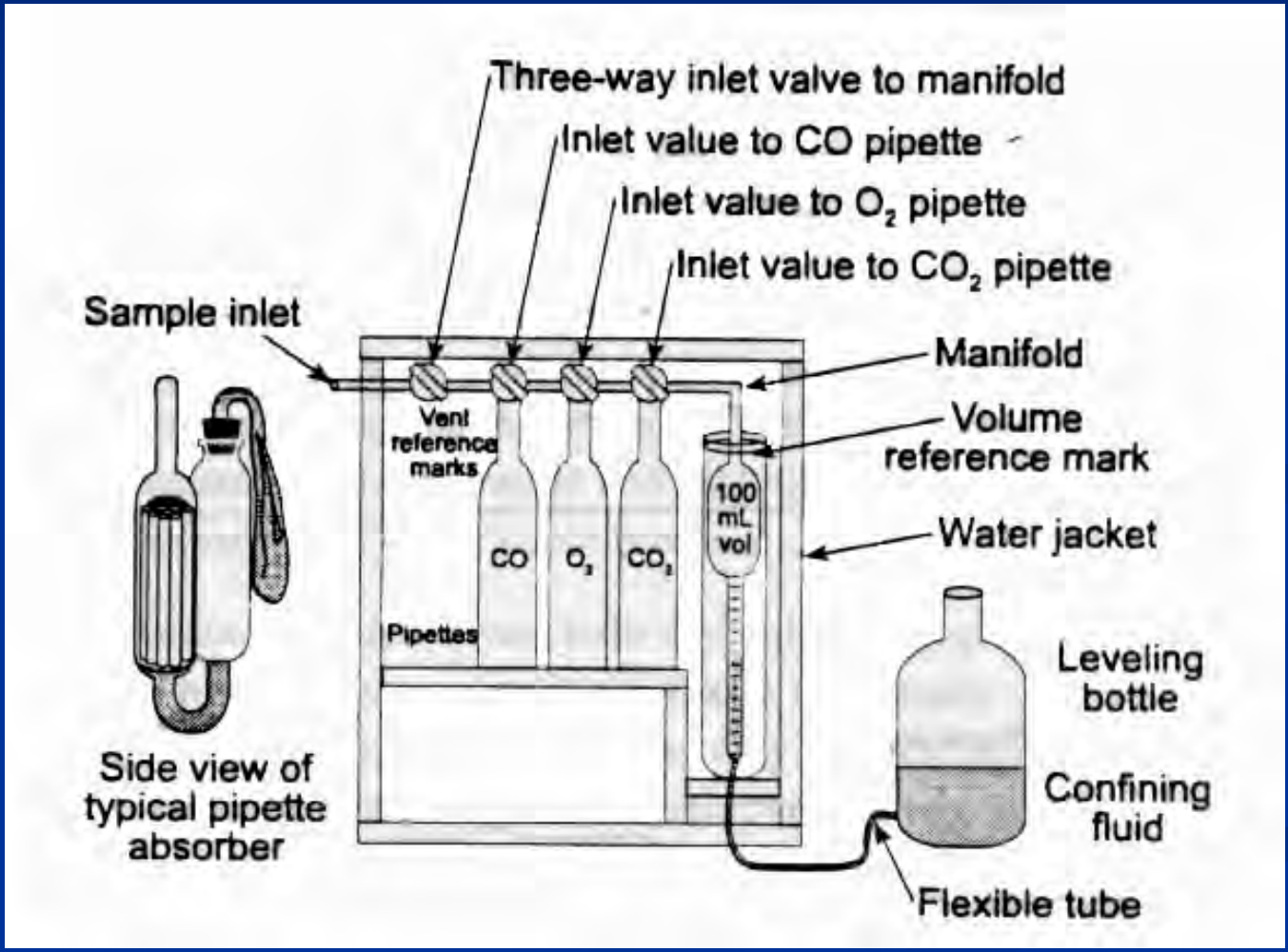
Federal Reference Method 3 History

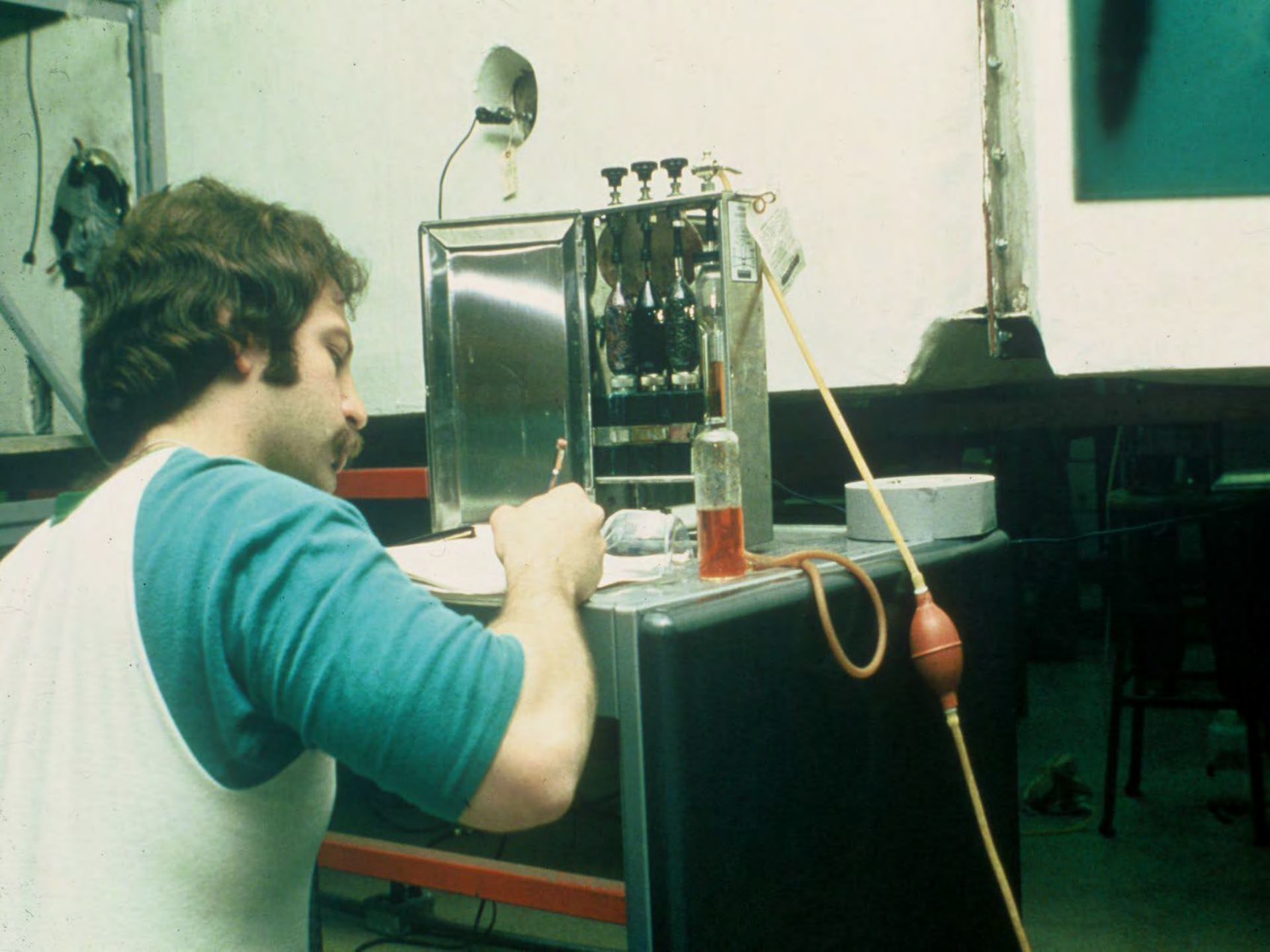
- 1970 FRM 3 Promulgated
- 1986 FRM 3A Instrumental
- 1990 FRM 3B Orsat for Correction Factor and Excess Air (F_o-Factor)
- 1996 FRM 3C Landfill Gas

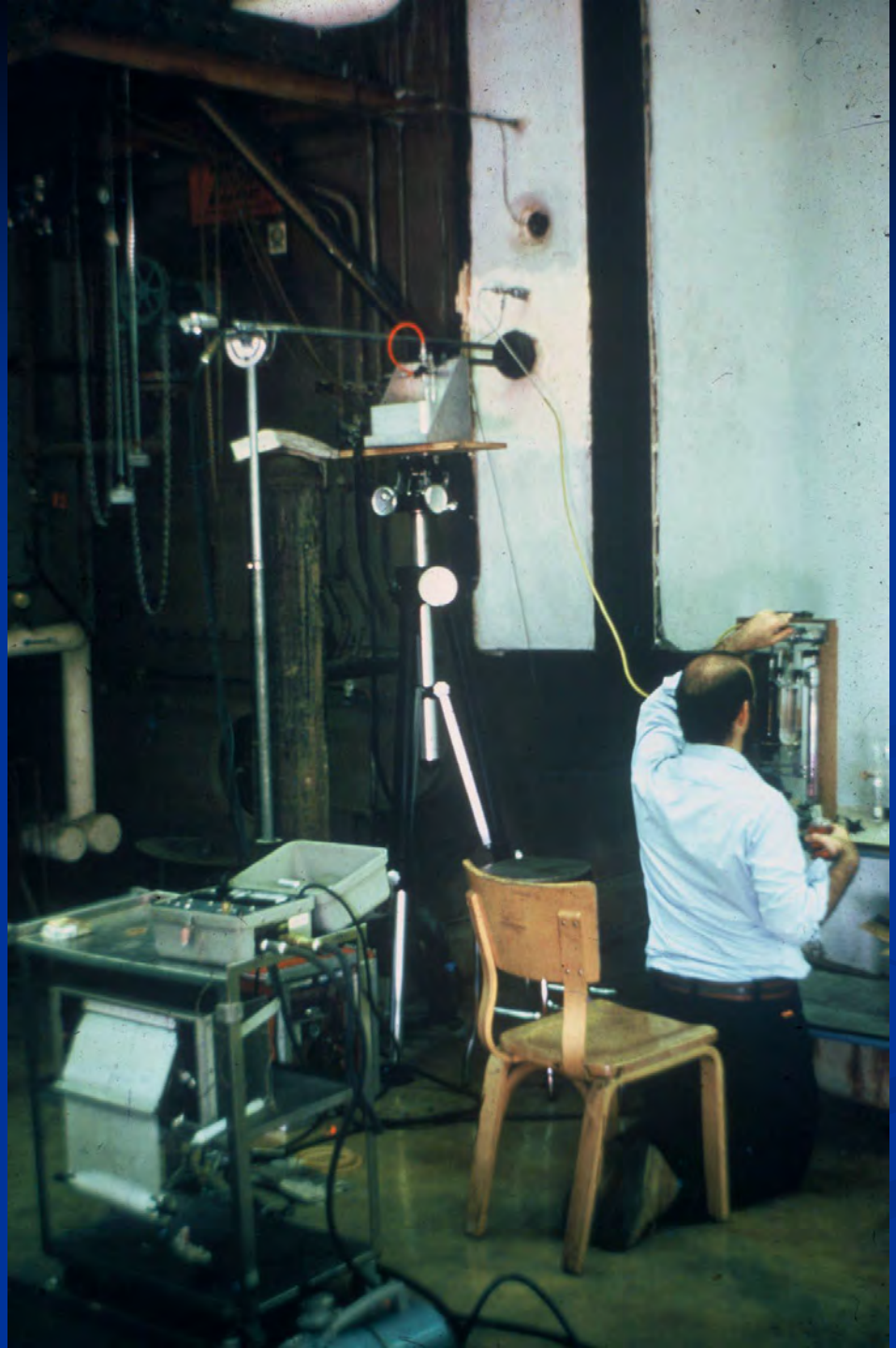
Federal Reference Method 3

- Gas analysis: measuring percent of O_2 and percent of CO_2 to determine the dry molecular weight of the flue gas (using Orsat Apparatus)

Orsat Analyser










'94 12 1


ENERAC 3000E
Integrated Emissions System
SET KEYS
PRIMARY FUELS
PRINTER
STACK KEYS
STACK PROBE
ELECTRICAL

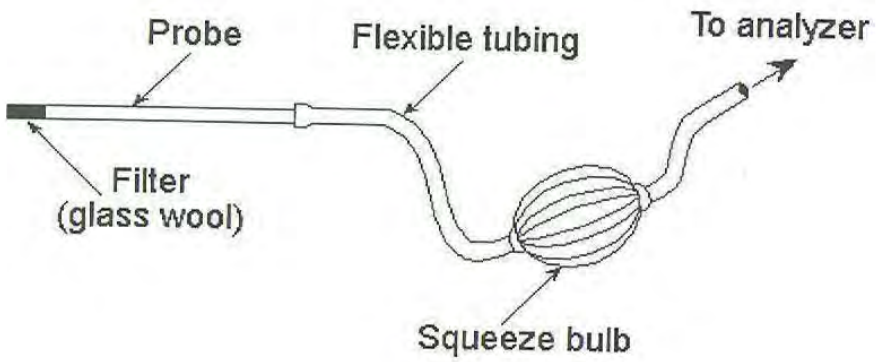
FRM 3 Sampling Techniques

- Single point grab sample
- Single point integrated sample
- Integrated multi-point sample

Single-Point Grab Sampling

1. Sample point should be a centroid of the cross-section or at a point at least 1 m from the wall of a large stack.
2. Place probe securely in stack and seal sampling port to prevent dilution of stack gas.
3. Purge sample line and attach to analyzer.
4. Aspirate sample into analyzer.

Single-Point Grab Sampling Train



Single-Point Integrated Sampling Train

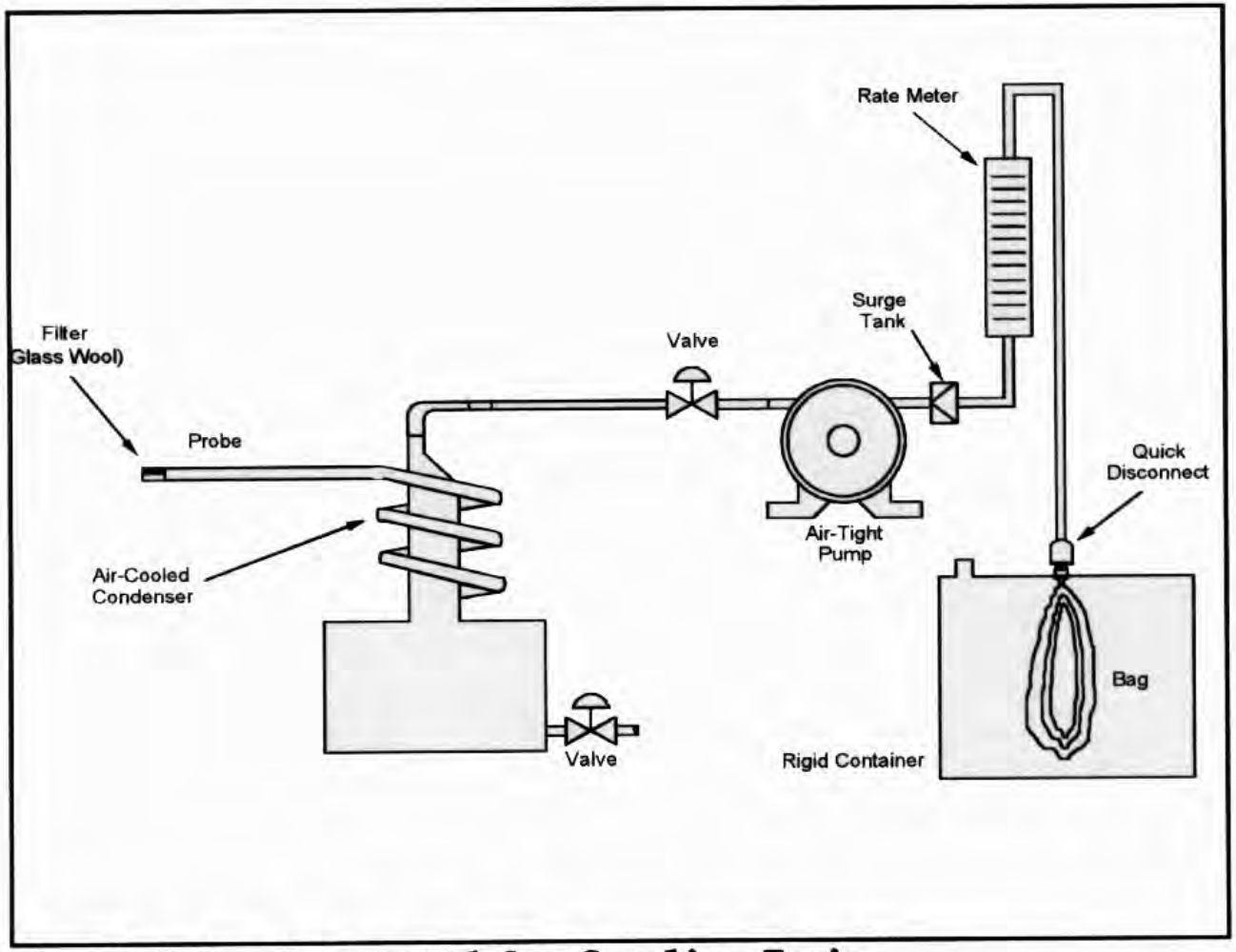


Figure 3-2. Integrated Gas-Sampling Train.

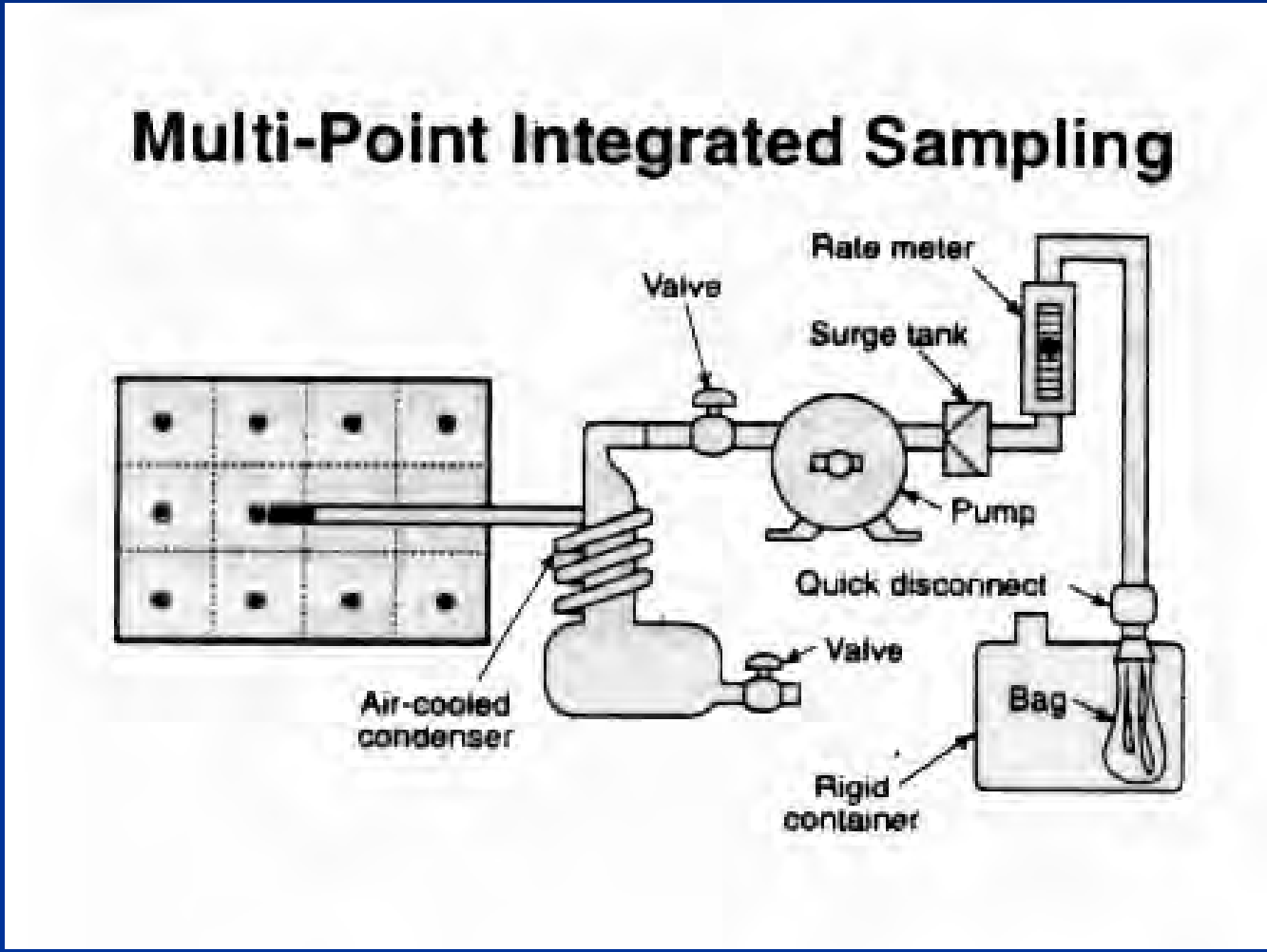
Single-Point Integrated Sampling

1. Sample point and probe placement is same
   as for single-point grab sampling.
2. Leak-check the flexible bag.
3. Leak-check the sampling train.

Single-Point Integrated Sampling

4. Connect probe to train and purge the system.
5. Connect evacuated flexible bag and begin sampling.
6. Sample at constant rate; collect 30 to 90 L of gas simultaneous with pollutant emission test.

Multi-point Integrated Sampling Train



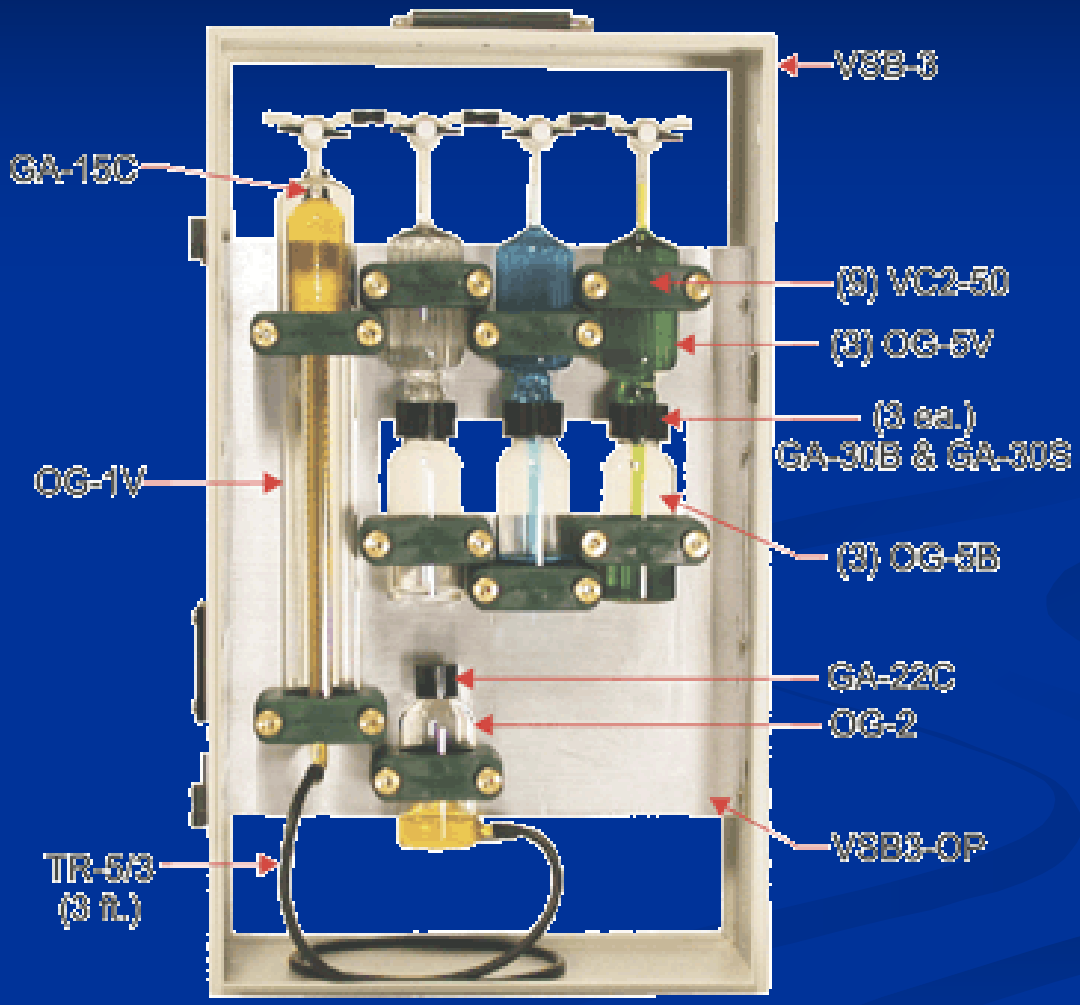
Multi-point Integrated Sampling

1. This procedure uses same sampling train and equipment preparation as the single-point integrated sampling method.
2. Locate sampling points according to Method 1.
3. Sample each point at the same rate and for the same time increment.
4. Collect 30 to 90 L of gas simultaneous with pollutant emission test.

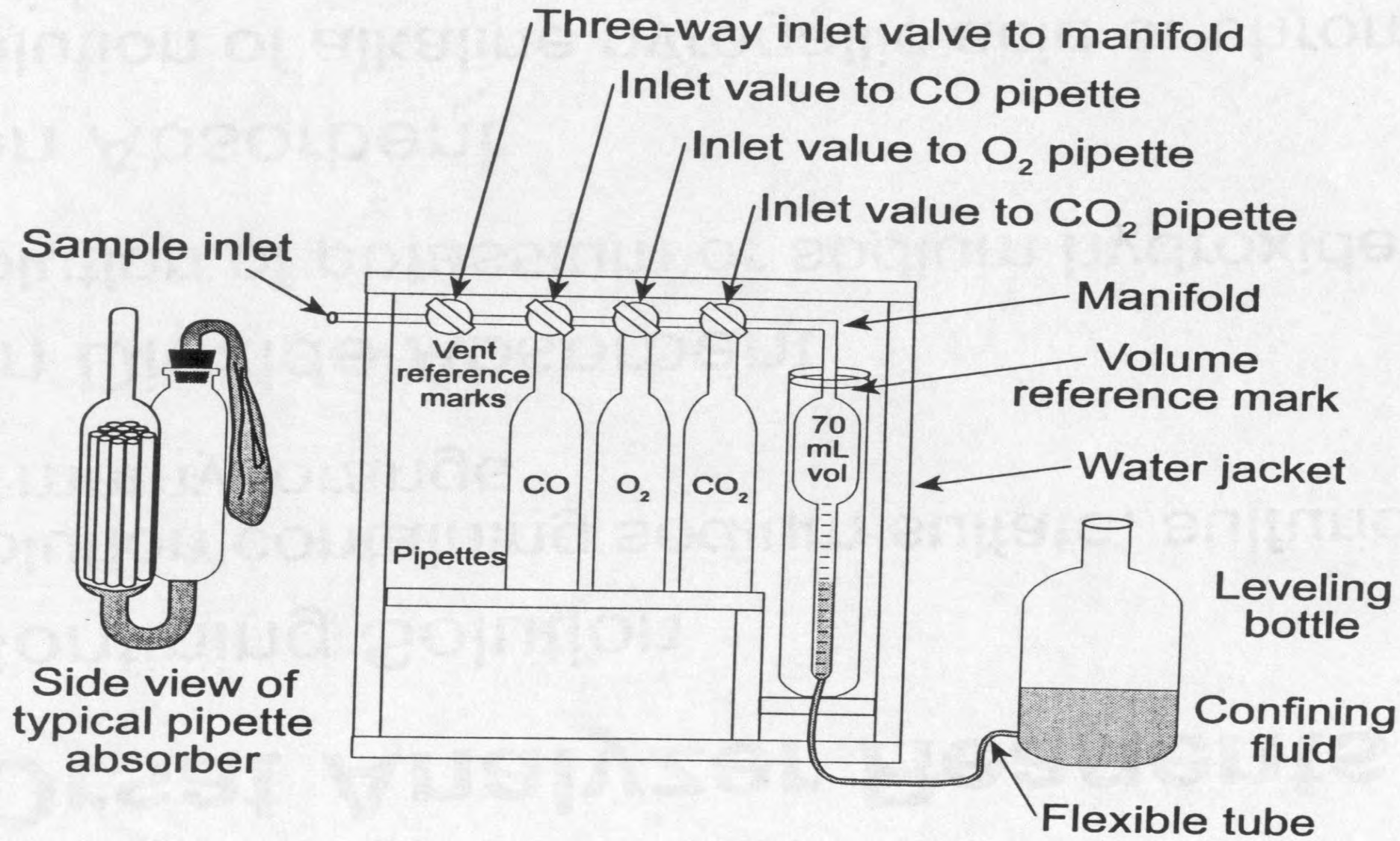
Multi-Point Continuous Integrated Sampling

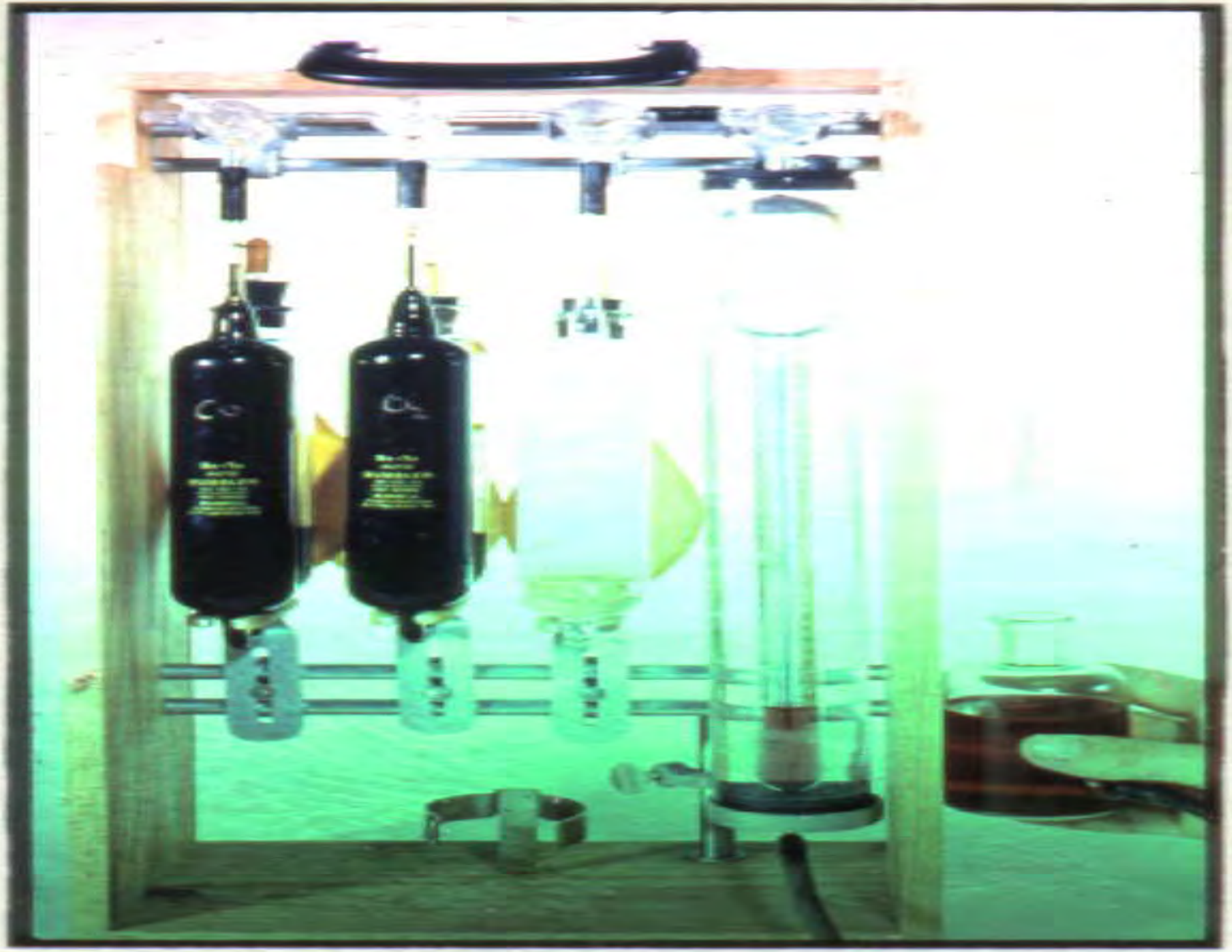
- Particulate sample and variations
- Modified Method 5 sampling
- VOST sampling
- For concentrations given to specific conditions (i.e., 12 % CO_2, 6 % O_2)
- For emission rate calculations (F-factor)
- For molecular weight determination

Orsat Analyzer



Orsat Analyzer





Orsat Analyzer Reagents

Reagent: Gas Confining Solution

A solution containing sodium sulfate, sulfuric acid and methyl orange

Reagent: Carbon Dioxide Absorbent

A solution of potassium or sodium hydroxide

Orsat Analyzer Reagents

Reagent: Oxygen Absorbent

A solution of alkaline pyrogallic acid or chromous chloride

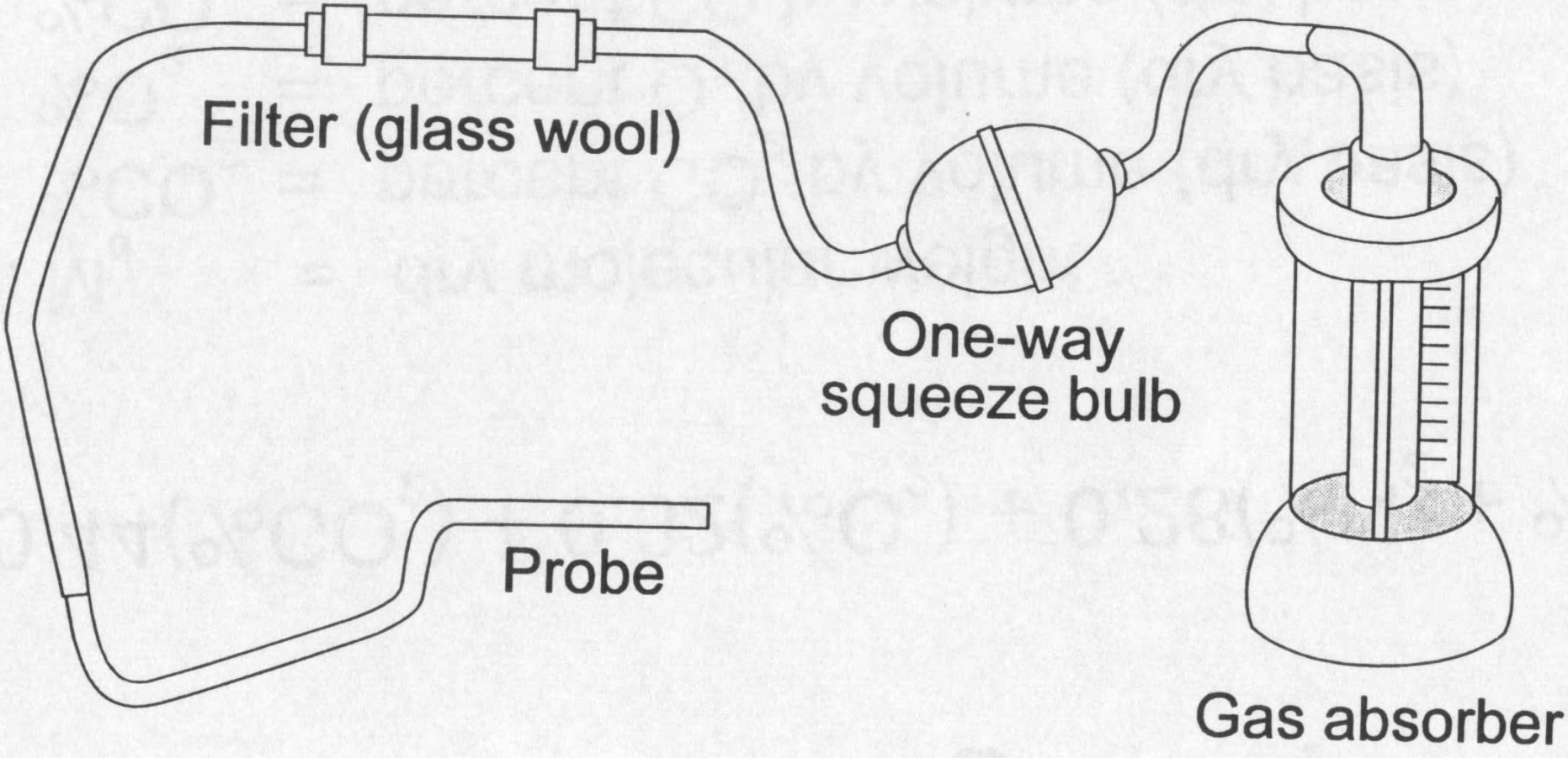
Reagent: Carbon Monoxide Absorbent

A solution of cuprous chloride or a sulfate solution

Fyrite Analyzer



Fyrite Analyzer



Dry Molecular Weight Equation

$$M_d = 0.44(\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO)$$

Where:	M_d	=	dry molecular weight
	$\%CO_2$	=	percent CO_2 by volume (dry basis)
	$\%O_2$	=	percent O_2 by volume (dry basis)
	%CO	=	percent CO by volume (dry basis)
	$\%N_2$	=	percent N_2 by volume (dry basis)
	0.44	=	molecular weight of CO_2 divided by 100
	0.32	=	molecular weight of O_2 divided by 100
	0.28	=	molecular weight of N_2 divided by 100
	0.28	=	molecular weight of CO divided by 100

Method 3 Data Uses

- Calculate molecular weight of the stack gas
- Emission rate correction
  - FRM 20 contains the equation to correct an emission rate to a % O_2 or % CO_2

$$C_{adj} = C_d[(20.9 - \%O_{2corr})/(20.9 - \%O_{2\ meas})]$$

Method 3 Data Uses

- Emission rate calculation
  - FRM 19 contains the equation to determine a heat input based emission concentration

$$E = C_d F_d [20.9/(20.9 - \%O_{2dry})]$$

Problems with FRM 3

- Leak in pump or bag
- Process gives off CO_2 or O_2
  - Cement plant- Cannot validate F_o
  - FGD scrubber- Cannot validate F_o
- Incomplete combustion cannot validate F_o- Too low for fuel
- Processes removing CO_2 or O_2

Method 3A

Determination of O_2 and CO_2 Concentrations in Emissions from Stationary Sources

(Instrumental Analyzer Procedure)

Applicability

For the determination of O_2 and CO_2 only when specified within the regulations

Principle

A sample is continuously extracted from the effluent stream. A portion of the sample stream is sent to an instrumental analyzer(s) for the determination of O_2 and CO_2 concentrations.

Analyzer Operating Principles

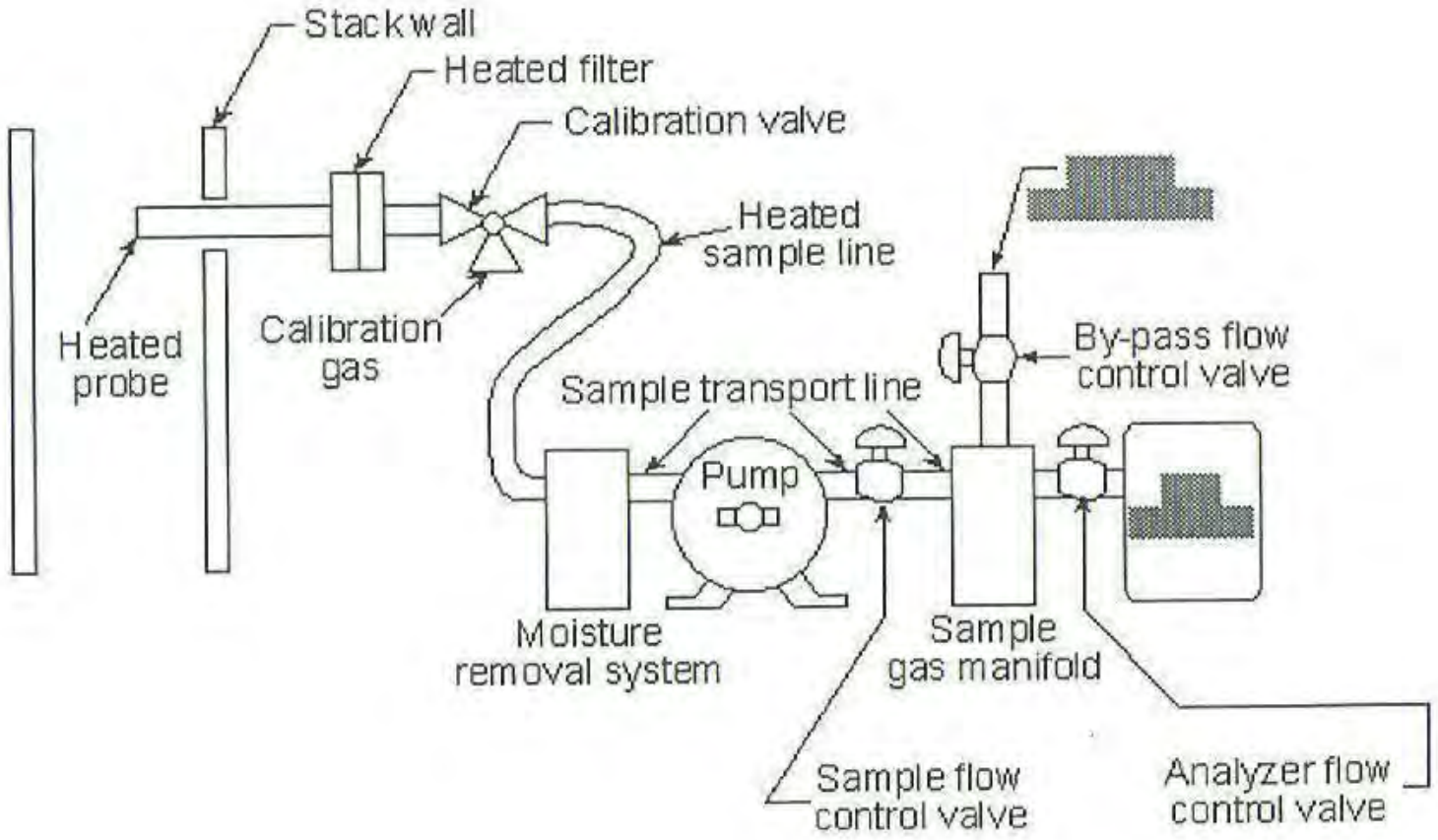
CO_2 Analyzers

- Nondispersive infra-red
- Polarography

O_2 Analyzers

- Paramagnetism
- Polarography
- Electrocatalysis


ENERAC 3000E
Integrated Emissions System
SET KEYS
PRIMARY FUELS
PRINTER
STACK KEYS
STACK PROBE
ELECTRICAL


Stackwall
Heated filter
Calibration valve
Heated sample line
Heated probe
Calibration gas
By-pass flow control valve
Sample transport line
Pump
Moisture removal system
Sample gas manifold
Sample flow control valve
Analyzer flow control valve

Performance Test Procedures

- Calibration error check
- Sampling system bias check
- Interference response check

Performance Test Criteria

Calibration Error –

- < ± 2% of span for zero, mid, high range gases
- (0) (40-60) (80-100) % of span

Sampling System

Bias Check –

- < ± 5% of span for zero and high range gases

Performance Test Criteria

Interference Response

< ± 2% of span

For CO @ 500 ppm
SO_2 @ 200 ppm
CO_2 @ 10%
O_2 @ 20.9%

Method 3A

Test Procedure

- Sample collection
- Zero and calibration drift test

Method 3B

Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air Using the Orsat Analyzer

Applicability

For determining CO_2, O_2, and CO from a gas stream from a fossil-fuel combustion process

The Fuel Factor

$$F_O = \frac{20.9 - \%O_2}{\%CO_2}$$

Percent Excess Air Equation

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

Where:
- $\%EA$ = percent excessive air
- $\%O_2$ = percent O_2 by volume (dry basis)
- $\%CO$ = percent CO by volume (dry basis)
- $\%N_2$ = percent N_2 by volume (dry basis)
- 0.264 = ratio of O_2 to N_2 in air, V/V

FRM 3B F_o Factors

Coal: Anthracite	1.016-1.130
Coal: Bituminous	1.083-1.230
Oil: Distillate	1.260-1.413
Oil: Residual	1.210-1.370
Gas: Natural	1.600-1.836
Gas: Propane	1.434-1.586
Gas: Butane	1.405-1.553
Wood	1.000-1.120
Wood Bark	1.003-1.130

FRM 3 Major Points

- Applicability to FFFSG (Sec. 1.1.1)
- Method modifications (Sec. 1.1.2)
  - A multi-point sampling method/ Orsat at each point
  - Using CO_2 or O_2 and stoichiometric calculations
  - Assigning value of 30.0

FRM 3 Major Points

- Sampling approaches (Sec. 1.2)
- Leak-check Tedlar bags (Sec. 2.2.6)
- Sampling point in the stack for single point grab (Sec. 3.1)
- Multi-point integration:
  >24 in. 12 Pts; <24 in. 8 Pts

FRM 3 Major Points

- Sampling at constant rate and same time as FRM 5 (Sec. 4.3)
- Analysis time 8 hours (Sec. 4.4)
- Leak-check Orsat (Section 6)
- F_o Factor (Method 3B)
- Can't use Fyrite (Method 3B)

FRM 3 Inspector Tools

- Field observation agency checklist
- Stack sampling nomographs for field estimations
- Fryite-type combustion gas analyzer

FRM 3 Tips

- Don't forget to take into account correction for altitude location of sampling port (0.1 in./100 ft)
- Stack gas pressure also requires determination of stack static pressure (P_g): $P_g/13.6$

FRM 3 Tips

- Leak check sampling bag
- Leak check sampling train lines before sampling
- Leak check Orsat analyzer
- Minimum 12 sampling pts. (>24 in.)
- Minimum 8 sampling pts. (<24 in.)

FRM 3 Tips

- Validate analytical data
  - Analyze ambient air ($O_2 = 20.9 \pm 0.3\%$)
  - Analyze against protocol gases ($\pm 0.2\%$)
  - F_o Calculation
  - Nomograph verification

FRM 3 Tips

- Analyze bag sample within 4 hours
- No more than 20 separate analysis for a given set of reagents
- Three separate analysis for each bag
  - ± 0.3% if CO_2>4%
  - O_2<15%
  - then ± 0.2%

Dismiss FRM 3 Stack Test

- Failed to calibrate Orsat analyzer
- Tedlar bag found to be leaking
- F_o outside of +/- 5 % of calculated value
- O_2/CO_2 outside of typical range

Compliance Test and Source Test Observation

FRM 4: Determination of Moisture Content in Stack Gases



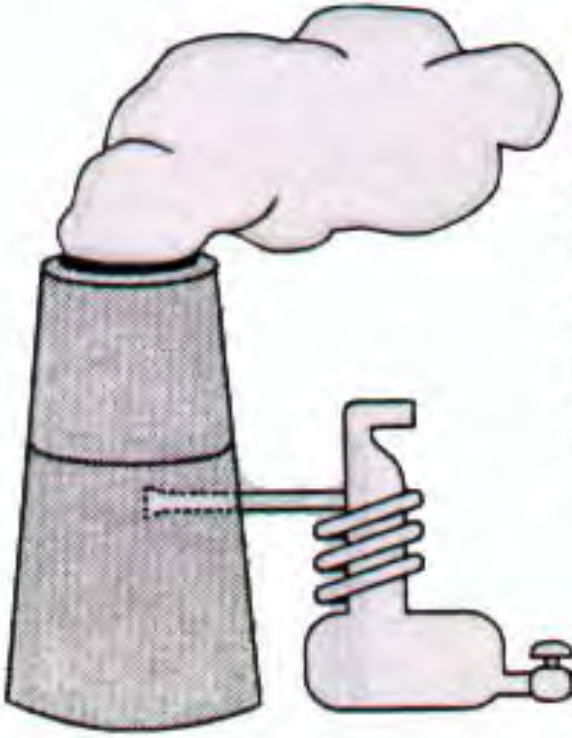
Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1
FRM 2
FRM 3
FRM 4
FRM 5
FRM 19

FRM Method 4



Method 4

Determination of moisture content of stack gas (by condensation method)

Applicability

For determining moisture content of stack gas.

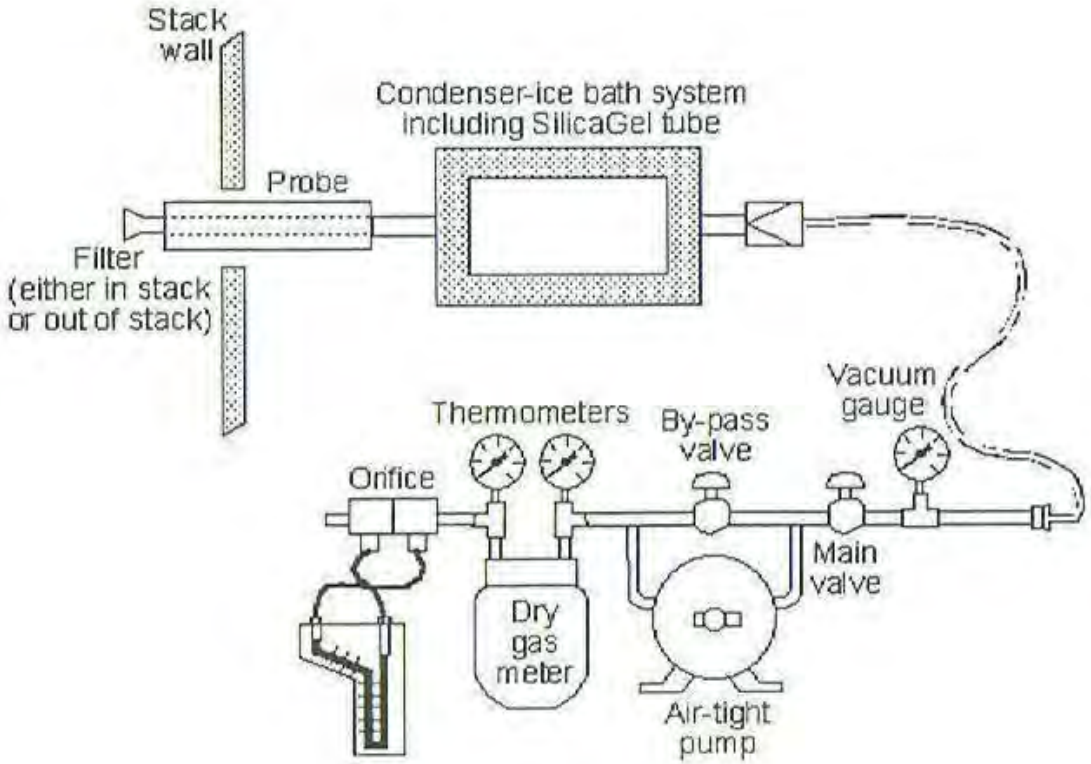
Two Methods in FRM 4

- Reference method
  (FRM 5 Condenser Methodology)
- Approximate Methodology
  - FRM 6 Impingers
  - Wet Bulb/Dry Bulb
  - Nomographs

Reference Method

- Used for accurate determination of moisture content
- Usually conducted simultaneously with a pollutant measurement run
- Results used to calculate the percent isokinetic and pollutant emission rate

Moisture Sampling Train (Reference Method)

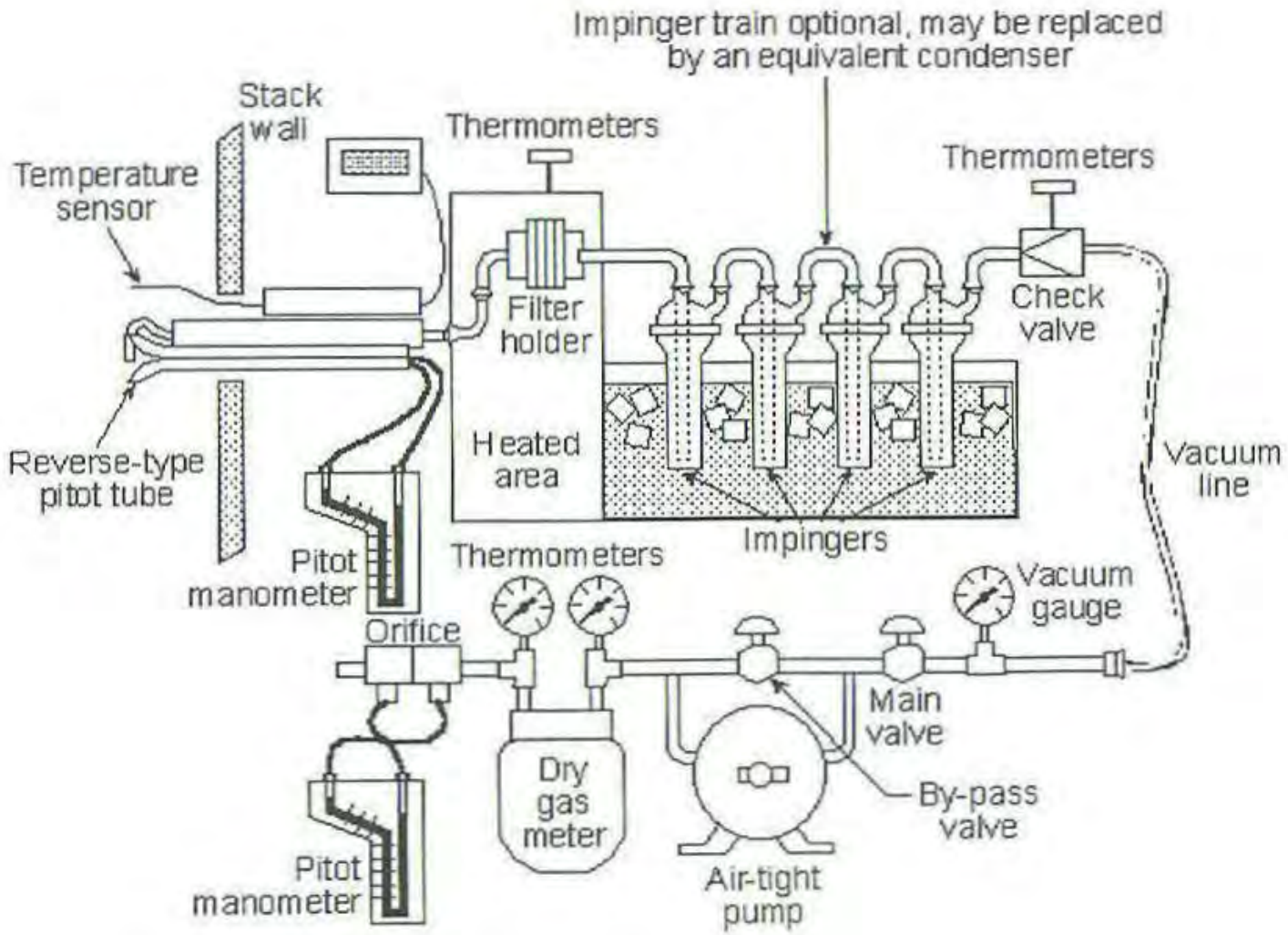


Procedure

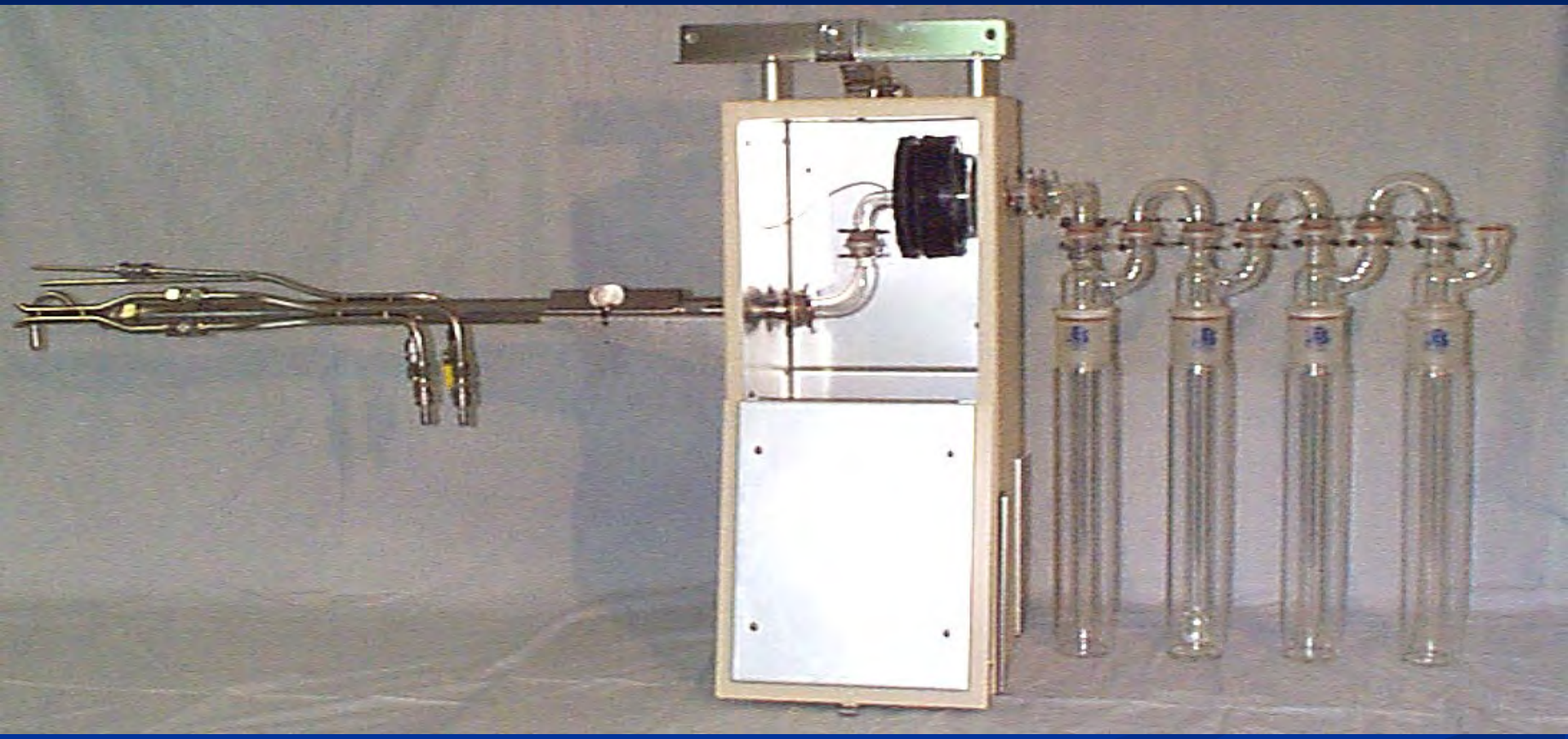
1. Determine traverse points using Method 1.
2. Select sampling time such that minimum gas volume of 21 scf will be collected at rate no greater than 0.75 cfm.
3. Leak-check sampling train (optional).

Procedure

4. Maintain sampling rate within 10% of constant rate
5. After sampling, leak-check sampling train (mandatory).
6. Verify the constant sampling rate.


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
Thermometers
Thermometers
Temperature sensor
Filter holder
Check valve
Heated area
Vacuum line
Reverse-type pitot tube
Impingers
Pitot manometer
Thermometers
Vacuum gauge
Orifice
Main valve
Dry gas meter
By-pass valve
Pitot manometer
Air-tight pump

Federal Reference Method 4



Volume of Water Vapor Condensed

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1 (V_f - V_i)$$

Where: K_1 $=0.001333\ m^3/ml$ for metric units
$=0.04715\ ft^3/g$ for English units

Volume of Water Vapor Collected in Silica Gel

$$V_{wsg(std)} = \frac{(W_f - W_i)RT_{std}}{P_{std}M_w}$$

$$= K_2(W_f - W_i)$$

Where: K_2 $=0.001335\ m^3/g$ for metric units

$=0.04715\ ft^3/g$ for English units

Sample Gas Volume

$$V_{m(std)} = V_m Y = \frac{(P_m)(T_{std})}{(P_{std})(T_m)}$$

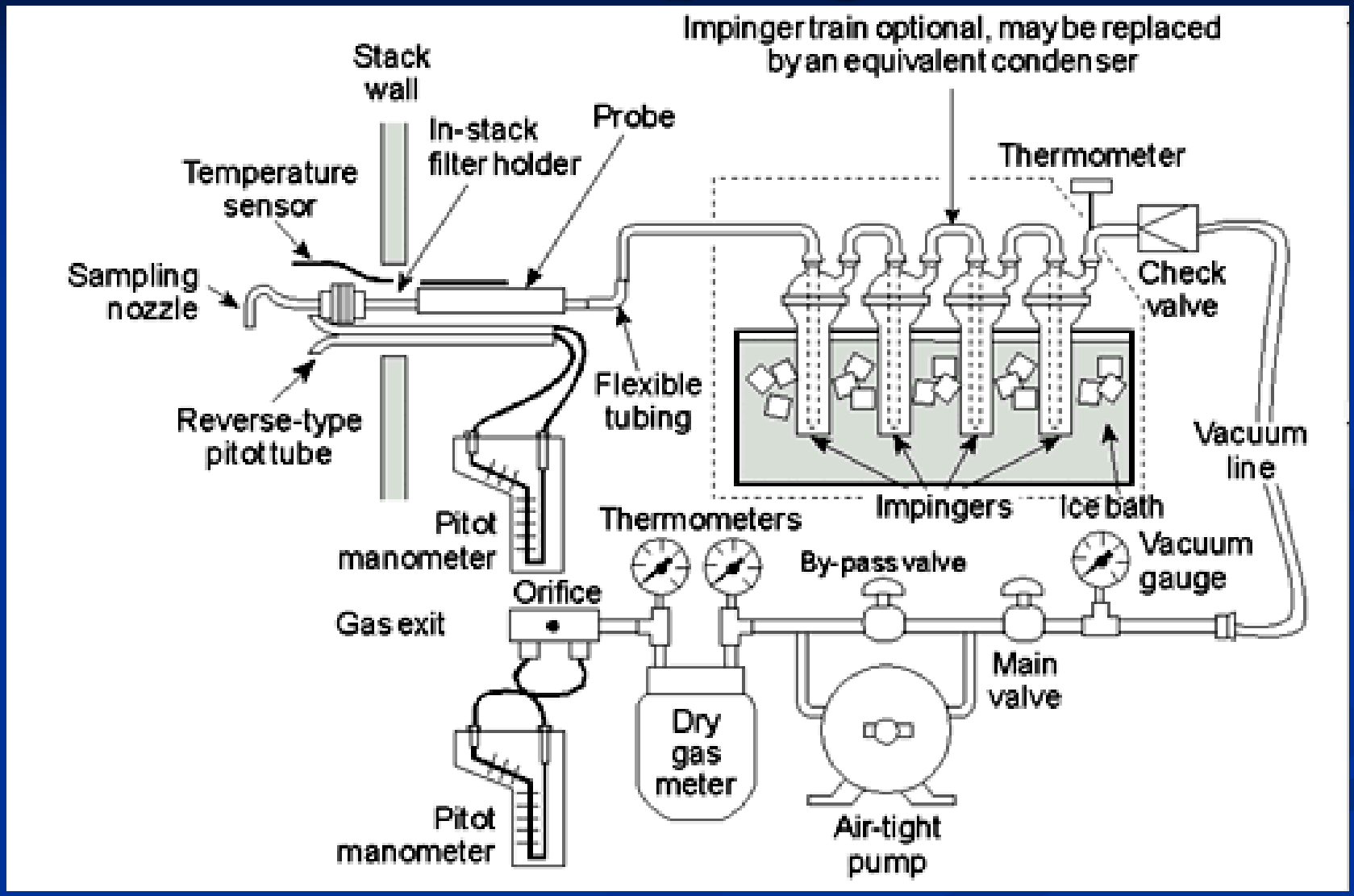
$$= K_3 Y \frac{V_m P_m}{T_m}$$

Where: K3 =0.3858 K/mmHg for metric units
=17.64 R/in. Hg for English units

FRM 4 Calculation

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}}$$

RM 5 Sampling Train



Approximation Methods

Used to estimate percent moisture to aid in setting isokinetic sampling rate using:

- Wet bulb- dry bulb
- Partial pressure technique (at saturation)
- Approximation sampling method

Wet Bulb – Dry Bulb Method

1. Measure the wet bulb temperature.
2. Measure the dry bulb temperature.
3. Estimate moisture content using psychometric chart

or

Calculate moisture content

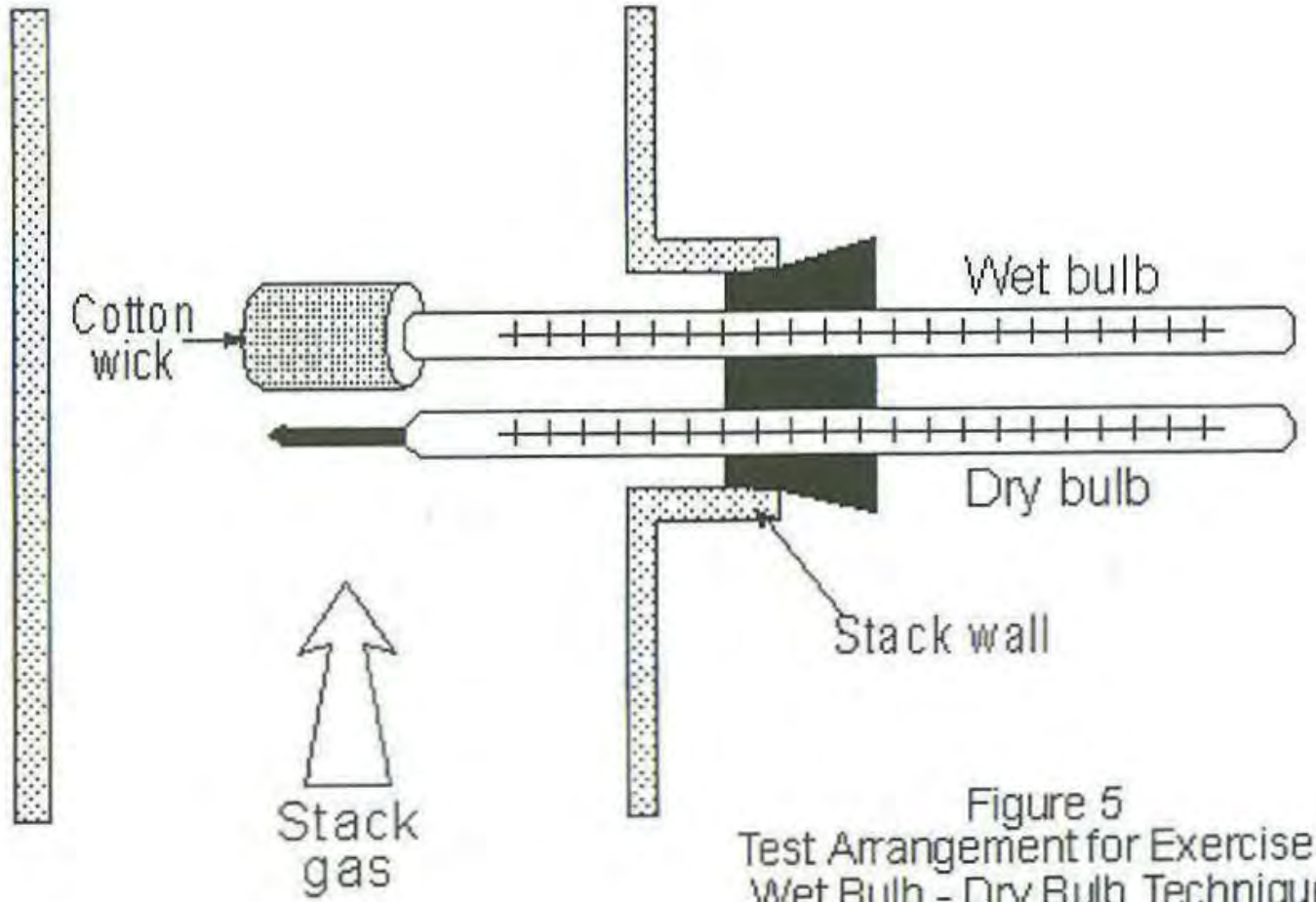
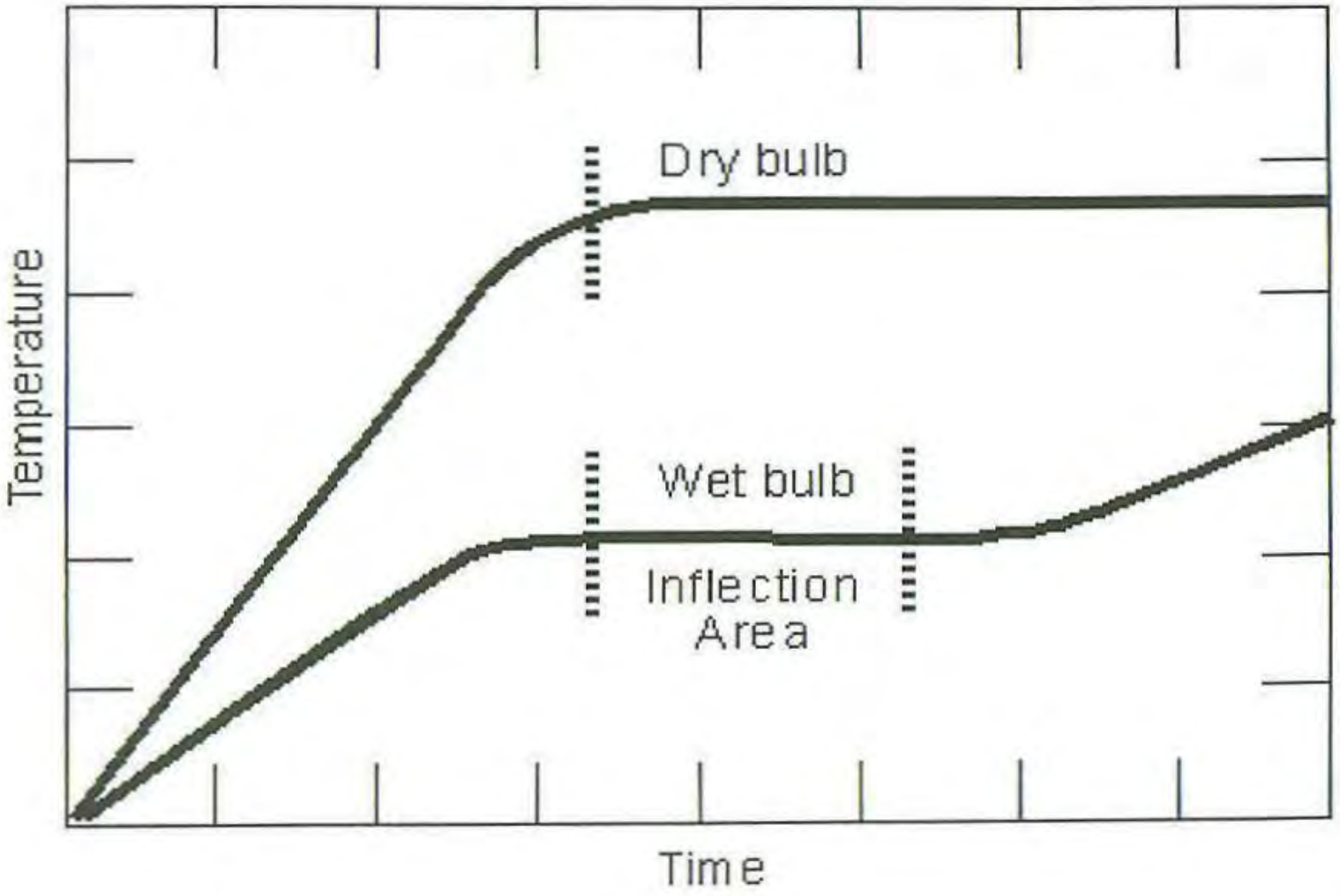
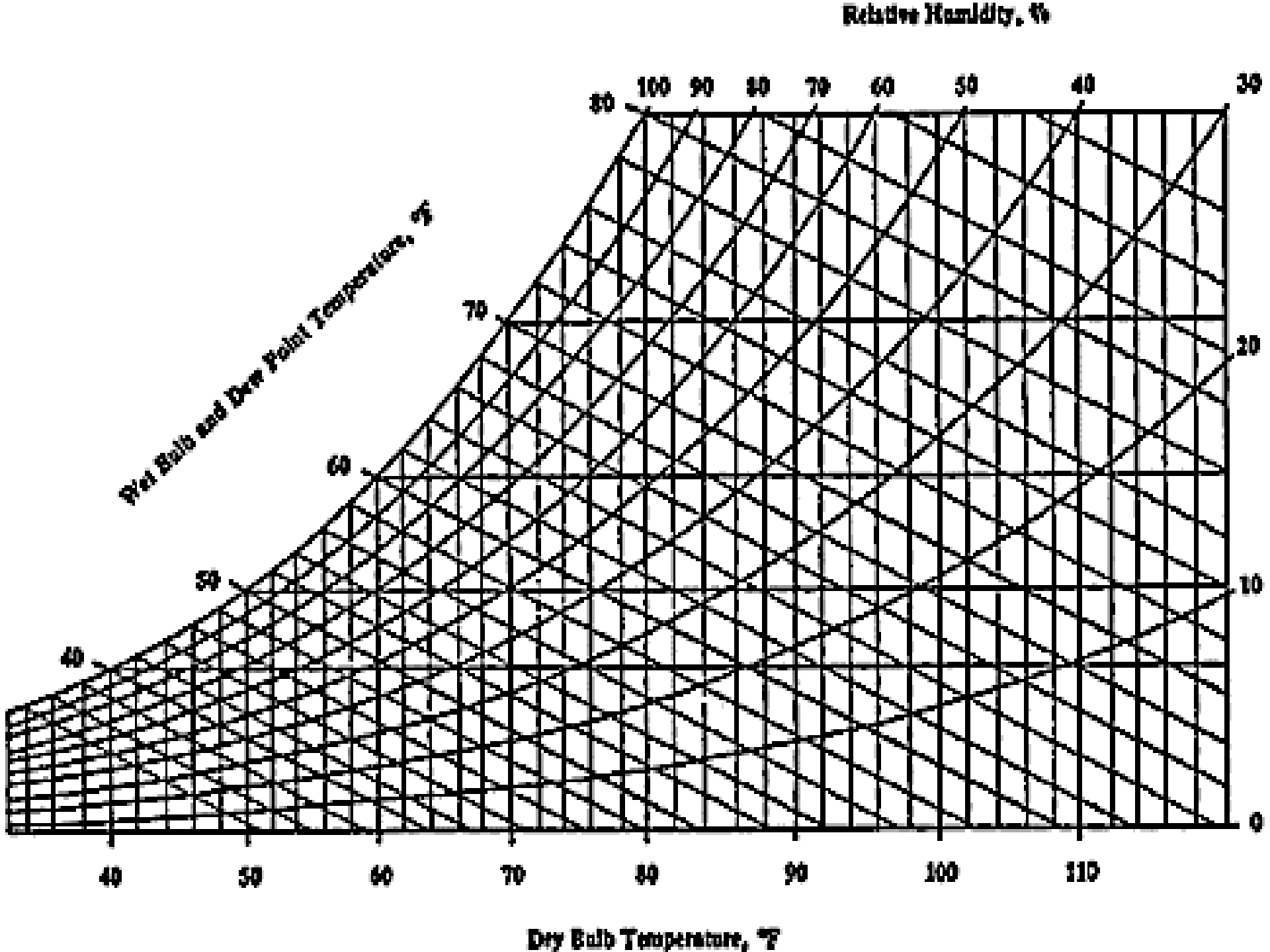


Figure 5
Test Arrangement for Exercise 3
Wet Bulb - Dry Bulb Technique
for
Moisture Measurement


Dry bulb
Wet bulb
Inflection
Area
Temperature
Time


Relative Humidity, %
100
90
80
70
60
50
40
30
20
10
0
Wet Bulb and Dew Point Temperature, °F
80
70
60
50
40
40
50
60
70
80
90
100
110
Dry Bulb Temperature, °F

Moisture Equation (Wet Bulb – Dry Bulb)

$$B_{WS} = \frac{v.p.}{P}$$

$$v.p. = s.v.p. - [(0.000367)(P)(t_S - t_P)\left(1 + \frac{t - 32}{1571}\right)]$$

s.v.p. = saturated water vapor pressure at the wet bulb temperature

P = absolute pressure in the stack

t_S = dry bulb temperature

t_W = wet bulb temperature

v.p. = water vapor pressure

Partial Pressure Method

- Assume saturation.
- Attach temperature sensor to reference method probe.
- Measure stack gas temperature at each traverse point.
- Calculate the average stack gas temperature.
- Determine moisture fraction using saturation vapor pressure table.

Moisture Equation – Partial Pressure

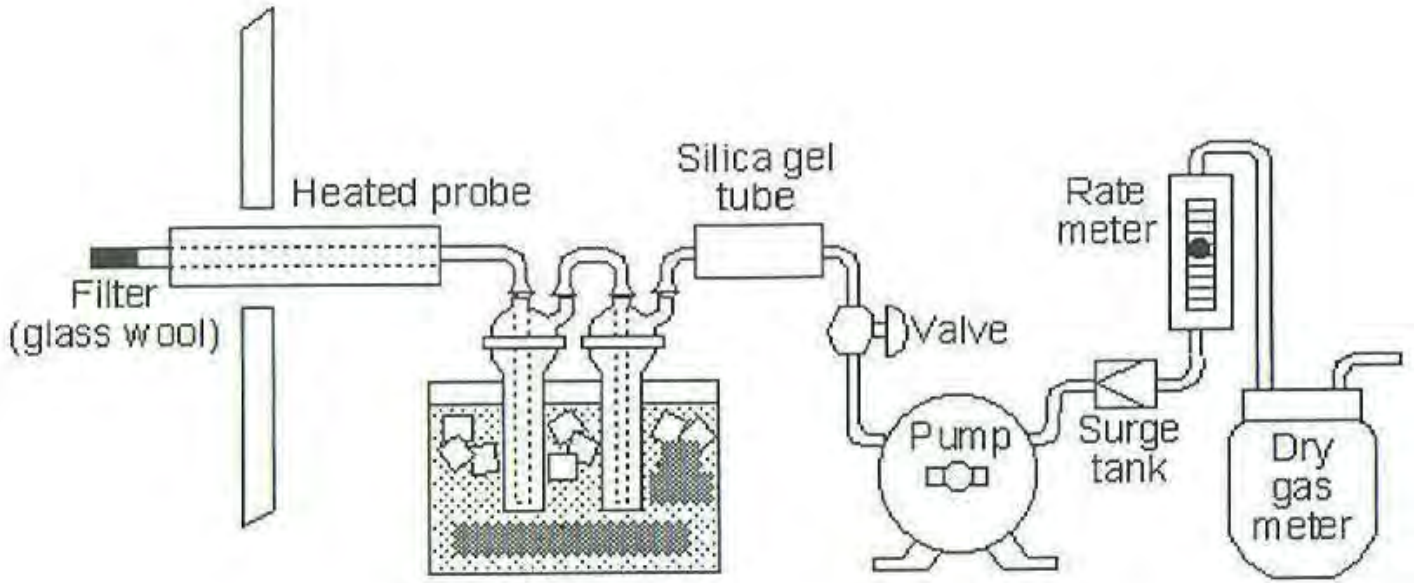
$$B_{ws} = \frac{s.v.p.}{P_s}$$

Where: B_{ws} = proportion (by volume) of water vapor in a gas mixture

s.v.p. = saturated vapor pressure of water at average stack temperature

P_S = absolute pressure of the stack

Moisture Sampling Train-Approximation Method



Procedure

1. Place 5.0 ml of distilled water in each impinger
2. Assemble and leak-check sampling train.
3. Sample at a constant rate of 0.07 cfm until a sample volume of 1.1 ft^3 is obtained.
4. Combine contents of impingers and measure volume to nearest 0.5 mL.

FRM 4 Equations

$$B_{ws} = \frac{V_{wc(std)}}{V_{m(std)} + V_{wc(std)}}$$

Calculating % Moisture Under Saturated Gas Stream

$$\%H_2O = 10^{(6.691 - (3144/(T_s + 390.86)))} / P_s * 100$$

FRM 4 Key Points

- Reference Method: Condenser Approach (Sec. 1.2)
- Approximation Method: Method 6 impingers, wet bulb/dry bulb, charts (Sec. 1.2)
- Saturated gas streams may give questionable results (Sec. 1.2)

FRM 4 Key Points

- Design of train (sec. 2.1.2)
- Number of traverse points (sec. 2.2.1)
- Minimum sample vol. (21 scf) and sampling rate (0.75 cfm) (Sec. 2.2.2)
- Sampling at a "constant sampling rate" (Sec. 2.2.4)

FRM 4 Key Points

- Leak rate determined from filter (Sec. 2.2.6)
- Excess Leak: throughout test or adjust volume (Sec. 2.2.6)
- Approximate Method is Modified Method 6 (Sec. 3)

FRM 4 Key Points

- Two calculations for saturated/ moisture droplet gas stream
  - One measurement on saturation conditions
  - One measurement on impinger technique
- Lower of these two values used in calculations

FRM 4 Inspector Tools

- Hand-held digital thermometer
- Field observation agency checklist
- Stack sampling nomographs for field estimations

FRM 4 Tips

- Don't forget to wipe moisture from the outside of each impinger before weighing
- Do not weigh U-tube connectors
- Condensibles other than water leads to positive bias in results (i.e., acid aerosols and condensable organics)
- Stack gases that are supersaturated or no demisting

FRM 4 Tips

- Typical moisture ranges
  - Coal: 5-15%
  - Oil: 8-10%
  - Gas: 8-10%
  - After wet scrubbers: 4-70%
  - Wood: 15-30%
  - Kilns: 30-40%
  - Sewage sludge incinerators: 5-30%
- Use wet/dry bulb and nomographs to verify moisture

Compliance Test and Source Test Observation

FRM 5: Particulate Emissions



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1
FRM 2
FRM 3
FRM 4
FRM 5
FRM 19

Federal Reference Method 5 Sampling Train




'94 5 19


'94 5 20


'94 6 19


'94 1 20


'94 12


36

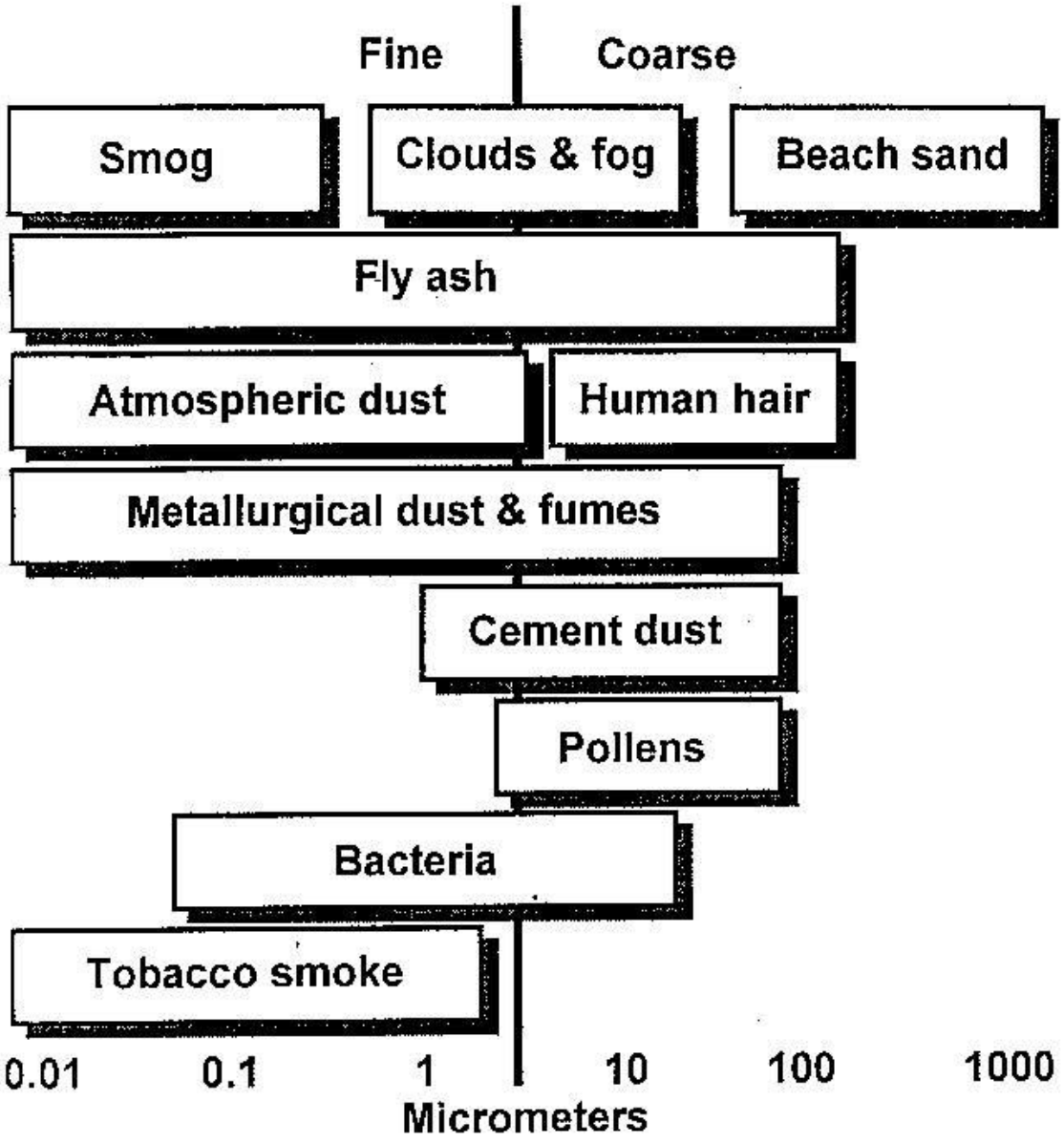
FRM 5 Sampling Train

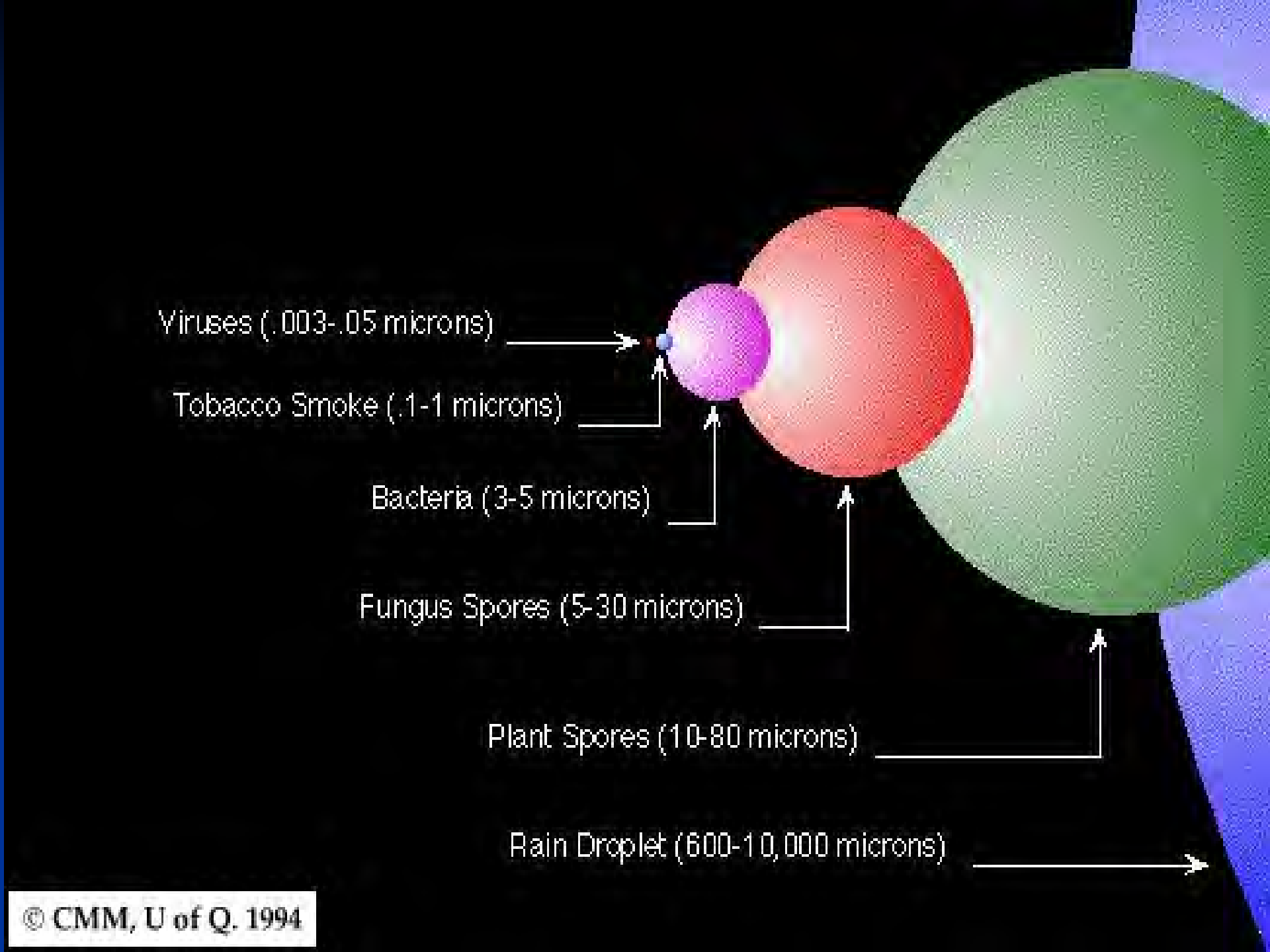


Particles

Discrete masses of solid or liquid matter

Examples: dust, smoke, mist, and fly ash


Fine
Coarse
Smog
Clouds & fog
Beach sand
Fly ash
Atmospheric dust
Human hair
Metallurgical dust & fumes
Cement dust
Pollens
Bacteria
Tobacco smoke
0.01
0.1
1
10
100
1000
Micrometers



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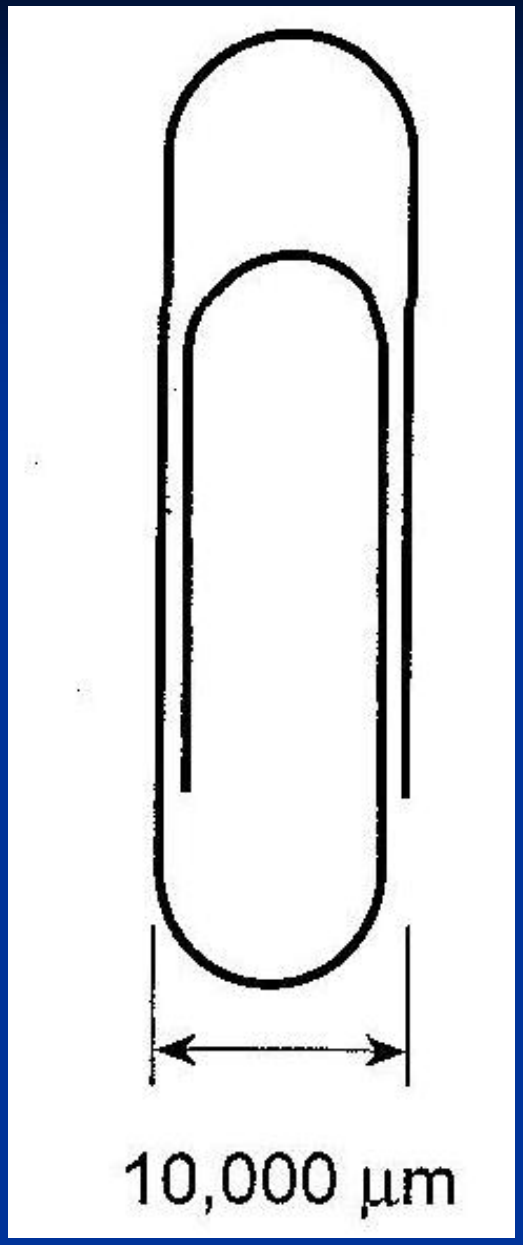
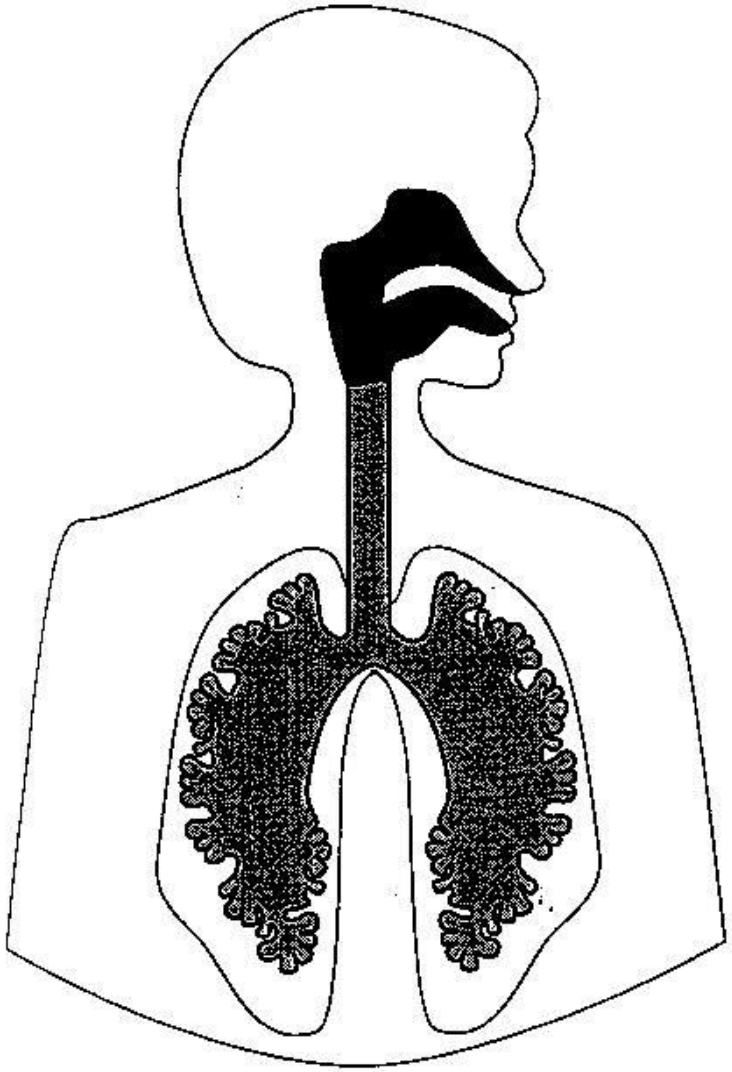
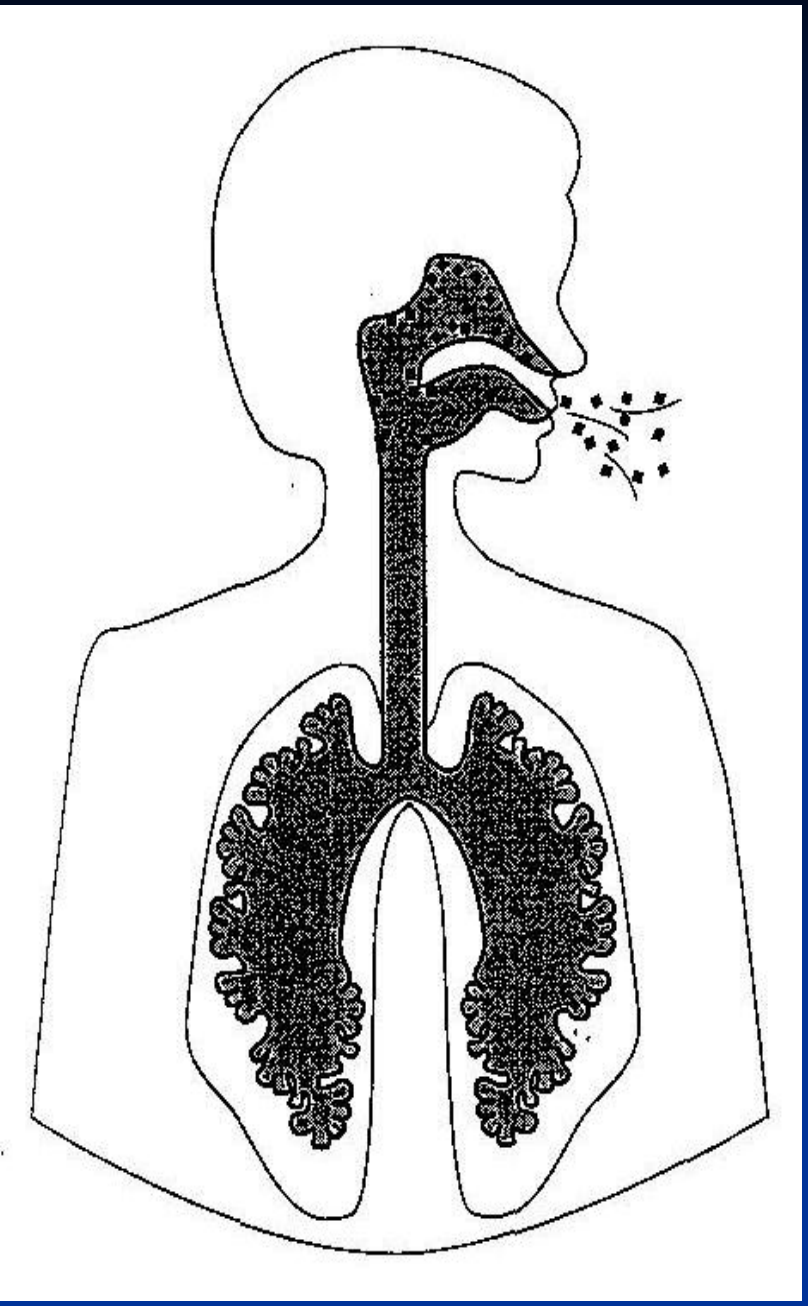


It would take 10,000 particles, each 1 micrometer (µm) in diameter, laid end to end, to stretch across the width of a small paper clip.

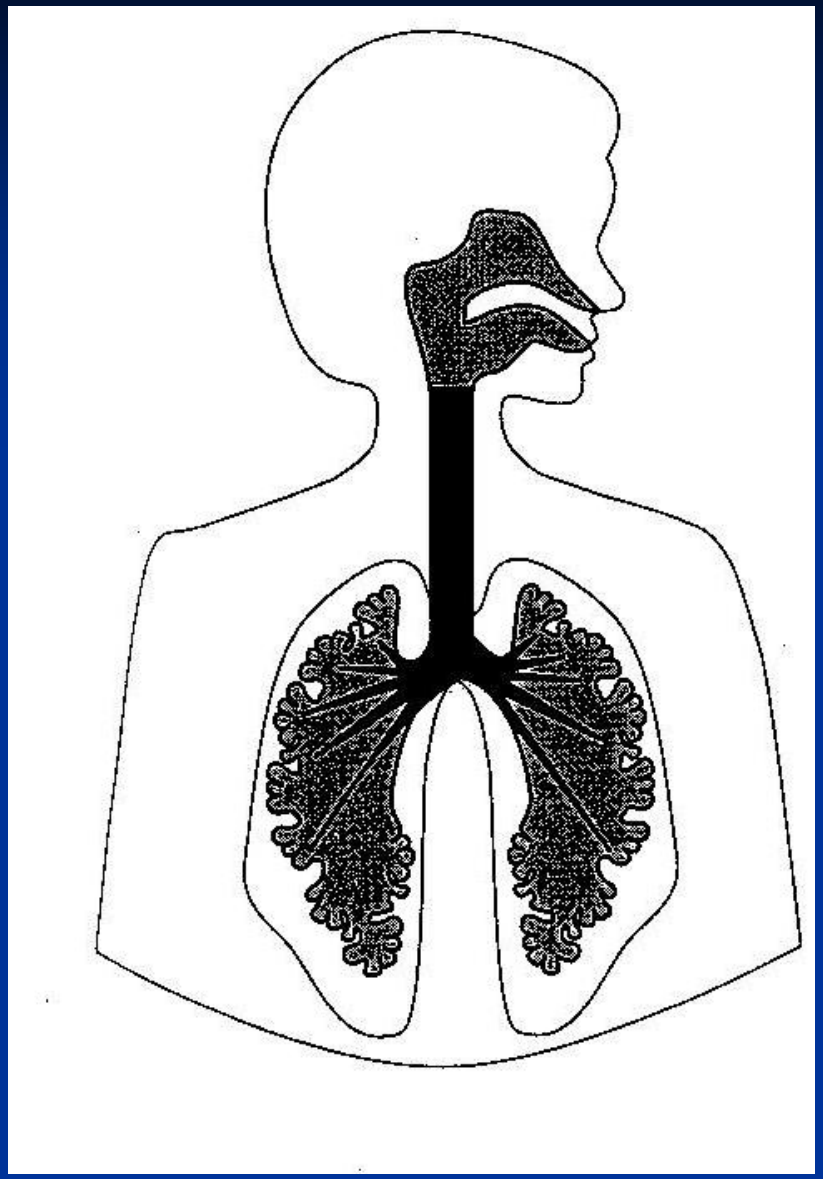


Collect in upper part of respiratory system



Particles collect moisture as they move through moist air of upper respiratory region, making them heavier and causing them to strike walls of throat, nose, etc.

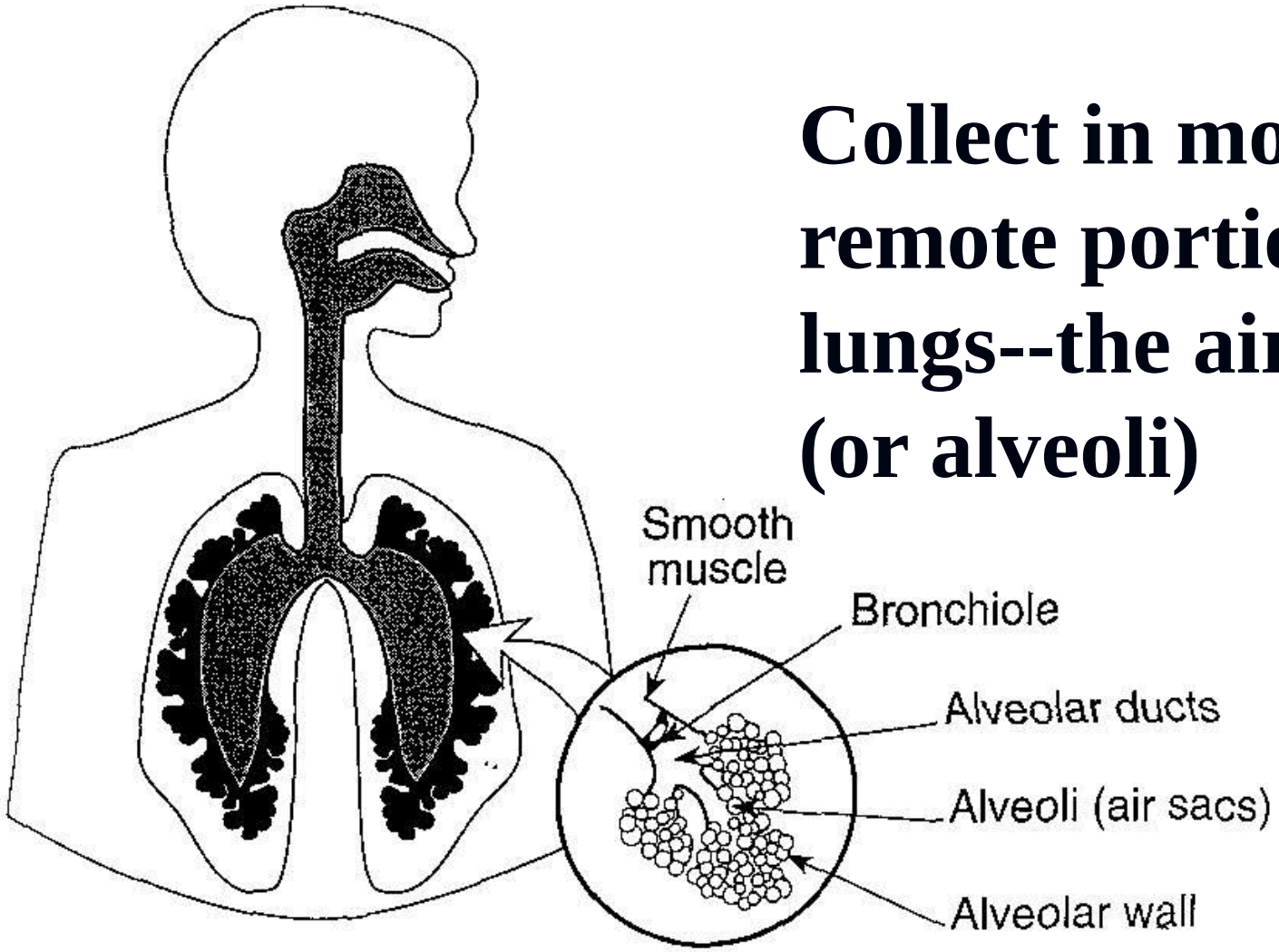
They are eliminated by sneezing, coughing, nose blowing, spitting, or by the digestive system.

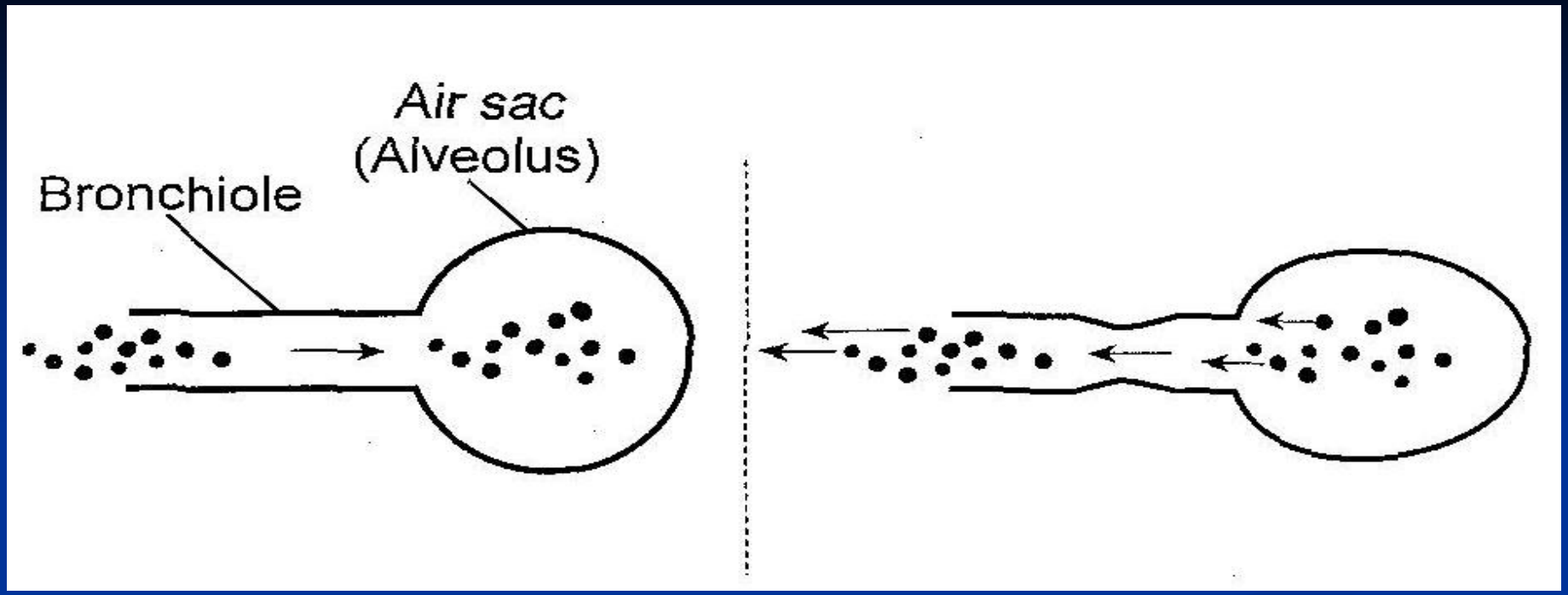


Particles 1-10 μm

Collect in middle part of respiratory system--the tracheobronchial region

Collect in most remote portions of lungs--the air sacs (or alveoli)





Particles with diameters of 0.5 µm or less float in the air sac and many are expelled with the next breath.

Health Effects - Nontoxic Particles

Concentration of Particles in $\mu g/m^3$	Effect
2000 $\mu g/m^3$ with 0.4 ppm SO_2 (24-hr avg) episodes of several days duration	Increase in deaths due to bronchitis
1000 $\mu g/m^3$ with 0.25 ppm SO_2 (24-hr avg) during episodes	Increase in mortality from all causes including respiratory and cardiac disease
300 $\mu g/m^3$ with 0.21 ppm SO_2 (annual avg)	Significant increase in bronchitis symptoms
130 $\mu g/m^3$ with SO_2 (annual avg)	Increase in frequency and severity of lower respiratory illness
100-200 $\mu g/m^3$ with 0.05 to 0.08 ppm SO_2 (avg seasonal levels)	Increase in incidences of bronchitis reported above this level

How Do We Define Particulate Matter?

- TPM?
- FPM?
- FPM-I?
- TPM-PM10?
- FPM-I-PM10?
- CPM?
- MCEM?

Definition of Particulate Matter

- Total Particulate Matter (TPM): The sum of the filterable particulate (i.e., front half of the FRM 5 sampling train) and the condensable particulate matter (i.e., the back half of the FRM 5 sampling train, including water and organic soluble extractions, Method 202)

Definition of Particulate Matter

- Filterable Particulate Matter (FPM): The mass of the filterable particulate matter (i.e., front half of the FRM 5 sampling train) that is captured on the filter at a temperature of 248 F +/- 25 F

Definition of Particulate Matter

- Filterable (In-stack) Particulate Matter (FPM-I): Particulate matter as measured by FRM 17 at stack temperature and pressure
- Total Particulate Matter PM-10 (TPM-PM10): Sum of the filterable PM-10 as measured by FRM 201 and 201A and the condensable particulate matter determined by FRM 202

Definition of Particulate Matter

- Filterable (In-Stack) Particulate Matter PM-10 (FPM-I-PM10): Particulate matter with an aerodynamic diameter of < 10 micrometers as measured by FRM 201 or 201A
- Condensable Particulate Matter (CPM): Particulate matter captured in the back half of the FRM 5 sampling train, including water and organic soluble extraction components, Method 202.

Definition of Extractable Particulate Matter

- Methylene Chloride Extractable Particulate Matter (MCEM): MCEM involves methylene chloride rinse of the probe and filter holder, extracting the condensable hydrocarbons collected in the impinger water and rises after the filter to the silica gel, all residue determined gravimetrically after evaporation of solvents (i.e., FRM 315)

History of FRM 5

- 1970 FRM 5: Filterable PM @ 248 F
- 1982 FRM 5A: PM @ 108 F for Asphalt Roofing, Pre-collector cyclone and trichloroethane (TCE) rinse
- 1986 FRM 5B: Nonsulfuric Acid PM with Sampling and Volitilization of Filter @ 320 F
- Reserved FRM 5C: Small Ducts (Reserved)
- 1984 FRM 5D: PM @ 248 F from Positive Fabric Filters

History of FRM 5

- 1985 FRM 5E: PM @ 248 F from Mineral Wool Plus Captured Condensible in 0.1 N NaOH (TOC)
  - Total Carbon @ 1740 F
  - Inorganic Carbon @ 300 F
  - $C_t = C_s + C_c$
- 1986 FRM 5F: Non-sulfuric acid PM @ 320 F with water rinse and ammonium sulfate substraction

History of FRM 5

- 1988 FRM 5G: PM @ 90 F from wood stoves using a dilution tunnel with 100-mm series filters
- 1988 FRM 5H: PM from wood stoves stack with 1st filter @ 248 F, then impingers followed by 2nd filter @ 68 F
- 1999 FRM 5I: Low level (<50 mg) PM using FRM 5 sampling train with 47-mm filter @ 248 F and paired sampling trains (< 10%)

Emission Generation Categories

- Transportation
- Stationary source fuel combustion
- Industrial processes
- Solid waste disposal
- Miscellaneous

Stationary Combustion Sources



Stationary Combustion Sources

Produce energy but no other products. Emissions result from fuel combustion.

- Fixed energy generating sources range in size from home heating furnaces to major power plants.
- Sources include commercial, institutional, industrial, and steam-electric power plants.
- Fuels used include coal, oil, natural gas, and wood. Other fuels such as liquefied natural gas, propane, process gas, etc. may also be used.

Industrial Processes

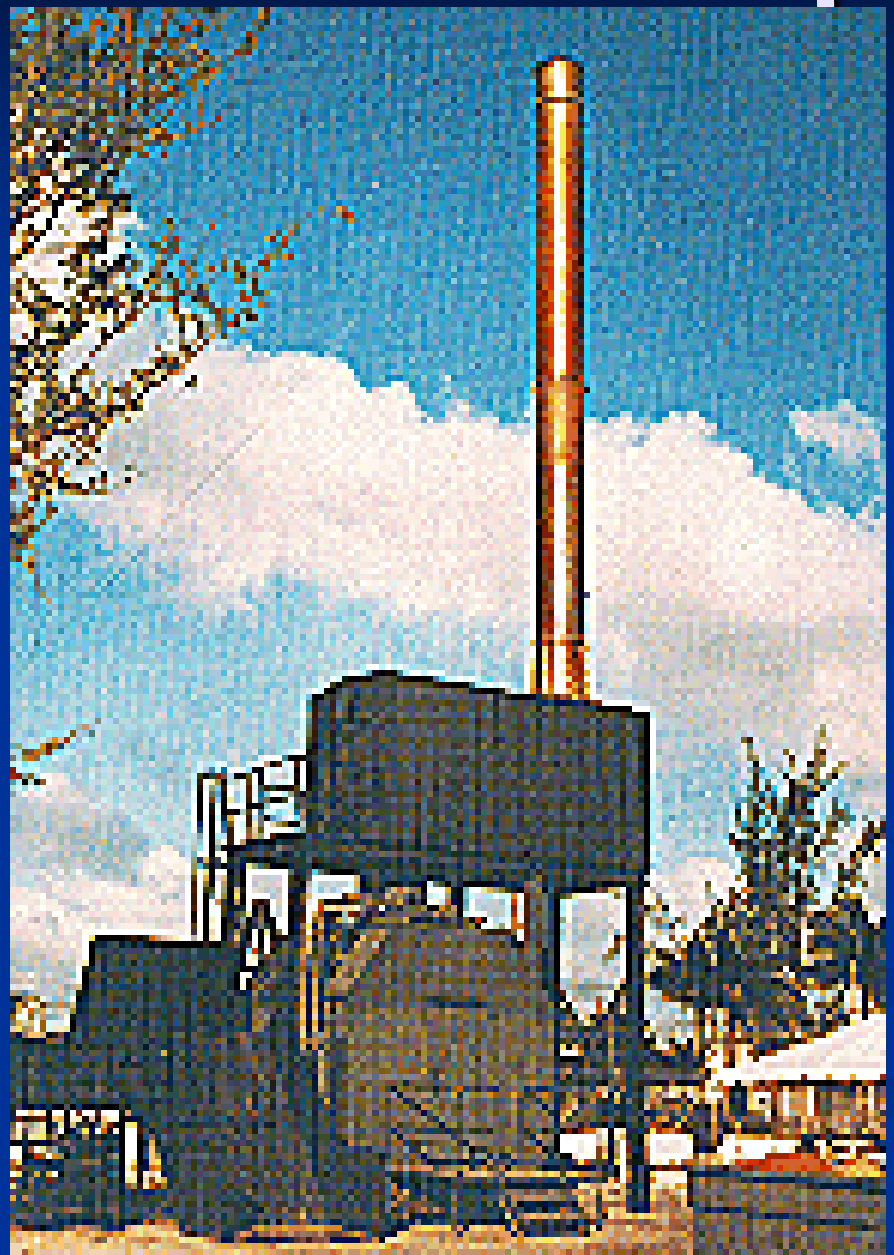


Industrial Processes

Emit pollutants in the course of manufacturing products

- Major sources include chemical processing, food and agricultural industries, metallurgical and mineral product factories, petroleum refining, petrochemical plants, petroleum storage, and wood-processing industries.
- Smaller sources include painting, dry-cleaning, and degreasing operations.

Solid Waste Disposal



Solid Waste Disposal

Facilities that dispose of unwanted products and by-products.
Emissions result from the disposal process
--usually burning.

Emission Generation Categories

- Transportation
- Stationary source fuel combustion
- Industrial processes
- Solid waste disposal
- Miscellaneous


10 17:05
50:11 01






'94 6 18

FRM 5 Sampling Train



Basic Operation of FRM 5

- Isokinetic Source Sampling
- "Iso" as denoting equality, similarity, uniformity. "Kinetic" is defined as of, pertaining to, or due to motion
  - $\Delta H = K \Delta p$

$$\Delta H = K \Delta p$$

SIMPLIFIED ISOKINETIC RATE EQUATION

Isokinetic Sampling and Bias

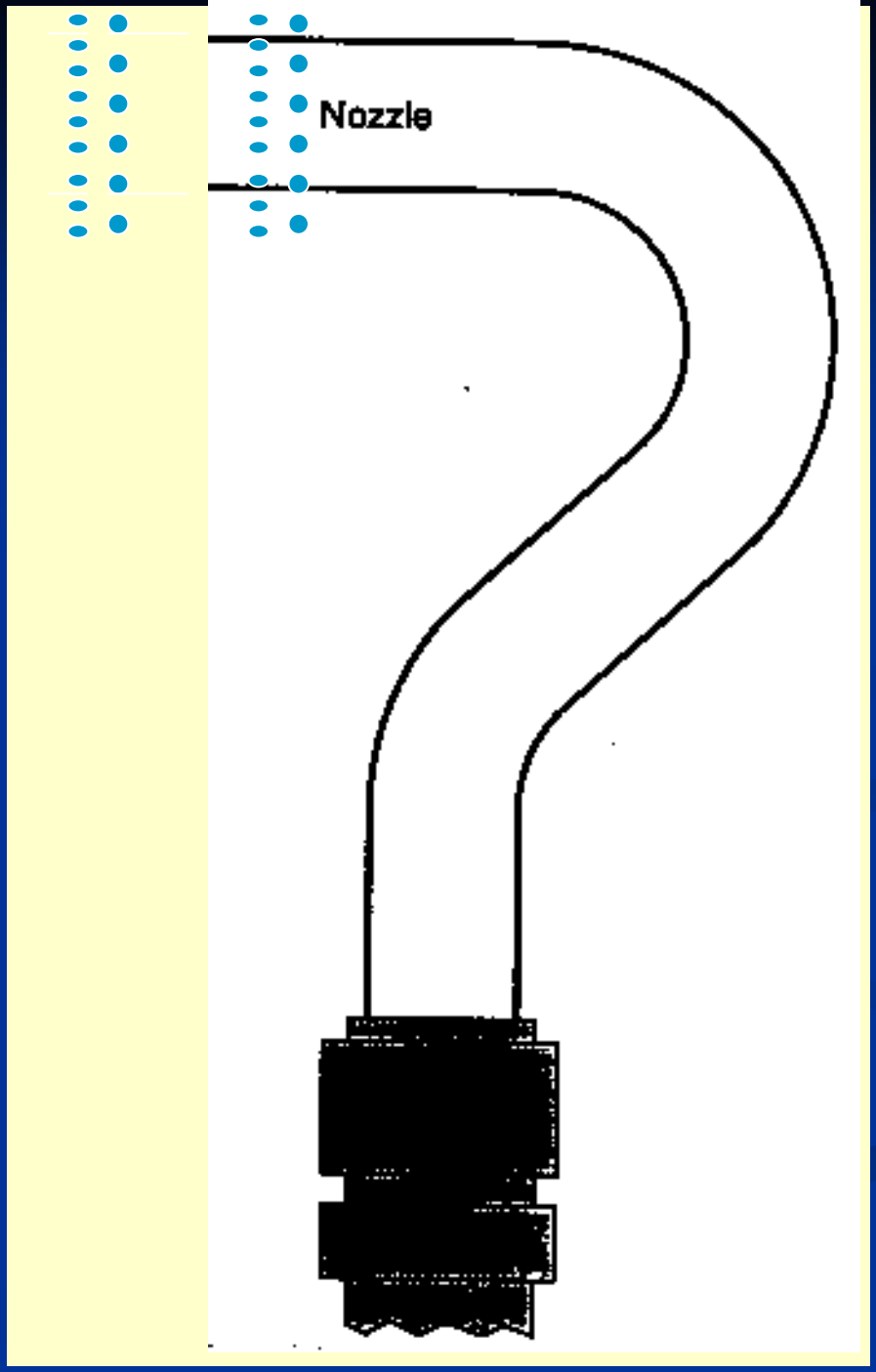
- To obtain average pollutant concentration, need parameters:
  - Quantity of mass emitted from stack
  - Total quantity of volume from stack

Isokinetic Sampling and Bias

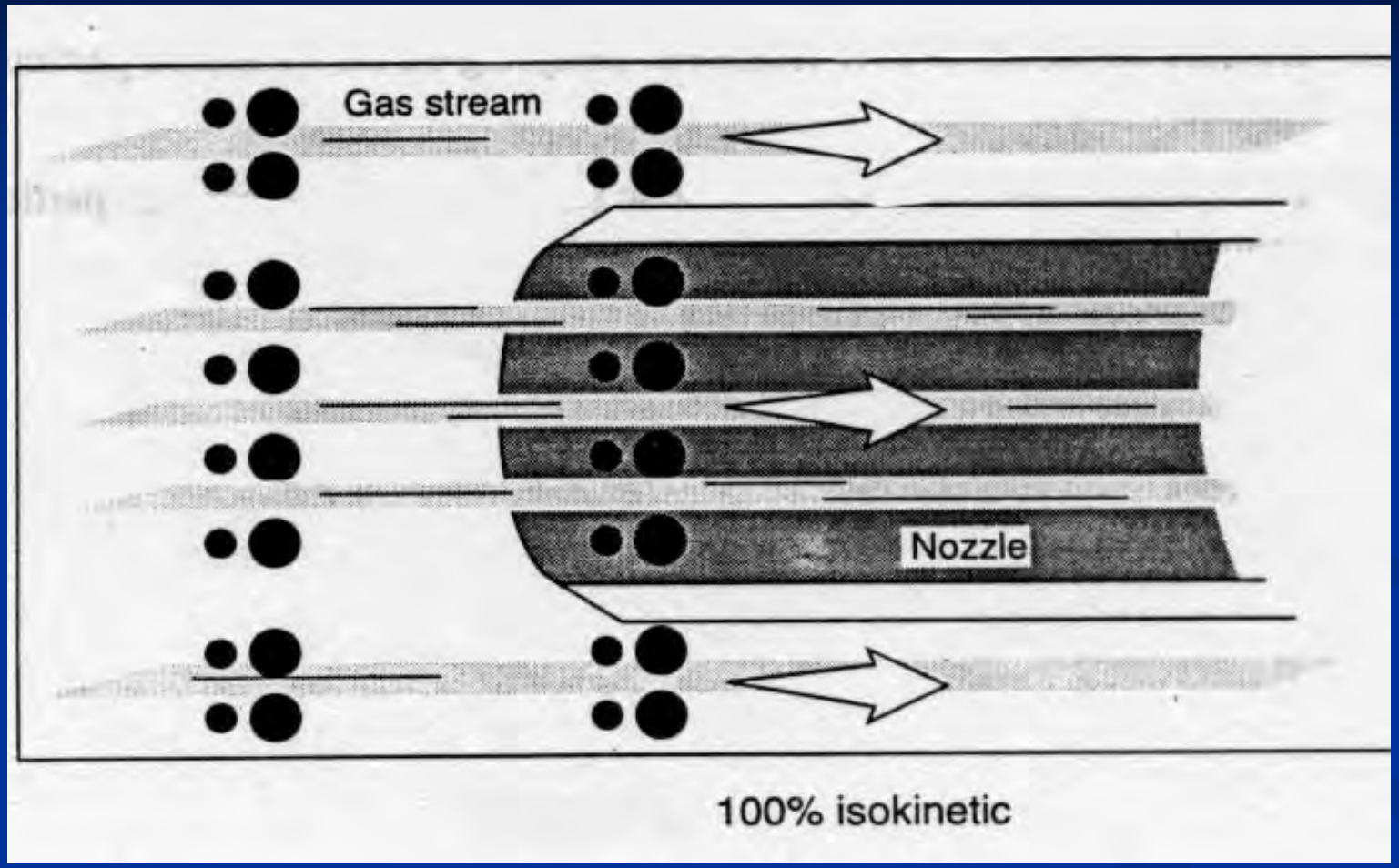
- Isokinetic sampling provides best approach for accurate data
- Pollutant mass rate (pmr)
  - pmr_a (Ratio-of-areas: A_n ratio A_s)
  - pmr_c (Ratio-of-conc.: m_n ratio A_n)

$V_n = V_s$

100% Isokinetic

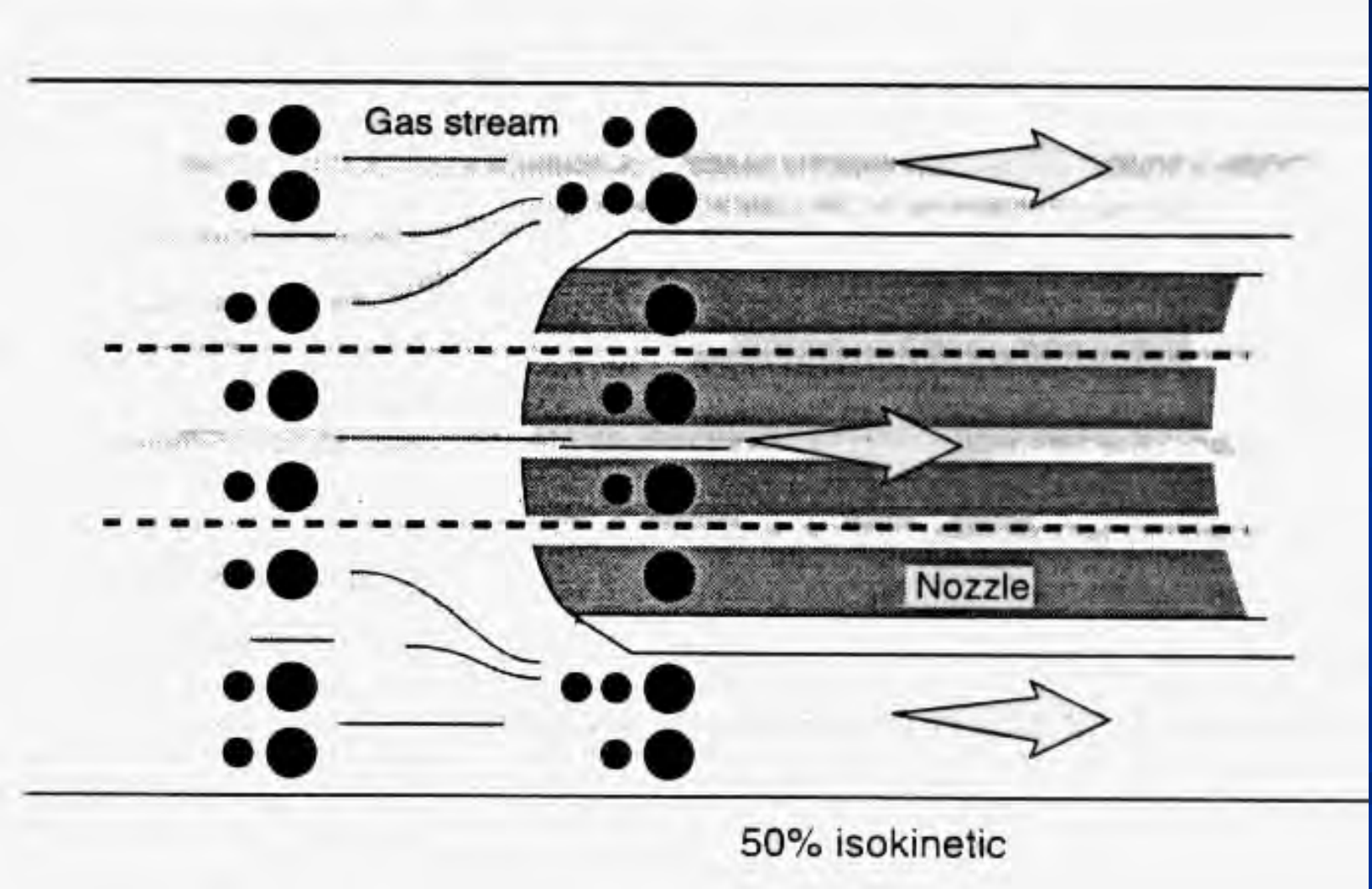


100 % Isokinetic



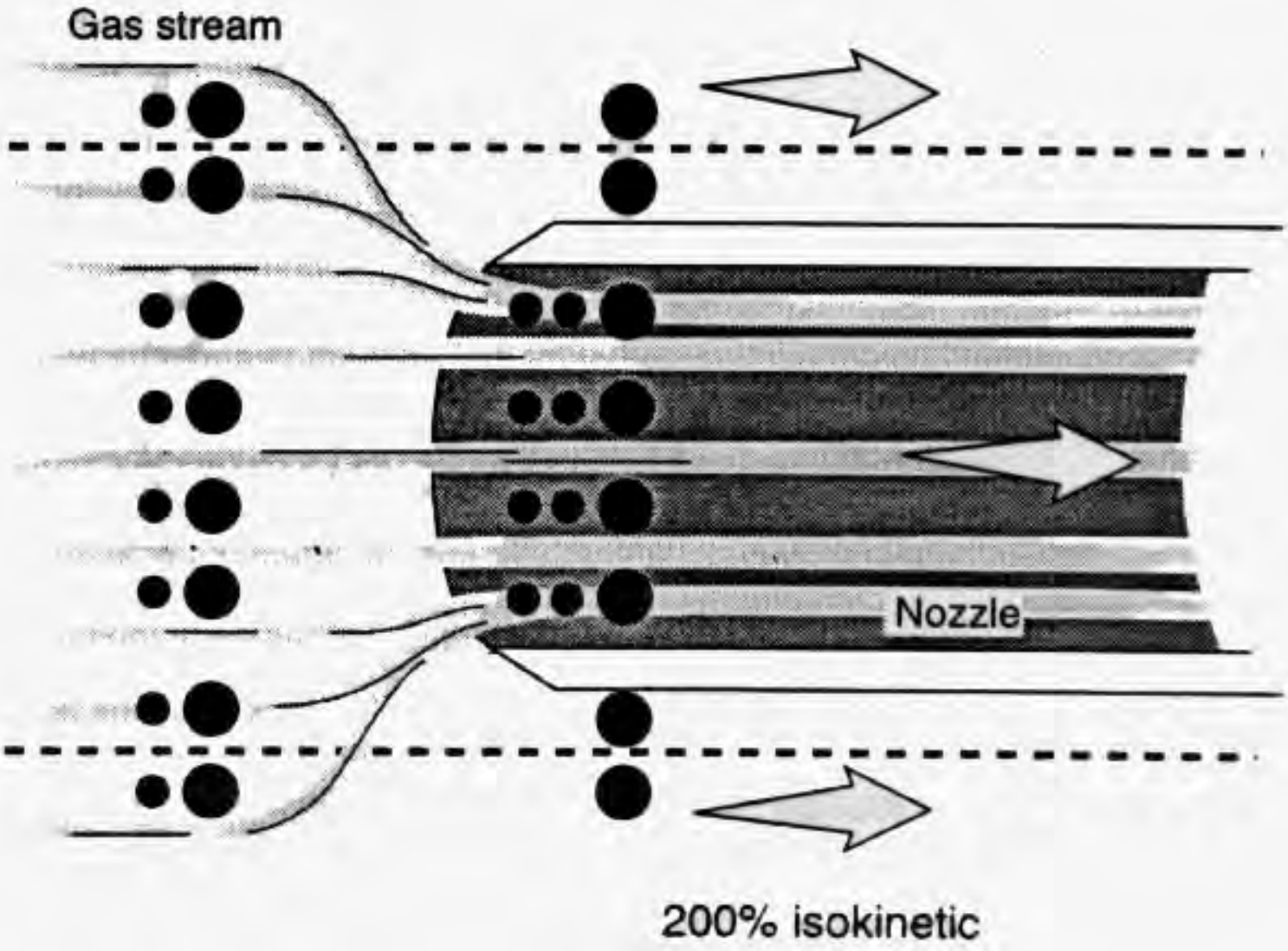
Vs=Vn

Sub-Isokinetic (50%)



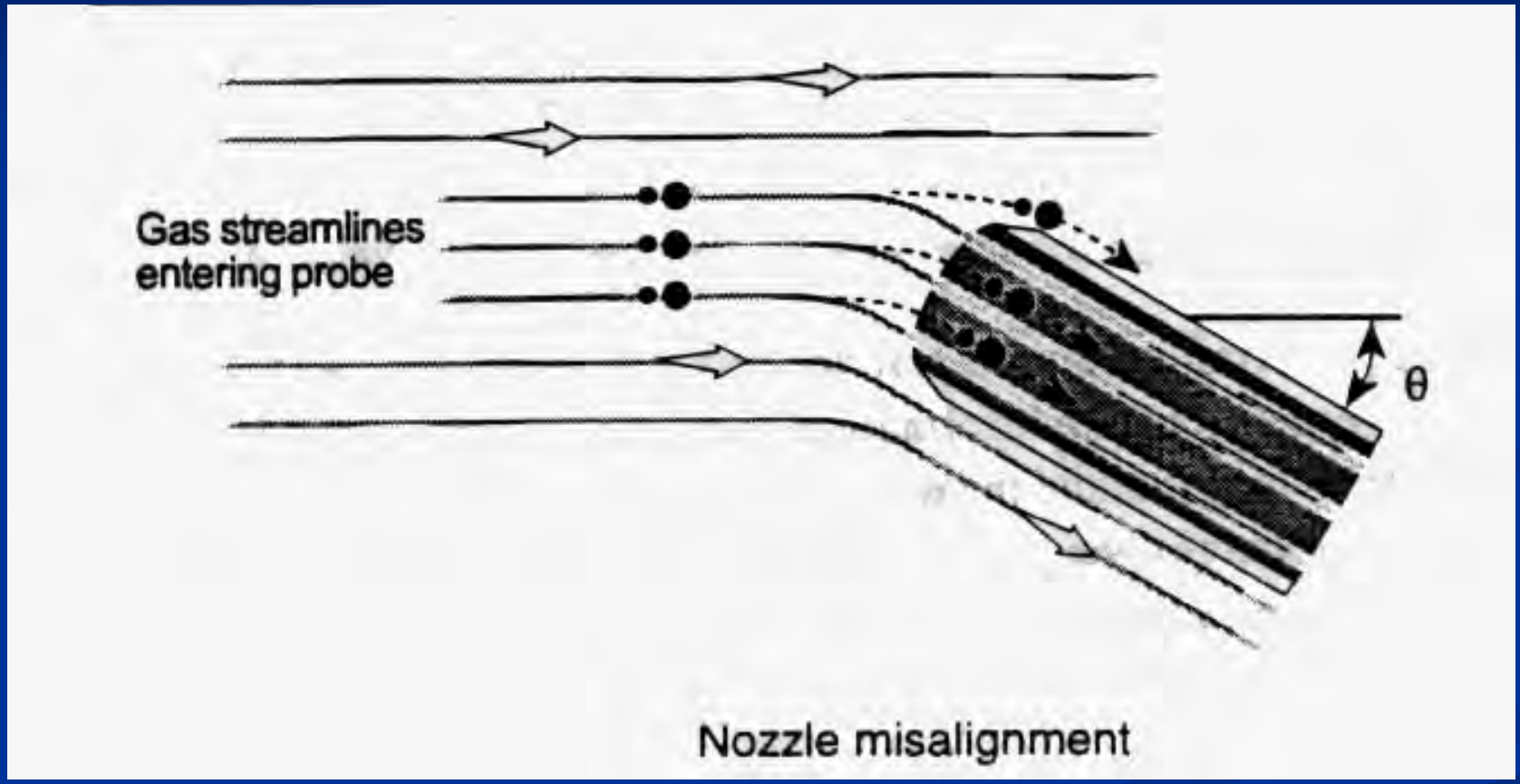
Vn=1/2Vs

Over-Isokinetic (200%)

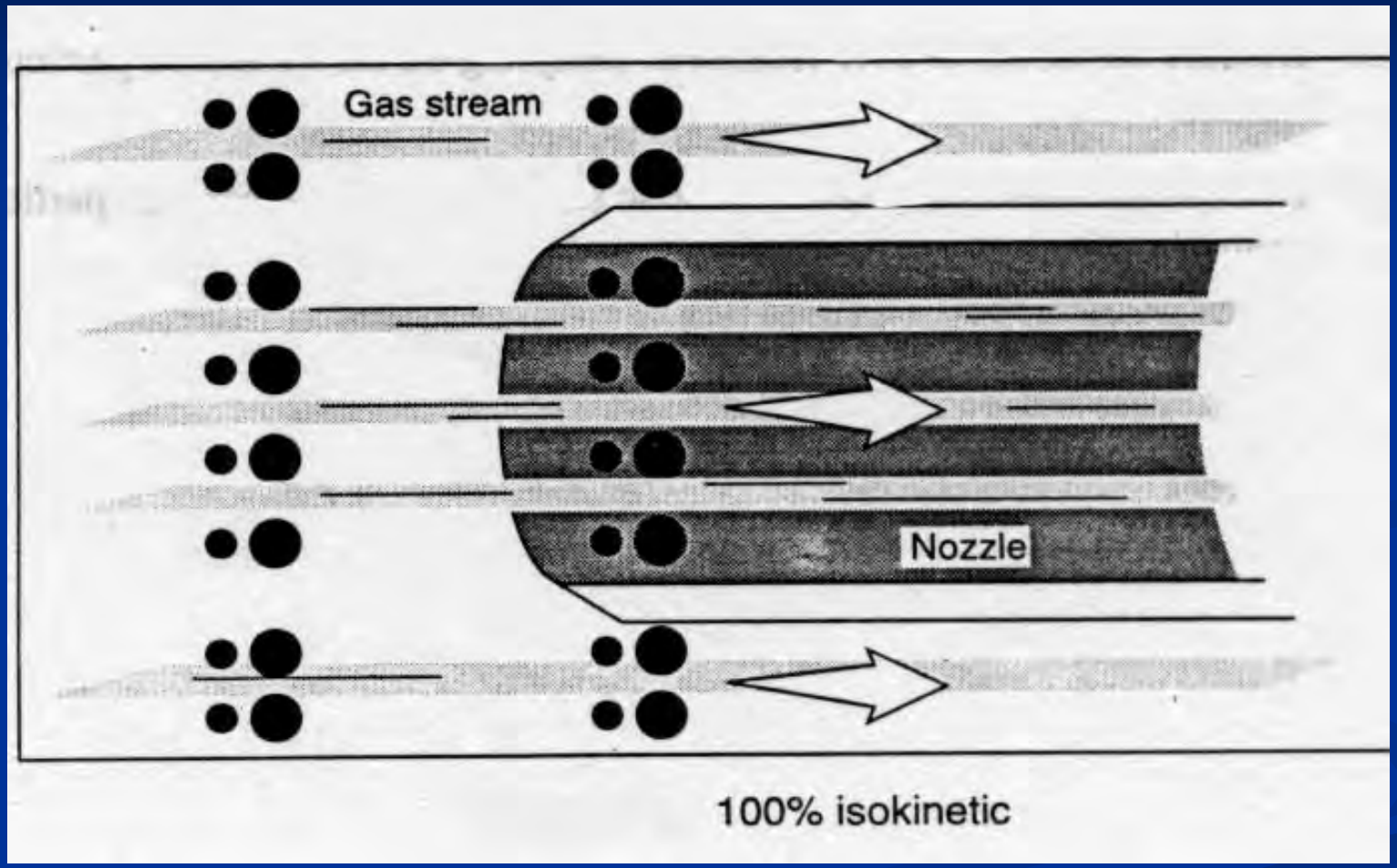


Vn=2Vs

Nozzle Misalignment



$\Delta H = K\Delta p$



Vs=Vn

Isokinetic Sampling

$$\% \text{ Isokinetic} = \frac{V_n}{V_s} \times 100$$

In Order To Take An Isokinetic Sample, We Must….

- Calculate the motion of the gas stream passing by the sampling system, and
- Recreate that motion in the sampling system

FRM 5 Isokinetic Rate Equation

$$\%I_{int} = 100 \frac{T_s V_{m(std)} P_{std}}{T_{std} v_s \theta A_n P_s 60 (1 - B_{ws(est)})}$$

$$\%I_{final} = \frac{100\ T_{s(avg)}\ K_3 V_{1c} + \left[\left(\frac{V_{m(avg)}}{T_{m(avg)}}\right)\left[P_{bar} + \frac{\Delta H}{13.6}\right]\right]}{60\ \theta\ V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

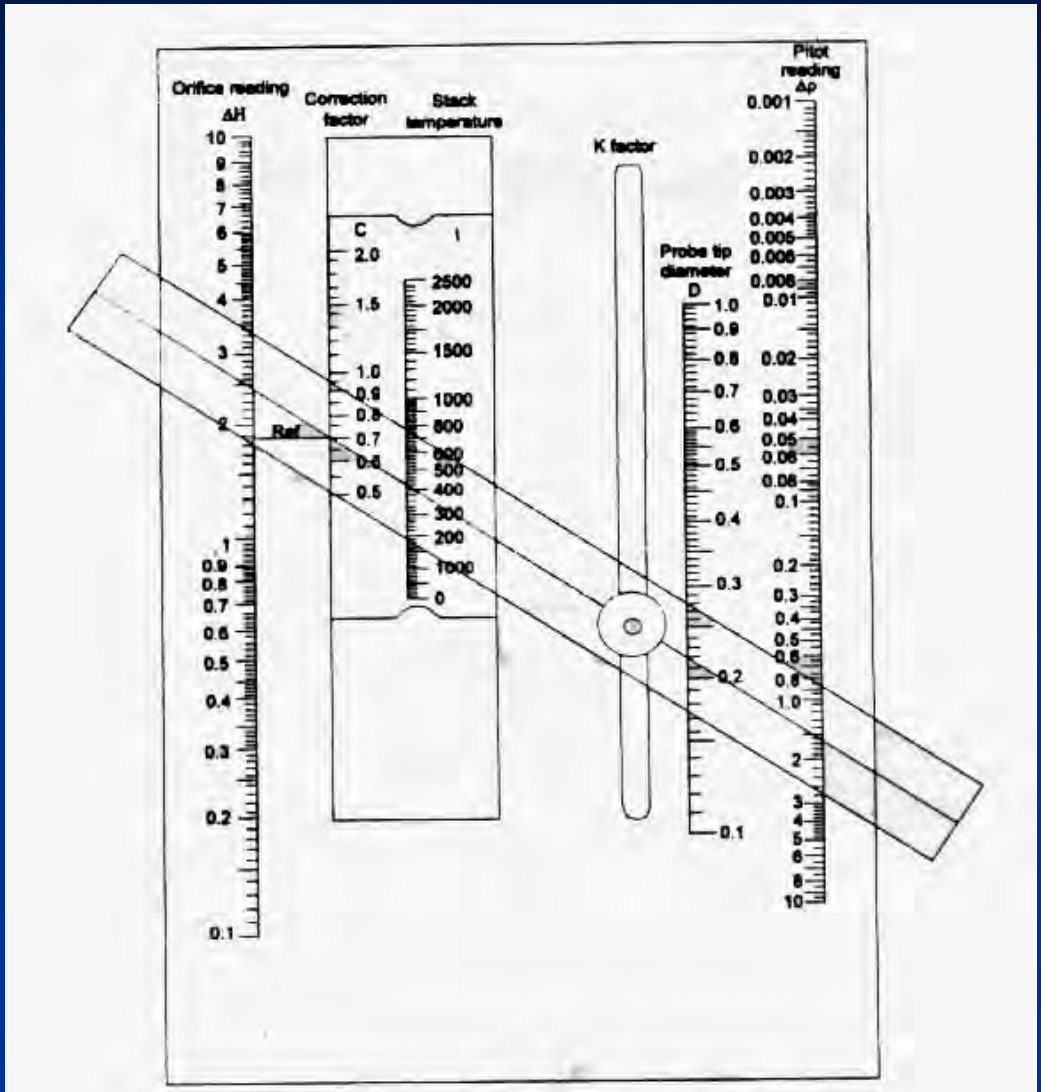
$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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

FRM 5 Isokinetic Rate Equation

- The relationship between "v_s" and "v_n" is the core understanding of FRM 5 isokinetic sampling
- Reading the "Δp" from the pitot tube and setting the proper "ΔH" on the meter box allows one to sample isokinetically

FRM 5 Nomograph



FRM 5 Isokinetic Rate Equation

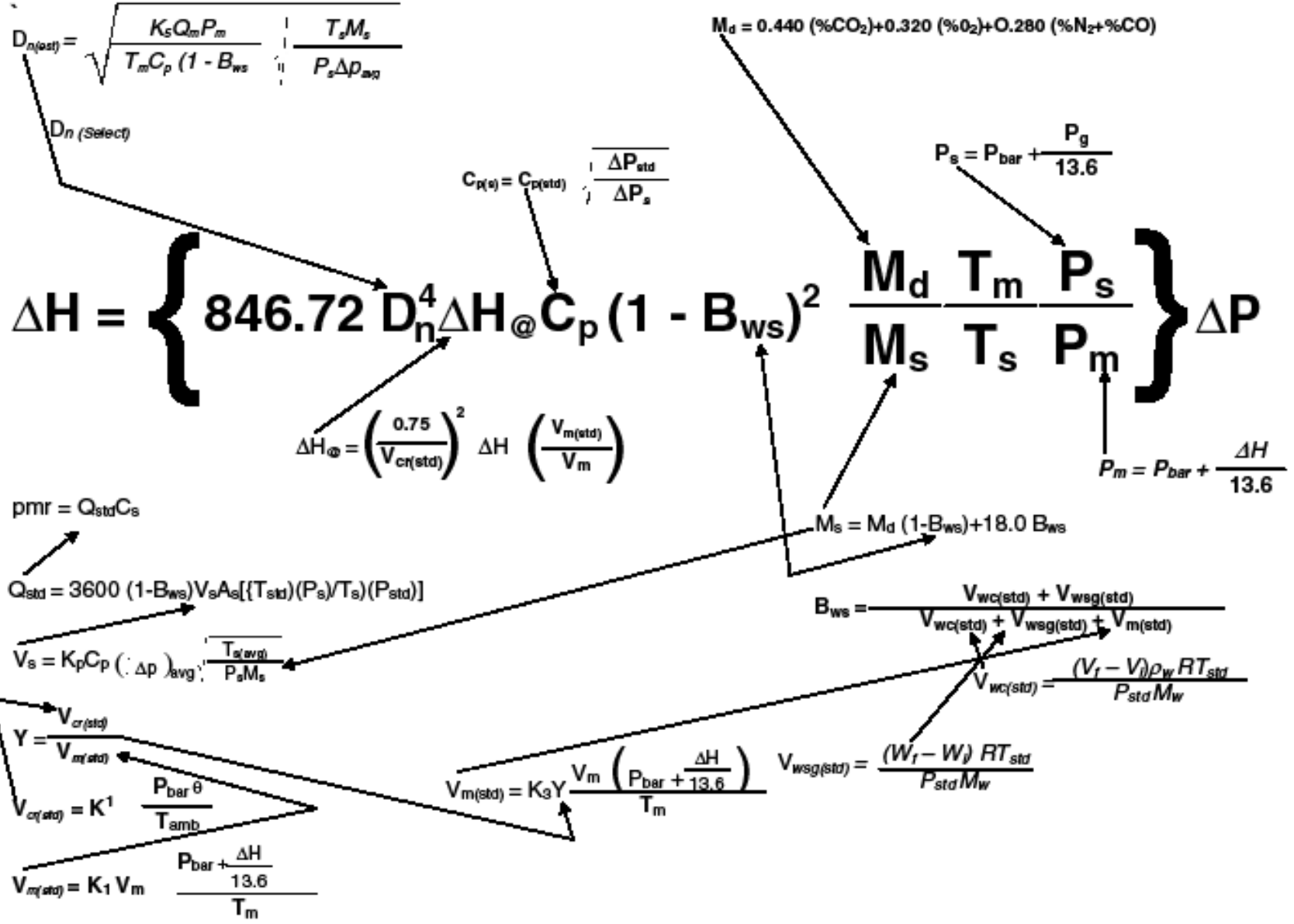
$$\Delta H = \left\{ 846.72\, D_n^{4}\, \Delta H_@\, C_p^{2} (1 - B_{ws})^2 \quad \frac{M_d}{M_s} \frac{T_m}{T_s} \frac{P_s}{P_m} \right\} \Delta P$$

FRM 5 Operation

Setting Δ H Based Upon Δ p Observation and Calculated K Factor

$$K = \frac{\Delta H}{\Delta p} = K_6 D_n{}^4 \Delta H_@ C_p{}^2 \left(1 - B_{ws}\right)^2 \frac{M_d T_m P_s}{M_s T_s P_m}$$

Federal Reference Method 5 Equations



FRM 5 Causes for not Meeting 100% Isokinetics

- Heavy grain loading, causing plugging of filter so can't achieve proper ΔH
- Large temperature variations not corrected in isokinetic rate equation

FRM 5 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 5 Causes for not Meeting 100% Isokinetics

- Leak in pitot or sampling lines (broken probe, lopsided filter, broken frit)
- Preliminary selection of wrong nozzle size

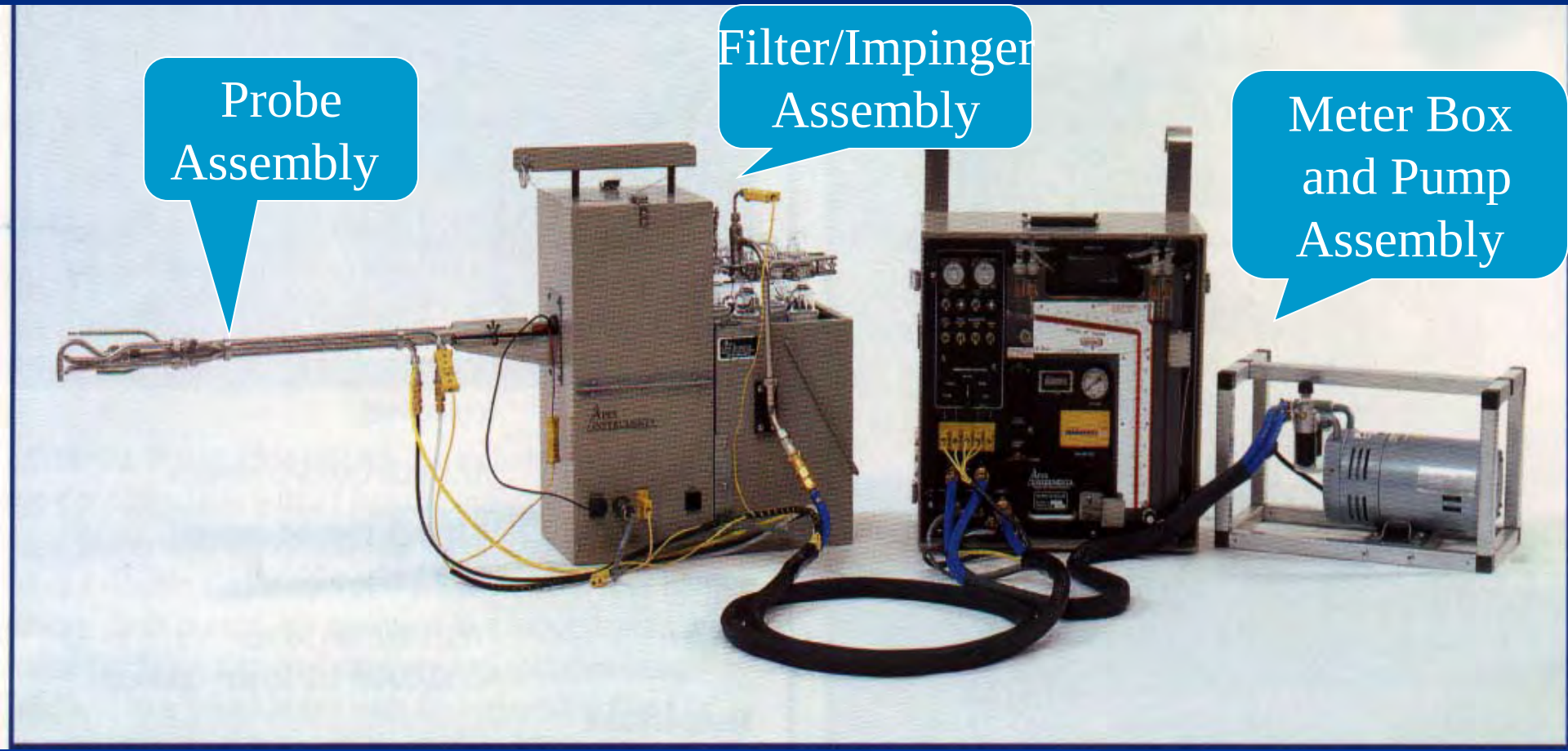
Difficulty in Maintaining Isokinetics

- Plugging of filter by particles
- Filter becoming wet:
  low box temperature
- Impinger stem too restricted

Difficulty in Maintaining Isokinetics

- Filter disc plugging
- Nozzle too small/large for velocity of stack gas

FRM 5 Sampling Train



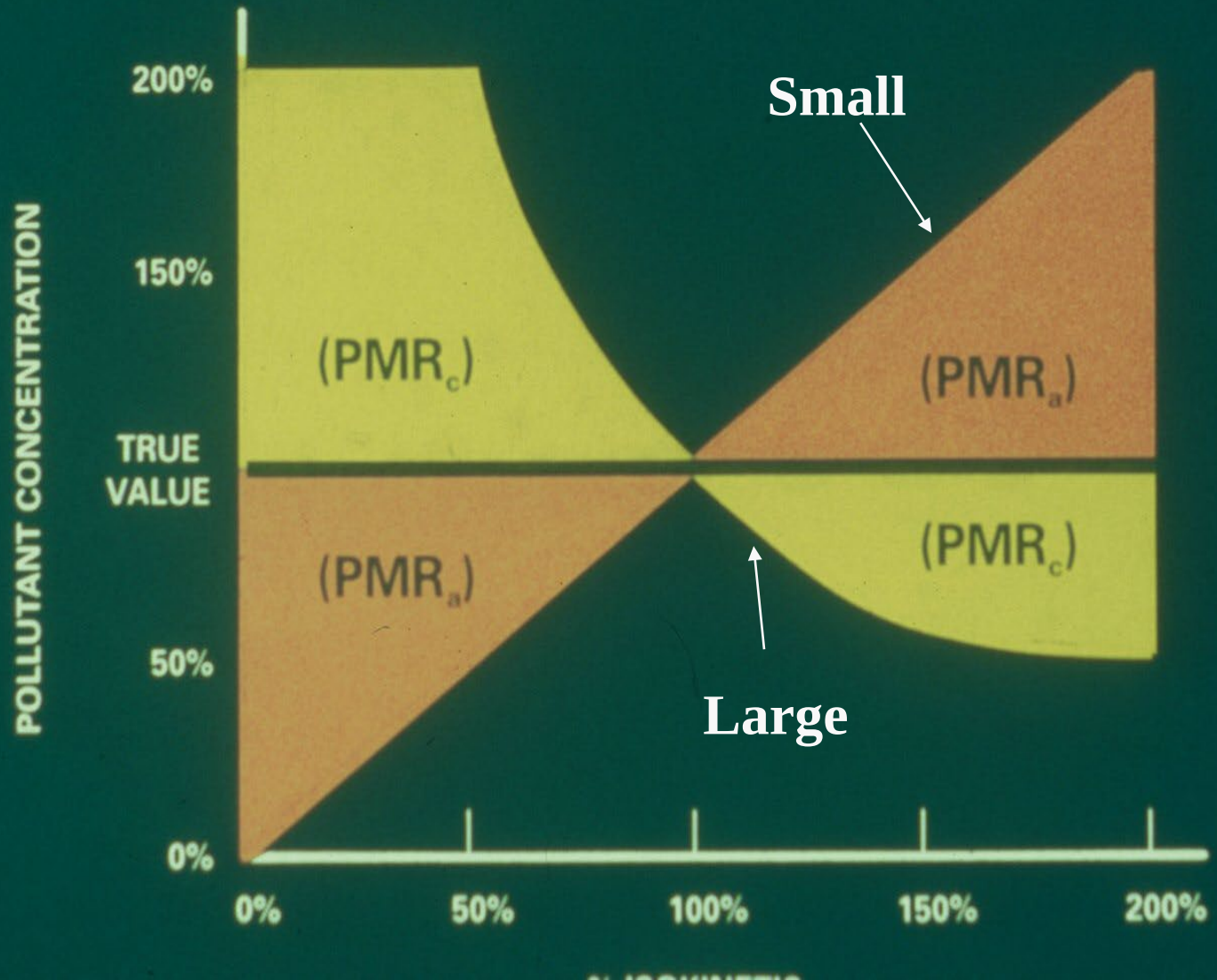
FRM 5 Sampling Train



Isokinetic Sampling and Bias

- To obtain average pollutant concentration, need parameters:
  - Quantity of mass emitted from stack
  - Total quantity of volume from stack
- Isokinetic sampling provides best approach for accurate data
- Pollutant mass rate (pmr)
  - pmr_a (Ratio-of-areas: A_n ratio A_s)
  - pmr_c (Ratio-of-conc.: m_n ratio A_n)

VS.
POLLUTANT CONCENTRATION



Errors in pmr Calculations Using FRM 5

- T_s: 1.4 %
- DGM: 1.0 %
- P_s: 0.4 %
- P_m: 0.4 %
- P_b: 0.2 %
- B_{ws}: 1.0 % Affects % Iso
- Δ H: 5.0 %
- D_n: 1.0 %
- Delta $H_@$: 1.5 %

FRM 5 Principle

- Particulate matter is drawn isokinetically from an applicable source and collected on a glass fiber filter maintained at regulated temperature (usually 120°C ±14°C)
- The particulate mass is determined gravimetrically after removal of uncombined water

FRM Method 5 Limits

- Particulate matter (PM) target catch as a concentration or amount of an analyte that can be determined with a specific degree of confidence to be different from zero

FRM 5

- "Front Half" is defined as particulate emissions
- Filter Temperature
  - 248°F
  - 320°F
- Isokinetic Sampling
  - $\text{Velocity}_{\text{nozzle}} = \text{Velocity}_{\text{stack}}$
  - 90% - 110%

FRM Method 5 Limits

- Designed for PM catches of > 50 mg
- Limits for FRM 5
  - Practical quantitation limit (PQL) of 3 mg
  - Methdod detection limit (MDL) of 1 mg
- Target catch for FRM 5 must be no less than 3 mg; If less, go to FRM 5I

Required Sampling

- Sampling duration: 60 –120 minutes
- Sampling rate: 0.50-0.75 dscfm
- Minimum sampling volume: 30 – 60 dscf
- Review 40CFR60/61 for minimum sampling duration, volumes and filter/gas temperatures
- Minimum sample volume dependent on analyte MDLs and expected concentrations

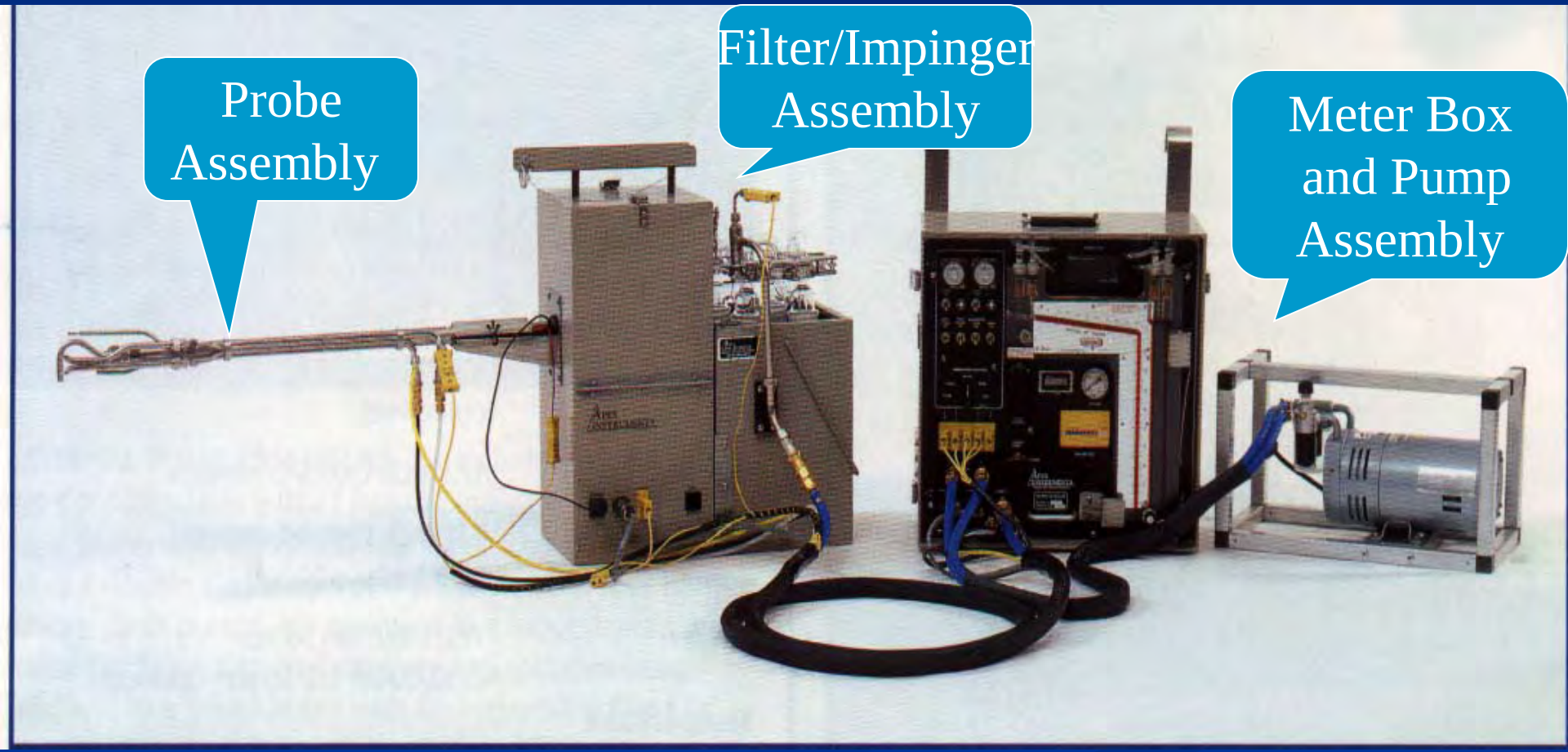
$$\Delta H = K \Delta p$$

SIMPLIFIED ISOKINETIC RATE EQUATION

Sampling Train Components

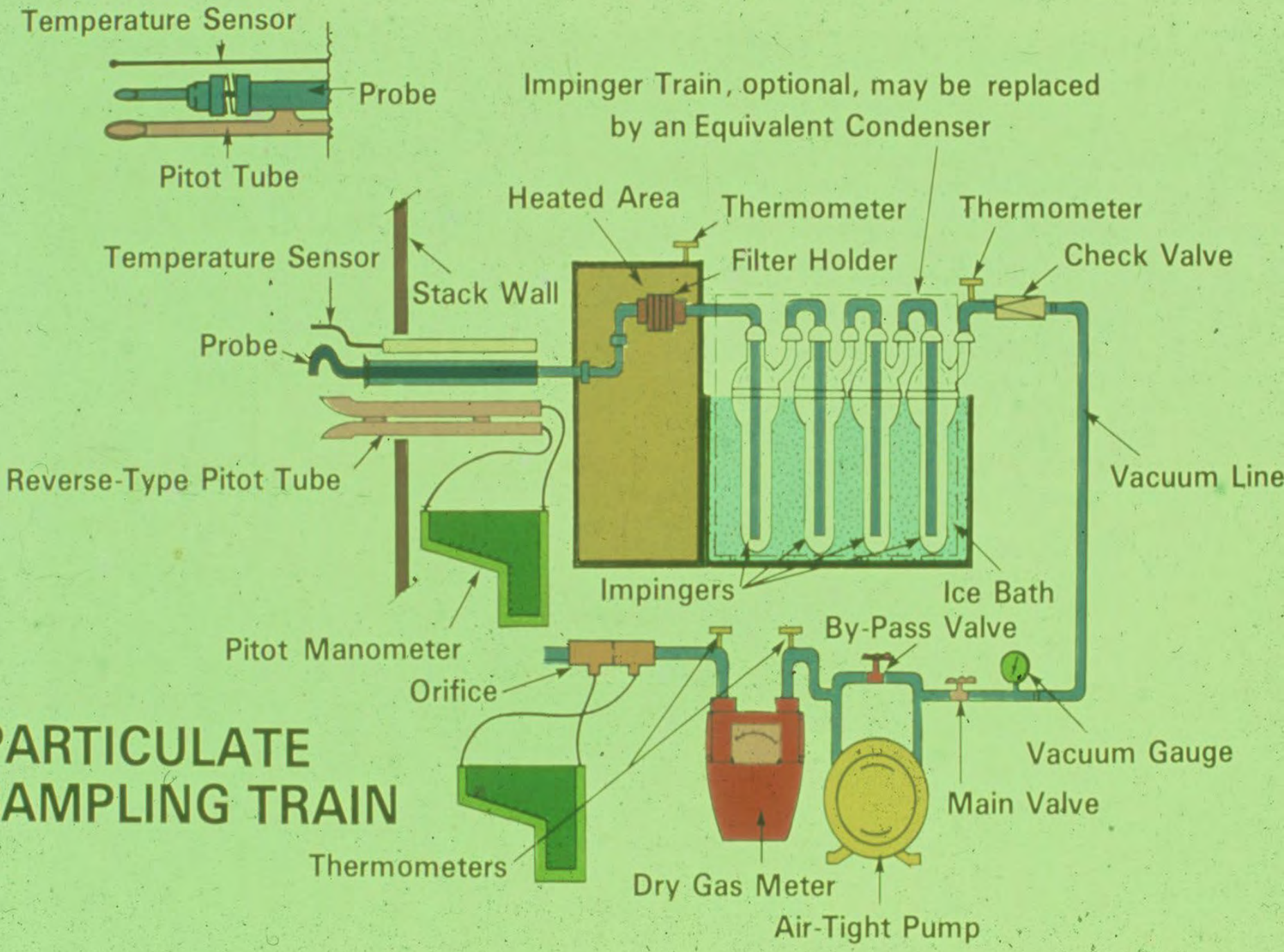
- The probe assembly
- The sample box
- The umbilical
- The meter box

FRM 5 Sampling Train



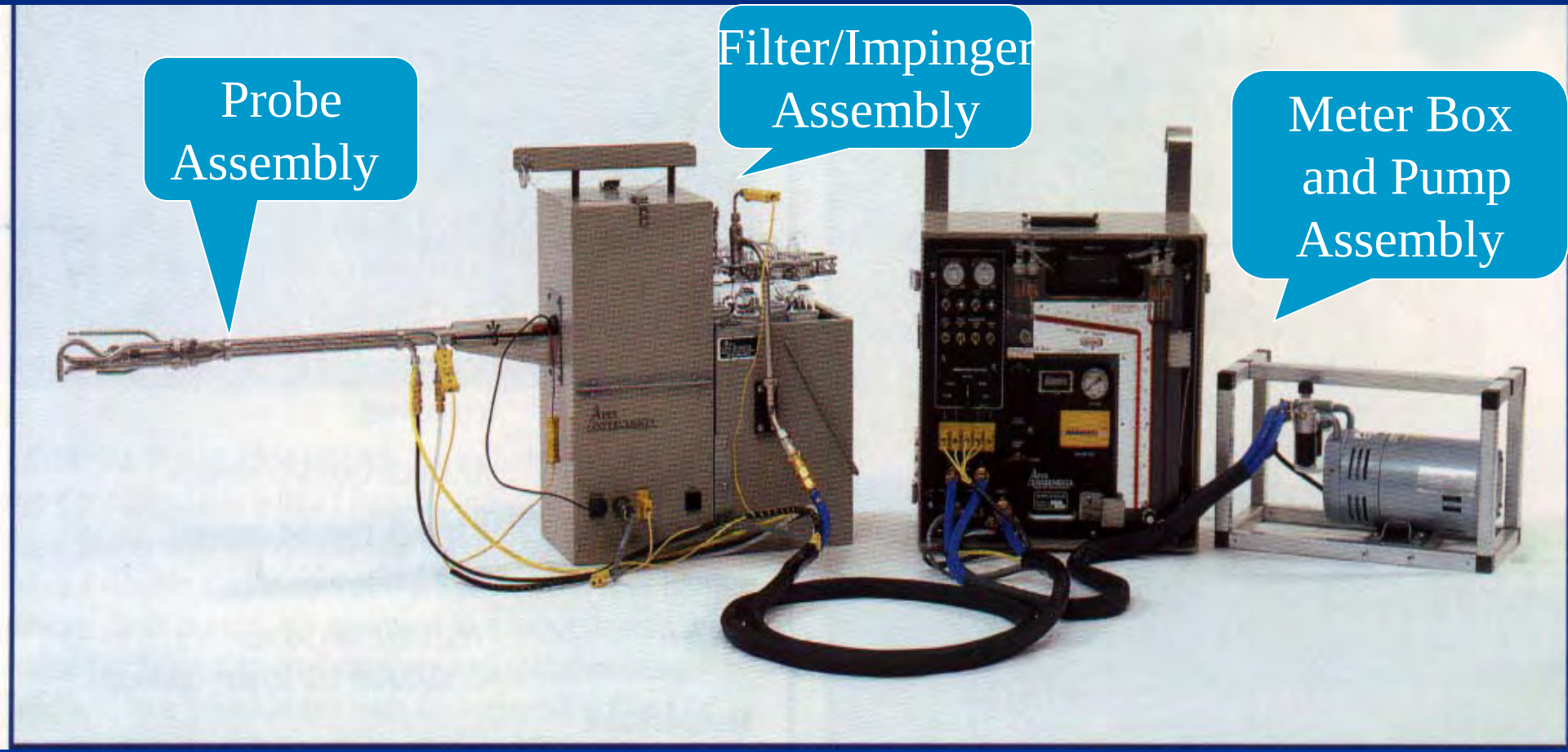
FRM 5 Sampling Train



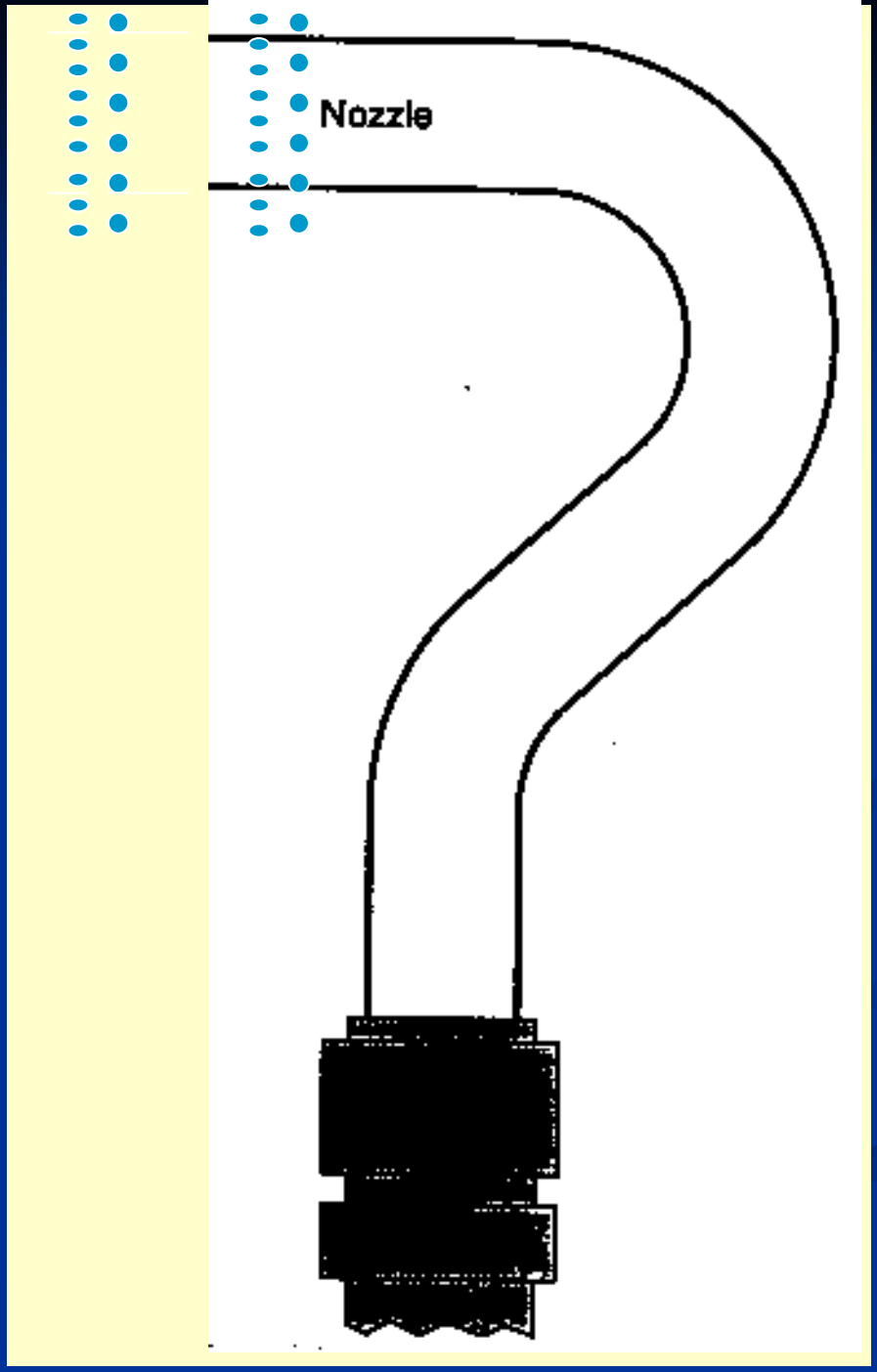


PARTICULATE SAMPLING TRAIN

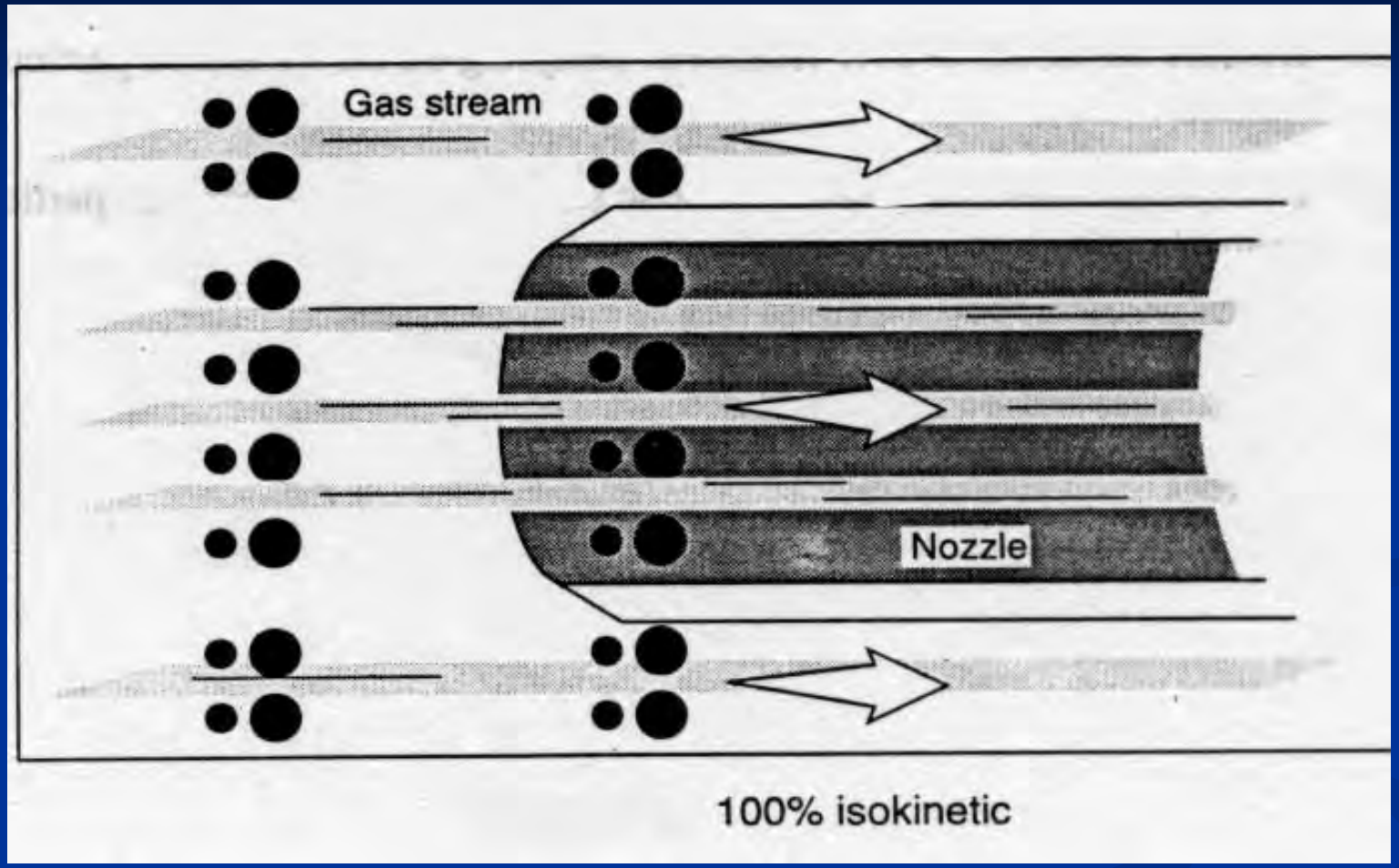
FRM 5 Sampling Train



$v_n = v_s$
100% Isokinetic

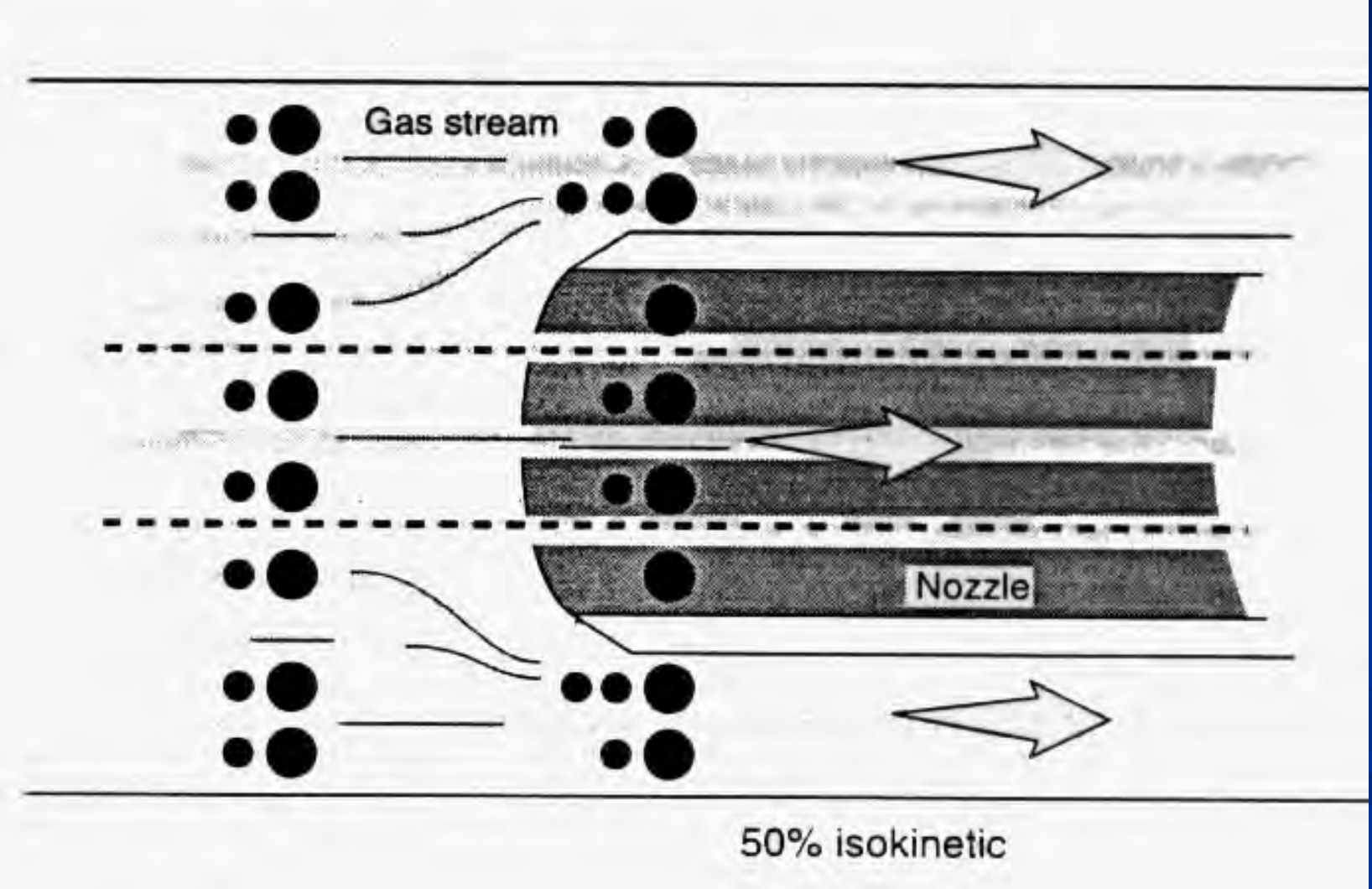


100 % Isokinetic



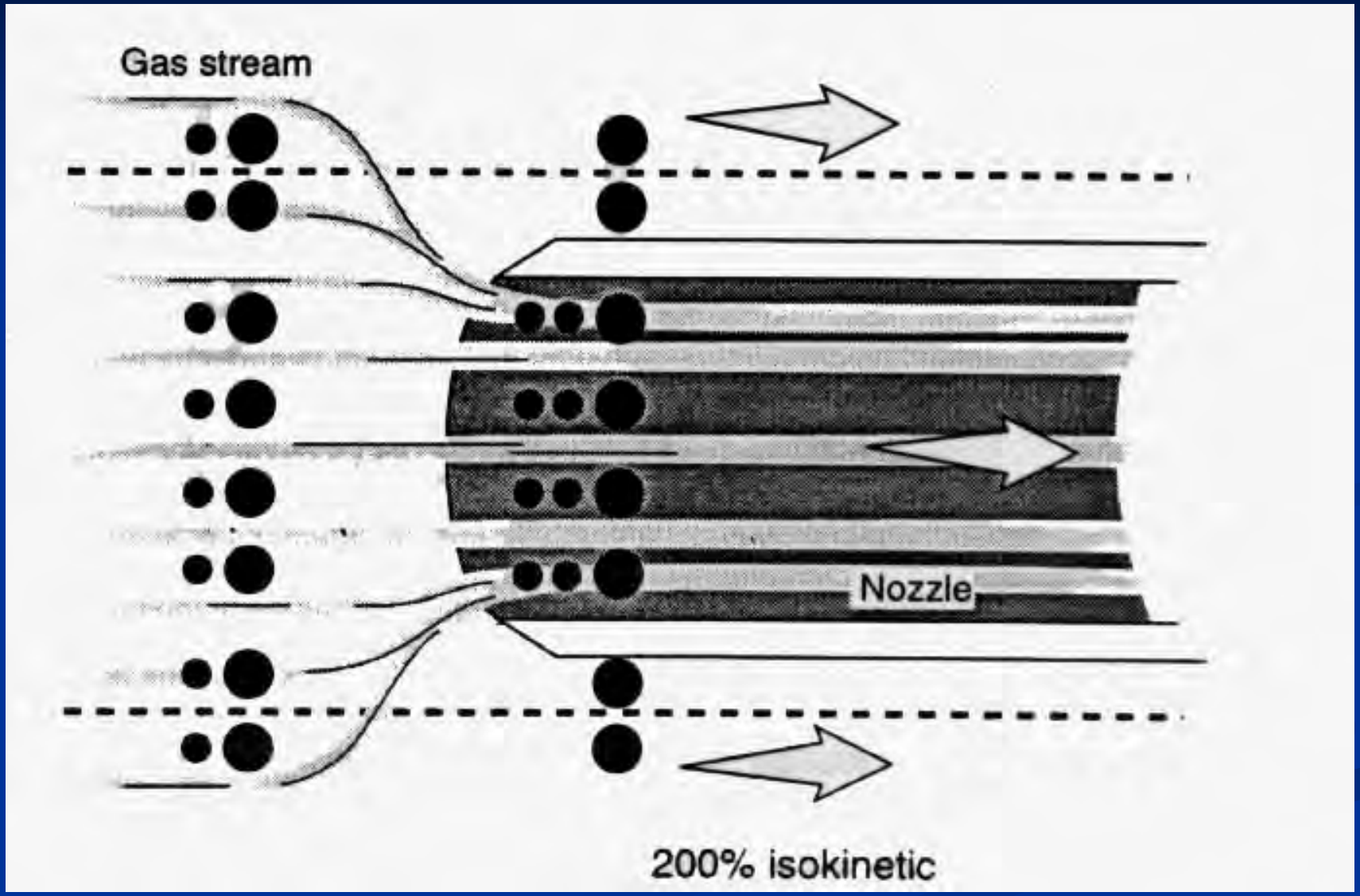
Vs=Vn

Sub-Isokinetic (50%)



Vn=1/2Vs

Over-Isokinetic (200%)



Vn=2Vs

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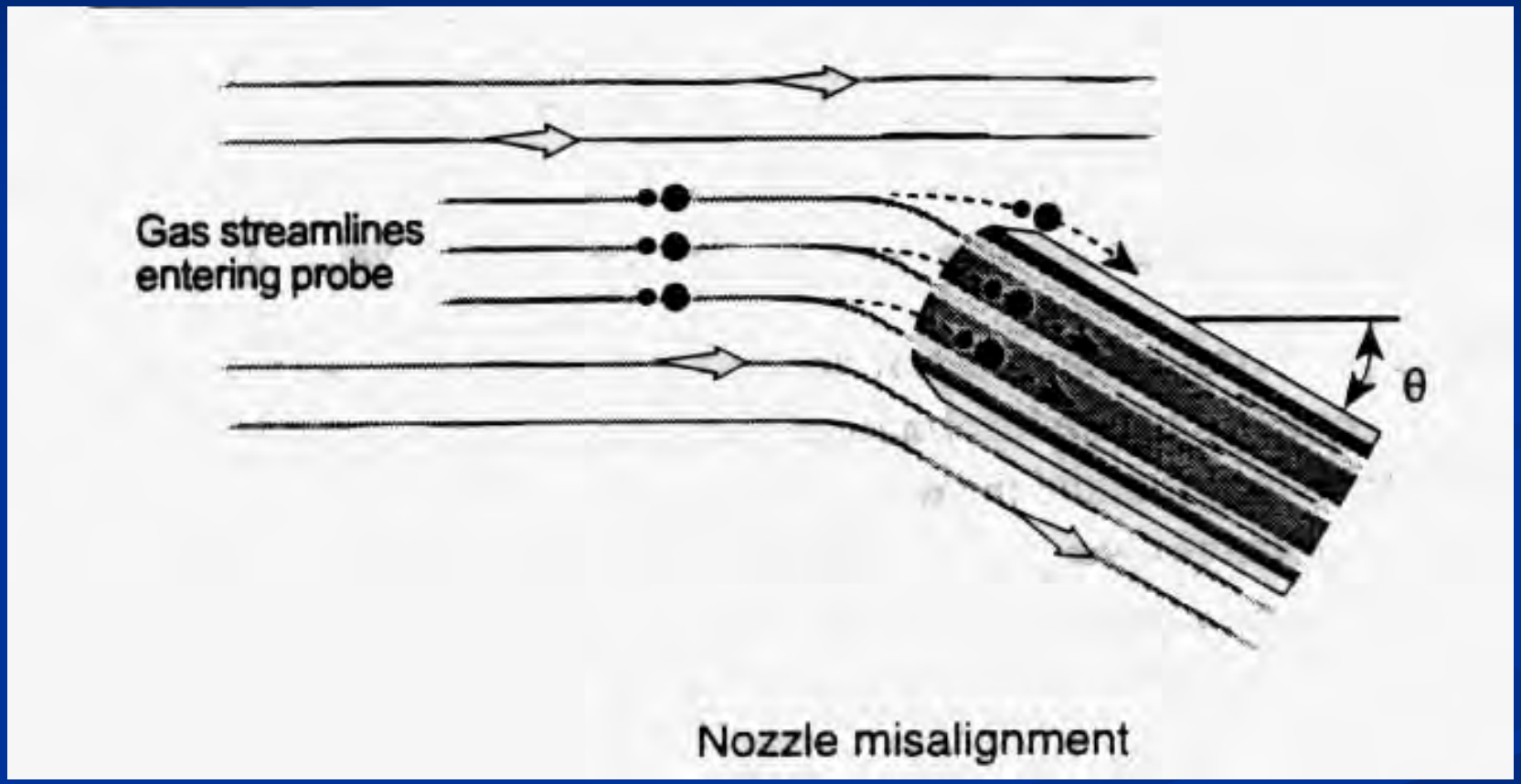
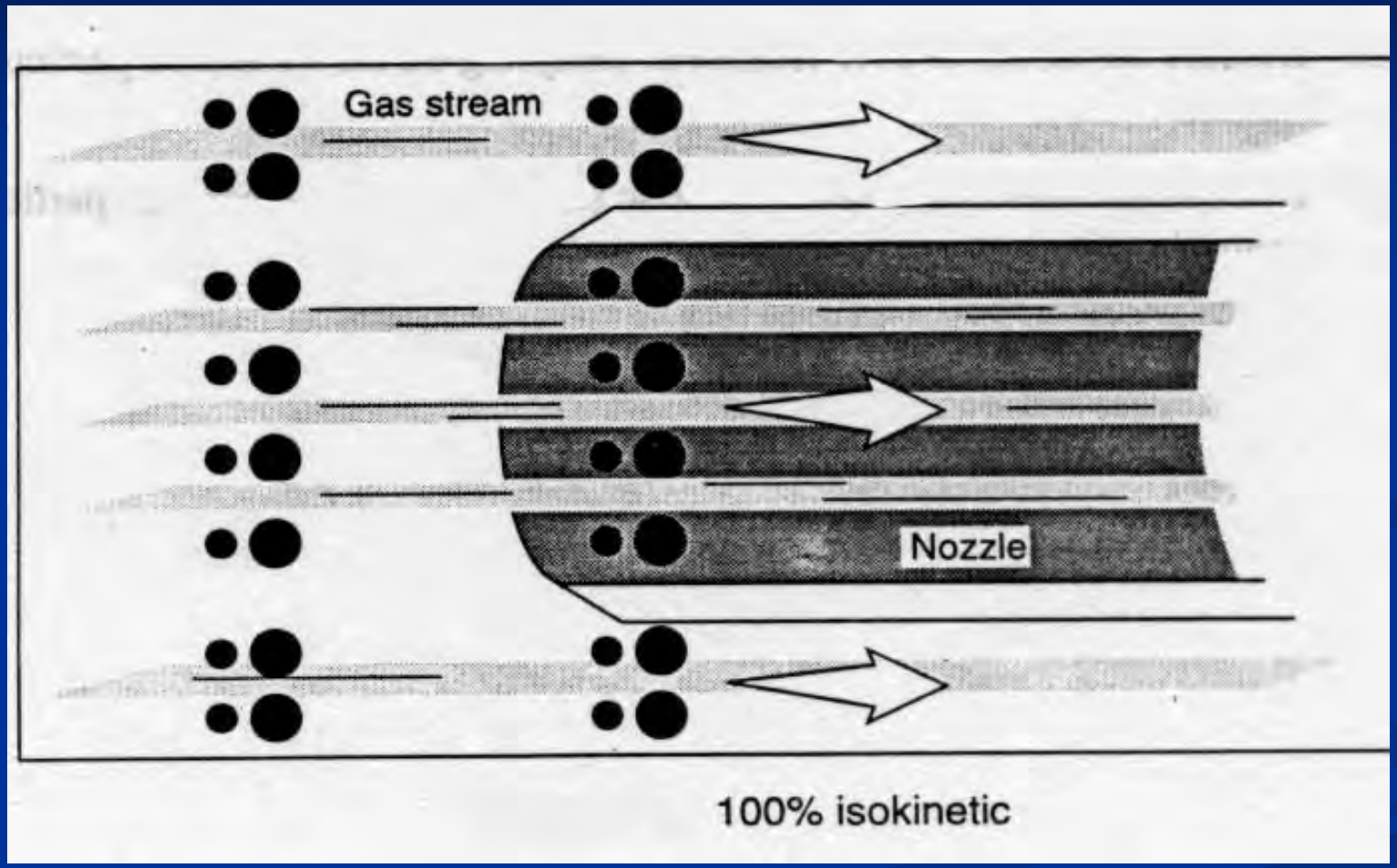


$\Delta H = K \Delta p$



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$$\%I_{final} = \frac{100\, T_{s(avg)} \left[K_3 V_{1c} + \left(\frac{V_{m(avg)}}{T_{m(avg)}} \right) \left[P_{bar} + \frac{\Delta H}{13.6} \right] \right]}{60\, \theta\, V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

$$D_{n(est)} = \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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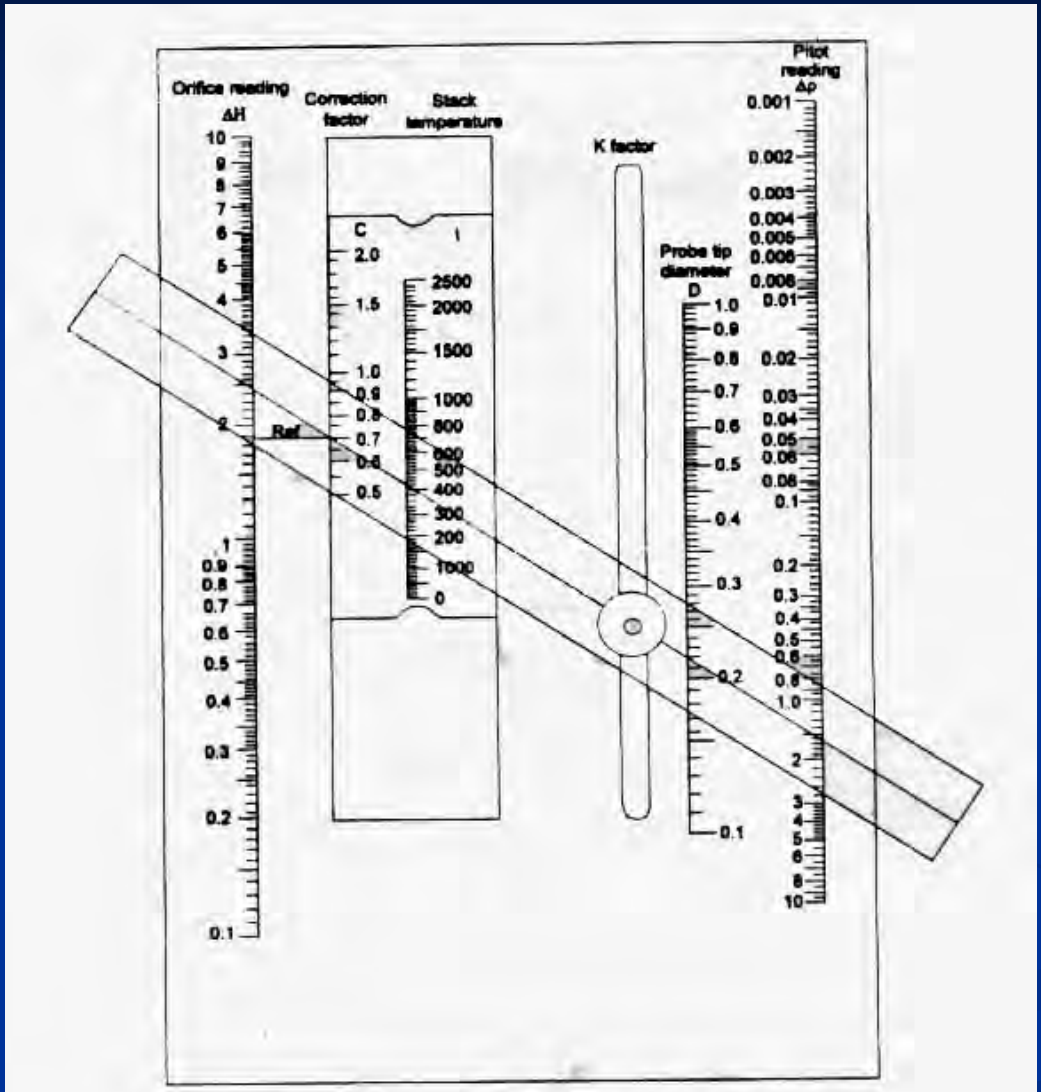
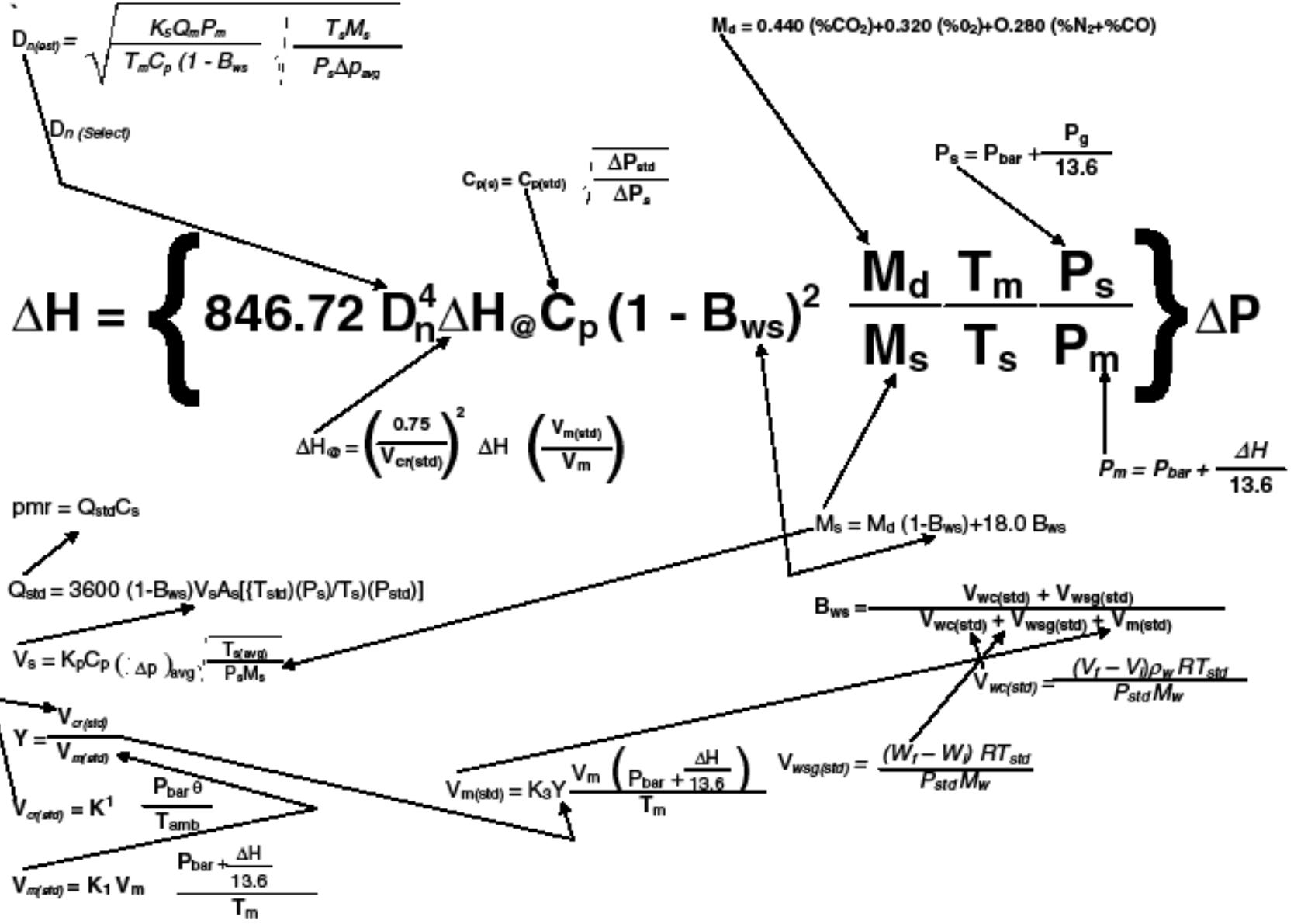
FRM 5 Nomograph



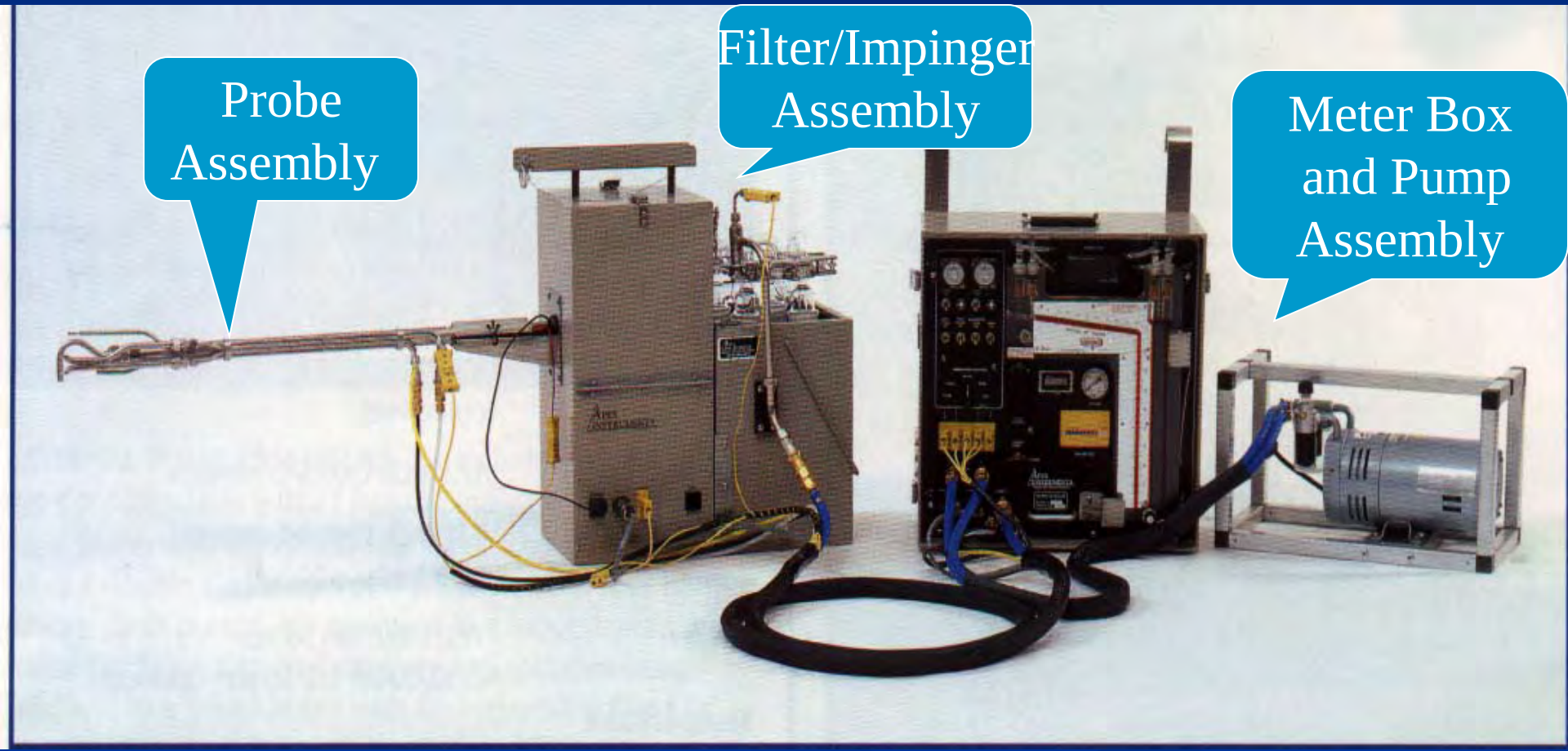
Federal Reference Method 5 Equations



FRM 5 Sampling Train



FRM 5 Sampling Train



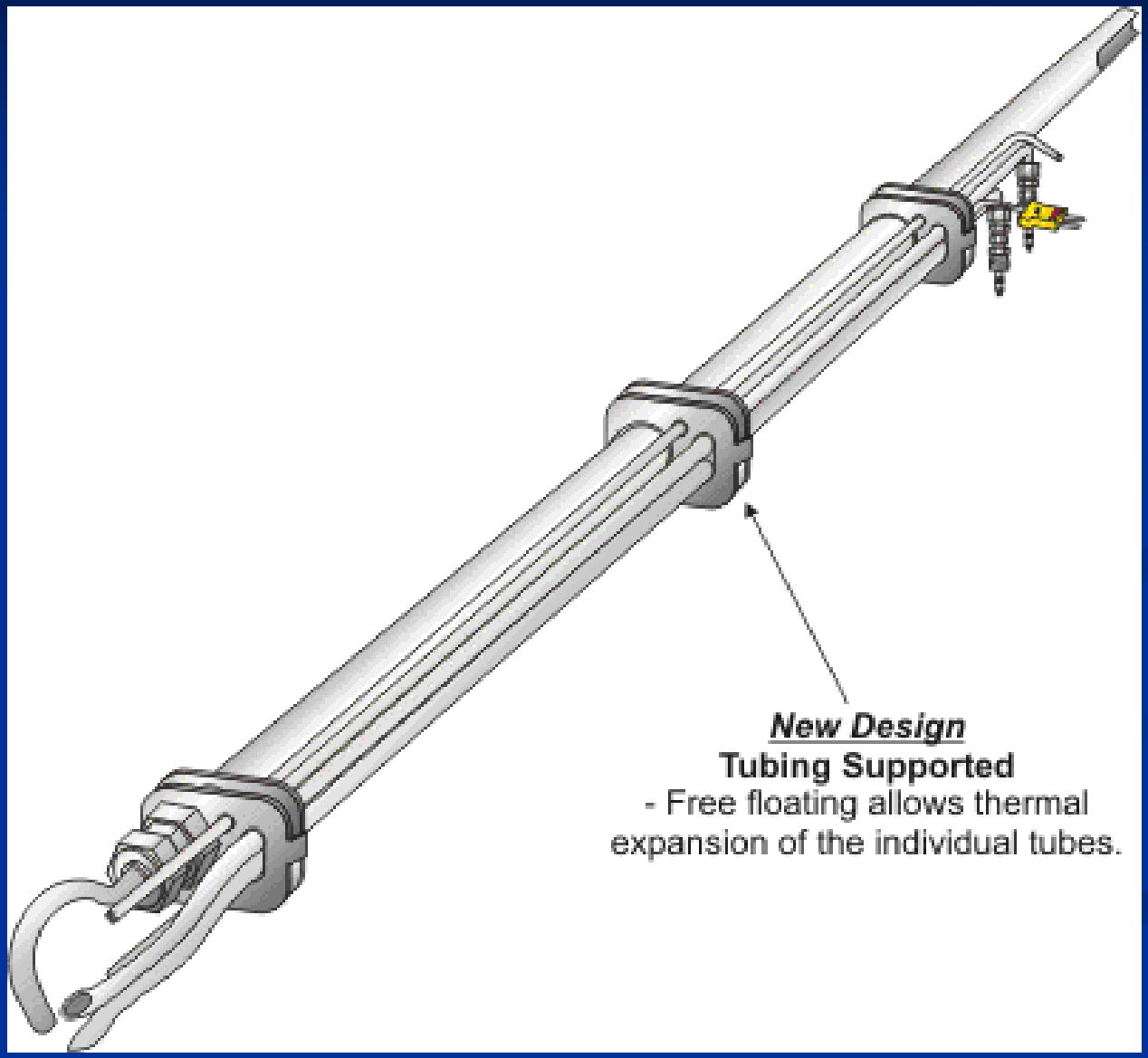
Sampling Train Components

- The probe assembly
- The sample box
- The umbilical
- The meter box

The Probe Assembly

- Nozzle
- Pitot Tube
- Thermocouple
- Probe liner
- Probe sheath

The Probe Assembly



FRM 5 Sampling Probe

- Typical diameter of 2.54 cm
- Should be stainless steel or equivalent
- Pitot tube must be firmly welded to probe
- Probe design to prevent accidental misalignment in gas stream

FRM 5 Sampling Probe

- Probe design to protect liner
- Material of construction determined by temperature/compounds being monitored
  - Borosilicate glass liners up to 480 C
  - Quartz liners up to 900 C
  - Teflon liners up to 350 C

Probe Liner

- **Borosilicate or quartz glass**
- **Heating System to maintain exit gas temperature of 120° C**
- **Borosilicate temperature to 480° C**
- **Quartz glass temperature to 900° C**

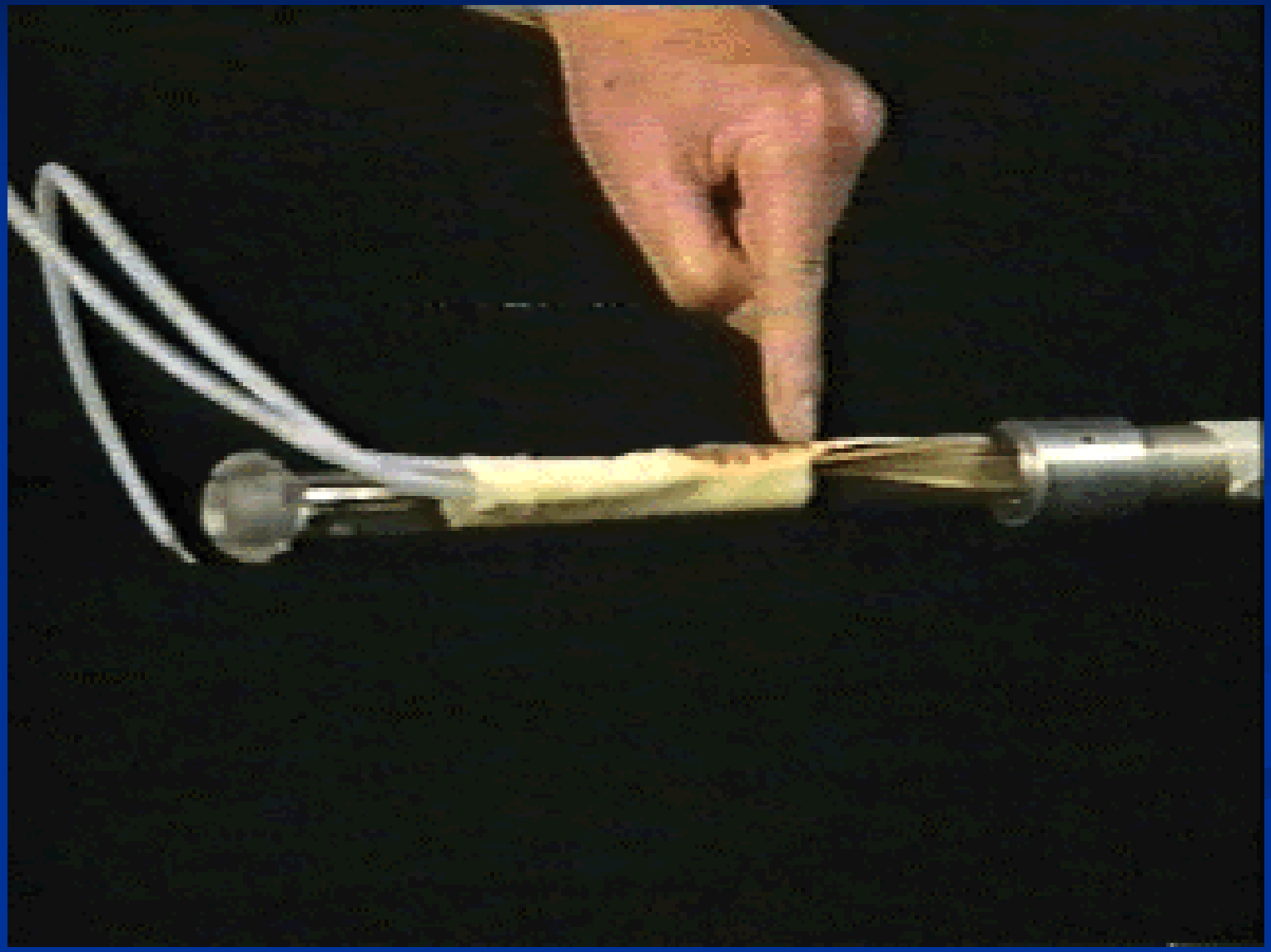
FRM 5 Sampling Probe

- Must have heating system capable of maintaining gas temperature of typically 120 C +/- 14 C
- Temperature must be calibrated

Probe Sheath

- Usually stainless steel
- Pitot tube welded to sheath to prevent misalignment
- Protects liner from breakage

Probe liner and sheath



FRM 5 Ceramic Probe Heater



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FRM 5 Sample Nozzle

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

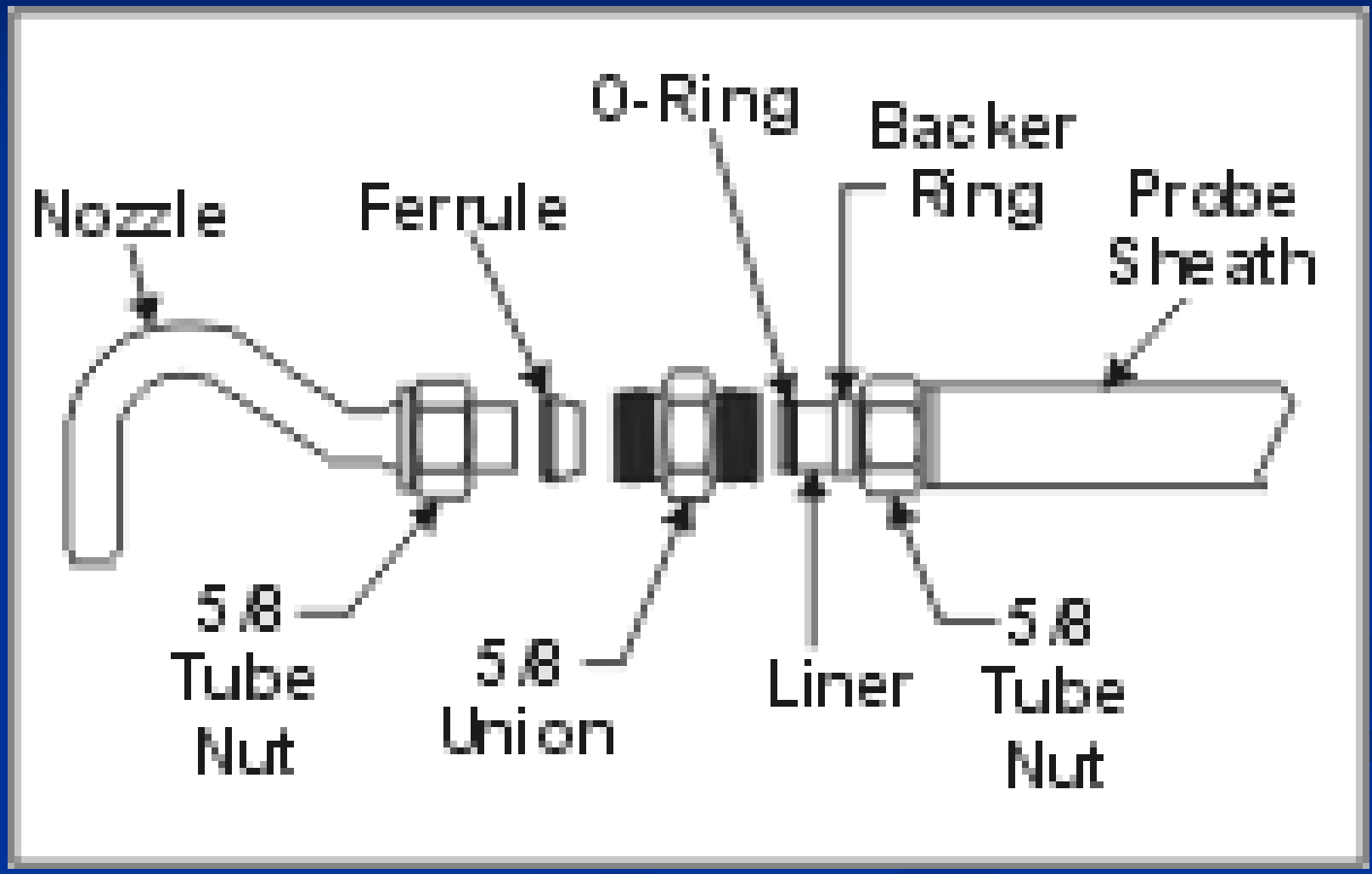
FRM 5 Sample Nozzle

- Range of nozzles (0.32-1.27 cm ID)
  - Nozzle must be calibrated
  - Measure 3 readings using micrometer (take average)
  - Low/high readings not exceed 0.004 inches

FRM 5 Sampling Nozzle



Sampling Nozzle













FRM 5 Sample Nozzle

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

$$D_{n(est)} = \sqrt{\frac{K_5 Q_m P_m \sqrt{T_s M_s}}{T_m C_p \left(1 - B_{ws}\right) \sqrt{P_s \Delta p_{avg}}}}$$

FRM 5 Isokinetic Rate Equation (Simplified)

$$D_{n(est)} = \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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FRM 5 Nozzle/Pitot Tube/Thermocouple Orientation

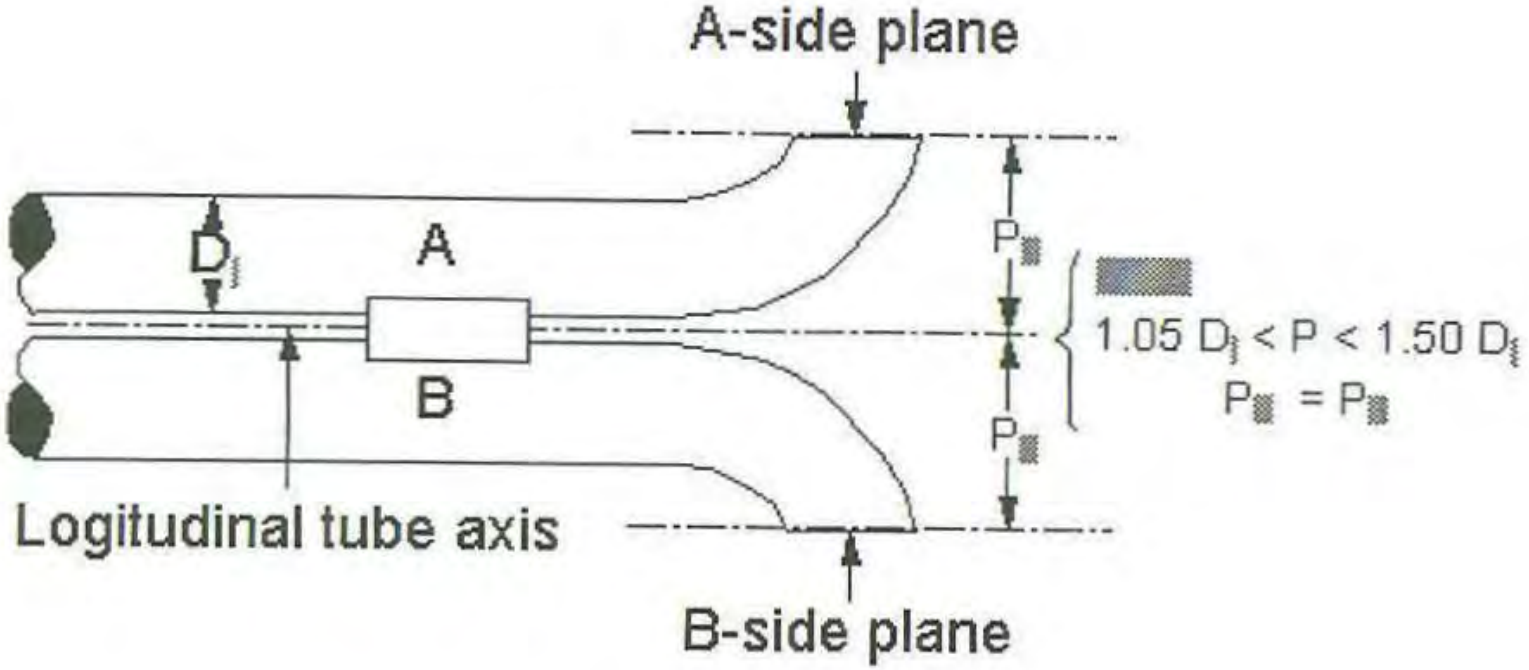
- Must meet certain design and configuration specifications
- Inspect during each test to verify orientation

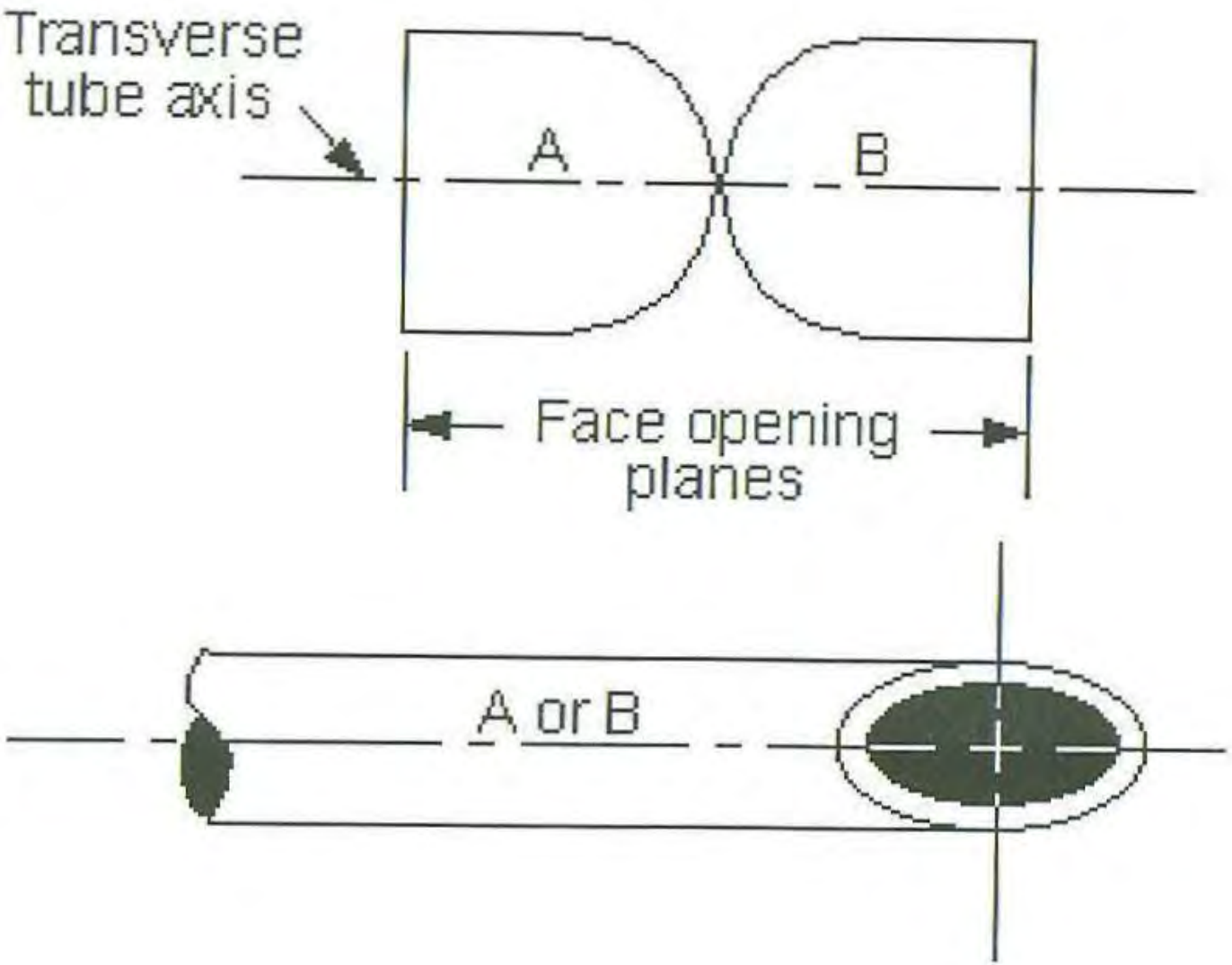


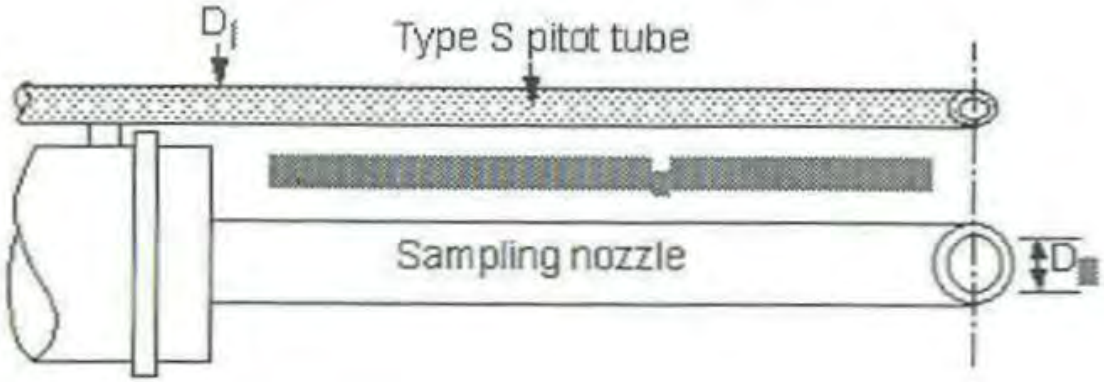
Type S Pitot Tube

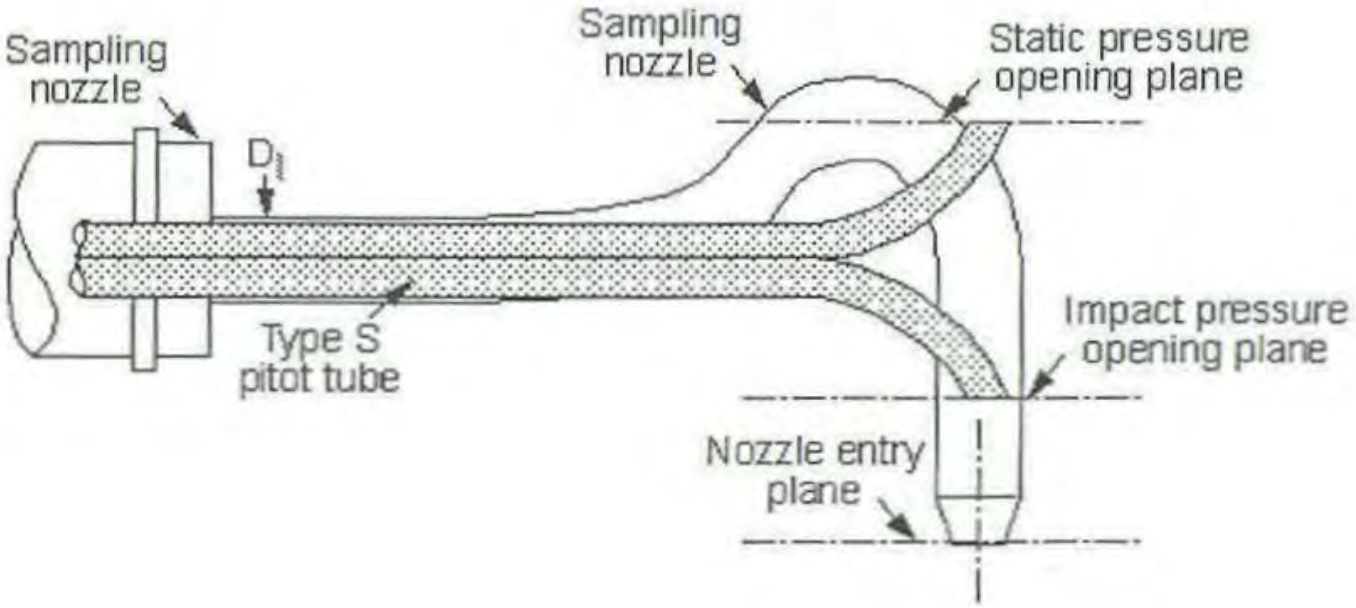
Design criteria for assigning

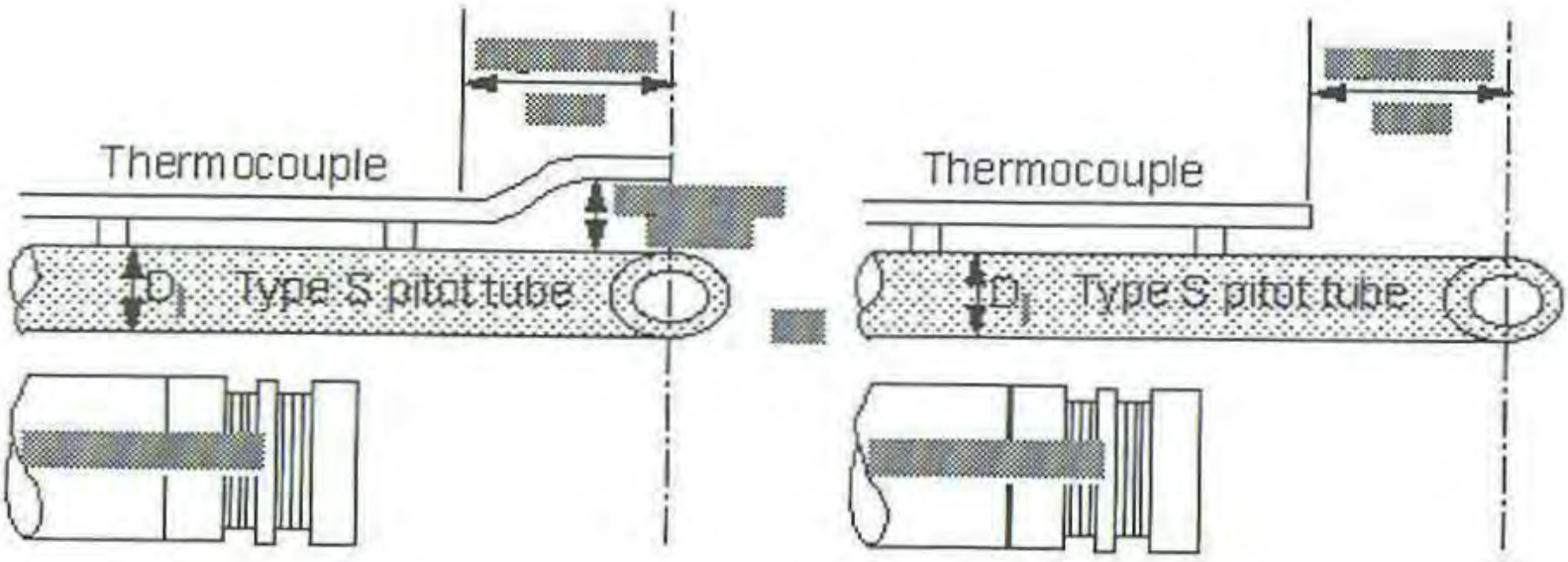
$$C_p = 0.84$$

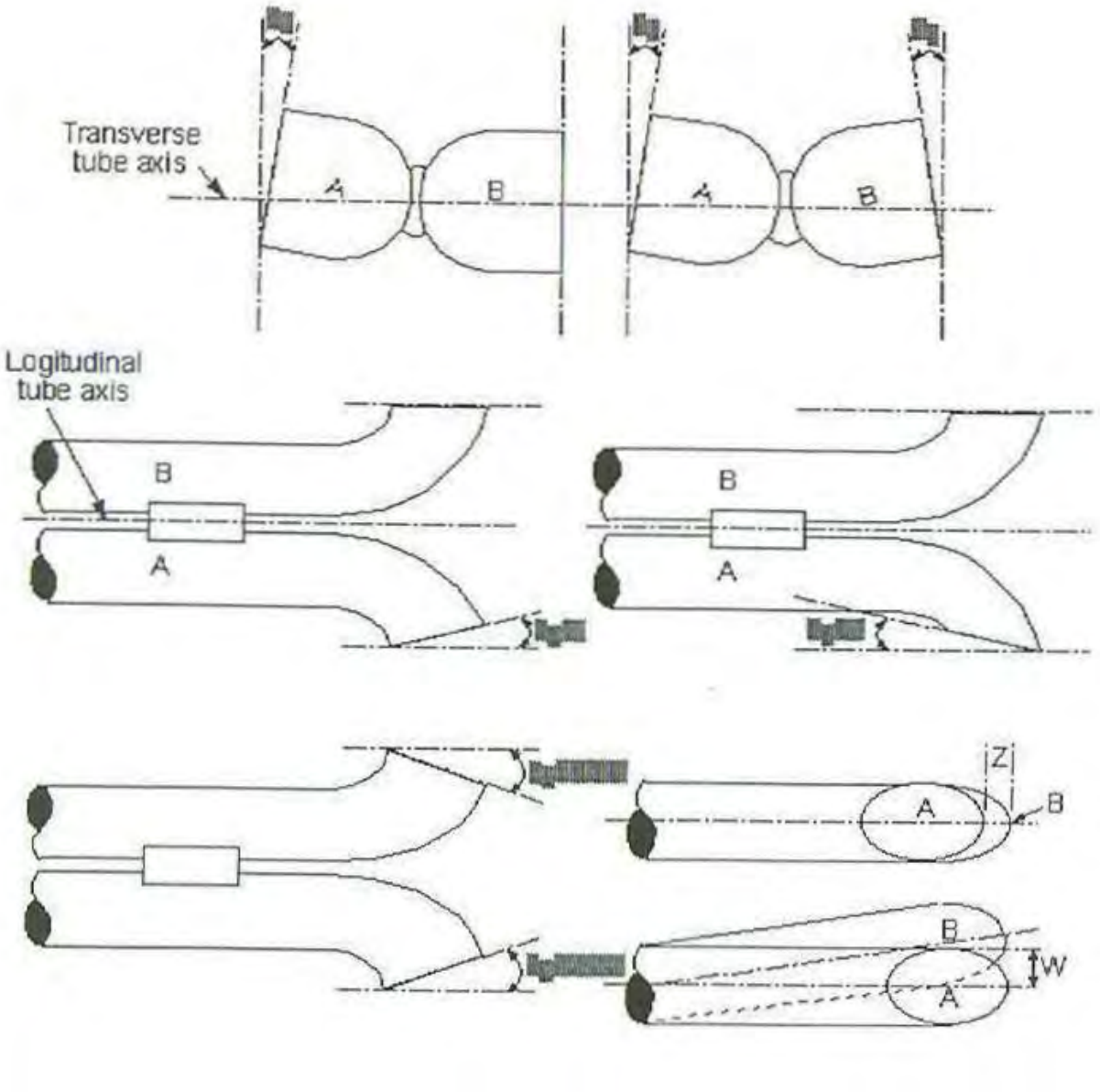

A-side plane
D
A
B
P
P
1.05 D < P < 1.50 D
P = P
Logitudinal tube axis
B-side plane


Transverse
tube axis
A
B
Face opening
planes
A or B


D_t
Type S pitot tube
Sampling nozzle
D_n


Sampling nozzle
D_n
Type S pitot tube
Sampling nozzle
Static pressure opening plane
Impact pressure opening plane
Nozzle entry plane


Thermocouple
D_1
Type S pitot tube
Thermocouple
D_1
Type S pitot tube


Transverse
tube axis
A
B
A
B
Logitudinal
tube axis
B
A
B
A
Z
A
B
B
W
A

Verification of Geometry of Type S Pitot Tube To Assign 0.84

- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375

Type S Pitot Tube Inspection Data Sheet

- With the S-Type pitot tube, determine whether it meets the design specifications to be able to assign a C_p of 0.84
- C_p may be determined in conjunction with standard pitot tube
- Identification number scribed on pitot tube

FRM 2 Velocity Equation

$$v_s = K_p C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s\,(avg)}}{P_s M_s}}$$

FRM 5 Sampling Train



Sampling Train Components

- The probe assembly
- The sample box
- The umbilical
- The meter box

The Sample Box

Heated Filter Box

- Heating element to maintain filter temperature of 120° C
- Filter Holder
- Flexibility for vertical and horizontal traverses
- Insulated

Impinger Box

- Provide support and protection for glassware
- Insulated
- Holding container for ice to cool impingers

FRM 5 Heated Filter Box

- Filter heating system capable of maintaining temperature typically 120 C +/- 14 C
- Temperature gauge capable of +/- 3 C
- May be separate from impinger system for convenience





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FRM 5 Heated Filter Box Desired Features

- Light weight, good insulation
- Positive probe alignment locking system
- Easy accessibility to all parts
- Good electrical system
- Durability/flexibility for vertical and horizontal stacks

FRM 5 Impinger System

- Material of construction depends upon compounds being tested
  - Glass, Teflon, stainless steel
- Design should allow for additional space for impingers beyond FRM 5 requirements
- Need for water drain tap

FRM 5 Impinger Assembly















FRM 5 Stainless Steel Impinger Assembly



FRM 5 Filter/Impinger Transport Case



FRM 5 Impinger Case



Problems

- Leak in sampling train:
  low gas volume (correct or void)
- Filter/probe temperature
  not within specification
- Contamination during sampling/recovery
  (nozzle scraps on nipple,
  dust falls on filter)

Problems

- Non-Isokinetics
  - Range outside of 90<I<110
    - If <90, bias high (large particles)
    - If >110, bias low (high sample volume)
  - Multiply E by < 90: corrected does not pass limit: accept test
  - Multiply E by > 110: corrected not greater than limit: accept test

FRM 5 Train Components/pmr Error

- P_{bar}: + 5.9%
- Δp: + 2.4%
- Moisture: + 1.4%
- Nozzle diameter: - 2.0%
- Isokinetic rate: - 5.0%

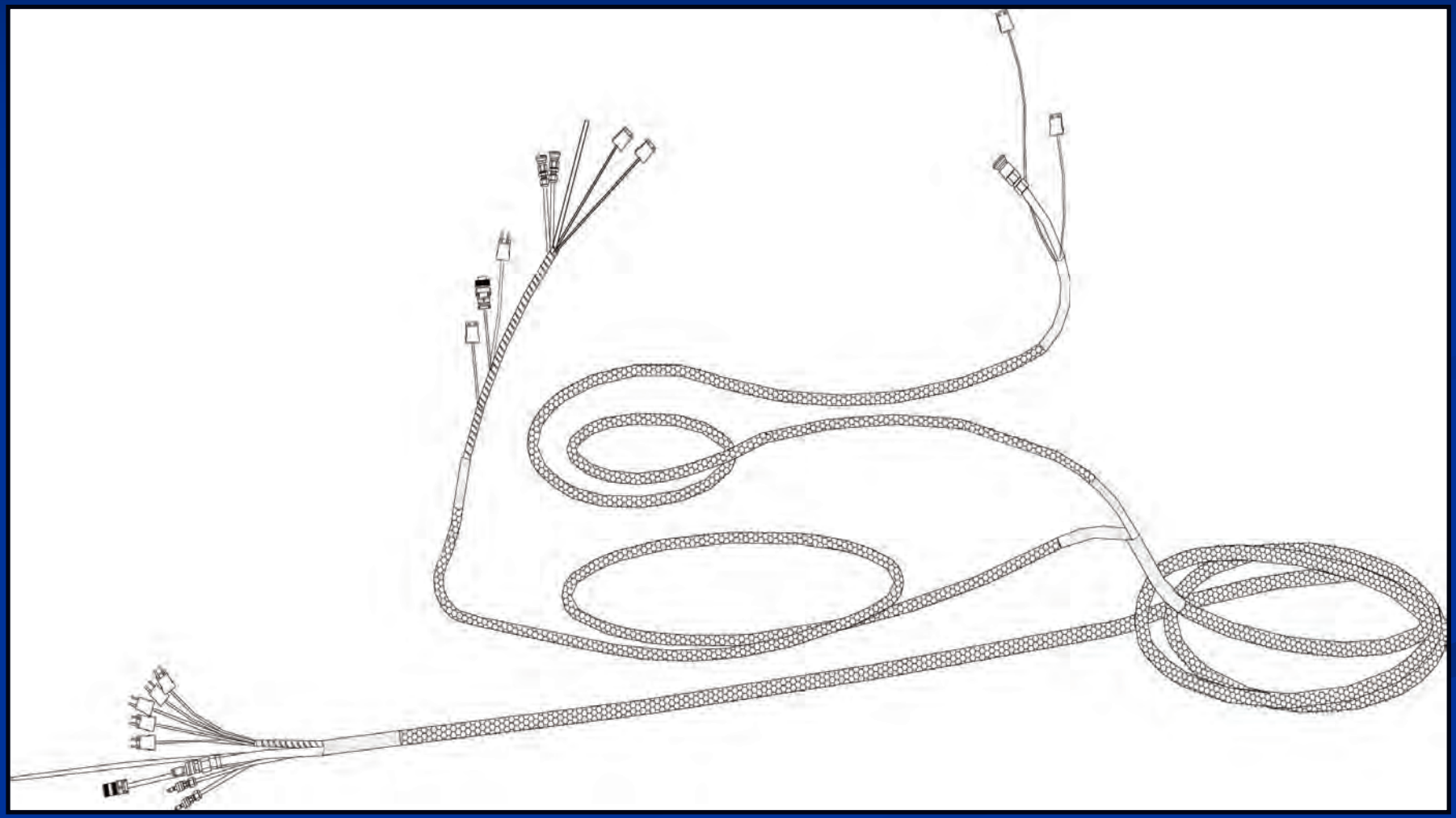
Sampling Train Components

- The probe assembly
- The sample box
- The umbilical
- The meter box

The Umbilical Line

- Sample lines
- Pitot lines
- Electrical connections
- Covered in a protective sheath

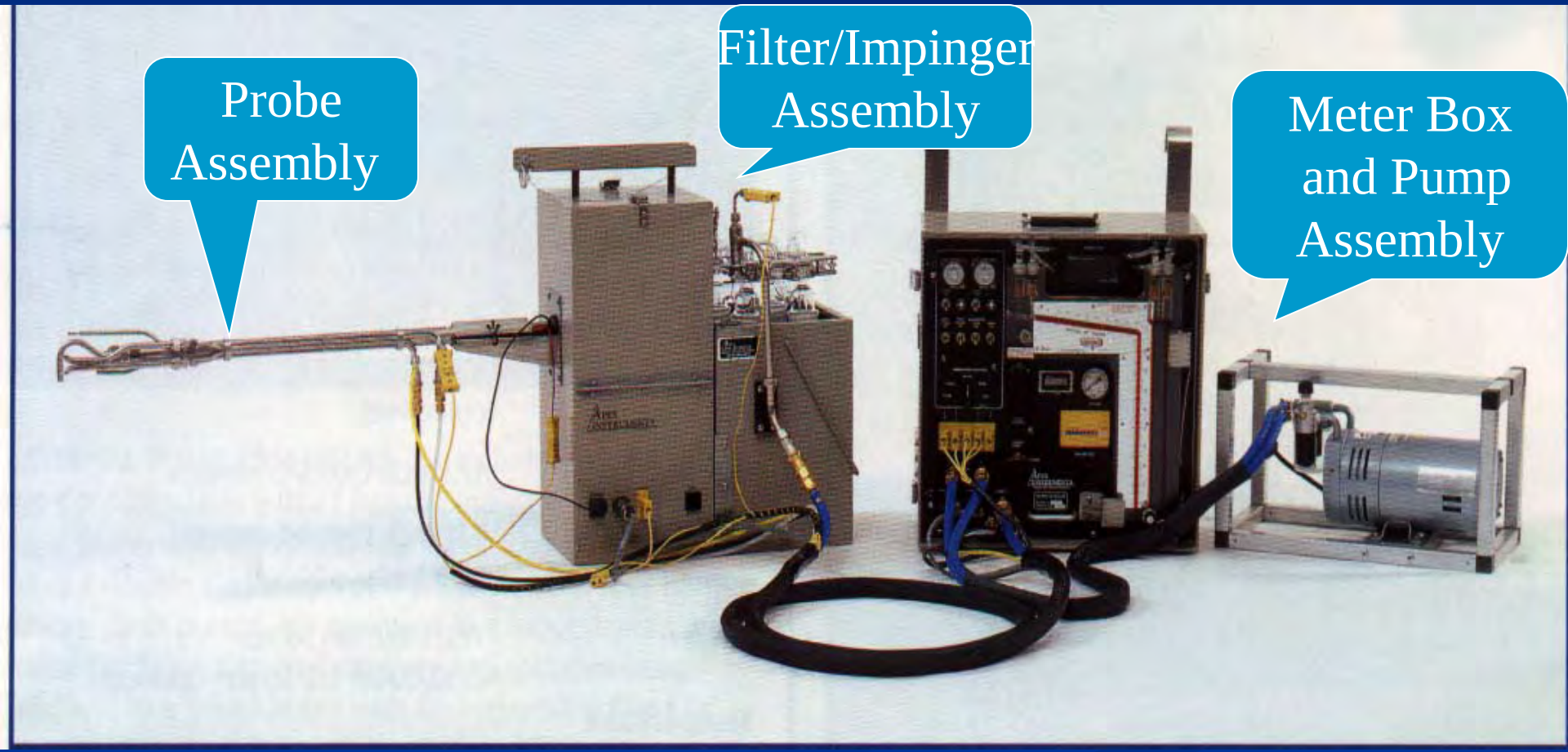
FRM 5 Transfer Line



FRM 5 Sampling Train



FRM 5 Sampling Train



The Meter Box

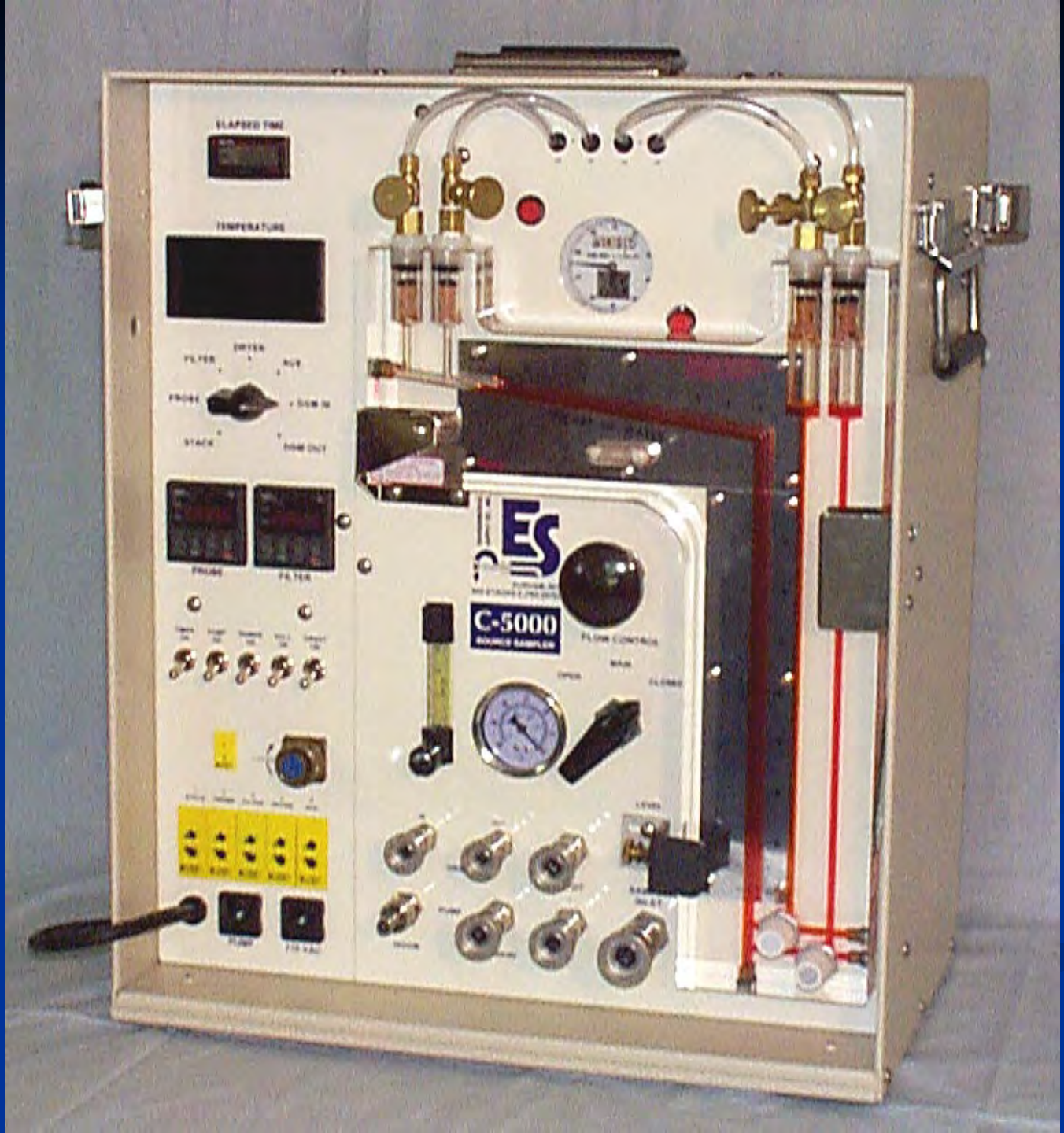
- Pump
- Dry gas meter
- Inclined manometer for Δp and ΔH readings
- Flow control valves
- Ports for integrated gas sampling

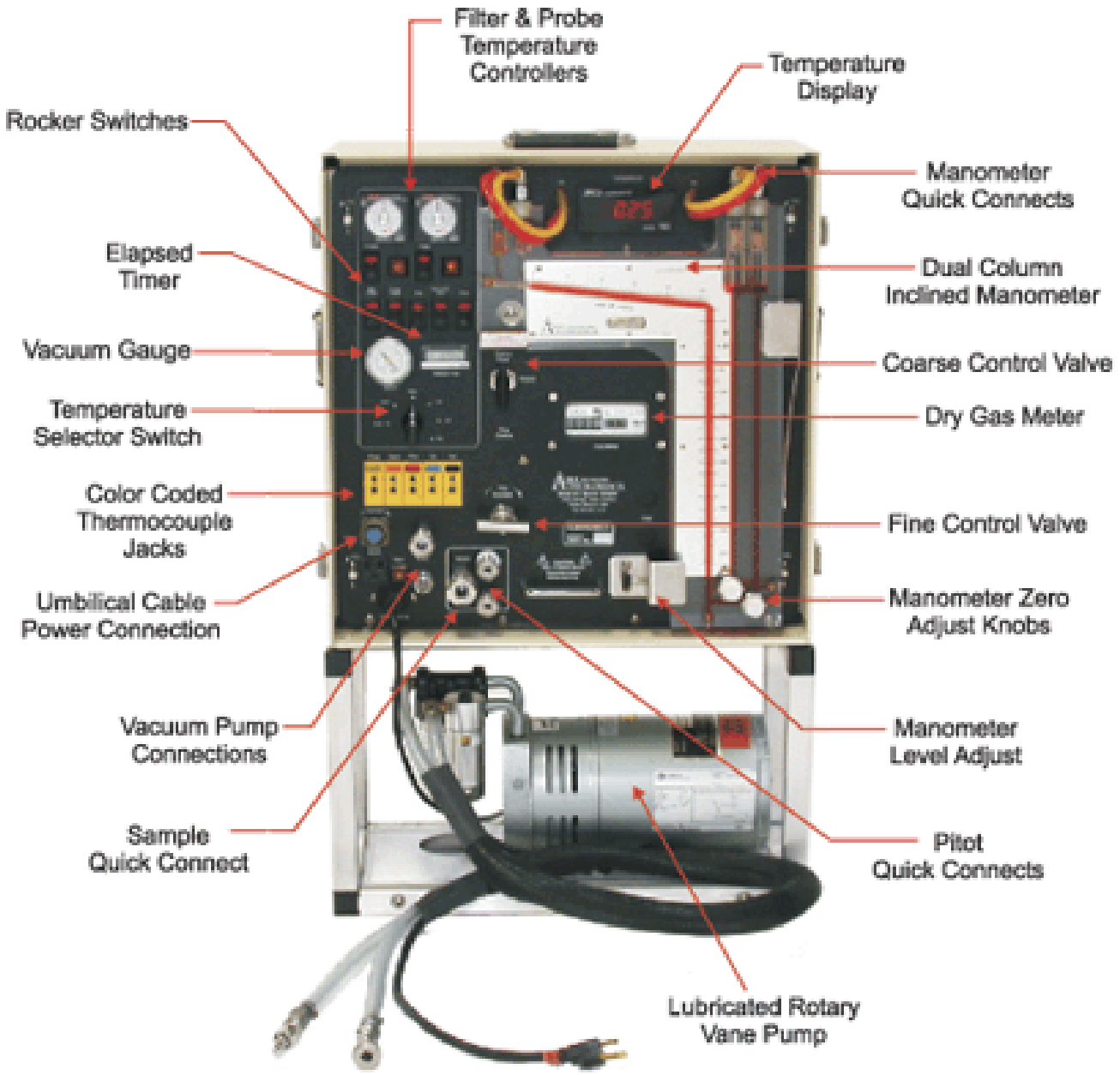
FRM 5 Meter Console Desirable Features

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

FRM 5 Meter Console Desirable Features

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


ELAPSED TIME
TEMPERATURE
C-5000


Filter & Probe Temperature Controllers
Temperature Display
Rocker Switches
Manometer Quick Connects
Elapsed Timer
Dual Column Inclined Manometer
Vacuum Gauge
Coarse Control Valve
Temperature Selector Switch
Dry Gas Meter
Color Coded Thermocouple Jacks
Fine Control Valve
Umbilical Cable Power Connection
Manometer Zero Adjust Knobs
Vacuum Pump Connections
Manometer Level Adjust
Sample Quick Connect
Pitot Quick Connects
Lubricated Rotary Vane Pump




Temperature
JENCO
765
Probe
Filter
INCHES OF WATER
Coarse Open
Flow Control
Gas Meter
Vacuum
Probe
Stack
Filter
Exit
Aux
APEX INSTRUMENTS


Flow Control
Gas Meter
Pump
Sample
CAUTION

FRM 5 Dry Gas Meter



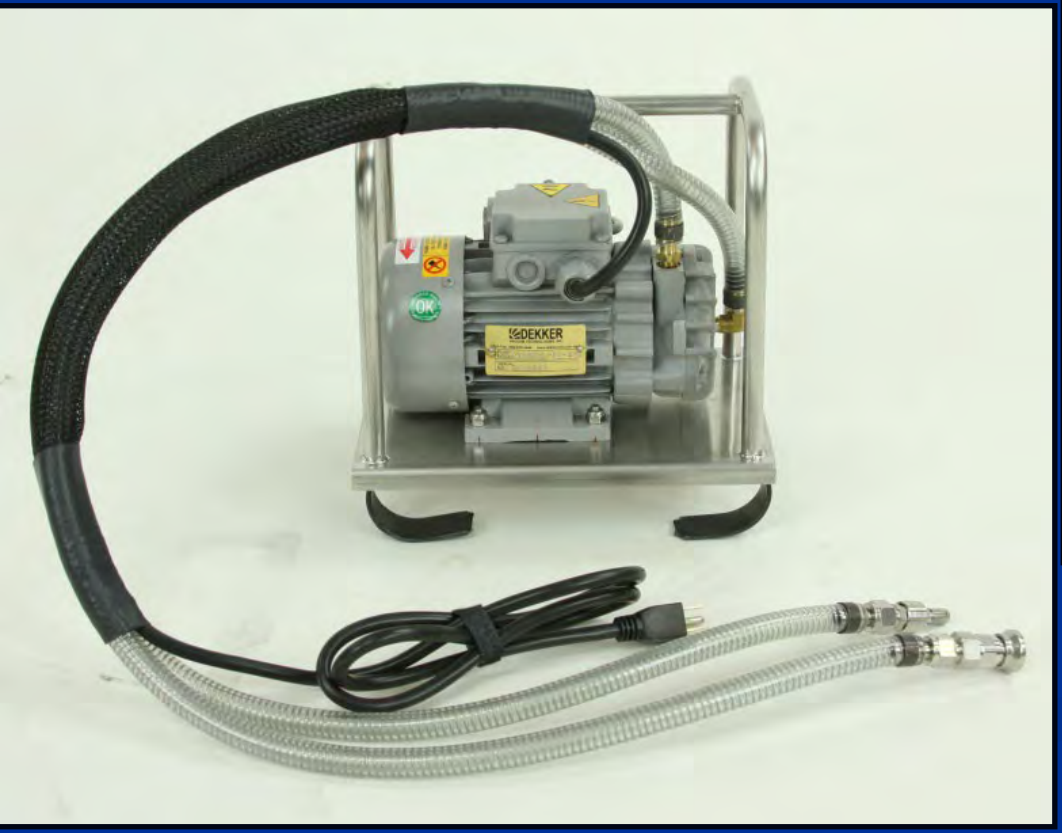

Fine
Increase
Suction
Sample


APEX INSTRUMENTS
Model 522 Source Sampler
Holly Springs, North Carolina
CALIBRATION RESULTS

FRM 5 Digital Meter Box

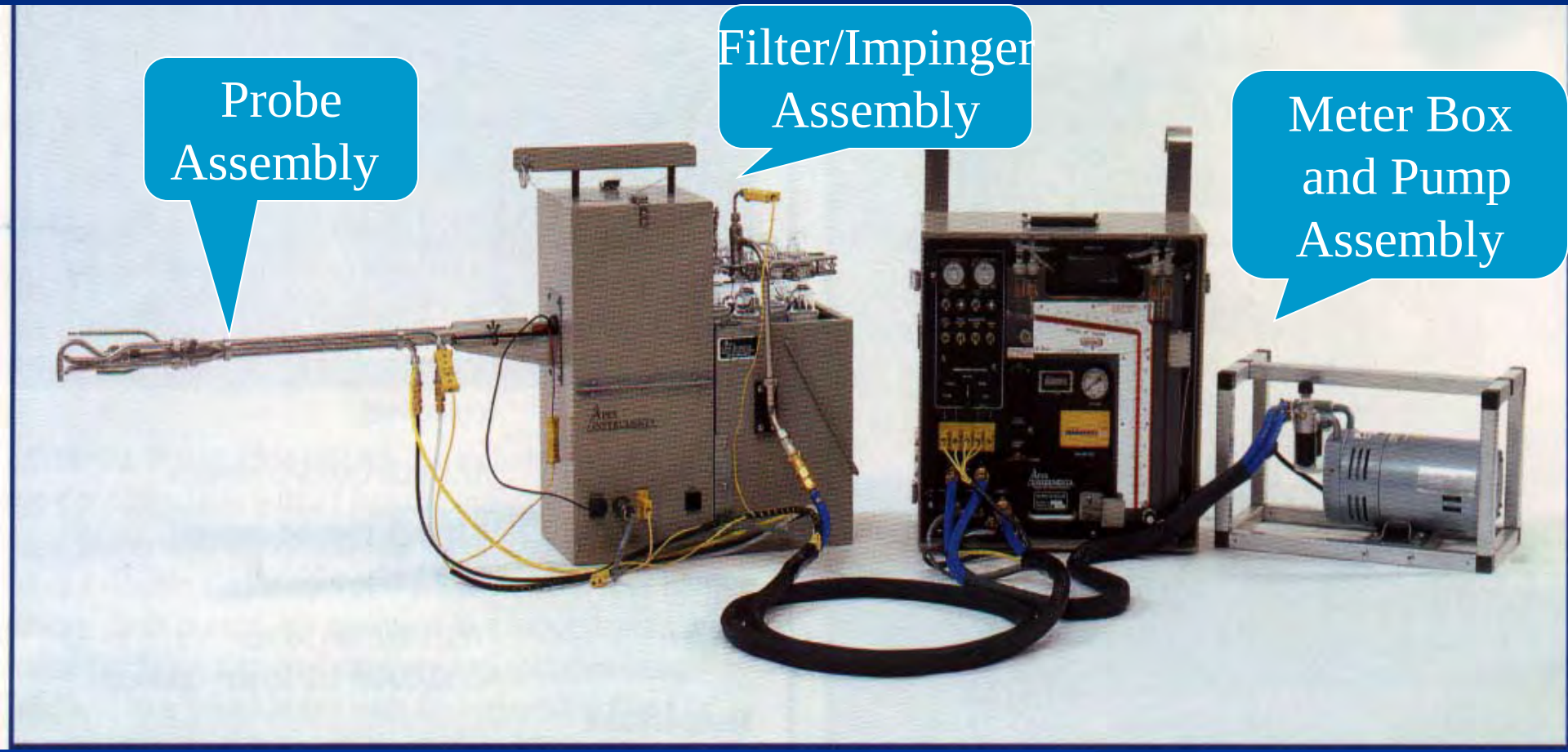


FRM 5 Sampling Pump





FRM 5 Sampling Train



Errors in pmr Calculations Using FRM 5

- T_s: 1.4 %
- DGM: 1.0 %
- P_s: 0.4 %
- P_m: 0.4 %
- P_b: 0.2 %
- B_{ws}: 1.0 % Affects % Iso
- Δ H: 5.0 %
- D_n: 1.0 %
- Delta $H_@$: 1.5 %

What Are the Significant Errors With FRM 5?

- Before obtaining the answer, the tester or observer needs to know three things to determine what is important in significant errors with FRM 5:
  - What is the data to be used for (i.e., proof of compliance, proof of violation, engineering evaluation etc.)?

What Are the Significant Errors With FRM 5?

- Know three things (cont'd):
  - What are the direction and magnitude of any biases?
  - What is the acceptable bias that will be allowed before rejecting the results?

Source Compliance

- If test results show compliance:
  - Any magnitude of bias in the data that increases measured results (high bias), accepted as compliance
  - (10 % for high bias and 5 % low bias)
- If test results shows violation:
  - Any magnitude of bias in the data that shows violation of standard, then test data can contain any level of low bias
  - (10 % for low bias and 5 % for high)

ERROR ANALYSIS OF SAMPLING PARAMETERS

Parameter	True value	Error	Erroneous value	Concentration (%)[a]	Q_s	Qs_{std}	Pollutant mass rate (%)[b]	Requirement
P_{bar}	30 in. Hg	1 in. Hg	31 in. Hg	+ 4.1	-1.6	+1.6	+5.9	±0.1 in. Hg
ΔH	30 in. Hg	1 in. H_2O	30.07 in. Hg	+ 0.2	-[c]	-[c]	+0.2	none
tm	528°R	5°R	533°R	- 0.9	-[c]	-[c]	-0.9	±5.4°F
Ps	30 in. Hg	2 in. H_2O	30.15 in. Hg	+ 0.1	-0.2	+0.2	+0.3	±1.36 in. H_2O
ts	600°R	10°F	610°R	- 0.4	+0.8	-0.8	-1.2	±1.5%
Δp	1 in. H_2O	0.1 in. H_2O	1.1 in. H_2O	- 2.5	+4.9	+4.9	+2.4	equip. spec.
Moisture	10%	1%	11%	+ 0.1	-0.2	+1.3	+1.4	±1%
Md	29	1% CO_2	29.15	+ 0.1	-0.3	+0.3	+0.4	±0.1%
Md	29	1% O_2	29.03	+ 0.1	-0.1	+0.1	+0.2	±0.1%
Md	29	1% CO	29	-	-[c]	-[c]	-	±0.1%
Mn	100 mg	1 mg	101 mg	1.0	-[c]	-[c]	1.0	±0.5 mg
Time	120 min	1 min	121 min	- 0.4	-[c]	-[c]	-0.4	none
Y	1.00	0.01	1.01	- 1.0	-[c]	-[c]	1.0	±2%
Cp	0.84	0.01	0.85	- 0.6	+1.2	+1.2	+0.6	±0.03
Nozzle diameter	0.250 in.	0.005 in.	0.255 in.	- 2.0	-[c]	-[c]	-2.0	±0.002 in.
Isokinetic	100%	10%	110%	- 5.0[d]	-[c]	-[c]	-5.0	±10%
F factor	5% O_2	1% O_2	6% O_2	+ 6.7[d]	N/A[e]	N/A[e]	N/A[e]	±0.1% O_2
F factor	10% O_2	1% O_2	11% O_2	+10.1[d]	N/A[e]	N/A[e]	N/A[e]	±0.1% O_2
F factor	15% O_2	1% O_2	16% O_2	+20.4[d]	N/A[e]	N/A[e]	N/A[e]	±0.1% O_2

Note: All errors are a theoretical calculation and it is assumed that a 2% error in isokinetics will cause a 1% error in both concentration and pollutant mass rate emissions. The percentage of error may vary slightly depending on the magnitude of the true value and the different assumptions made.

[a] Error due to calculation and combined isokinetic bias.

[b] Error due to calculation and combined isokinetics bias.

[c] No effect on the measured value.

[d] Lb/10^6 Btu is actually a concentration standard.

[e] N/A - not applicable.

Example #1 (Stack Temperature)

- Asphalt plant with concentration standard of 0.04 g/scf
- Team measured stack temperature at 350 F, but correct temperatlure was 320 F
- Question: How much error?
  - From Table, -0.4 %/10 F
  - Therefore, -1.2 % total error
  - Little effect!

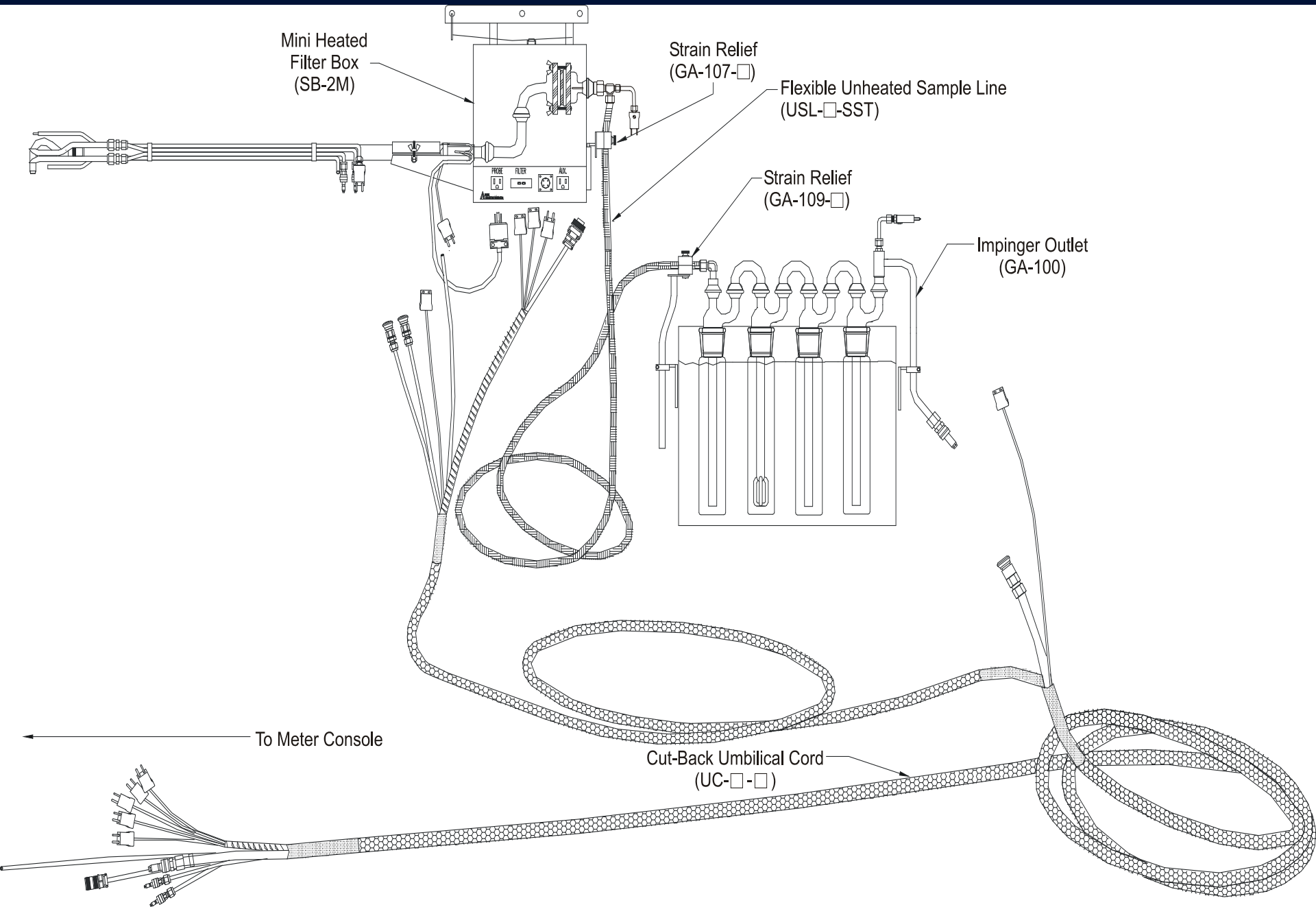
Example #2 (Orifice Meter)

- Dry dog food plant
- Allowable mass emissions 5 lbs/hr
- DGM "Y" determined to be 0.91, but tester using 0.97
  - From Table, 1.0 % error for each 0.10
  - Therefore, 6 % bias high error
  - May want to reject test!

Calibration Laboratory for DGM "γ" and Orifice Meter "ΔH@" Determinations



FRM 5 Flex Train

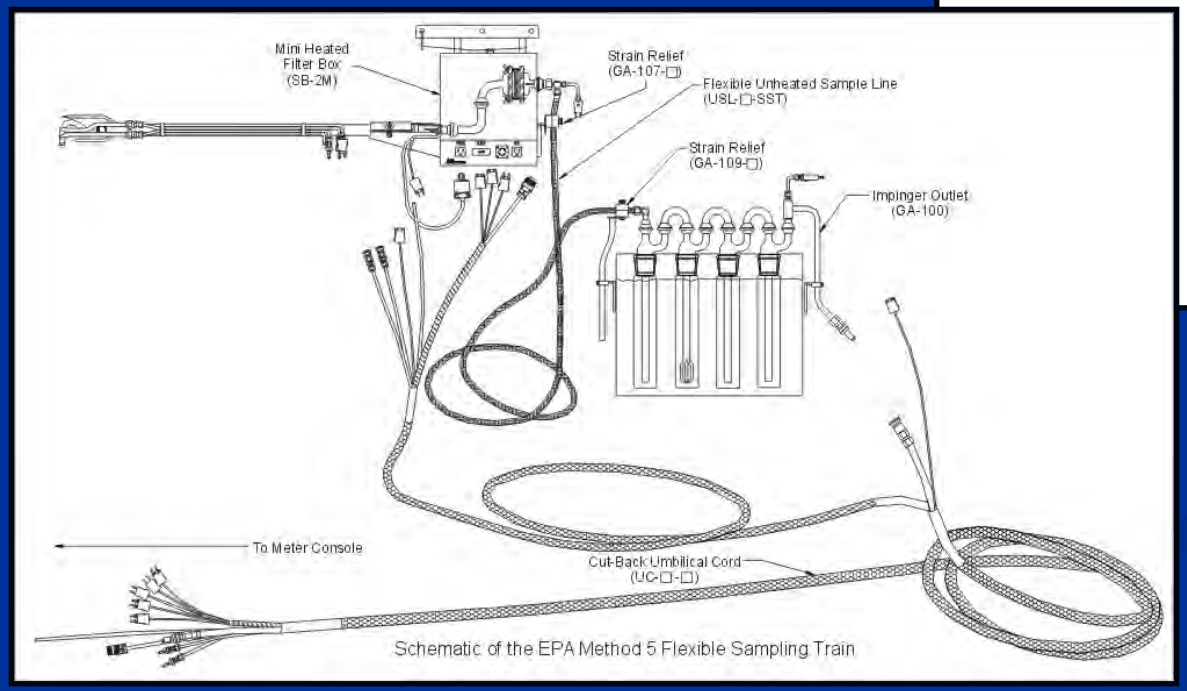






FRM 5 Flex Train

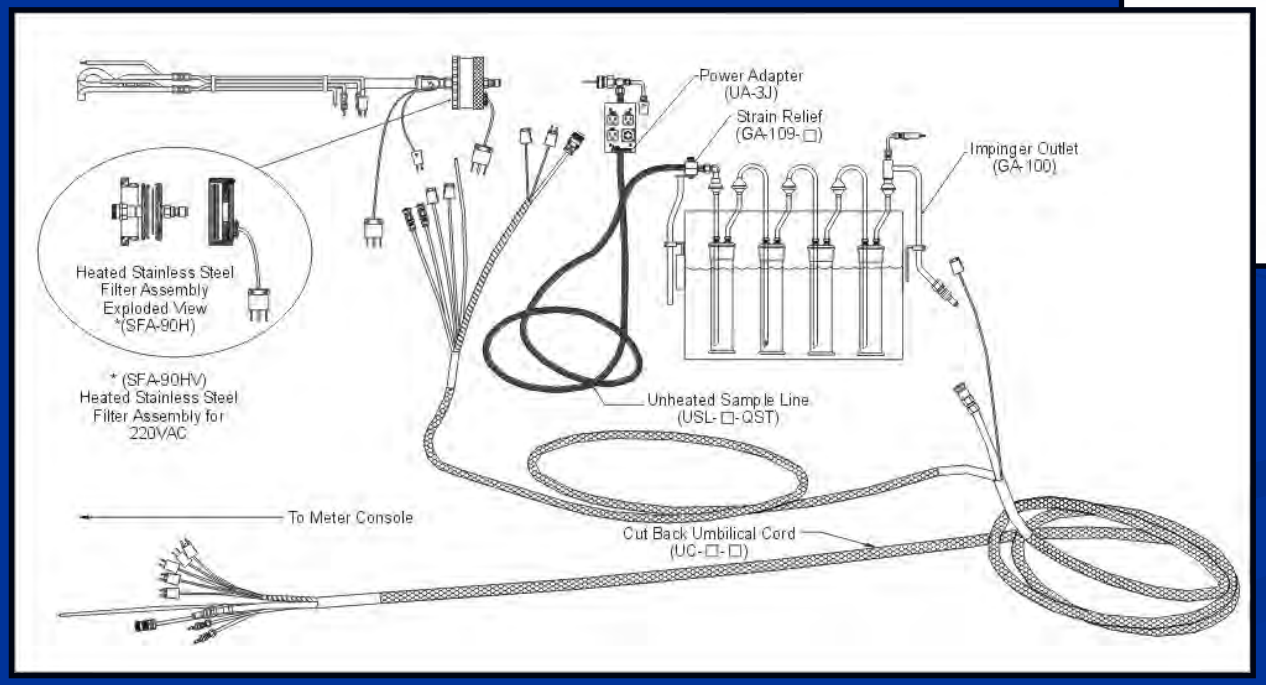




Schematic of the EPA Method 5 Flexible Sampling Train

FRM 5 Compact Train





FRM 5 Recovery

- Note final DGM reading
- Leak check sampling system
- Remove probe from sampling train
- Sample train removed to recovery area
- Nozzle removed and brushed 3-6X with acetone into sample bottle

FRM 5 Recovery

- Probe brushed and rinsed with acetone 3-6X into sample bottle
- Front half of filter brushed and rinsed with acetone into sample bottle with nozzle/probe rinse
- Filter removed carefully and placed into petri dish. Filter disc scrapped to remove filter particles which are added to dish

FRM 5 Recovery

- Liquids in impingers measured either by weight or volume-normally discarded. Can be saved if further analysis required
- Silica gel weighed either in impinger or returned to sample jar

FRM 5 Sample Recovery Items





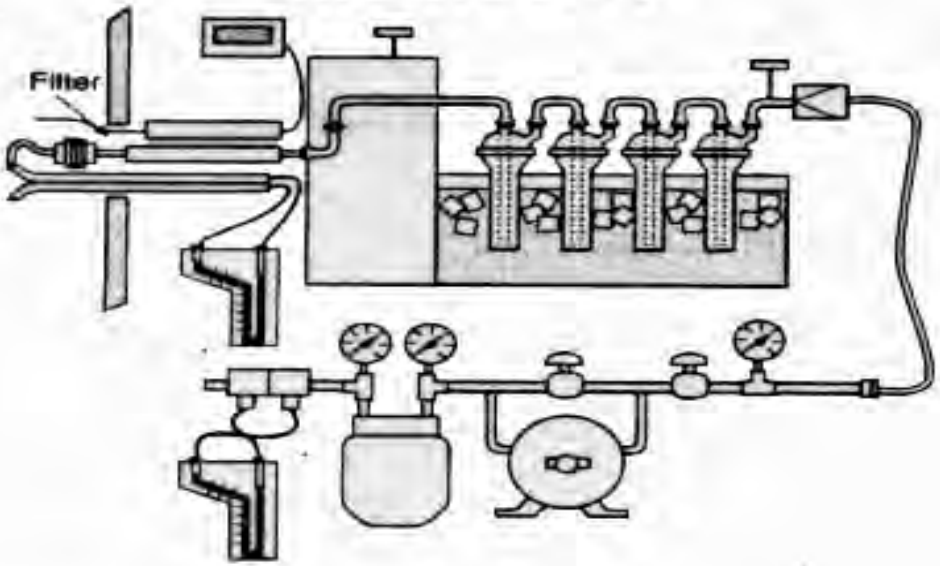




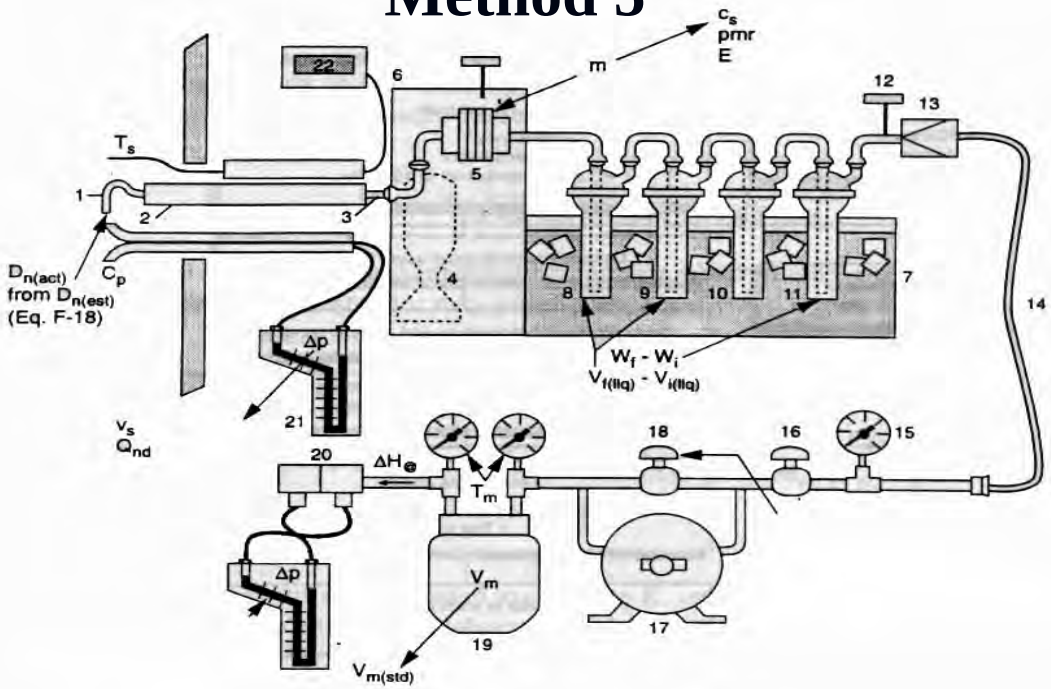




Method 17



Method 5

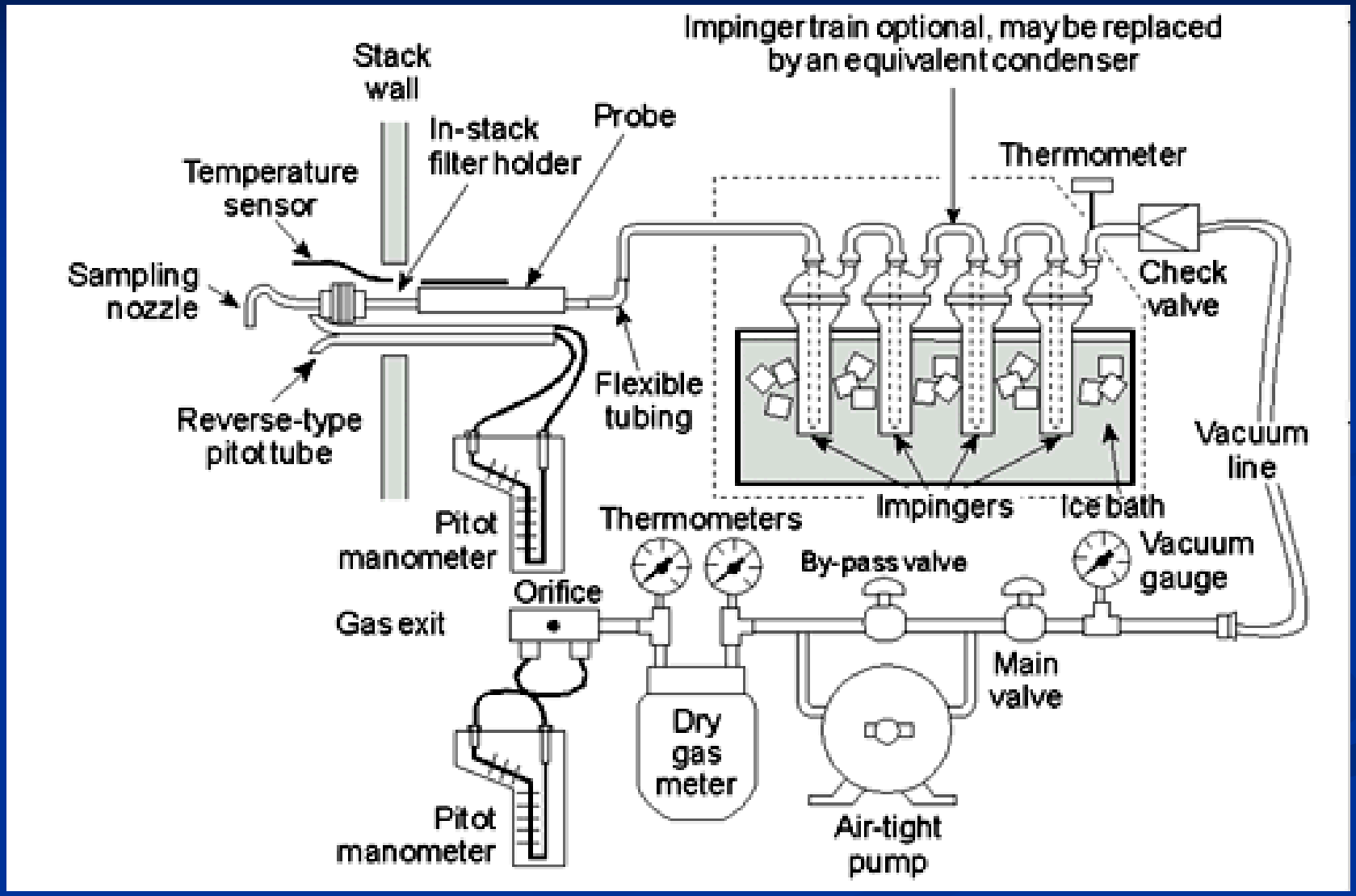


Method 17

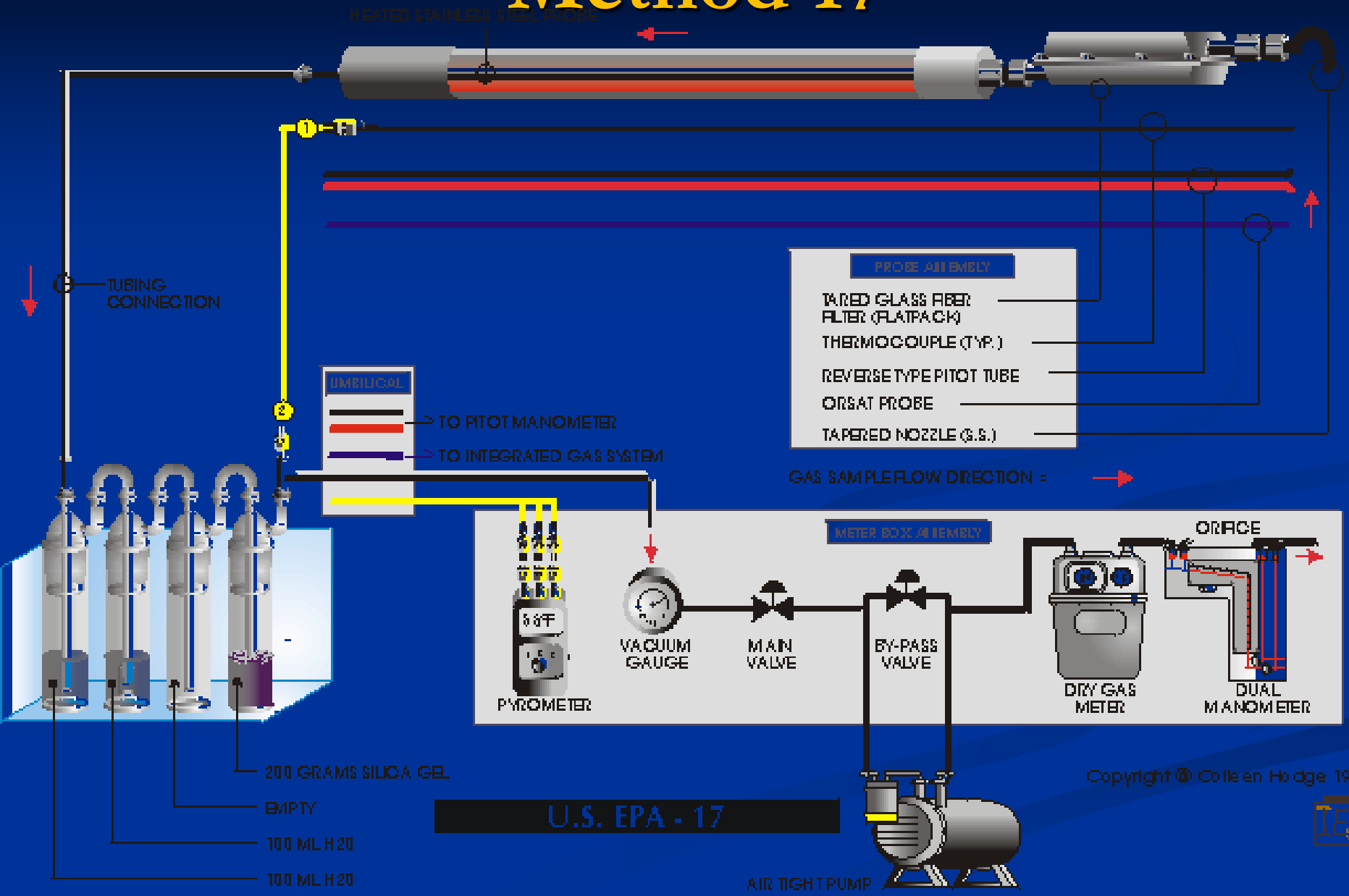
In-stack Filter Applicability

In sources where particulate matter concentration is independent of temperature

FRM 17


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
In-stack filter holder
Probe
Temperature sensor
Thermometer
Sampling nozzle
Check valve
Reverse-type pitot tube
Flexible tubing
Vacuum line
Pitot manometer
Thermometers
Impingers
Ice bath
By-pass valve
Vacuum gauge
Orifice
Gas exit
Main valve
Dry gas meter
Pitot manometer
Air-tight pump

Method 17



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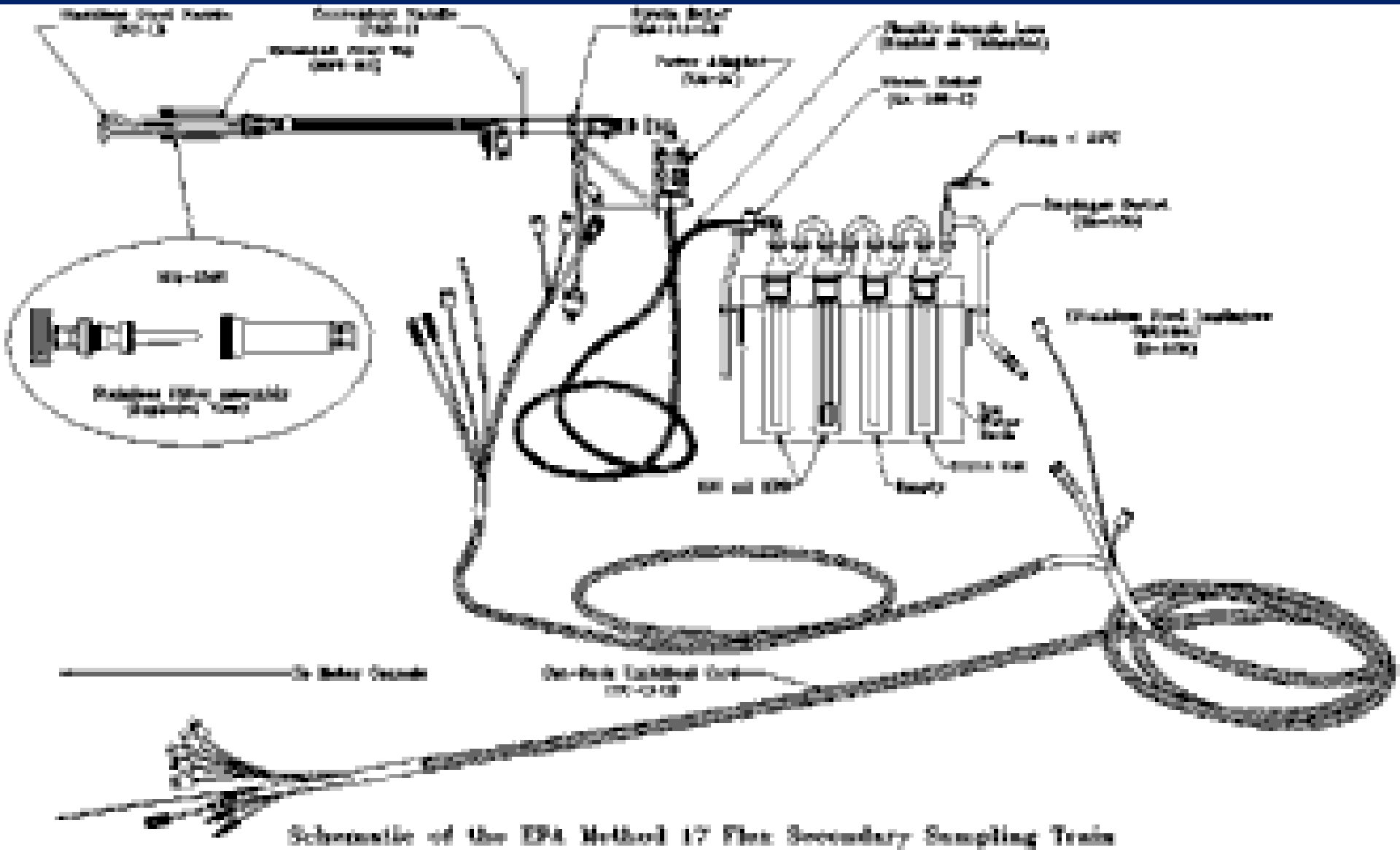
FRM 17 In-stack Filters



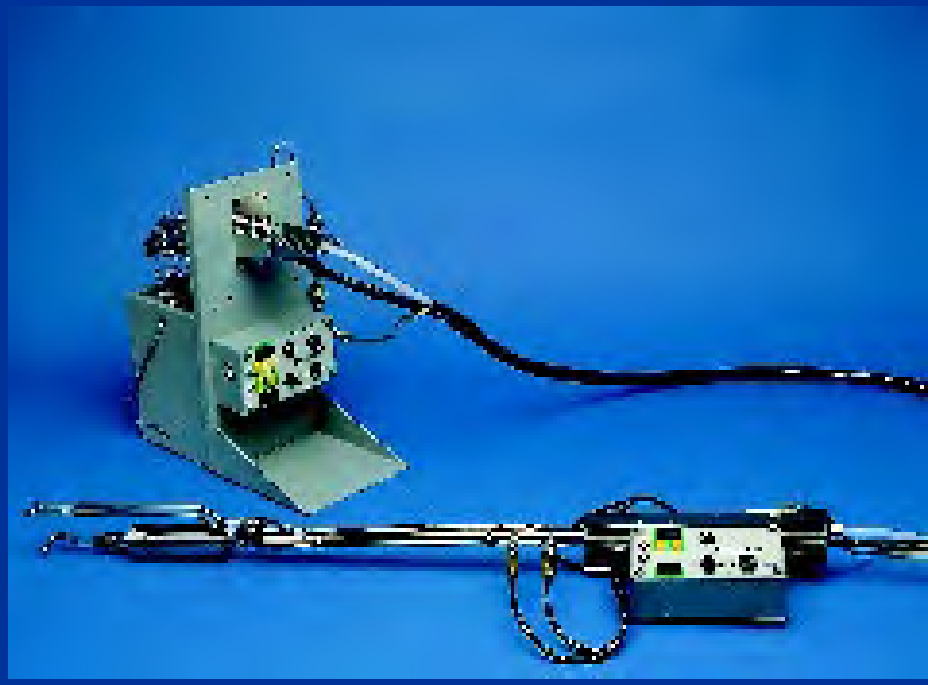
FRM 17 Flex Train



Automatic Federal Reference Method 5 (AFRM5)

Automatic Sampling Train "AST"





AST Features

- Automatically adjust isokinetic rates
- Automatically records flow rates, temperatures, and pressures
- Calculates all data; no manual manipulation
- Available in Method 5 or Method 17 configurations

AST Benefits

- No mistake sampling
- All calculations are microprocessor-based
- No manual data, no recording errors
- Results = time and money savings

AST

- Same components as typical Method 5
- Probe with various liner materials heated by 48 volts DC
- Sample box/ice bath contains node boxes for control of heaters and sensors for temperature and pressure

AST

- Glassware
  - “Standard” impingers
- Umbilical cable
  - Carries electronic signal and sample gas
- Control console
  - Houses microprocessor, pump, gas meter, and transformer

AST Applicable Methods

- Any isokinetic test procedure
  - Particulates - Method 5 or 17
  - Aerosol mists - Method 8
  - Fluorides - Method 13A or B
  - Halides and halogens - Method 26A
  - Metals - Method 29
  - PCDD/PCDFs - Method 23

AST Applications

- Aluminum industry primary reduction plant sources include
  - "Pot" line roof vent monitors Method 14 for HF - long duration test procedure usually over 24 hours
  - AST can provide unattended operation over entire test

Other AST Aluminum Applications

- Carbon bake
  - Method 315 for organics - tests are 2-4 hours duration
- Baghouse/scrubbers
  - Numerous test locations with long duration

AST Aluminum Applications

- Eliminates data calculation errors
- No increased labor requirements
- Use of AST has improved data quality

AST Applications

- Power plants
  - Used for Method 5 or Method 17 particulates flow rate RATA's
- Chemical process
  - All EPA methods, plus some research and development

AST Measurements

- Automatically monitors and displays
  - Stack gas temperature
  - Velocity pressure of stack gases
  - Absolute stack gas pressure
  - Stack gas flow rate
  - Sample gas flow and volume
  - Percent isokinetic

Method 5I Low PM Concentrations

- Initial Federal Register notice - December 30, 1997
- FRM 5I promulgation in 1999 with Maximum Achievable Control Technology (MACT) Hazardous Waste Incinerator (HWI) Rule
- EPA contact: Dan Bivins (919) 541-5244

Method 5I Low PM Concentrations

- Validated for Hazardous Waste Incinerators (HWI)
- Application - Calibrating PM CEMS
- Accuracy improved through:
  - Improved sampling handling procedures
  - Light weight sample filter assembly which is weighted entirely
  - Use of low residue grade acetone

Method 5I Low PM Concentrations

- Description
  - Isokinetic sampling using FRM 5 sampling equipment
  - Paired sampling trains
  - Lightweight out-of-stack filter (47 mm) assembly in FRM 5 hot box
  - Entire filter assembly weighing
  - Design for stack with < 50 mg PM (below 45 mg/dscm, ~0.02 gr/dscf)

Method 5I Low PM Concentrations

- Components:
  - Pyrex filter inlet
  - Viton seal ring
  - 47-mm filter paper
  - Stainless steel filter frit
  - 47-mm stainless steel clamp
  - Held together by Teflon tape seal
- Designed to be weighted as a single unit

Method 5I Low PM Concentrations

- Limits for FRM 5
  - Practical quantitation limit (PQL) of 3 mg
  - Methdod detection limit (MDL) of 1 mg
- Therefore, the target catch must be > 3 mg by adjusting sampling time or sampling rate

FRM Method 5I Potential Interferences

- Attention to filter housing during handling, sampling, and port changes
- Balance room conditions
  - Relative humidity < 50 %
  - Same person perform weighting before and after test
  - Electrostatic charges minimized during sample weighting

FRM Method 5I Quality Control (QC) Requirements

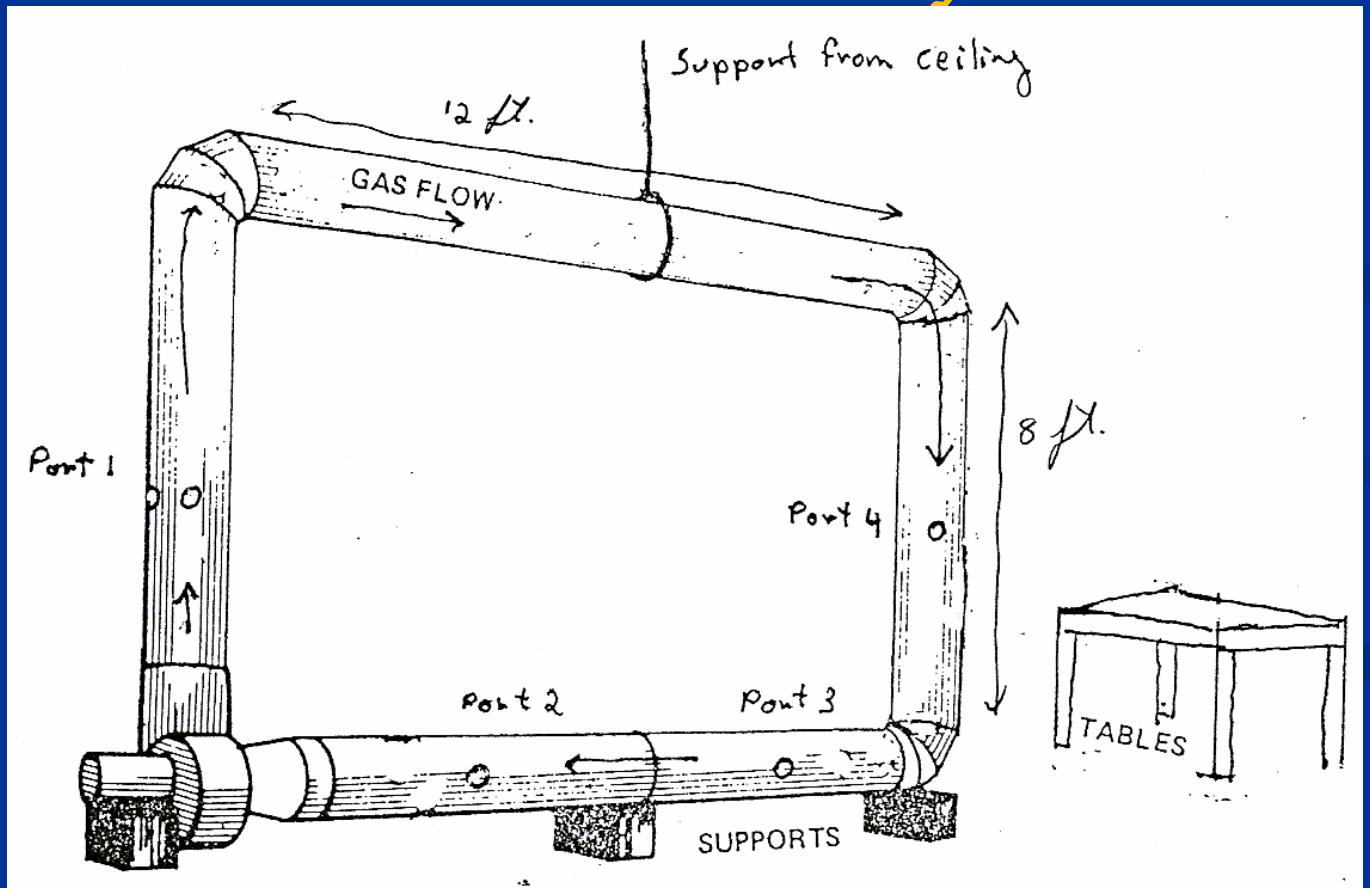
- Same as FRM 5
- Recommended field bias blank train. Similar train, taken to field, prepared, leak checked, and recovered but no sampling of source emissions
- Relative standard deviation
  - RSD=100% $|(C_a-C_b)|/(C_a+C_b)$
  - Acceptable limits of < 10%

FRM 5 Sampling Train



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

Review of Laboratory Exercise





Ten (10) Laboratory Stations

- Station #1: Nozzle Diameters
  - All readings within 0.004 inches
- Station #2: DGM γ Determination
  - Temperature ° R
- Station #3: Orifice ΔH@ Determination
  - Temperature ° R

Ten (10) Laboratory Stations

- Station #4: Stack Gas Velocity and Volumetric Flow Rate
  - Assume Traverse Points from Station # 10
  - Assume Bws = 3 %, Md = 30, Ts = 75 ^{o}F
- Station #5: Pitot Tube Calibration
  - Sample point is 6 inches into duct

Ten (10) Laboratory Stations

- Station #6: Stack Gas Moisture
  - Three Methods
    - Wet Buld/Dry Bulb Calculations
    - Nomograph
    - Psychrometric Chart
- Station #7: Pitot tube Inspection
  - Keep Pitot Tube Level

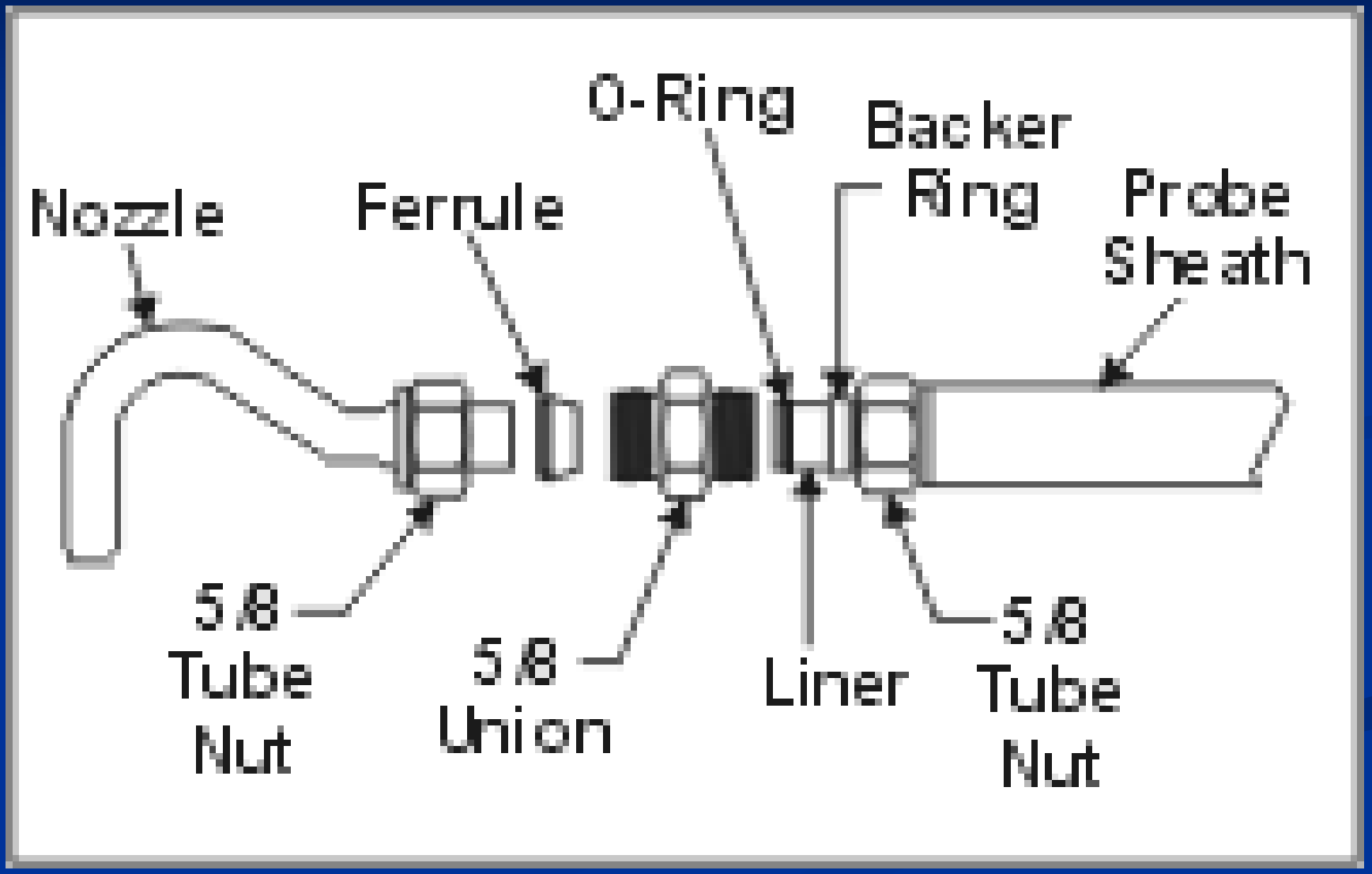
Ten (10) Laboratory Stations

- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: Traverse Point Determination
  - Use 12-24 inch diameter stack

Classroom Stations

- Station #1: Nozzle Diameters
  - All readings within 0.004 inches
- Station #2: DGM γ Determination
  - Temperature ° R
- Station #3: Orifice ΔH@ Determination
  - Temperature ° R

Sampling Nozzle













FRM 5 Sample Nozzle

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

FRM 5 Isokinetic Rate Equation (Simplified)

$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

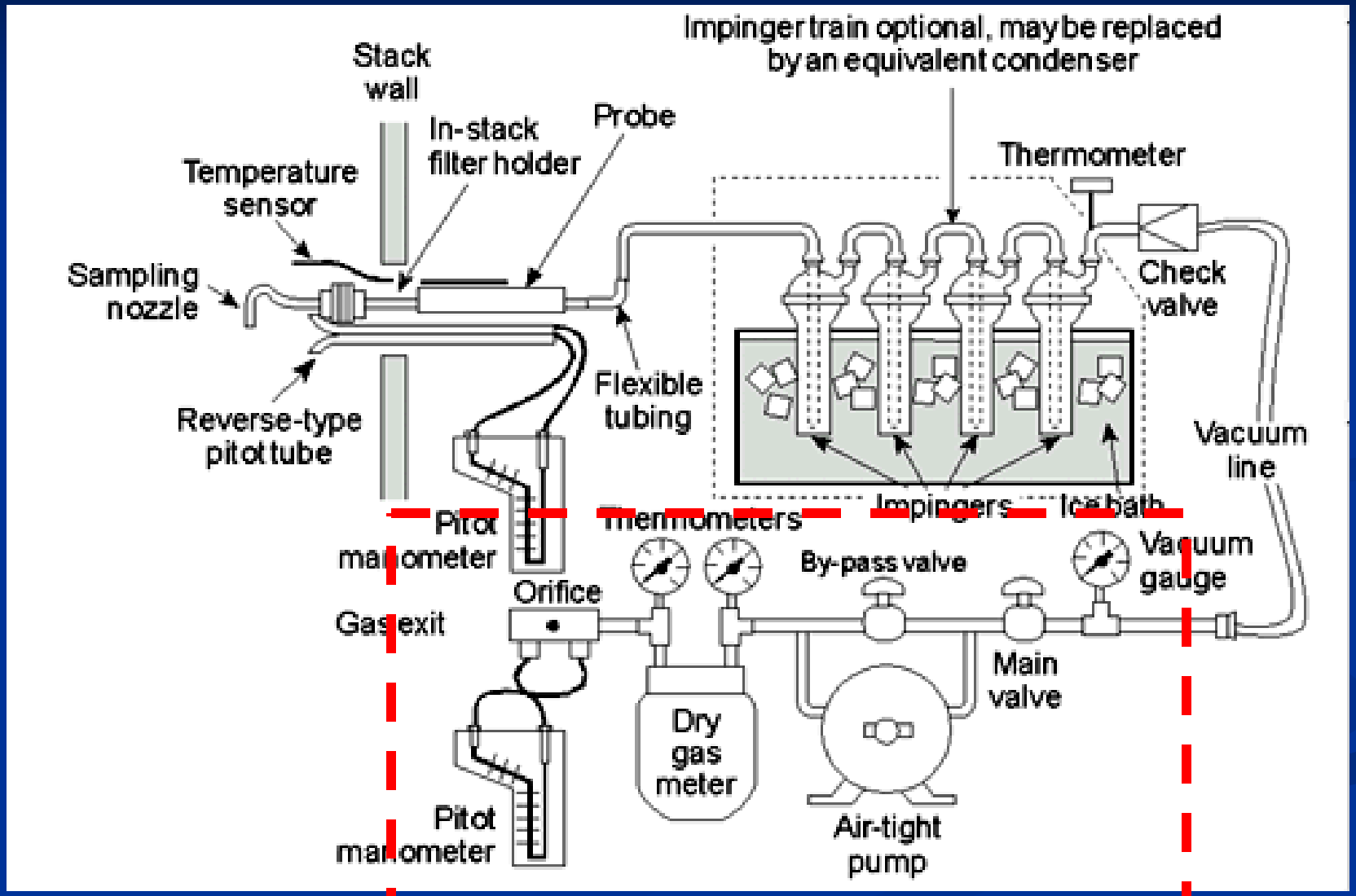
$$\Delta H = \left\{ 846.72\, D_n^{\,4}\, \Delta H_@\, C_p^{\,2} (1 - B_{ws})^2 \quad \frac{M_d}{M_s} \frac{T_m}{T_s} \frac{P_s}{P_m} \right\} \Delta P$$



Classroom Stations

- Station #1: Nozzle Diameters
  - All readings within 0.004 inches
- Station #2: DGM γ Determination
  - Temperature º R
- Station #3: Orifice ΔH@ Determination
  - Temperature º R

Meter Box


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
In-stack filter holder
Probe
Temperature sensor
Thermometer
Sampling nozzle
Check valve
Flexible tubing
Reverse-type pitot tube
Vacuum line
Impingers
Ice bath
Pitot manometer
Thermometers
By-pass valve
Vacuum gauge
Orifice
Gas exit
Main valve
Dry gas meter
Pitot manometer
Air-tight pump


Flow Control
Gas Meter
Pump
Sample
CAUTION




Memorex
FORMATTED
FORMATEE
2SHD




Fine
Increase
Suction
Sample

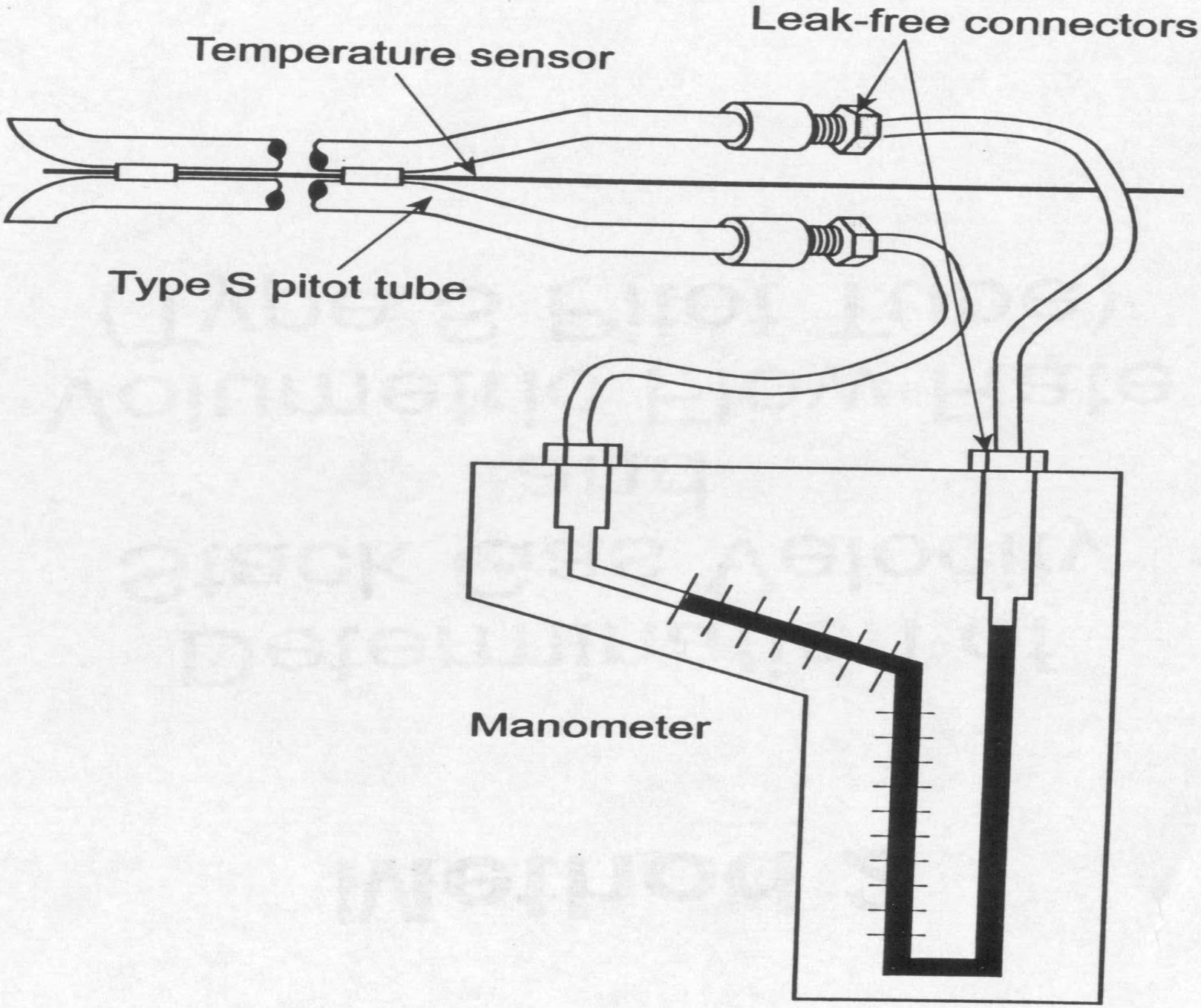

APEX INSTRUMENTS
Model 522 Source Sampler
Holly Springs, North Carolina
CALIBRATION RESULTS


'04 3 25

Classroom Stations

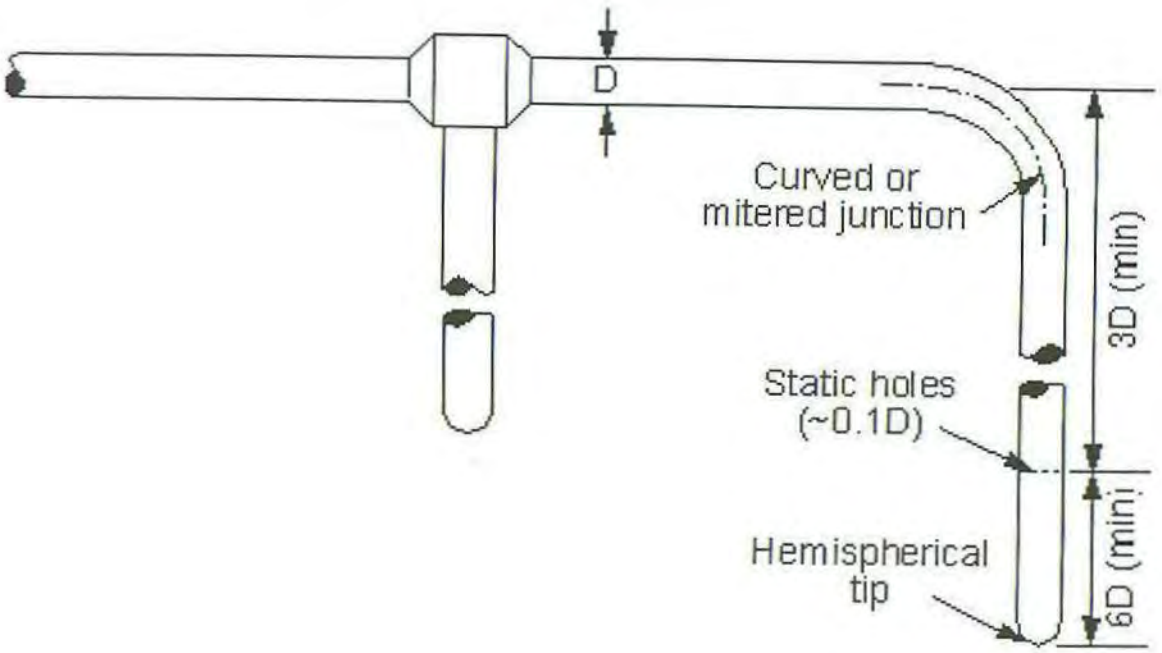
- Station #4: Stack Gas Velocity and Volumetric Flow Rate
  - Assume Traverse Points from Station # 10
  - Assume Bws = 3 %, Md = 30, Ts = 75 °F
- Station #5: Pitot Tube Calibration
  - Sample point is 6 inches into duct



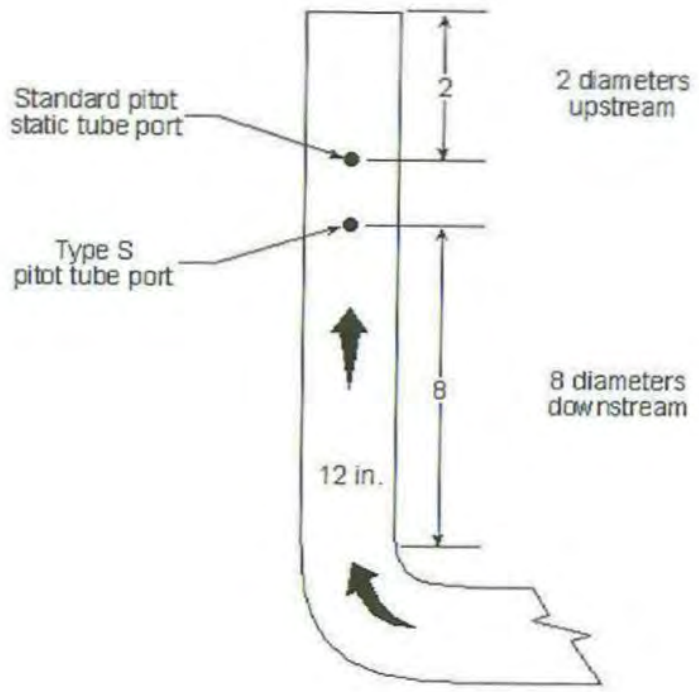

Leak-free connectors
Temperature sensor
Type S pitot tube
Manometer

Pitot Tube Calibration

Calibrate in wind tunnel against standard pitot tube


D
Curved or
mitered junction
3D (min)
Static holes
(~0.1D)
Hemispherical
tip
6D (min)

Calibration Duct



PITOT TUBE IDENTIFICATION NUMBER: _____ DATE: _____

CALIBRATED BY: _____

	"A" SIDE CALIBRATION			
RUN NO.	Δ_{Pstd} cm H_2O (in. H_2O)	$\Delta_{P(s)}$ cm H_2O (in. H_2O)	$C_{p(s)}$	DEVIATION $C_{p(s)} - \bar{C}_p(A)$
1				
2				
3				
		$\bar{C}_p$ (SIDE A)		

	"B" SIDE CALIBRATION			
RUN NO.	Δ_{Pstd} cm H_2O (in. H_2O)	$\Delta_{P(s)}$ cm H_2O (in. H_2O)	$C_{p(s)}$	DEVIATION $C_{p(s)} - \bar{C}_p(B)$
1				
2				
3				
		$\bar{C}_p$ (SIDE B)		

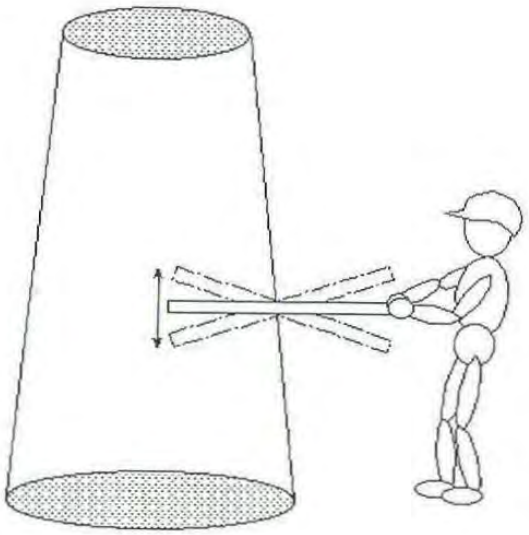
$$\text{AVERAGE DEVIATION} = \sigma\,(\text{A OR B}) = \frac{\sum_{1}^{3} \left| C_{p(s)} - \bar{C}_p(\text{A OR B}) \right|}{3} \leftarrow \text{MUST BE} \leq 0.01$$

$$\left| \bar{C}_p\,(\text{SIDE A}) - \bar{C}_p\,(\text{SIDE B}) \right| \leftarrow \text{MUST BE} \leq 0.01$$

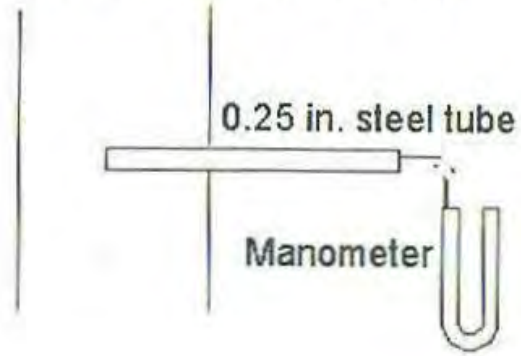
Figure 2-9. Pitot tube calibration data.

$$C_{p(s)} = \left[\frac{\Delta p_{std}}{\Delta p_s} \right]^{1/2} C_{p(std)}$$

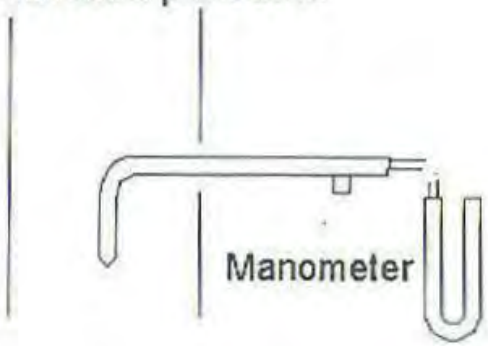
Careful of Pitch Angle



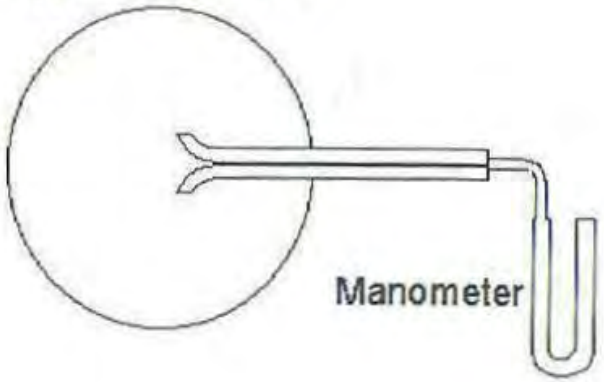
Pressure probe and gauge



Standard pitot tube



Type S pitot tube



$$P_s = P_b + \frac{P_g}{13.6}$$

Classroom Stations

- Station #6: Stack Gas Moisture
  - Three Methods
    - Wet Bulb/Dry Bulb Calculations
    - Nomograph
    - Psychrometric Chart
- Station #7: Pitot tube Inspection
  - Keep Pitot Tube Level

Stack Gas Moisture Approximation Methods

- Used to estimate percent moisture
- Wet bulb- dry bulb
- Partial pressure technique

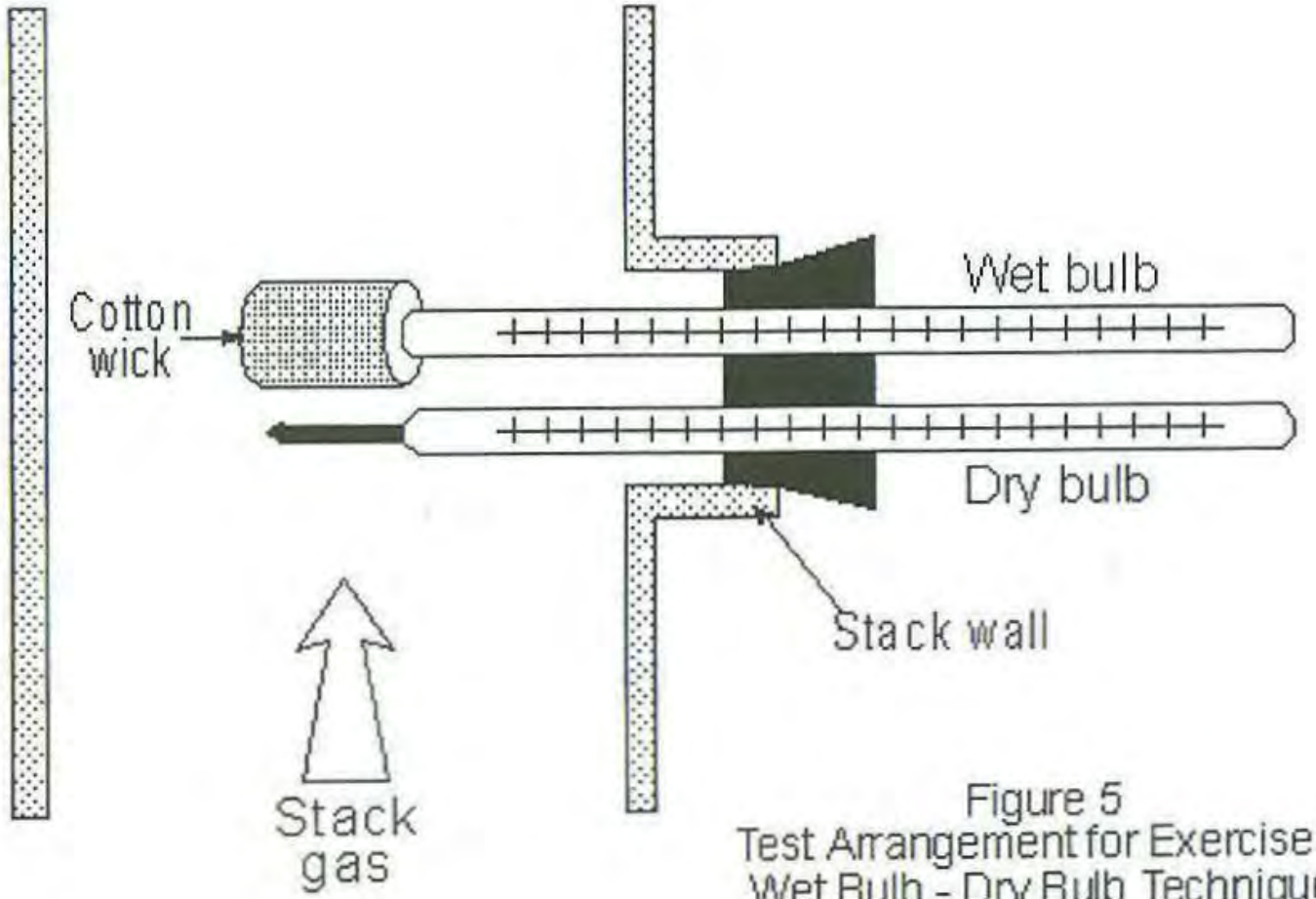
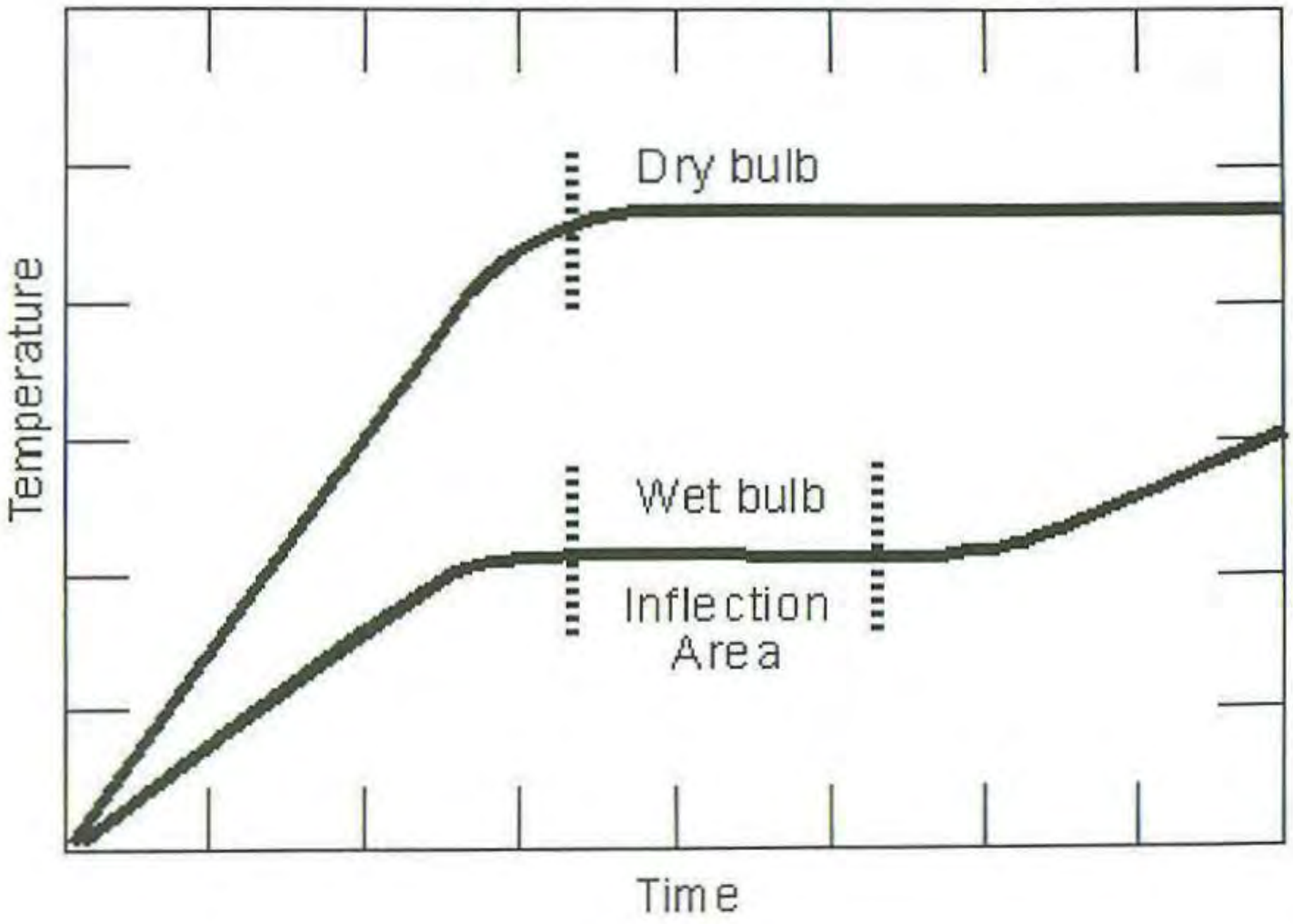
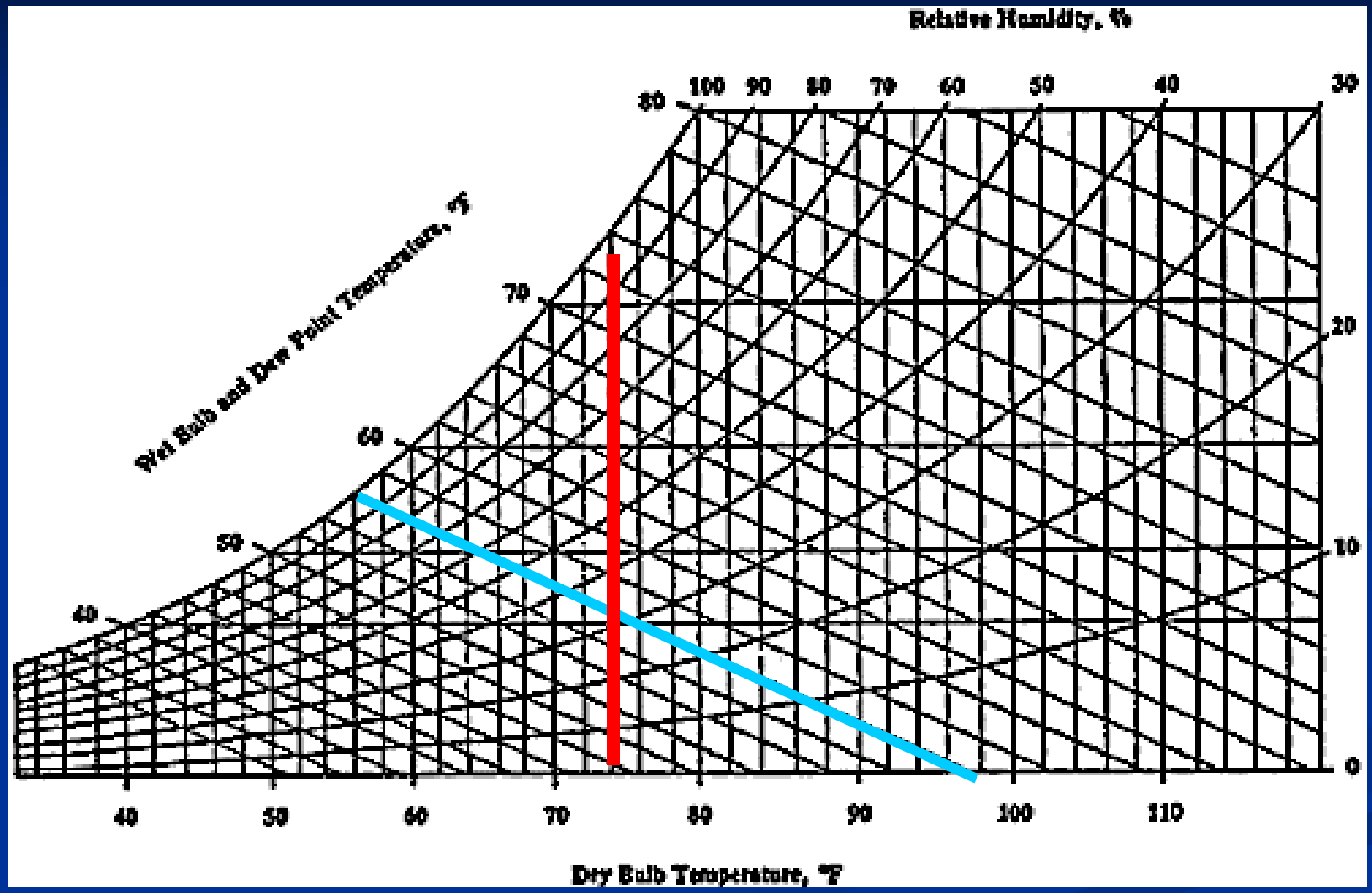


Figure 5
Test Arrangement for Exercise 3
Wet Bulb - Dry Bulb Technique
for
Moisture Measurement

Wet Bulb – Dry Bulb Method

1. Measure the wet bulb temperature.
2. Measure the dry bulb temperature.
3. Estimate moisture content using psychometric chart


Dry bulb
Wet bulb
Inflection
Area
Temperature
Time


Relative Humidity, %
100
90
80
70
60
50
40
30
20
10
0
Wet Bulb and Dew Point Temperature, °F
80
70
60
50
40
40
50
60
70
80
90
100
110
Dry Bulb Temperature, °F

Moisture Equation (Partial Pressure Method)

$$B_{WS} = \frac{v.p.}{P}$$

$$v.p. = s.v.p. - (0.000367)(P)(t_S - t_P)\left(1 + \frac{t - 32}{1571}\right)$$

Where:

s.v.p. = saturated water vapor pressure at the wet bulb temperature

P = absolute pressure in the stack

t_S = dry bulb temperature

t_W = wet bulb temperature

v.p. = water vapor pressure

If Gas Saturated, Then…

- Measure stack gas temperature at each traverse point.
- Calculate the average stack gas temperature.
- Determine moisture fraction using saturation vapor pressure table.

Moisture Equation – Partial Pressure

$$B_{ws} = \frac{s.v.p.}{P_S}$$

Where: B_{ws} = proportion (by volume) of water vapor in a gas mixture

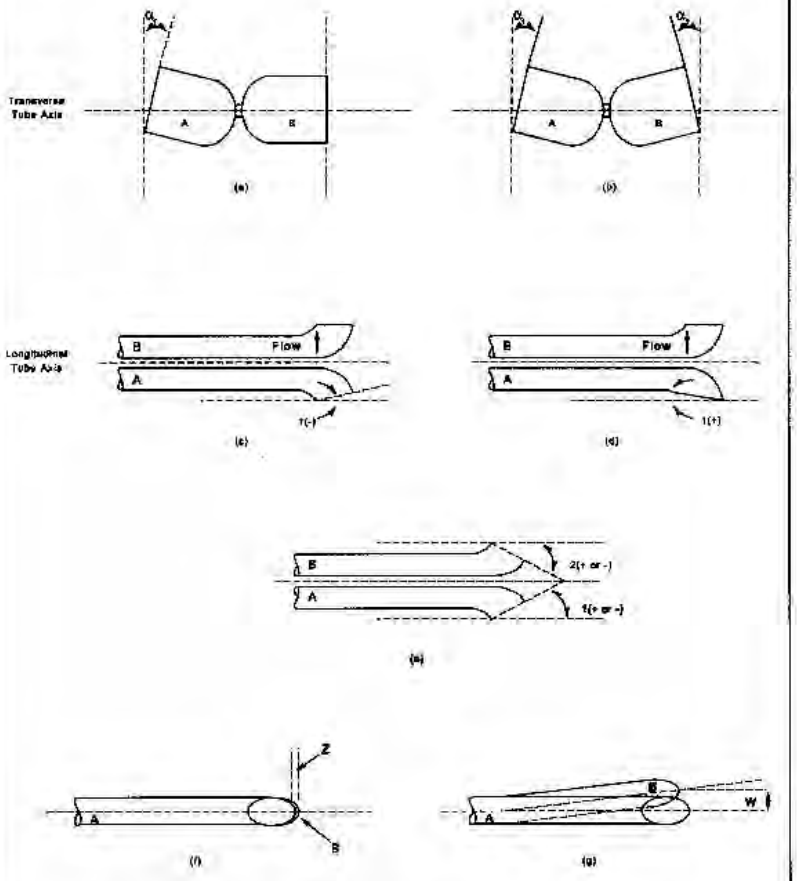
s.v.p. = saturated vapor pressure of water at average stack temperature

P_S = absolute pressure of the stack

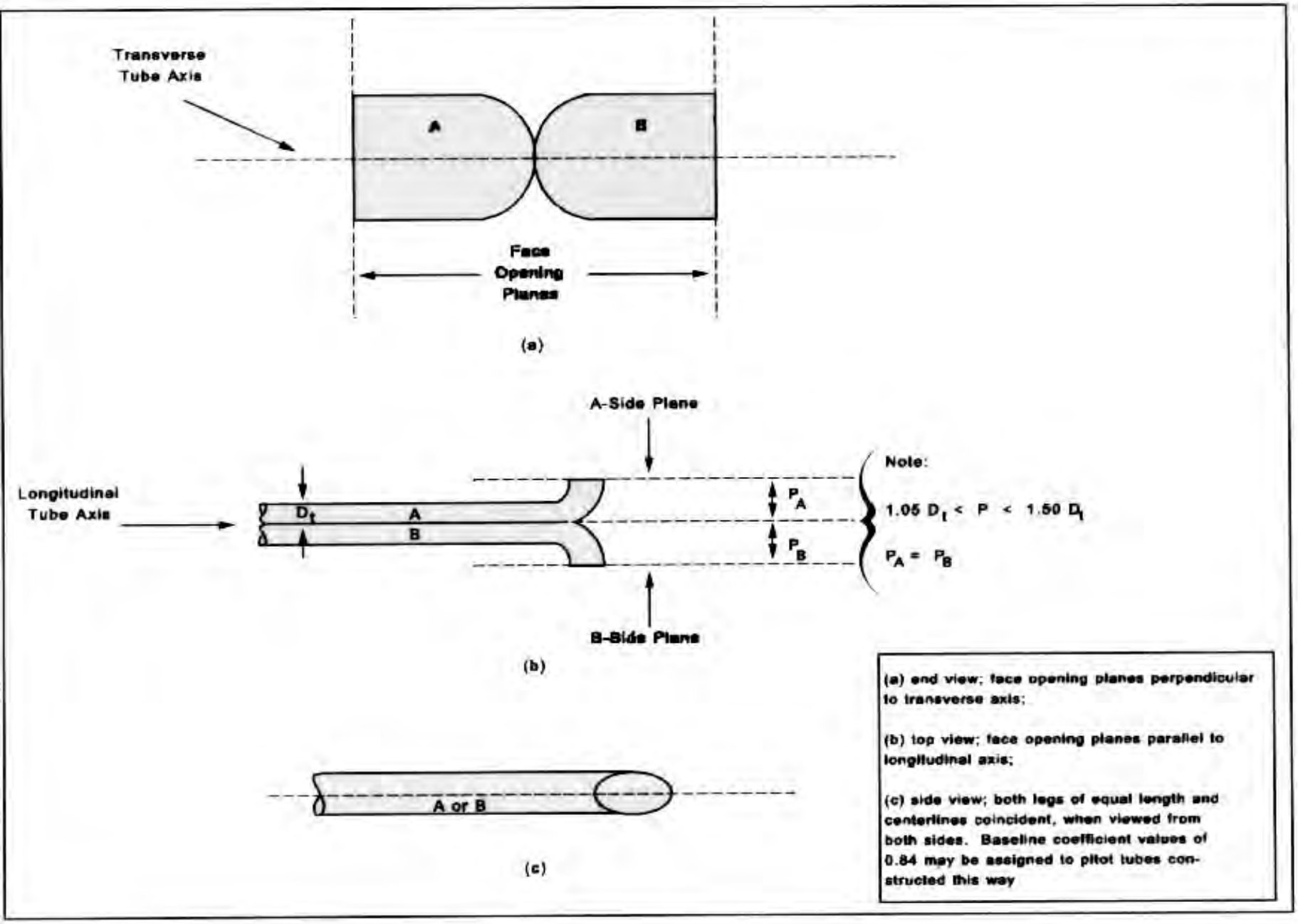
Classroom Stations

- Station #6: Stack Gas Moisture
  - Three Methods
    - Wet Buld/Dry Bulb Calculations
    - Nomograph
    - Psychrometric Chart
- Station #7: Pitot tube Inspection
  - Keep Pitot Tube Level





The types of face-opening misalignment shown above will not affect the baseline value of Cp(s) so long as α_1 and $\alpha_2 \leq 10°$, and $\leq .5$ z < 0.32 cm (1/8 in.), and w < 0.08 cm (1/32 in.) (reference 11.0 in Section 16.0).


Transverse
Tube Axis
A
B
Face
Opening
Planes
(a)
A-Side Plane
Longitudinal
Tube Axis
D_t
A
B
P_A
P_B
Note:
$1.05\ D_t < P < 1.50\ D_t$
$P_A = P_B$
B-Side Plane
(b)
A or B
(c)
(a) end view; face opening planes perpendicular to transverse axis;
(b) top view; face opening planes parallel to longitudinal axis;
(c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way

Verification of Geometry of Type S Pitot Tube To Assign 0.84

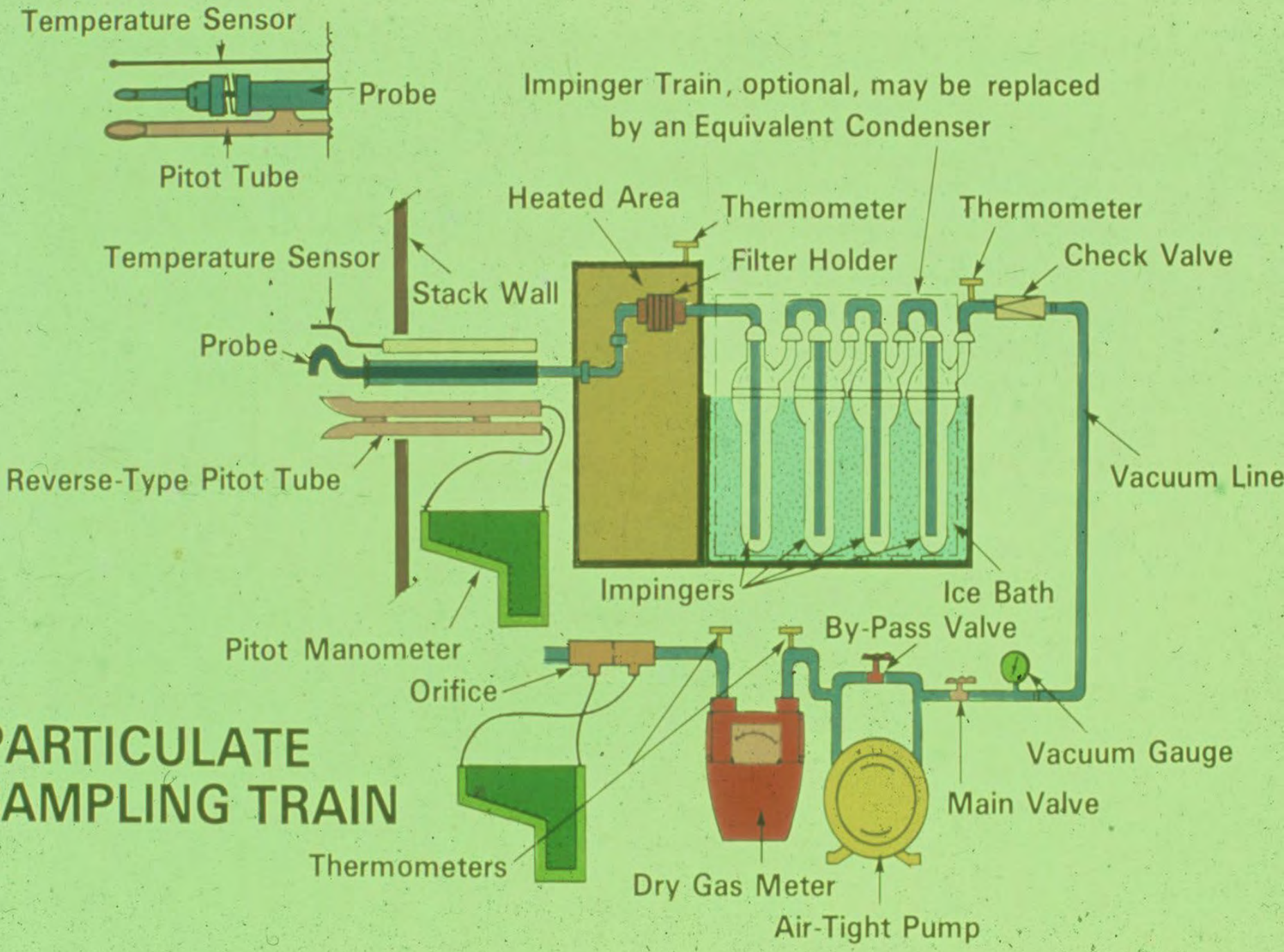
- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375


'94 3 25


'04 3:24

Laboratory Stations

- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: Traverse Point Determination
  - Use 12-24 inch diameter stack



PARTICULATE SAMPLING TRAIN




'94 3 25


EXIT

Laboratory Stations

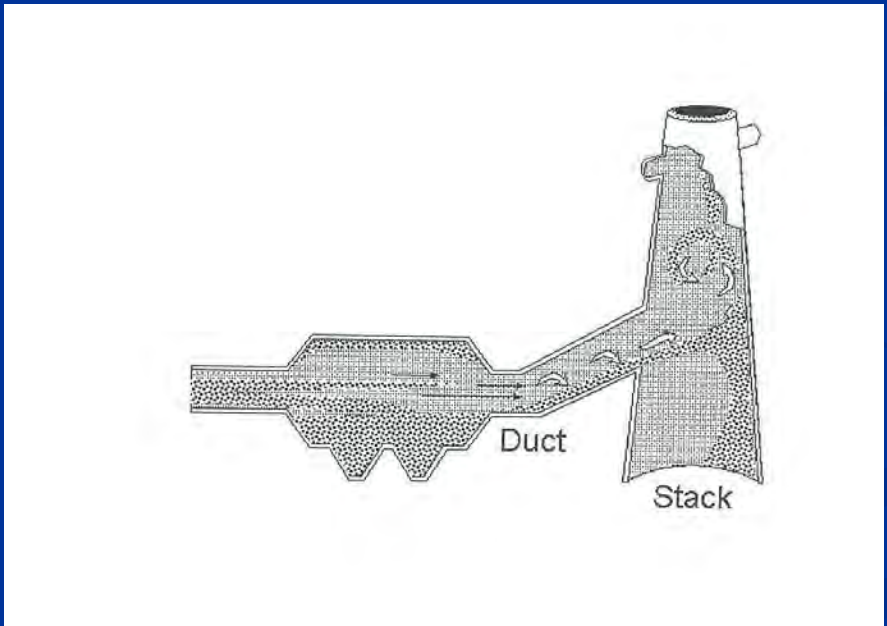
- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: Traverse Point Determination
  - Use 12-24 inch diameter stack



Laboratory Stations

- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: Traverse Point Determination
  - Use 12-24 inch diameter stack

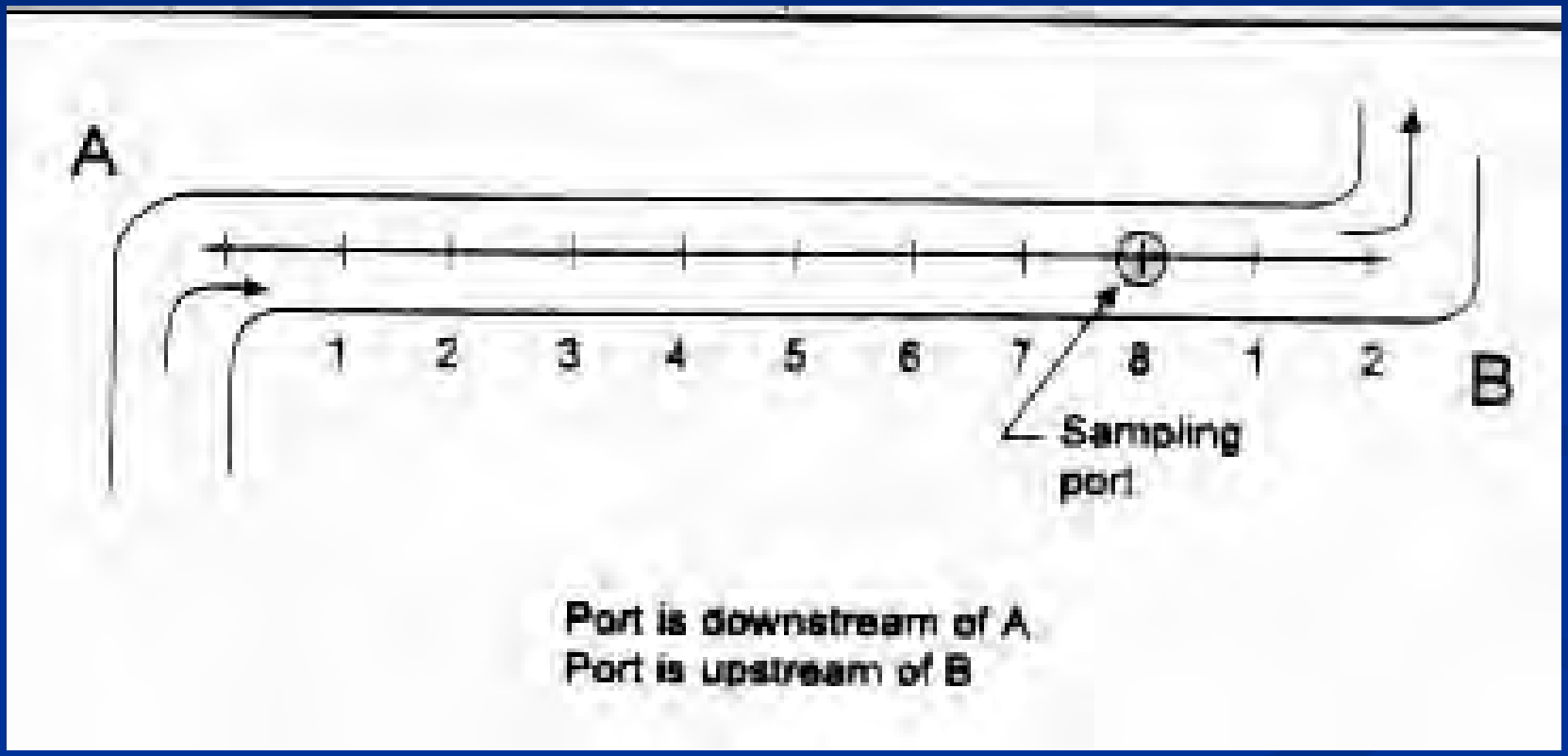
Determine the Number and location of sampling points

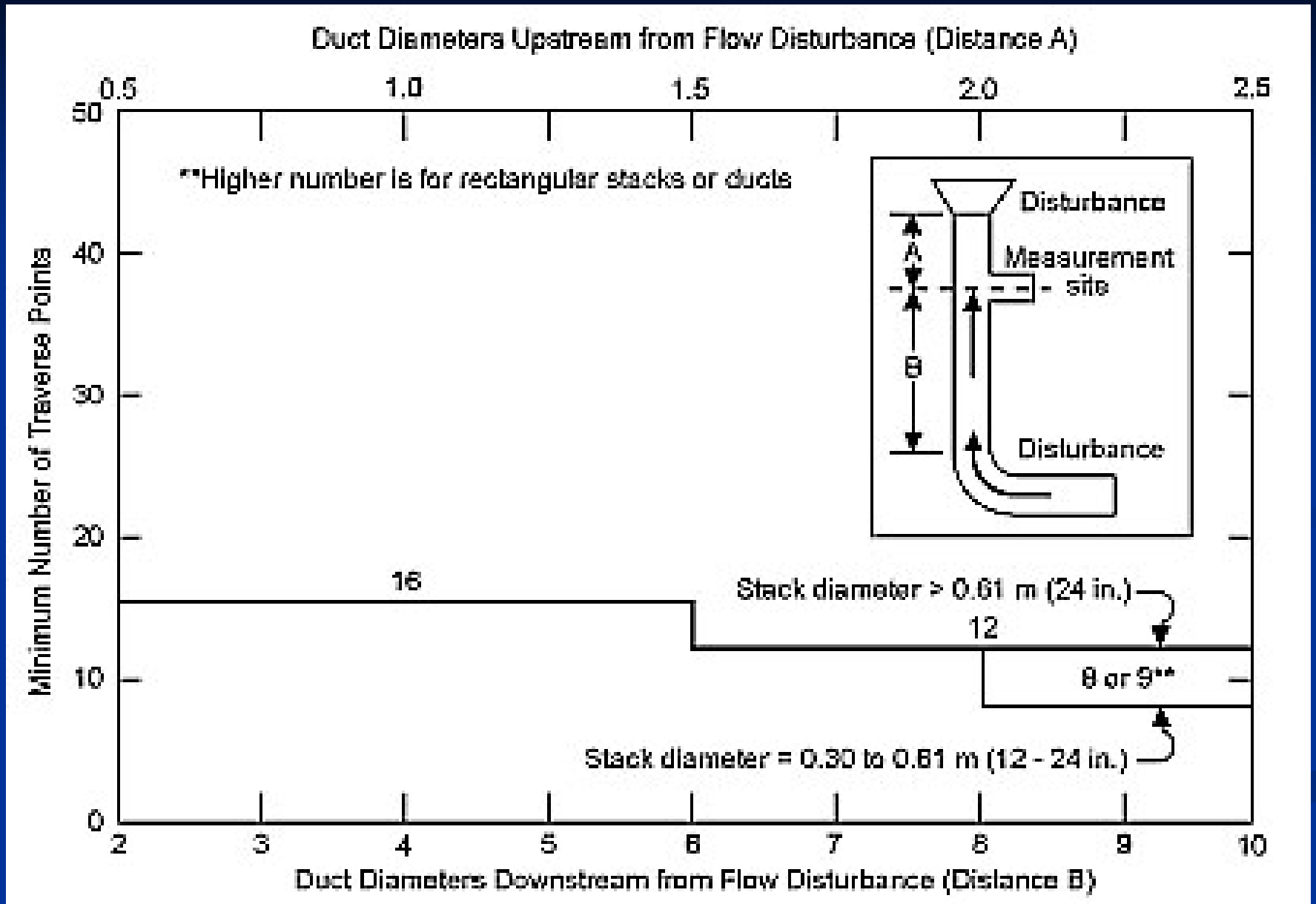


1 ft diameter duct

- Exhaust enters 10.75 ft from outlet
- Sampling port 1.75 ft from top

Ideal Siting Criteria




Duct Diameters Upstream from Flow Disturbance (Distance A)
0.5
1.0
1.5
2.0
2.5
50
40
30
20
10
0
Minimum Number of Traverse Points
**Higher number is for rectangular stacks or ducts
Disturbance
A
Measurement site
B
Disturbance
16
Stack diameter > 0.61 m (24 in.)
12
8 or 9**
Stack diameter = 0.30 to 0.61 m (12 - 24 in.)
2
3
4
5
6
7
8
9
10
Duct Diameters Downstream from Flow Disturbance (Distance B)

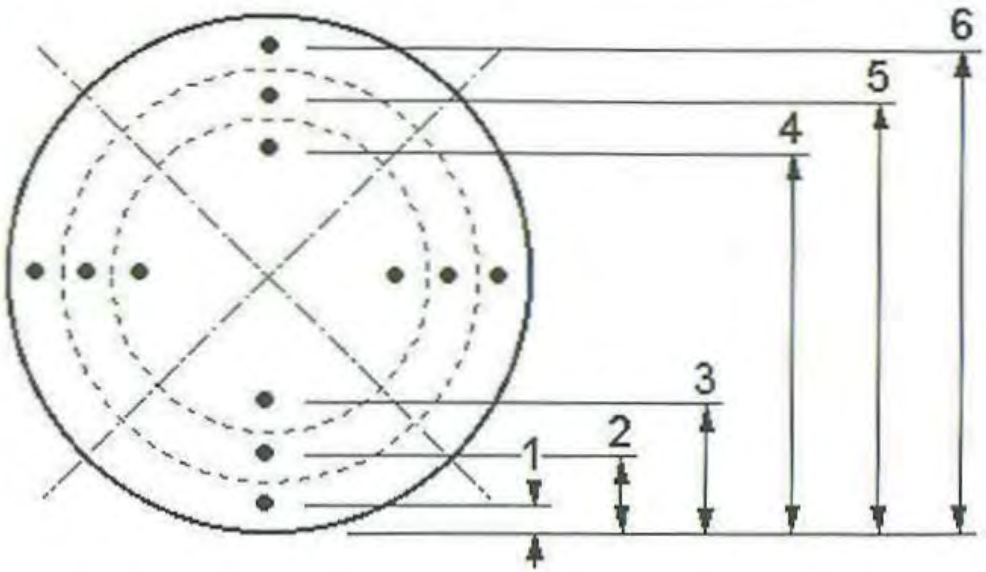
QUESTION?

- How many points need to be sampled ?

Cross-Sectional Layout and Location of Traverse Points

Pt. 60, App. Meth. 1

Traverse Point	Distance, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6



Traverse Point Location

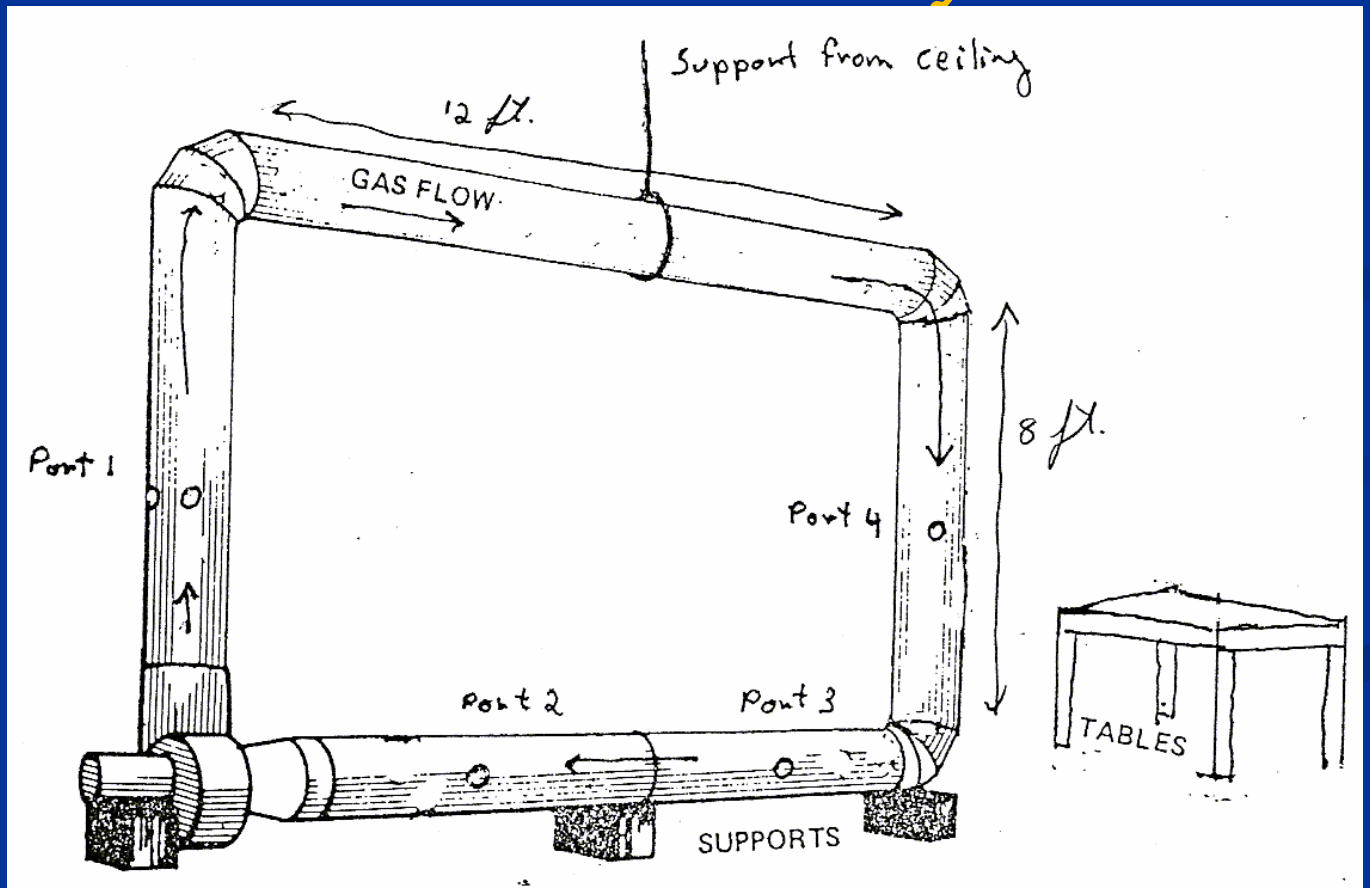
Table 1-2 Location of Traverse Points in Circular Stacks

(Percent of stack diameter from inside wall to traverse point)

Traverse point on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

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

Review of Laboratory Exercise



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

Course #468

Defining Volatile Organic Compounds (VOCs)

How Do We Define HAPs

- CAAA of 1990, Title III now contains a list of 186 HAPs containing both organic and inorganic analytes

CAAA of 1990 Number of HAPs in Each Volatility Class

Volatility Class	Number of HAPs in Class
Volatile (VV/V)	106 (56%)
Semi-Volatile (SV)	65 (35%)
Non-Volatile [Particles] (NV)	17 (9%)
	188

Organic Compounds

- Organic compounds (OCs) are those compounds which have a carbon-carbon bond
- Toxic air pollutants are those pollutants known or suspected to cause cancer or other serious health effects
- Many organic compounds are toxic air pollutants

Testing for VOCs Difficult

- Some State and Federal Regulations are based upon VOC emissions, not TOC or TNMOC
- The terms TOC, VOCs, NMOCs etc. are often erroneously applied interchangeably
- There is no straightforward way to measure the VOC emissions since there is no way to separate all VOCs by vapor pressure

Testing for VOCs Difficult

- All of the reference methods for organic compounds have inherent limitations that restrict their applicability
- There is no one method that can satisfy characterization of organic emissions from an industrial source

Historical Definition of VOCs

- 1970-1980's: Vapor pressure > 77 mm Hg. CAA of 1970 provided for NAAQS for HCs
- 1971: EPA's develop SIP program including definition for VOCs (~ 77 mm Hg)

Historical Definition of VOCs

- Late 1980's: Photochemical reactivity (40CFR51.100) and excluding freons
- 1990's: Clean Air Act Amendments of 1990 definition of hazardous air pollutants (HAPs), including VOCs

40CFR51.100

- "Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compound other than the following:
  - Methane, ethane, methylene chloride, CFCs, HCFCs, HFCs, etc.

Organic Chemistry

- "*…Organic chemistry is the chemistry of the compounds of carbon.*"
- Historically, chemical compounds were divided into two groups:
  - Inorganic compounds were those obtained from minerals;
  - Organic compounds were those obtained from animal sources, that is, from materials produced by living organisms. They all contain the element carbon.

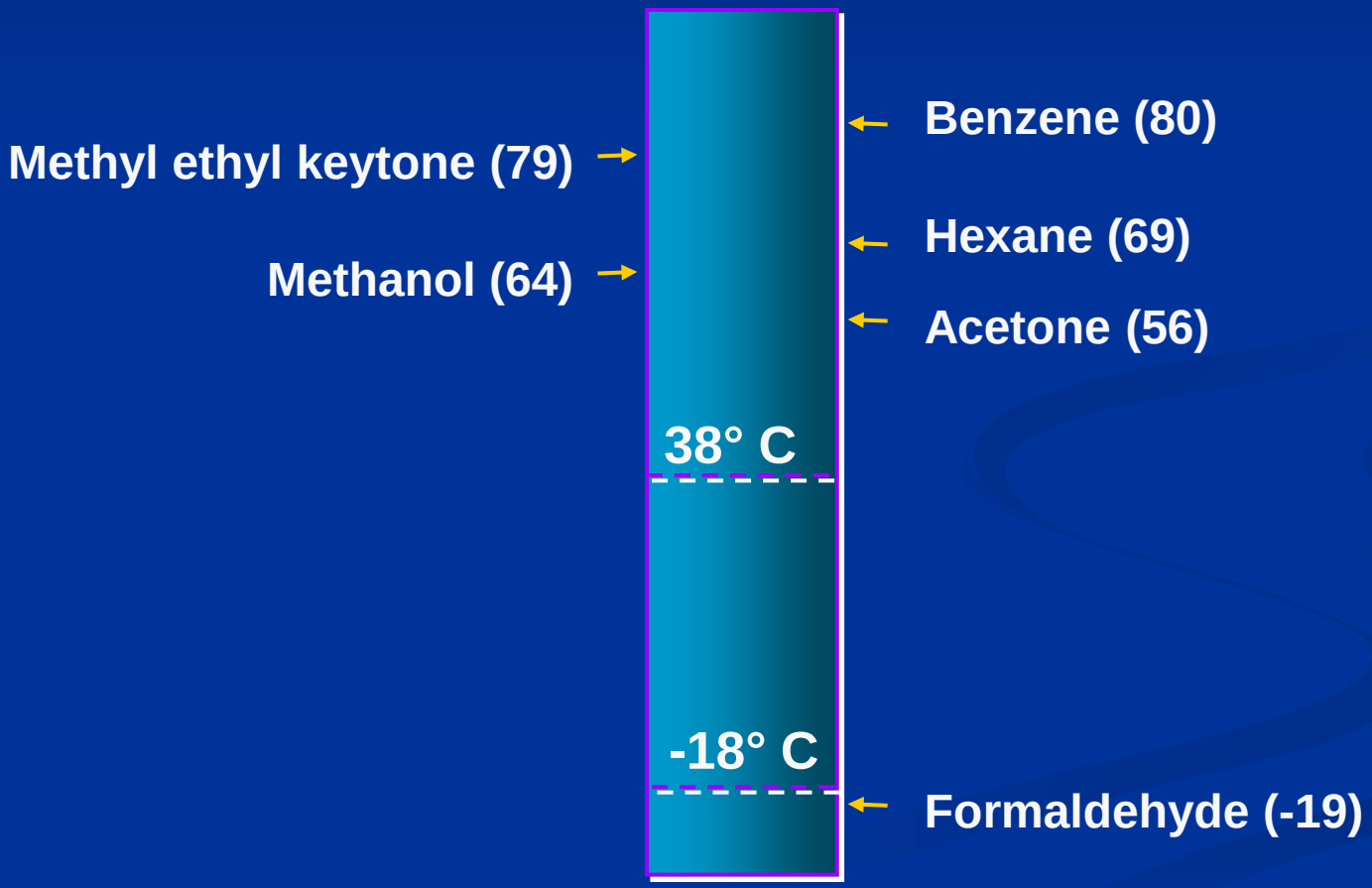
Historical Definition of VOCs

- 2000's: Various state agencies define VOCs (0.1 mm Hg to 77 mm Hg) by:
  - Vapor Pressure (in mm Hg at 25°C)
  - Boiling Point Temperature (°C)

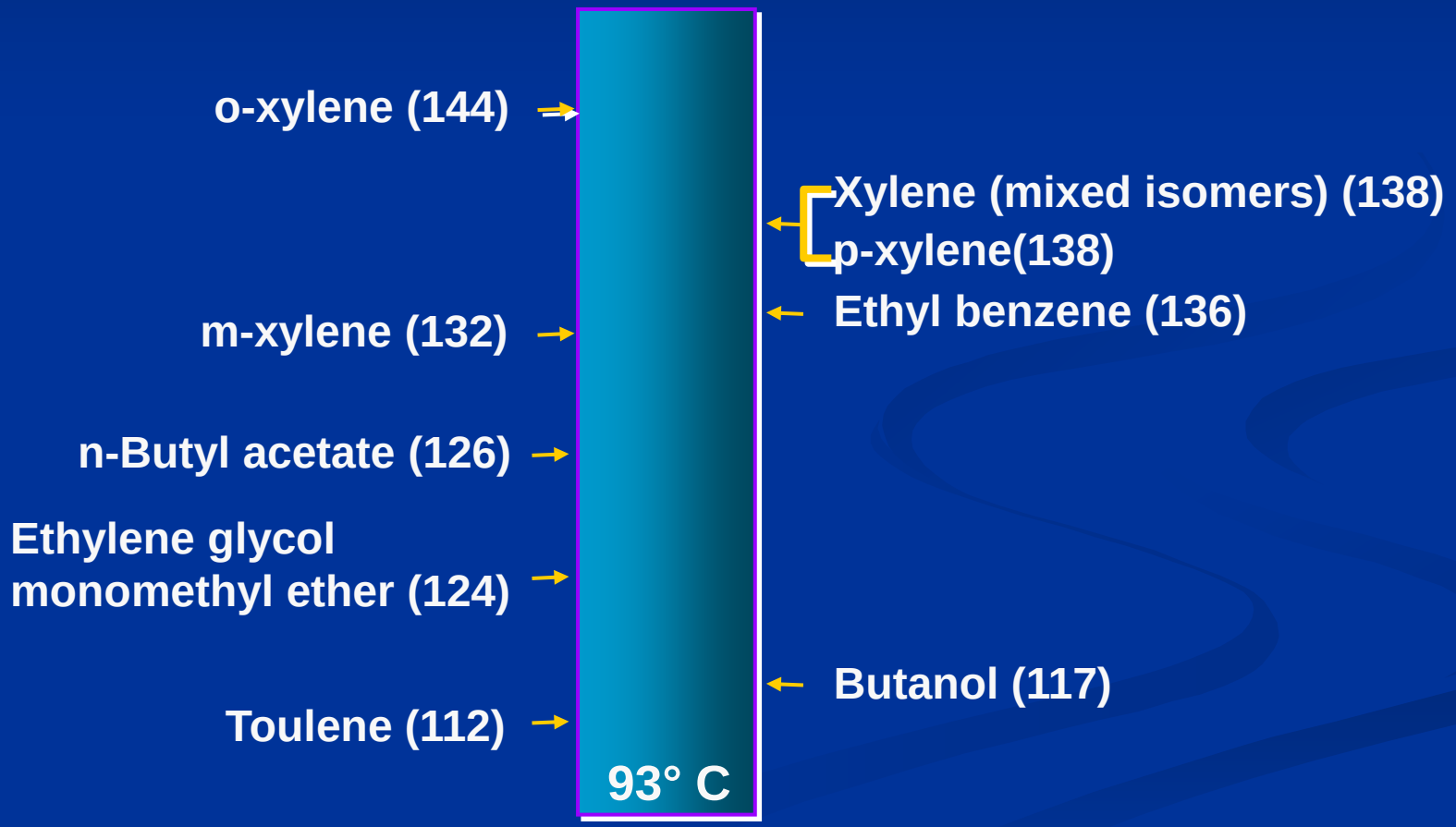
General Classification of VOCs

Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	> 10^{-1}	< 200°C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	200 - 500°C
Particles (NV)	< 10^{-7}	> 500°C

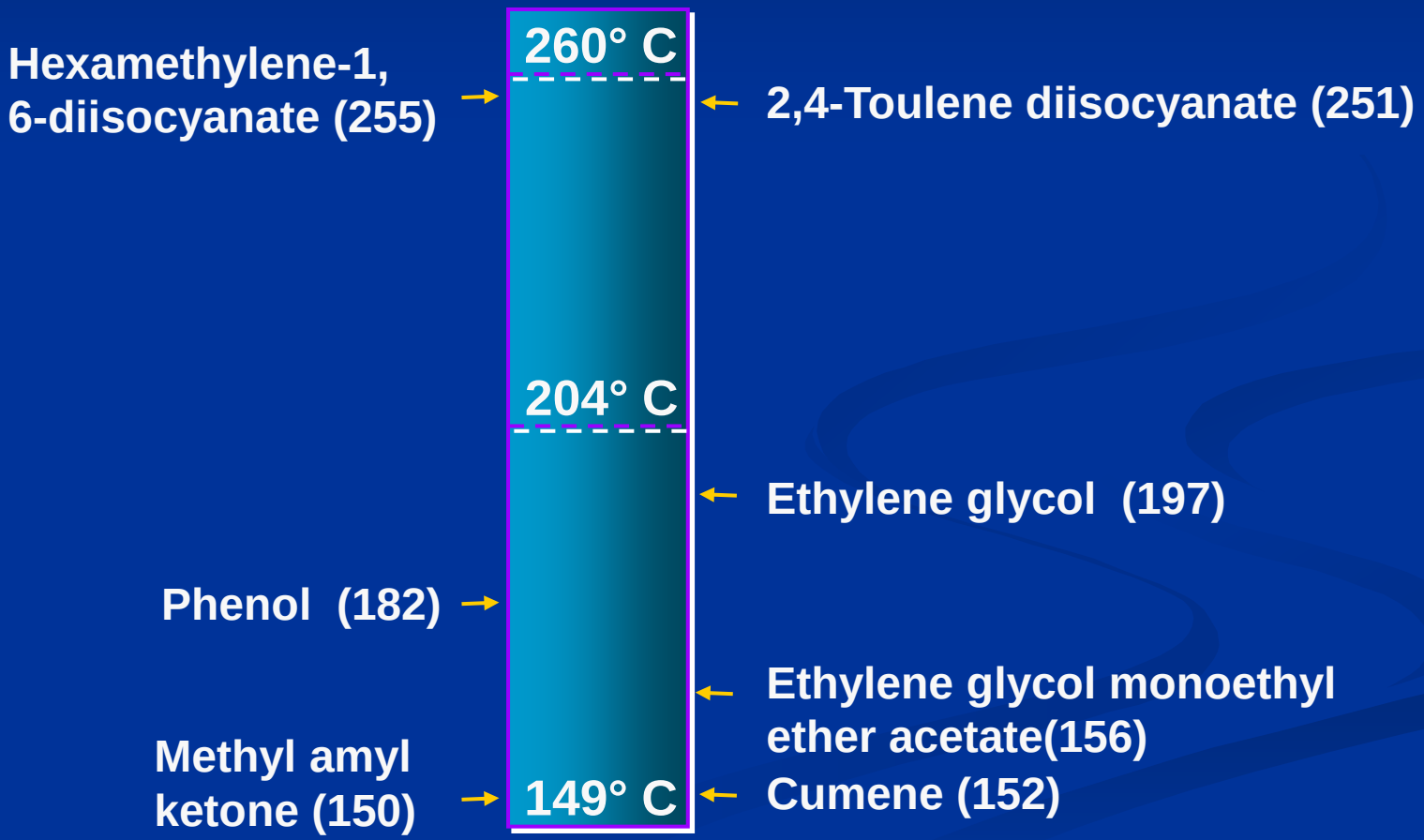
Boiling Points of Volatile Organic Compounds



Boiling Points of Volatile Organic Compounds



Boiling Points of Semi-volatile Organic Compounds



Six (6) Key Factors to Consider in Test Method Selection

1. The chemical composition of the VOCs being tested
2. The expected concentration range of the VOCs being emitted
3. The chemical properties (i.e., vapor pressure, boiling point, solubility etc.) of the emitted VOCs

Six (6) Key Factors to Consider in Test Method Selection

4. The characteristics of the effluent (i.e., temperature, moisture, $\%CO_2$ etc.)
5. The advantages and disadvantages of each of the test methods
6. The state and federal testing requirements documented in their regulations

Methods Associated with Monitoring VOCs

- FRM 18: Individual Organic Compounds by Gas Chromatography
- FRM 25: Measurement for Total Gaseous Nonmethane Organic Emissions
- FRM 25A: Total Gaseous Organic Concentration by Flame Ionization Analyzer

Methods Associated with Monitoring VOCs

- FRM 25B: Total Gaseous Organic Concentration by Non-Dispersive Infrared Analyzer (NDIR)

Methods Associated with Monitoring VOCs

- SCAQMD Method 25.3/EPA's CTM 035: Low-level Concentration of VOCs
- SW-846, Method 0010 and 0030: Semi-volatiles and volatile organic compounds respectively
- FRM 315: Polycyclic Organic Matter (POM) by MCEM

Definitions

- Volatile Organic Compounds (VOCs): Organic compounds that participate in atmospheric photochemical reactions and have vapor pressure (vp) > 10^{-1} mm Hg
- An organic compound that participates in atmospheric photochemical reactions. The exempt compounds are listed in 40CFR51.100

Definitions

- Semi-volatile Organic Compounds (SVOCs): Organic compounds with v.p. 10^{-1} to 10^{-7} mm Hg and b.p 200-500 ^{o}C
- Those organic compounds which can be quantified by SW-846, Method 0010 and analyzed by SW-846, Method 8270D

Definitions

- Polycyclic Aromatic Hydrocarbons (PAHs) or Polycyclic Organic Matter (POM): Organic compounds with more than one benzene ring and which have a boiling point > 200 C
- Methylene Chloride Extractable Matter (MCEM): Organic compounds which are extracted by $MeCl_2$

Definitions

- Total Hydrocarbons (THCs): Sum of total organic compounds containing only C and H
- Total Non-Methane Organic Compounds (TNMOCs): Sum of all VOCs and all exempt compounds excluding methane
- Total Non-Methane/Non-Ethane Organic Compounds (TNM/NEOCs): Sum of total VOCs and exempt compounds excluding methane and ethane

Definitions

- FRM 18 results can be converted to mass emission rates since this method reports concentrations in terms of the actual organic compounds. We know the molecular weight of each analyte along with volumetric flow rate to get VOC mass flow rate.
- Total Organic Compounds (TOCs): Organic compounds detected by a flame ionization analyzer (FIA)

Definitions

- Hazardous Air Pollutants (HAPs): Those compounds identified in the Clean Air Act Amendments of 1990, Title III list of 186 HAPs

Applicability of Organic Sampling Methods

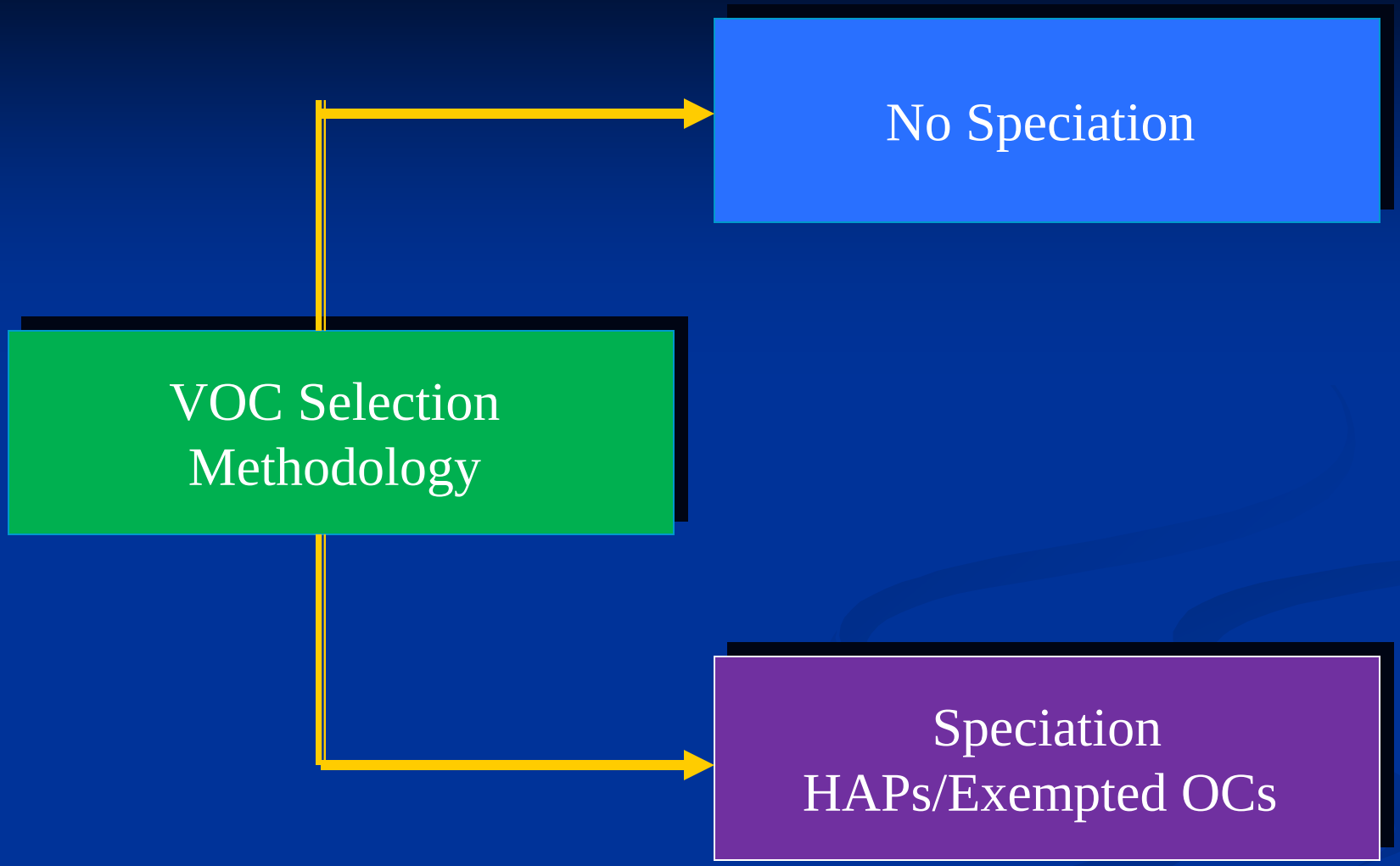
FRM	Conc. Range
FRM 25 B	0.5-10 %
FRM 25	50 ppm-10 %
FRM 18	1 ppm – 1 %
FRM 25 A	50 ppm – 1 %
Method 25.3 (CTM 035)	< 1 ppm

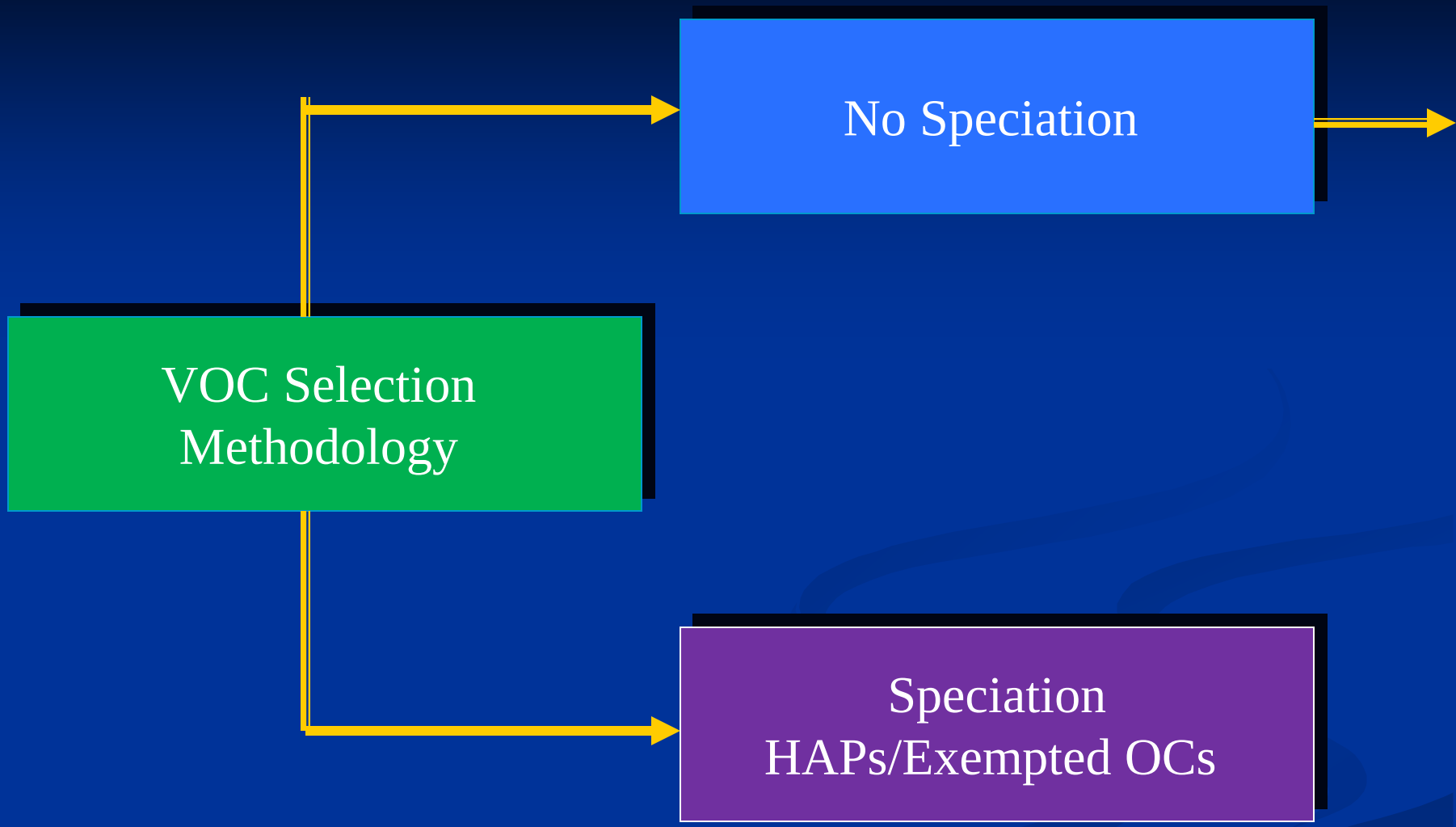
Applicability of Methods

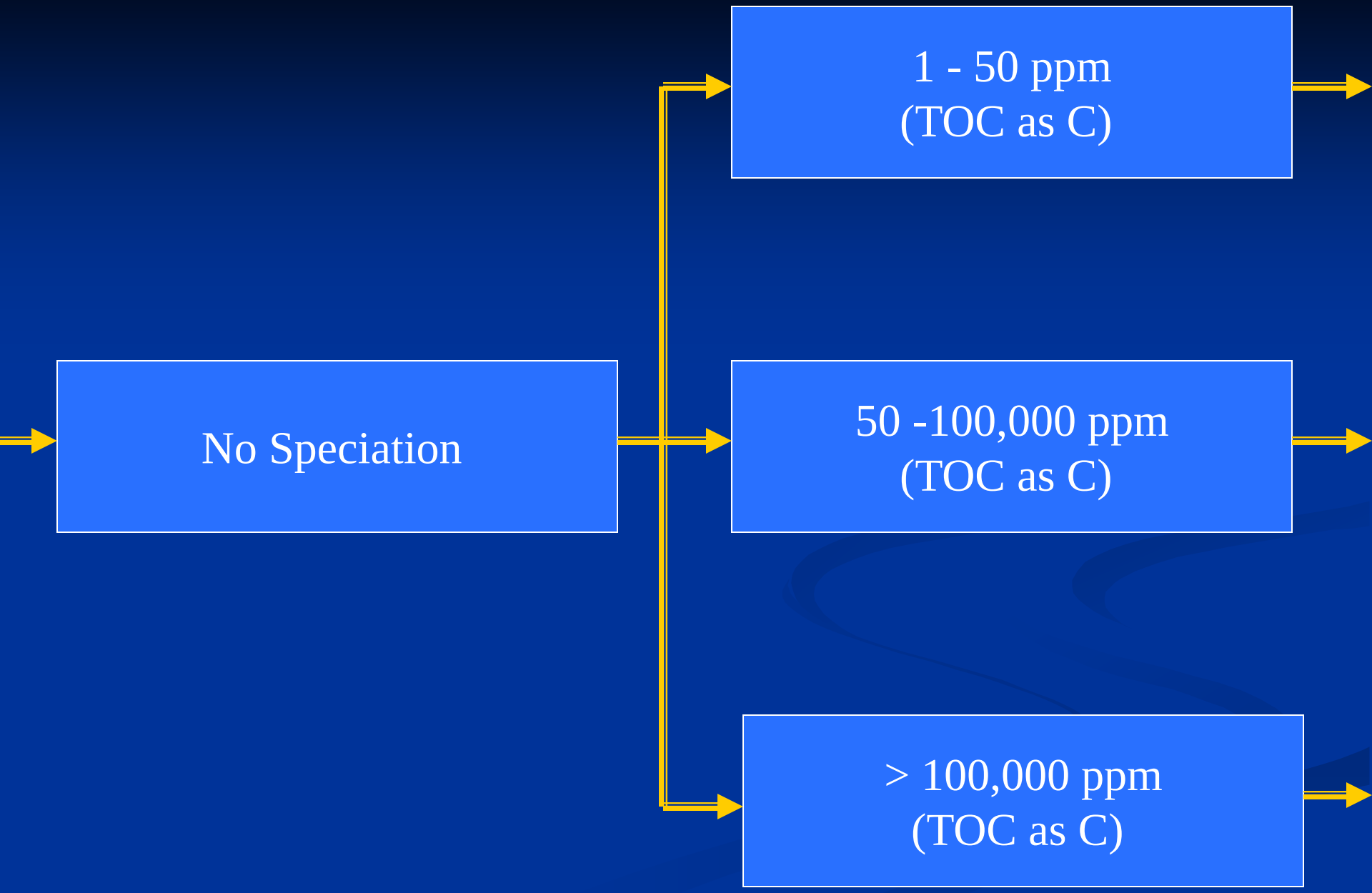
	FRM 18	FRM 25	FRM 25A
Measures…	VOCs	TGNMO	THC
Principle…	GC/MD	GC/FID	FID
Carbon Resp…	1:1	1:1	Var.
Results Exp As..	VOC	As C	Cal Gas

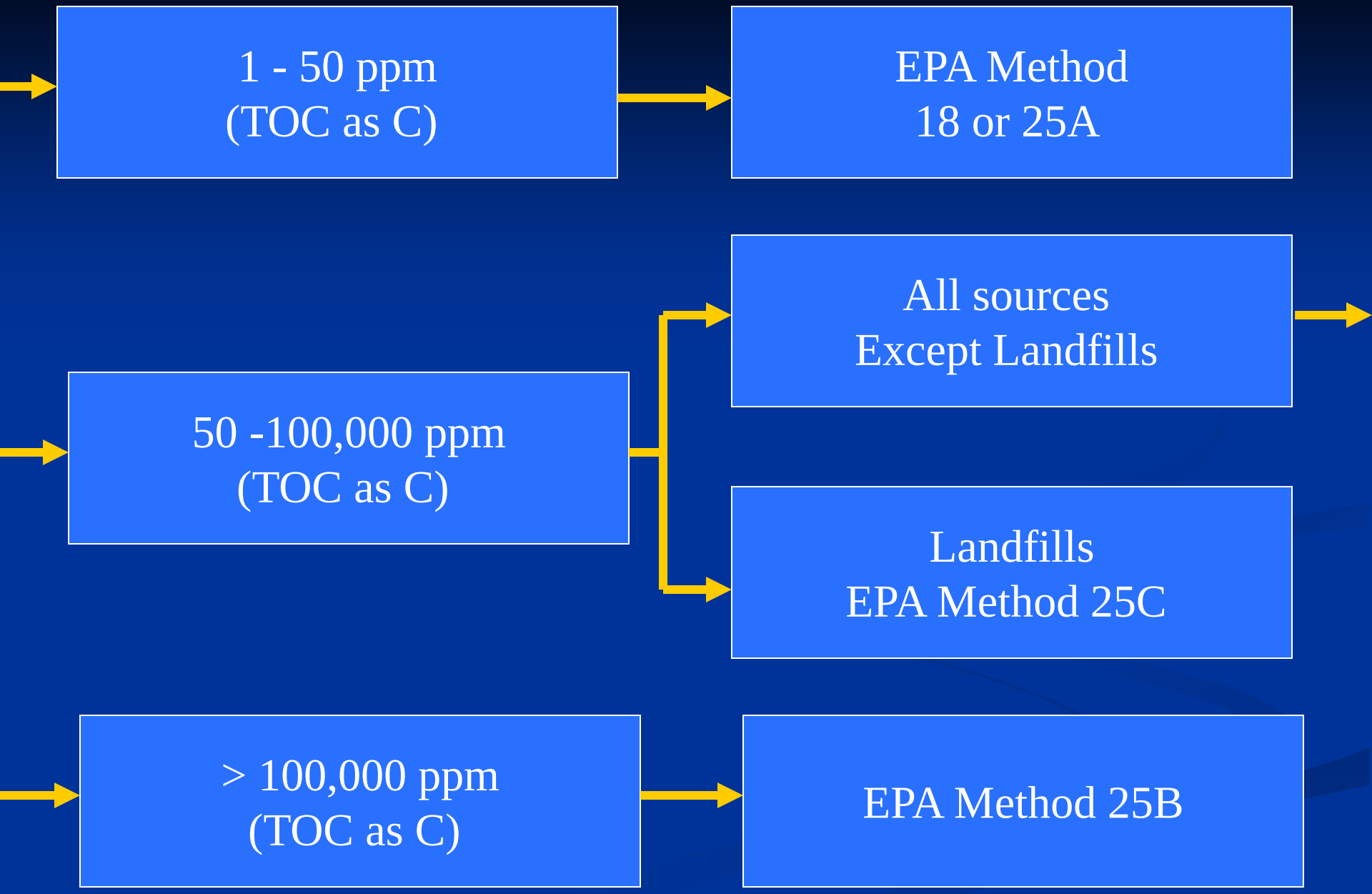
Applicability of Methods

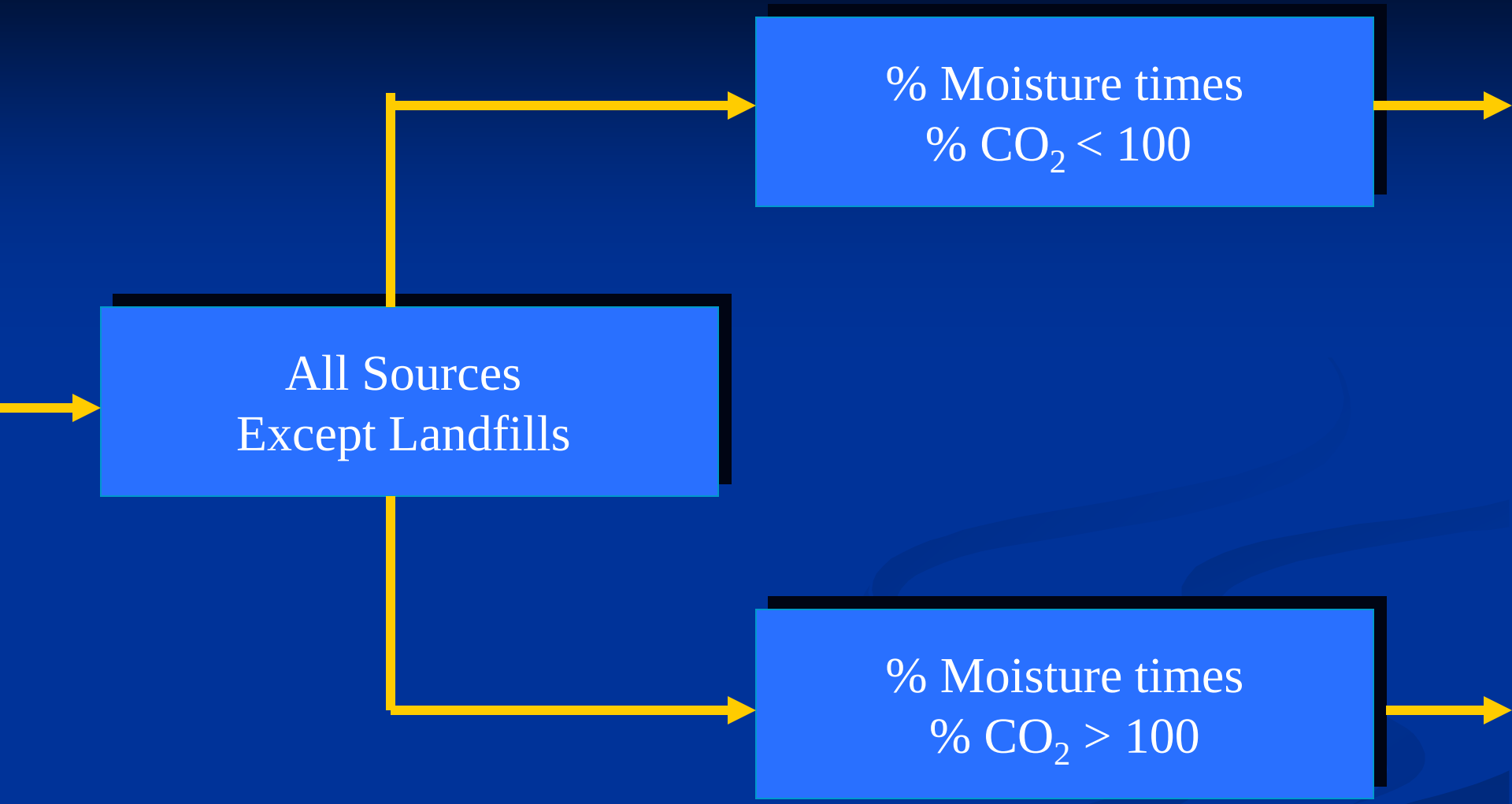
Nature of Emission	Report Emission As	Affected Facility
VOCs unknown/variable	Propane	Asphalt Plants Cement Plants Resource Rec Bakeries
Single VOC > 75 %	That single VOC	SOCMI
Single VOC < 75 %	Surrogate	Surface Coat Graphite Art

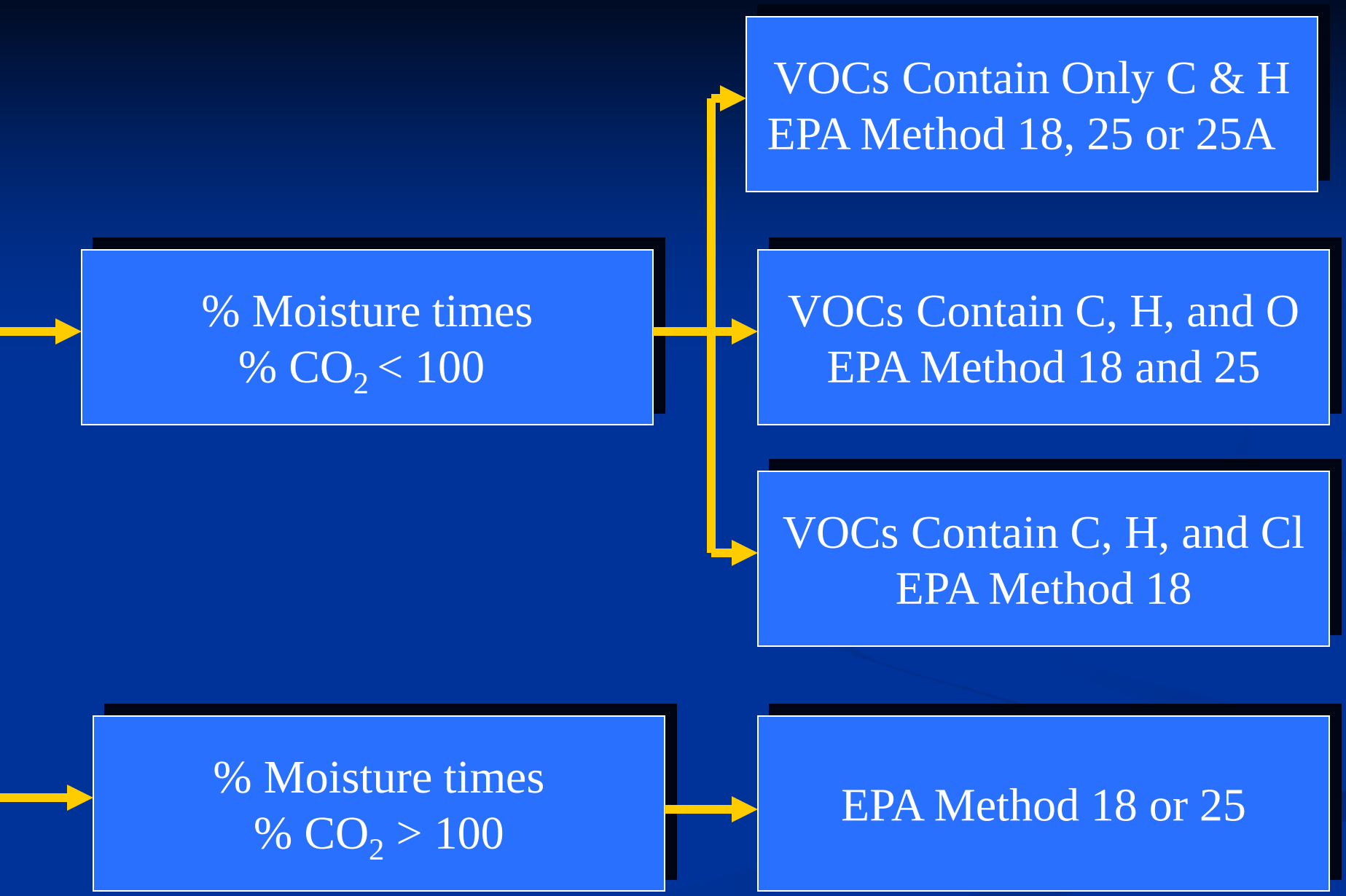

No Speciation
VOC Selection Methodology
Speciation HAPs/Exempted OCs

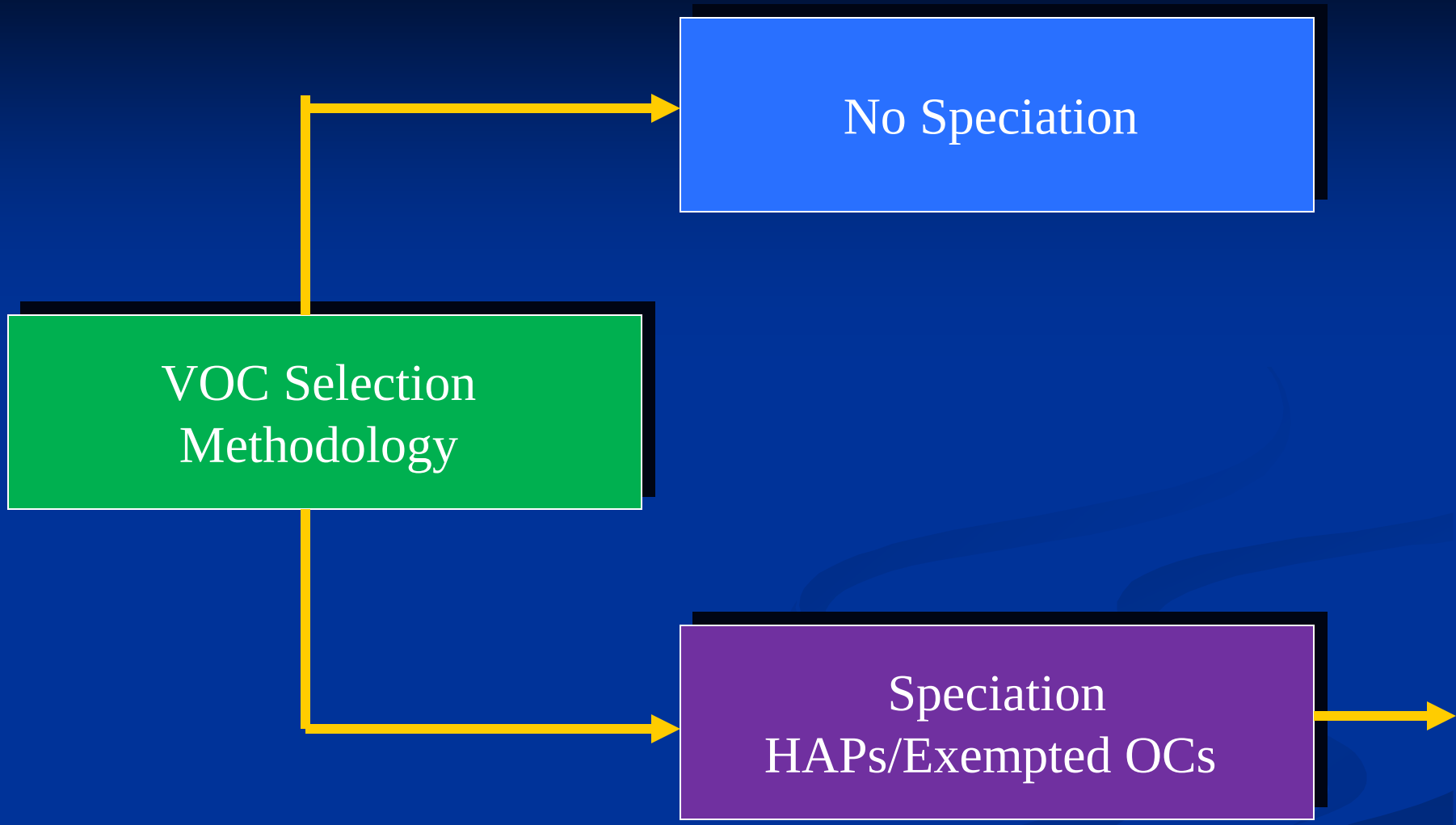

No Speciation
VOC Selection Methodology
Speciation HAPs/Exempted OCs

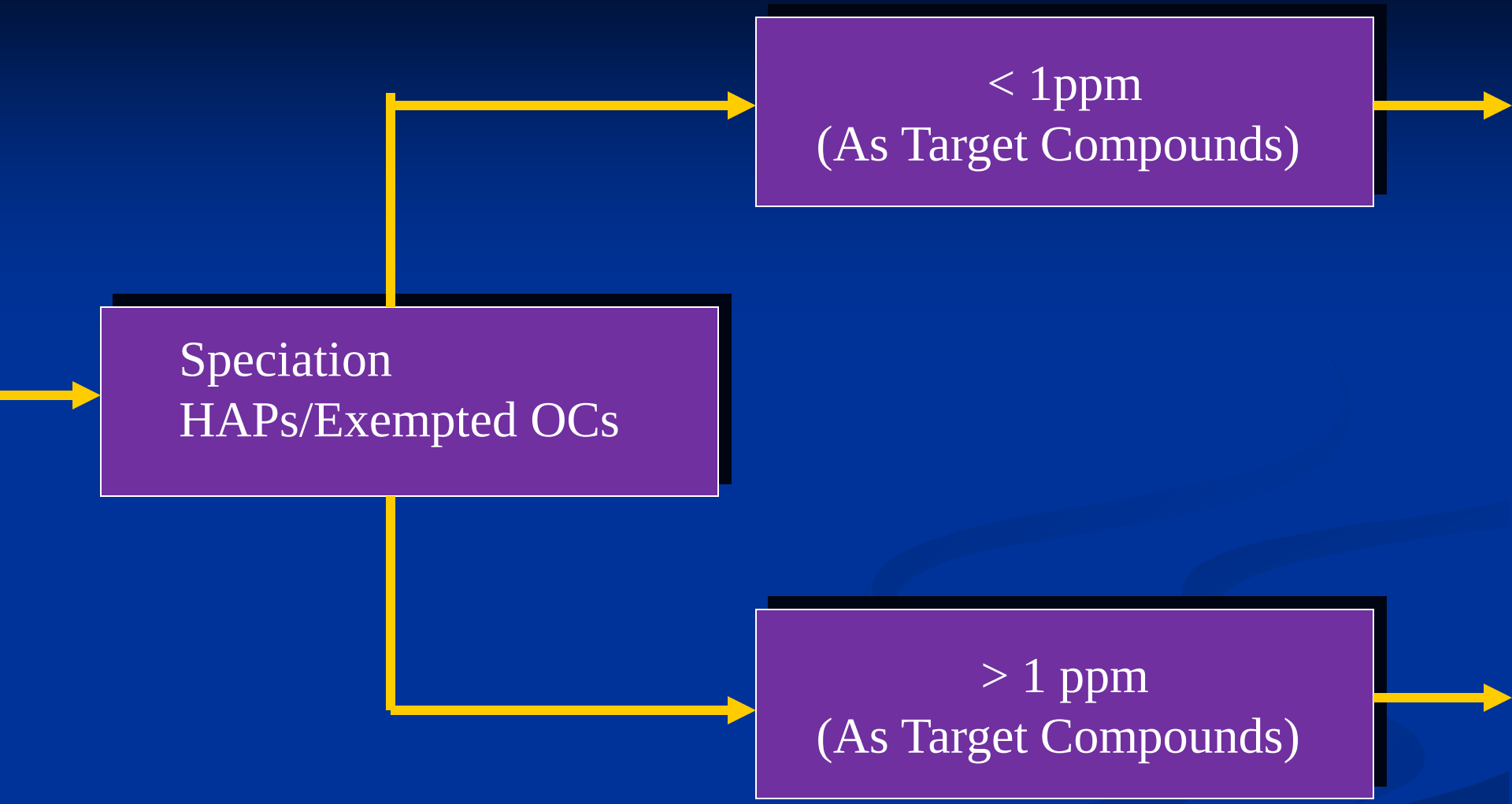

No Speciation
1 - 50 ppm
(TOC as C)
50 -100,000 ppm
(TOC as C)
> 100,000 ppm
(TOC as C)


1 - 50 ppm
(TOC as C)
EPA Method
18 or 25A
All sources
Except Landfills
50 -100,000 ppm
(TOC as C)
Landfills
EPA Method 25C
> 100,000 ppm
(TOC as C)
EPA Method 25B


% Moisture times
% CO_2 < 100
All Sources
Except Landfills
% Moisture times
% CO_2 > 100


VOCs Contain Only C & H
EPA Method 18, 25 or 25A
% Moisture times
% CO_2 < 100
VOCs Contain C, H, and O
EPA Method 18 and 25
VOCs Contain C, H, and Cl
EPA Method 18
% Moisture times
% CO_2 > 100
EPA Method 18 or 25


No Speciation
VOC Selection Methodology
Speciation HAPs/Exempted OCs


< 1ppm
(As Target Compounds)
Speciation
HAPs/Exempted OCs
> 1 ppm
(As Target Compounds)

< 1ppm
(As Target Compounds)

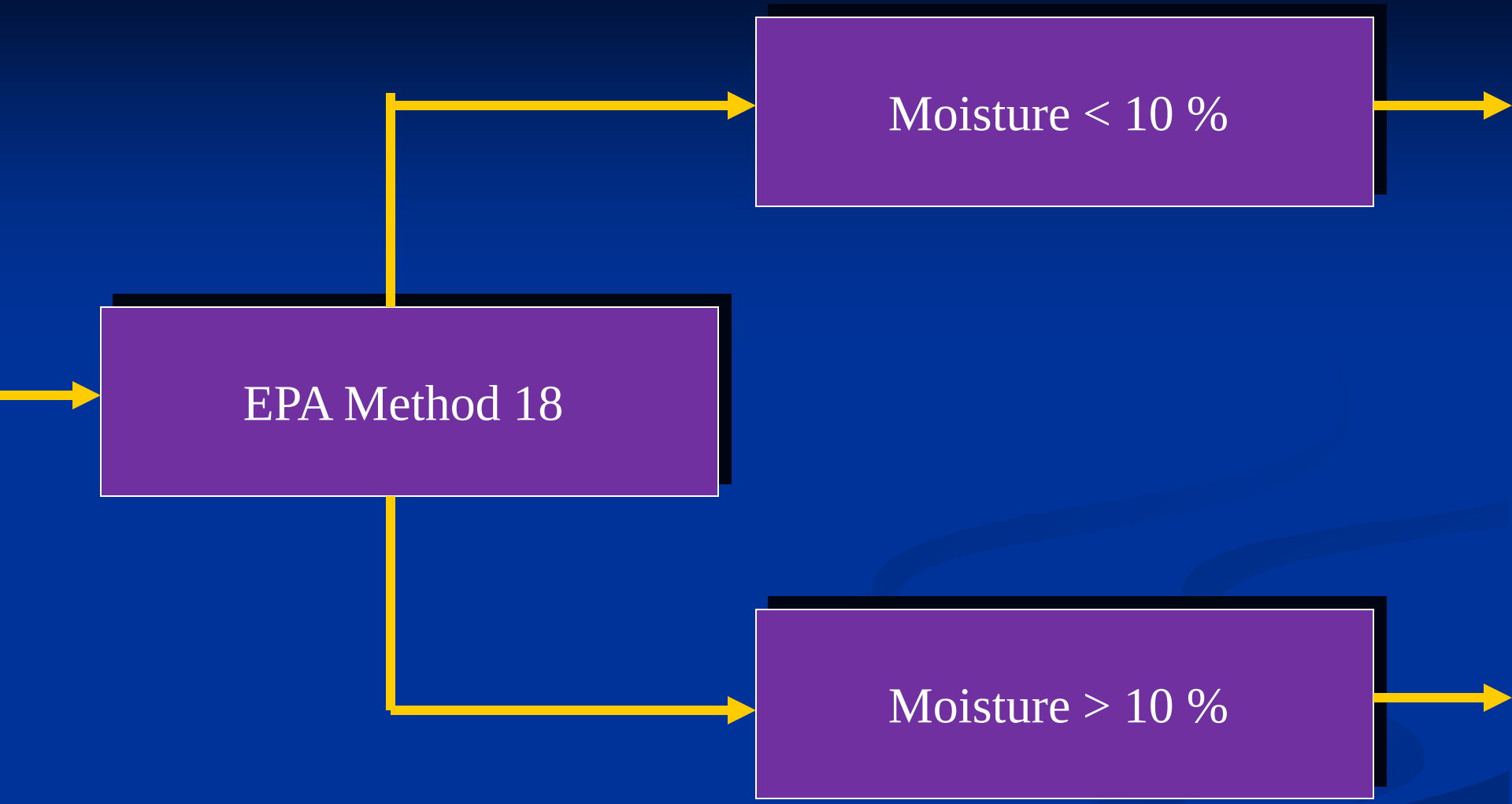
bp >200 C; vp <10^{-1} mm Hg
Method 0010

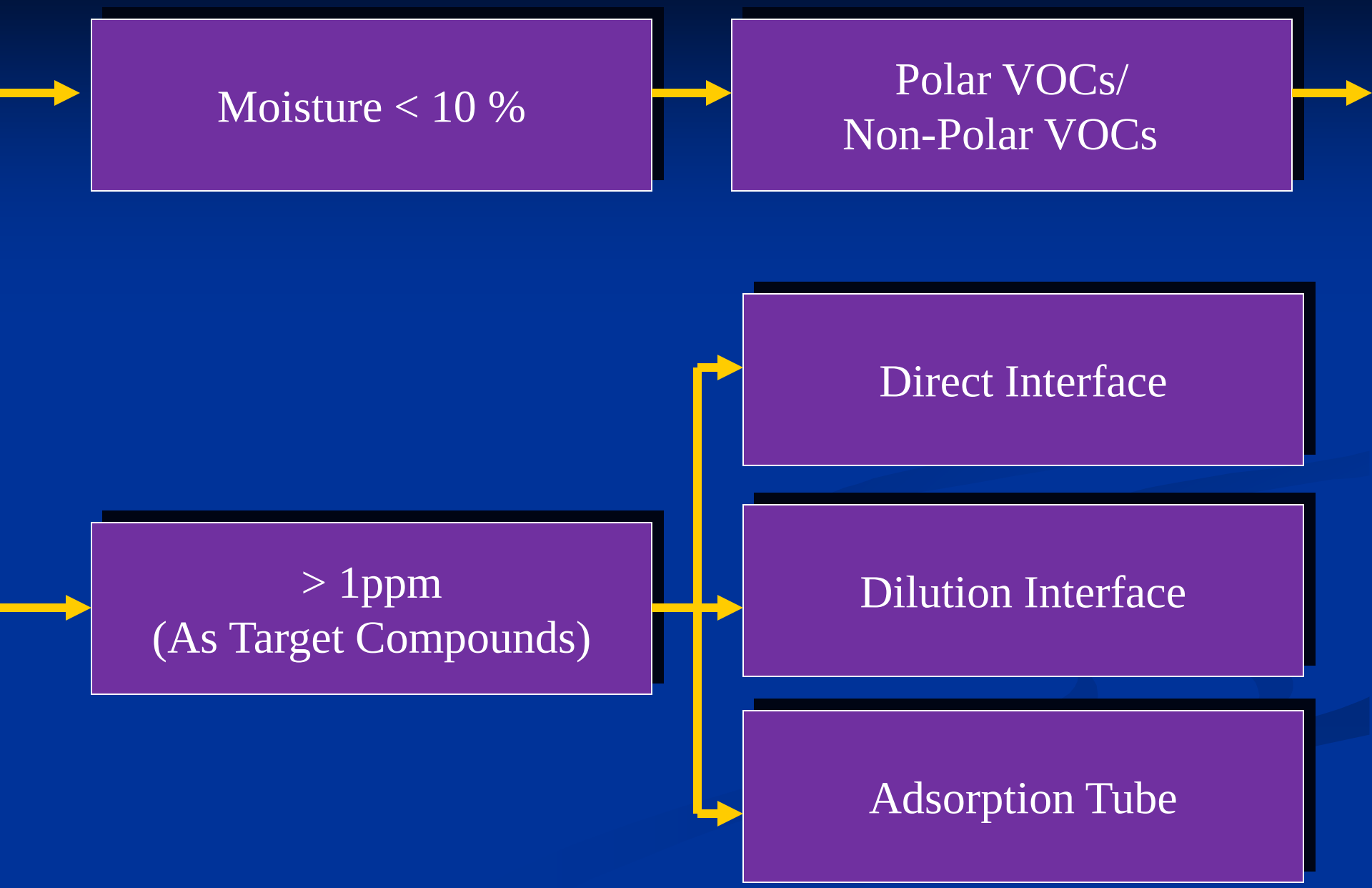
bp <200 C; vp > 10^{-1} mm Hg
Method 0030

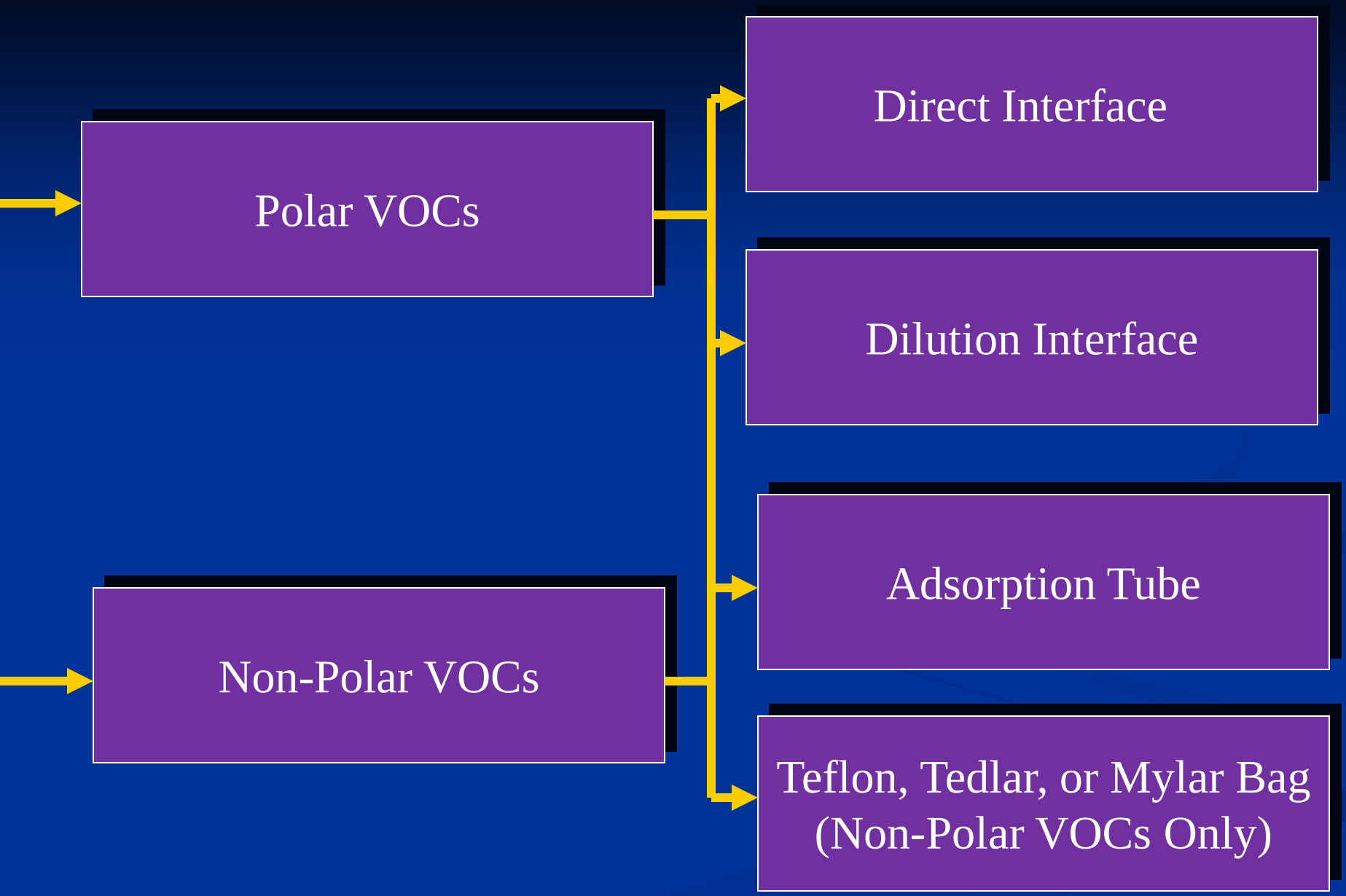
> 1ppm
(As Target Compounds)

Aldehydes/Ketones
Method 0011

Other VOCs
EPA Method 18


Moisture < 10 %
EPA Method 18
Moisture > 10 %


Moisture < 10 %
Polar VOCs/
Non-Polar VOCs
> 1ppm
(As Target Compounds)
Direct Interface
Dilution Interface
Adsorption Tube


Polar VOCs
Non-Polar VOCs
Direct Interface
Dilution Interface
Adsorption Tube
Teflon, Tedlar, or Mylar Bag
(Non-Polar VOCs Only)

Reporting of Emissions?

- "As Carbon?"
- "As TGNMOCs?"
- "As Propane?"
- "As VOCs?"
- "As THCs?"
- "As……What?"

Reporting of Emissions

- FRM 18, because of the GC/MS analysis, reports results in terms of the concentration of specific organics
- FRM 25 is a method for measuring total gaseous nommethane organic compounds (TGNMOCs) with a GC column and FID. Therefore, a one-to-one response of all carbon atoms in the sample are as methane (i.e., carbon counter) .

Reporting of Emissions

- FRM 25A involves determining total hydrocarbons concentrations by introduction of the sample directly into the FID without a GC step to speciate. Results are expressed in terms of the gas used to calibrate the FID (usually methane or propane). FRM 25A does not provide a one-to-one response for all of the carbon atoms present in the sample.

Reporting of Emissions

- FRM 18 results can be converted to mass emission rates since this method reports concentrations in terms of the actual organic compounds. We know the molecular weight of each analyte along with volumetric flow rate to get VOC mass flow rate.

Reporting of Emissions

- For FRM 25, we need to know the VOC-to-carbon weight ratio to get VOC mass emission rate.
  - Methanol molecular weight = 32
  - Carbon molecular weight = 12
    - 32/12 = 2.67 VOC to carbon weight ratio. We would multiply everything by 2.67 to calculate VOC mass emission rate

Reporting of Emissions

- Converting FRM 25A results to " as VOCs" mass flow is similar to FRM 25 except one must take into account not only the molecular weight factor, but also the relative response factor (RRF) for the FID between the analytes in the gas stream and the calibration gas.

Relative Response Factors

VOC	C:O Ratio	RRF
Methane	1:0	1.00
Propane	1:0	1.00
Formalde	1:1	0.00
Methanol	1:1	0.40
Ethanol	2:1	0.70
MEK	4:1	0.75
Ethy. Ox	2:1	0.50
CO	1:1	0.00

Suggested Reporting of Emissions

- For federally regulated source (i.e., NSPS, NESHAPs, MACT etc.), report VOC emissions according to the specific subpart
- If VOC emissions are unknown, highly variable nature, the results should be reported in terms of propane (i.e., Incinerators, boilers, asphalt plants, cement plants, and recovery boilers etc.)

Suggested Reporting of Emissions

- If composition of the effluent is known and a single VOC > 75%, then emissions reported in terms of that compound (i.e., SOCMI facilities etc.)
- If composition of the effluent is known and a single VOC < 75%, then emissions reported in terms of a surrogate compound (i.e., surface coatings, graphic arts etc.)

Suggested Reporting of Emissions

- If testing is for control device efficiency, then emissions can be reported "as carbon" or "as VOCs."
- If testing is to determine if a source is subject to a regulation whose applicability is based upon VOC emission rates, to determine compliance with VOC emission rate standard, or to set permit fees, then the results must be reported "as VOCs" rather than "as carbon."

Suggested Reporting of Emissions

- This means one has to take into account molecular weight (MW) and for FRM 25A, relative response factor (RRF) in determining VOC emission rate.
  - Reporting as carbon in such circumstances would understate the impact of the emissions on the environment and therefore, would lead to incorrect conclusions regarding compliance or rule applicability.

Reporting of Emissions

Example Calculation 1

Calculating the VOC mass emission rate from a source emitting mostly ethanol (C_2H_5OH) using EPA Method 25A data in terms of propane…

$$\left(\frac{\left(\frac{\text{ppmvw as } C_3H_8}{(1-B_{ws})}\right)(K_{M25A})(MW_C)(Q_{sd})}{385.3\text{x}10^{6}}\right)\left(\frac{MW_{C_2H_5OH}}{(\#\text{ C atoms}_{C_2H_5OH})(MW_C)}\right)\left(\frac{RRF_{C_3H_8}}{RRF_{C_2H_5OH}}\right)=\frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

$$\left(\frac{\left(\frac{\text{ppmvw as } C_3H_8}{(1-B_{ws})}\right)(3)(12.01)(Q_{sd})}{385.3\text{x}10^{6}}\right)\left(\frac{46.07}{(2)(12.01)}\right)\left(\frac{1.00}{0.70}\right)=\frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

Reporting of Emissions

Example Calculation 2

Calculating the VOC mass emission rate from a source emitting mostly ethanol (C_2H_5OH) using EPA Method 25 data in terms of carbon…

$$\left(\frac{\left(\frac{\text{ppmvw as C}}{(1-B_{ws})}\right)(MW_C)(Q_{sd})}{385.3\text{x}10^{6}}\right)\left(\frac{MW_{C_2H_5OH}}{(\#\text{ C atoms}_{C_2H_5OH})(MW_C)}\right)=\frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

$$\left(\frac{\left(\frac{\text{ppmvw as C}}{(1-B_{ws})}\right)(12.01)(Q_{sd})}{385.3\text{x}10^{6}}\right)\left(\frac{46.07}{(2)(12.01)}\right)=\frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 18



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1 FRM 2 FRM 3 FRM 4 FRM 5 FRM 18



Survey Canister Sampling



Applicability

- Provides concentration data on approximately 90% of total gaseous organic mass emitted from an industrial source
- Does not include techniques to identify and measure trace amounts of organic compounds (< 1 ppm) , such as those found in building air and fugitive air emission sources

Applicability

- FRM 18 is a generic method which is wide open for quantifying speciated organic compounds
- FRM 18 is a "self-certifying" method….."performance-base" method! Most all other VOC methods are "procedure-base!"
- "Regulatory science" vs. "measurement science!"

Applicability

- FRM 18 will not determine compounds that are
  - Polymeric (high molecular weight)
  - Analytes that can polymerize before analysis
  - Analytes that have very low vapor pressure at stack or instrument conditions ($< 10^{-3}$ mm Hg)

Principle

- Based on separating components of a gas mixture in a gas chromatographic column and measuring separated components with suitable detector (i.e., FID, ECD, PID, MS, IT etc.)
- Uses retention time (RT) as the identification technique compared to standards

Overview Items

- FRM 18 requires analysis of an EPA audit cylinder prior to sample analysis
- FRM 18 strongly suggest/requires performing pre-survey to help identify analytes/column/detector [All tentatively identified compounds (TICs) with peaks > 5%]
- FRM 18 requires conducting a recovery study to meet 70-130 %

Overview Items

- FRM 18 provides concentration (usually in terms of "ppm") for speciated organics
- Mass emission rate can be provided as long as FRM 1 and 2 are incorporated into the monitoring program

Overview Items

- FRM 18 identifies only those analytes for which sampling and analysis is specifically conducted
- FRM 18 can't be used if emissions are unknown
  - FRM 18 (CH3OH,MW=32) 100 ppm x 32 = 3200
  - FRM 25 (C,MW=12) 100 ppm x 12 = 1200
  - Error: 62 %

Overview Items

- FRM 18 requires calibration of analytical system with 3 standards which bracket the concentration of the analyte in the source
  - Neat
  - Gas cylinder dilution
  - Flash vaporization
- FRM 18 requires determination of RRFs for each analyte

Overview Items

- FRM 18, for tube sampling, requires determination of collection efficiency (CE). Tubes (800/200 mg) with no more than 10% of analyte concentration on back portion

Overview Items

- FRM 18 requires determination of recovery study for all methodologies
  - Direct interface: Mid-level gas at probe then analyzer/2 injections (+/- 10%)
  - Bags: Of the 3 sample bags, choose one and spike all analytes into bag (40-60 % of avg. conc. of 3 bags). Recovery 70-130 %
  - Adsorbent tubes: Two sampling trains: Spiked/40-60 % of expect conc. and unspiked; three runs; 70-130 % recovery

Overview Items

- FRM 18 pushes you to using direct injection, Tedlar bags or adsorbents as sampling options
- FRM 18 allows correction of emissions to "Recovery Study" results: Reported emissions = FRM 18 Conc./R
- For solid adsorbent, no more than 10% of analyte found on back tube

Overview Items

- All tubing used in the sampling train must be Teflon…no Tygon tubing allowed
- Aluminized Mylar bags are recommended for low concentration bag sampling because of low permeation rate
- Canister sampling can only be used during survey, not for compliance application

Method Criteria

- Range: 1 ppm to upper limit of GC detector (saturation of detector limiting factor; upper limit can be extended by dilution)
- Sensitivity: minimum detection limit or signal-to-noise ratio 3:1

Method Criteria

- Precision: 5 to 10% RSD of mean value (usually 5% with experience GC operator)
- Accuracy: 10% audit sample value
  - EPA audit samples are available
  - Candace Sorrell (919-541-1064), email: sorrell.candace@epa.gov
- Must conduct recovery study
  - 70-130 % recovery criteria

Interferences

- Resolution interferences
  (may be eliminated by GC column selection and column physics)
- Contamination of analytical system (checked by periodic analysis of blanks)

Interferences

- Cross-contamination from analysis of high to low concentration (prevented by purging system between analysis)
- Water vapor
  (correction factor developed)

FRM 18 Overview

- To determine the concentration of discrete volatile organic compounds (VOCs) in the sample
- Generic GC method
- Pre-survey recommended/required
  - Confirms identity of target analytes and concentration > 5 % peak height
  - Qualitative by RT, quantitative by internal/external calibration technique

FRM 18 Overview

- For speciated VOCs
- Any combination of
  - Sampling techniques, GC Columns, and detectors (Wide open method)
  - Source decides combination as long as recovery criteria are met (70-130%)
  - Recovery performed once per source

FRM 18 Sampling Methods

- Integrated bag
- Glass sampling flask
- Adsorbent tubes
  - Charcoal
  - Silica Gel
  - Florisil®
  - CarboTrap® 300
  - Tenax® TA

(Must perform recovery study for each sampling approach)

FRM 18 Sampling Methods

- Liquid Trapping Media
  - Sulfuric acid for amines
  - Cadmium hydroxide for reduced sulfurs compounds
  - 2,4-Dinitrophenylhydrazine for aldehydes and ketones

FRM 18 Sampling Methods

- Direct Interface: Sample continuously pumped to gas chromatographic (GC) by heated line
  - Analysis conducted on discrete gas samples from sample loop (~ 1mL)
  - All compounds must be separated by one column/detector combination

FRM 18 Sampling Methods

- Dilution Interface: Same as direct interface, but used with extremely high concentrations of target analytes

Using FRM 18

- Know The Characteristics of the Source (Pre-Survey)
  - Specific analytes known
  - Chemical and physical properties of emissions known (i.e., BP, VP etc)
  - Matrix of source known (i.e., % H2O, stack temperature, part. loading etc.)
  - Perform survey with direct injection, Tedlar bags or canisters and identify all TICs with peaks > 5 %

Using FRM 18

- Select Sampling and Analytical Finish for Targeted Analytes
  - State of PA flow chart
  - Determine analytical finish for TICs
  - For solid adsorbents, select through literature resin and tube design
    - Breakthrough volume, desorption efficiency, capacity of adsorbent, design of 800 mg/200 mg
- Perform laboratory evaluation for analyte recovery (Not required by FRM 18)

Using FRM 18

- Perform An Audit of EPA's Gas Cylinder for Target Analytes (This is a Performance Evaluation [PE] Audit)
  - Analysis must agree within 10 % of certified gas values
  - Three analysis must agree within 10 % of each other
- Calibrate all Sampling Components
  - Dry gas meters, flow meters, thermocouples etc.

Using FRM 18

- Conduct Recovery Study (Once/source) For Selected Methodology
  - Direct Interface: Mid-level gas at entrance of probe; Must meet 5 % recovery
  - Tedlar Bag: Spike 1 bag at 40-60 % of emission standard; Must meet 70-130 % recovery
  - Tube Sampling: Two sample trains, 3-runs, one train spiked (40-60% mass); Must meet 70-130 % recovery

Using FRM 18

- Sampling
  - Verify non-cyclonic flow at sampling location
  - If mass emission required, perform FRM 1 and 2
  - Sample
    - Assemble sample train, Leak check, Purge probe, Sample at constant rate/single point, Take necessary data during sampling, Post leak check, Fill out COC, Chill samples if applicable

Using FRM 18

- Calibration of Analytical System and Analysis
  - Calibrate system using minimum of 3 standards that bracket the concentration of analyte in source
  - Determine relative response factor for each target analyte
  - Must identify all TICs > 5 %
  - Determine collection efficiency of 1 tube by analyzing back section. No more than 10 % on back section
  - Correct data to recovery study value

Sampling Flask/Canister

- Samples can be collected in pre-cleaned 250 mL double-ended sampling flask or canisters
  - Cleaning of flask: methylene chloride, soap solution, furnace (500 C for 1 hour)
- Sampling performed by either:
  - Evacuated flask procedure
  - Purged flask procedure

Evacuated Flask/Canister Sampling Procedure

- Flasked/canister cleaned
- Attach "T-connection" to inlet of flask/canister
- Attach 6 mm O.D. borosilicate sampling probe with 12 mm O.D. enlargement at end containing glass wool plug for particle control
- Probe placed > 1 meter from side wall of stack

Evacuated Flask Sampling Procedure

- Use rubber suction bulb to purge probe
- Open stopcock to fill flask/canister
- Heated canister used by NCASI for quantifying methanol, xylenes, acetone, benzene and methyl ethyl ketone (MEK)
- SCAQMD Method 25.3 applicable also

Purge Flask Sampling Procedure

- Attach end of flask to a rubber suction bulb
- Attach probe used in evacuated flask procedure to inlet of flask

Purge Flask Sampling Procedure

- Purge flask, then close stopcock near suction bulb
- Close stopcock near probe
- Tape stopcocks to prevent leakage

Flexible Bag Sampling Procedure

- Pre-survey samples collected in Tedlar® or aluminized Mylar flexible bags
- Flexible bag certification
  - Use new bag
  - Leak check all bags

Flexible Bag Sampling Procedure

- Check for contamination by filling with nitrogen
- Analyze 24 hours later with GC

Bag Sampling

- Assemble sampling train
- Leak check both the bag and container
- Place probe > 1 meter from inside wall
- Purge probe line
- Evacuate container containing flexible bag

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Bag Sampling

- Sample three bags (proportional sampling to stack flow, single point sampling)
- Analyze bag in triplicate
- Spike one of the bags for recovery determination
- Store for hold time period
- Analyze in triplicate


10. 11. 1999

Recovery Study For Bag Sampling

- Recovery must be 70-130%; Field values adjusted to recovery value
- Must analyze performance evaluation (PE) sample (EPA Audit Sample) prior to analysis of stack gas sample
- Audit analyses must agree with the audit concentrations within 10%

Bag Sampling with High Condensation Stacks

- Heat sampling box containing sample bag to stack temperature
- Maintain temperature of bag until analysis (Similar to heated canister approach)
- Add dropout impinger to collect condensate (must be analyzed for VOCs along with bag analysis)

Direct Interface Sampling and Analysis

- Apparatus: Sample probe (~ 6.4 mm), sample line, sample pump, sample valve, flow meters, and heated box
- Assemble equipment and leak check
- Heat sample probe, line, and sample box to 1 to 3°C above stack temperature

Direct Interface Sampling and Analysis

- Perform analysis of mid-level calibration gas through the sample line behind probe outlet.
- Response should be +/- 10% of true value and two readings must be within +/- 5%

Direct Interface Sampling and Analysis

- Response to calibration gas analysis should be accurate to within 10 %
- Reconnect probe, analyze stack gas
- Analysis of stack gas must agree with the two analyses to within 5 %

Direct Interface/Dilution Sampling and Analysis

- Same apparatus as direct interface except a dilution system is added between heated sample line and the gas sampling valve
- Apparatus arranged so either a 10:1 or 100:1 dilution of source gas can be directed to the GC analyzer

Direct Interface/Dilution Sampling and Analysis

- Verify accuracy of dilution system by analyzing calibration gas with agreement within 10 % of expected value
- Analyze low concentration calibration gas into analyzer twice
- Analysis should be within 5 % of each other

Adsorbent Tube Procedure

- Samples are collected in adsorbent tube containing specific amounts of adsorbents packed as primary and secondary sections (Dual bed tubes)
  - 800/200 mg for charcoal tubes
  - 1040/260 mg for silica gel tubes

Adsorbent Tube Procedure

- Tube design left up to user and selection of resin as long as:
  - Breakthrough volume determined;
  - Desorption efficiency determined; and
  - Capacity of adsorbent determine under stack conditions (i.e., temperature, moisture etc.)

Adsorbent Tube Design

- Adsorbents such as Tenax® GC or XAD-2® can also be used
- Typical tube design is 90 mm X 6 mm
- Dual sampling trains
- Dual components of tubes (< 10% in back tube)
- Audit analysis of +/- 10%

Nature of Ideal Adsorbents

- Very high surface area
- Irregular shape
- Non-polar
- Non-reactive
- Granular

Nature of Ideal Adsorbents

- High capacity
- Inert
- Non-corrosive
- Readily activated
- Easy release

Advantages of Adsorbent Technology

- Small sample configuration
- First element in sampling train
- Large selection of adsorbents
- Better water management
- Large database

Typical Adsorbents

- Organic polymer adsorbent
- Inorganic adsorbent
- Carbon adsorbents

Classification of Adsorbents

- Weak (50 m^2/g)
  - Tenax®, Carbopack C®, Anasorb®
- Medium (100-500 m^2/g)
  - Carbopack B®, chromosorbs
- Strong (> 1000 m^2/g)
  - Carbosieve S-III®, Carboxen®

Typical Organic Polymeric Adsorbents

- Tenax-GC® or Tenax-TA®
- Porapack Q®
- Carbon molecular sieve
- XAD® series

Weaknesses of Tenax® Adsorbent

- Poor desorption of highly polar compounds
- Possibly retains O_2 leading to sample oxidation
- Limited to specific range of VOCs

Weaknesses of Tenax® Adsorbent

- Possible background contamination
- Low breakthrough volume for many of the analytes of interest

Weaknesses of XAD® Series Adsorbent

- Thermal stability questionable
- Breakthrough extensive for < C7

Inorganic Adsorbents

- Silica gel
- Alumina
- Fluorisil
- Carbon molecular sieves

Weaknesses of Silica Gel Adsorbent

- Limited use in high moisture stacks
- Thermal breakdown of silica gel
- Solvent extraction
  means dilution of sample

Weaknesses of Carbon Molecular Sieve Adsorbent

- Holds onto very volatile compounds
- Solvent extraction means dilution
- Desorption efficiency decreases with analytes that have boiling points (BP) > 100°C

Carbon Adsorbent

- Activated carbon
- Carbon molecular sieve
- Carbonaceous polymeric adsorbents

Limitation of Carbon Base Adsorbents

- High surface area causes artifact formation
- High background contamination possible
- Very high affinity for water
- High catalytic activity

Limitation of Carbon Base Adsorbents

- Incomplete sample recovery during solvent extraction
- Impurities in solvents used during extraction
- Solvent extraction means dilution

Common Adsorbents Used in Air Pollution Studies

- Carbon
- Tenax-TA®
- Porapack Q®
- Polyurethane foam

Common Adsorbents Used in Air Pollution Studies

- Carbon molecular sieve
- XAD® Series
- Carbosieve S-III® /Carbotrap® /Carbotrap C® (Carbotrap 300®)

Adsorbent Selection-Capture Process (Analyte Boiling Point)

- Carbosieve S-III ® for VOCs with boiling points between -15°C to 80°C
- Carbotrap® for VOCs with boiling points between 0°C to 100°C
- Carbotrap C® for VOCs with boiling points between 80°C to 250°C

Adsorbent Selection-Capture Process (Analyte Boiling Point)

- Tenax-TA® for VOCs with boiling points from 30°C to 200°C
- XAD-2® for VOCs with boiling points from 120°C to 350°C

Supelco Carbotrap® 300

Carbotrap C®	Carbonaceous material	Heavy Organics (> C_{12})
Carbotrap®	Carbonaceous material	C_5 to C_{12}
Carbosieve S-III®	Carbon molecular sieve	C_2 to C_6

Adsorbent Recovery
Two Process Recoveries

- Thermal Desorption
  - Entire sample analyzed
  - More readily automated
  - Only one analysis

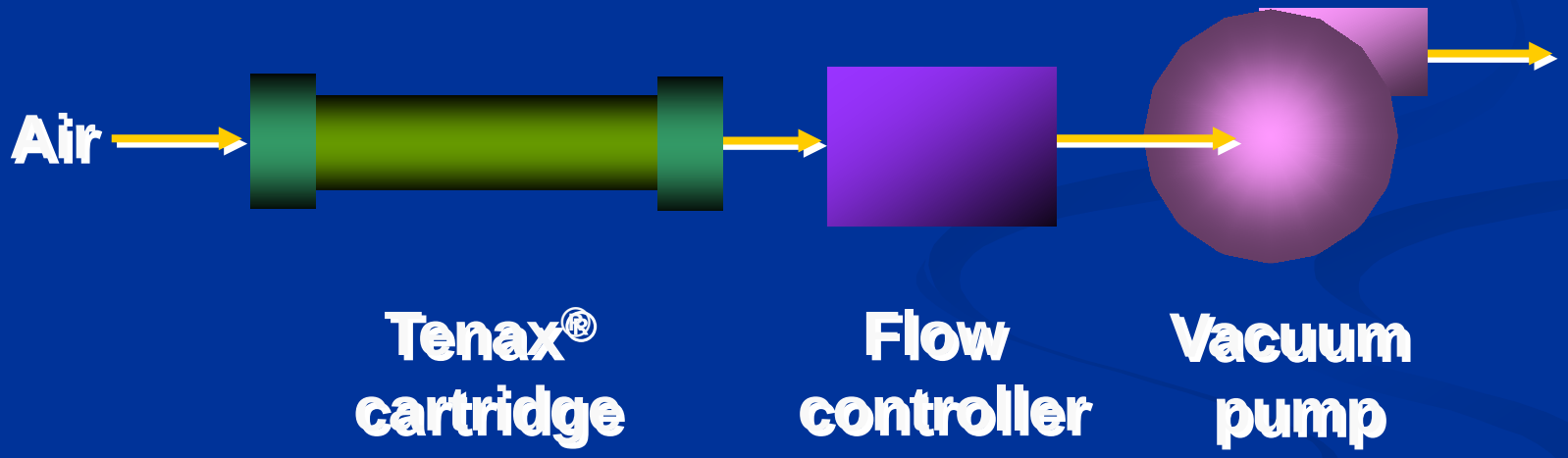
Adsorbent Recovery Solvent Extraction

- Solvent Extraction
  - Able to adjust concentration
  - Replicate analysis
  - No thermal desorbtion breakthrough products
  - However, dilute sample

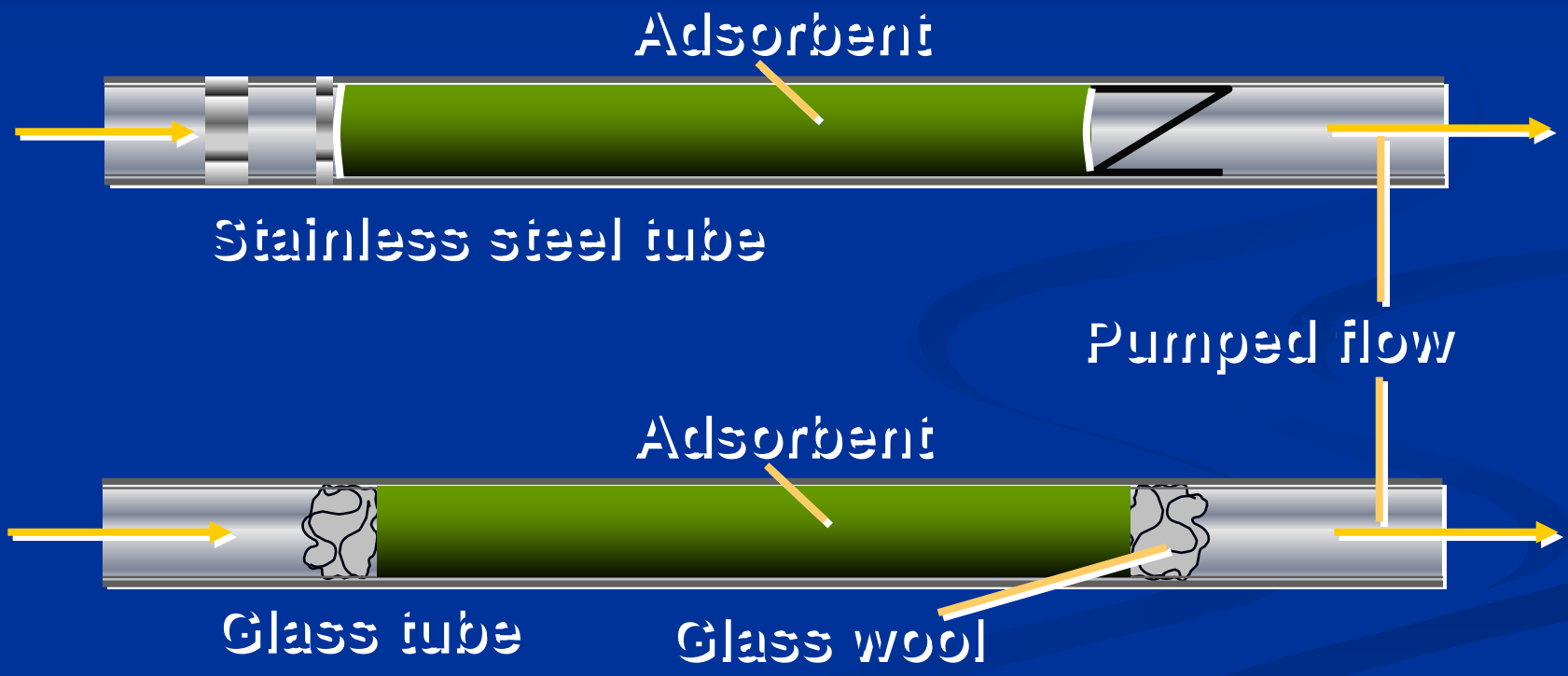
Adsorbent Tube Sampling Train

- Heated probe (~ 6 mm I.D.), in-stack or out-of-stack filter (heated), flexible tubing, leakless sample pump, rotameter, and adsorption tube
- All temperature and flow measuring devices must be calibrated

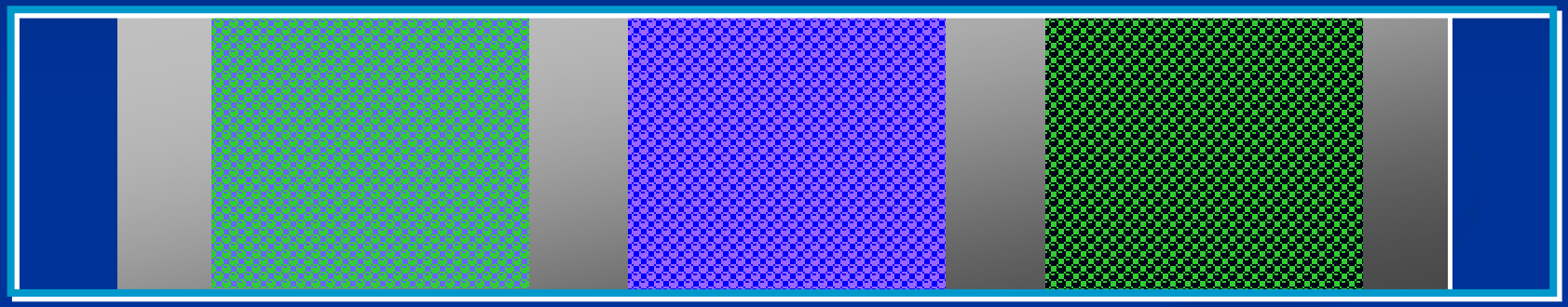
Active Sampling System Utilizing Solid Adsorbents

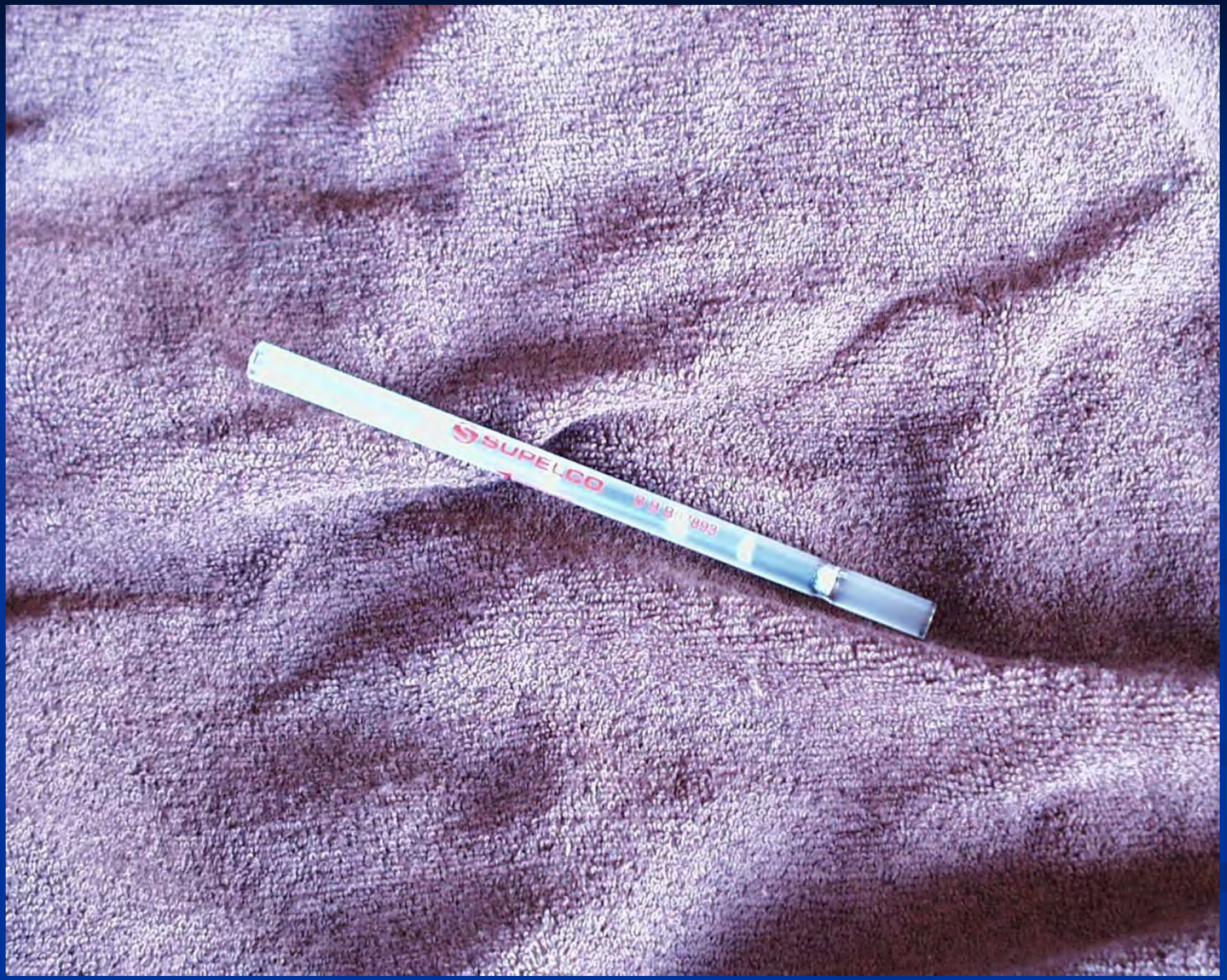


Single Tube Design- Glass/Stainless Steel



Multi-bed Adsorbent Trap




SUPELCO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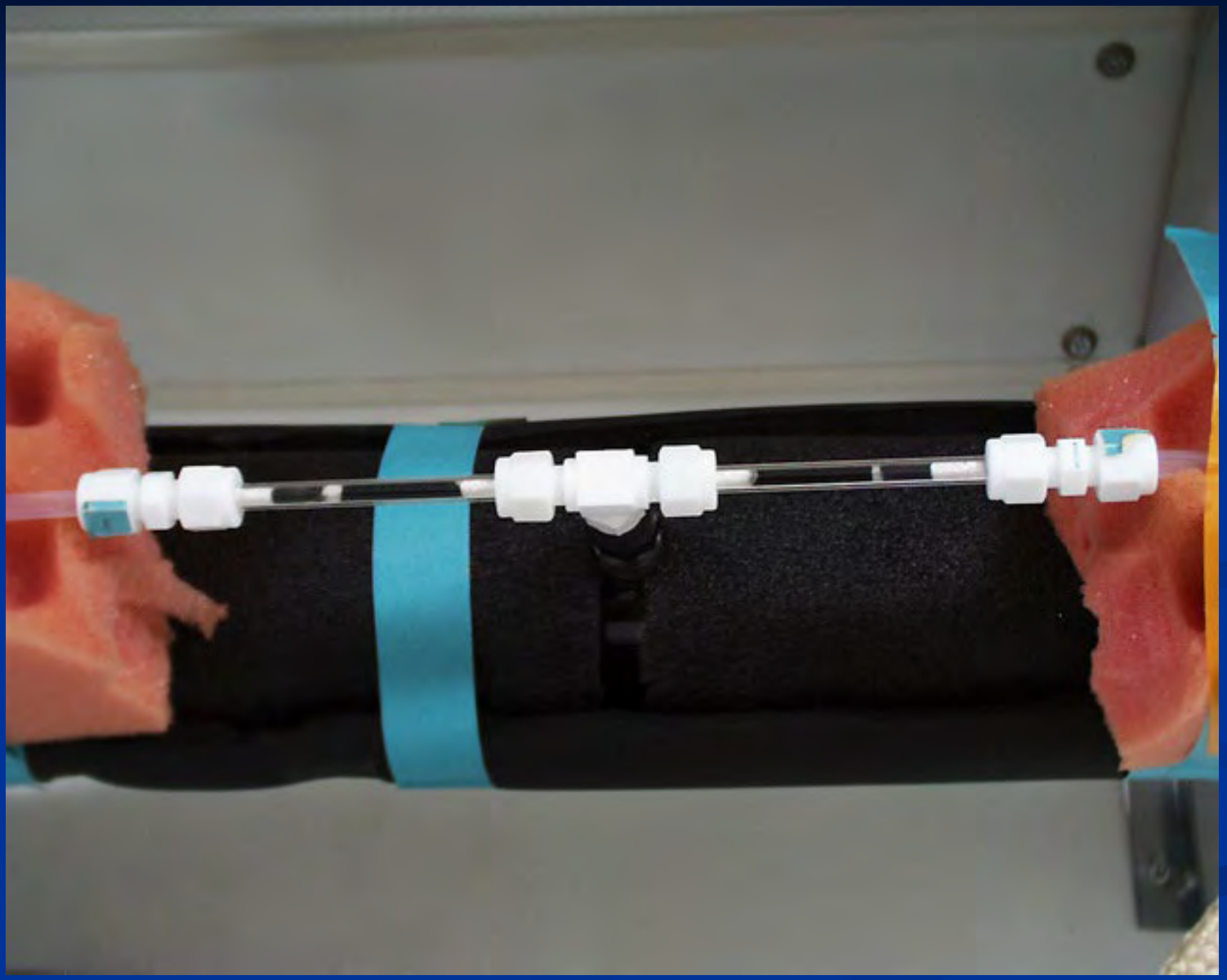



SUPELCO INC
SUPELCO INC
SUPELCO INC
SUPELCO INC

Adsorbent Tube Sampling

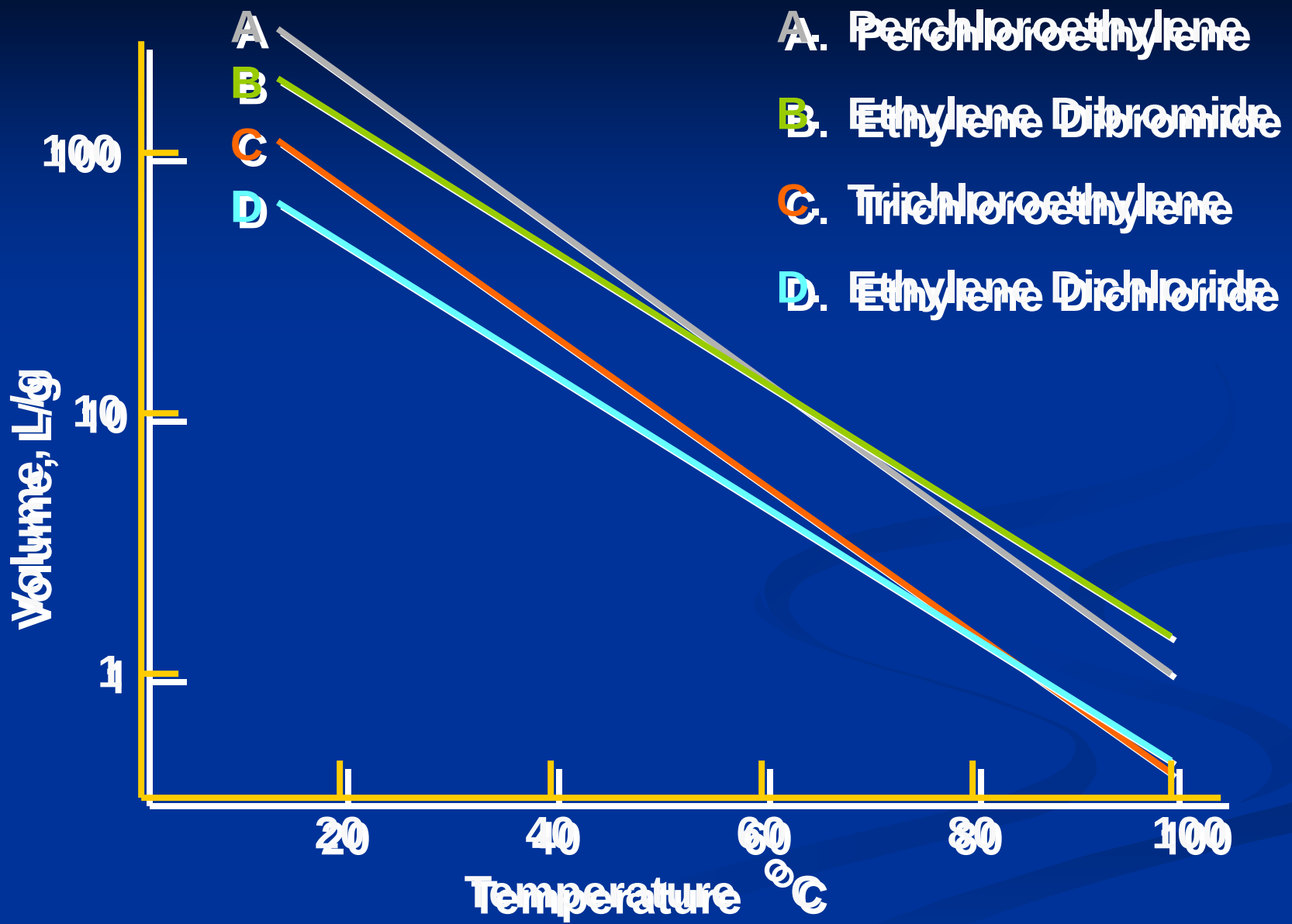
- Strengths
  - Sample compact and easy to use
  - Sample returned to laboratory for analysis
  - Good sample storage time

Adsorbent Tube Sampling

- Weaknesses
  - Quantitative recovery poor
  - Breakthrough possible of interested analytes
  - Moisture may effect sample recovery

Breakthrough Volume

- Breakthrough volume is when the analyte entering the adsorbent bed is also leaving the adsorbent bed at the same rate


A
B
C
D
A. Perchloroethylene
B. Ethylene Dibromide
C. Trichloroethylene
D. Ethylene Dichloride
100
10
1
Volume, L/g
20
40
60
80
100
Temperature °C

Published Breakthrough Volumes (at 20°C)

- Vinyl Chloride 0.6 L/g
- p-Dichlorobenzene 820 L/g
- Chlorobenzene 184 L/g
- Benzene 36 L/g
- Carbon Tetrachloride 27 L/g

Safe Sample Volume

- Safe sample volume is the published breakthrough volume (liters/gram of adsorbent) divided by 1.5 times the weight of the adsorbent used in the system

Published Safe Sample Volumes

- Vinyl Chloride <1.0 L/g
- p-Dichlorobenzene 290.0 L/g
- Chlorobenzene 74.0 L/g
- Benzene 14.0 L/g
- Carbon Tetrachloride 11.0 L/g

Adsorbent Tube Sampling

- Determine "breakthrough volume" in order to calculate sampling time and volume
- Perform recovery study of the analytes of interest during the actual field test
  - Two identical sampling trains collocated in stack

Adsorbent Tube Sampling

- Recovery study (Two sampling trains)
  - One train spikes (all compounds of interest) and the other unspiked train
  - Amount of analyte spiked should be 40-60% of mass expected to be collected by unspiked train
  - Field data adjusted with recovery value (R)

Adsorbent Tube Sampling

- Sample the stack gas with the collocated sampling trains for a total of 3 runs
- Determine the fraction of spiked compound recovered (R)
- Criteria of 70<R<130% must be met in order for sampling technique to be used for specific analyte
- < 10% in back half of adsorbent tube
- Audit analysis agrees within +/- 10%

Direct Interface Sampling

- Strengths
  - Sampling provides for immediate analysis
  - Minimize loss or alteration to analytes during sampling
  - Method of choice for steady state processes when duct temperature is below 100°C and organics suitable for GC analysis

Direct Interface Sampling

- Weaknesses
  - GC at site, can't integrate sample, non-steady state, poor recovery

Tedlar® Bag Sampling

- Strengths
  - Sample collected over time and has same compounds and concentrations as stack emissions
  - Sample may be returned to laboratory for analysis
  - Multiple analysis

Tedlar® Bag Sampling

- Weaknesses
  - Tedlar® bags awkward and bulky for shipment, stability of compounds, can't do polar

Recovery Studies

- Direct Interface: Mid-level calibration point for 1 analysis (+/- 10%) repeated twice (+/- 5%)
- Bags: After three analysis, choose bag, spike at 40-60% of avg. concentration (70-130 % recovery), field data adjusted to R value
- Solid Adsorbent: Two identical sampling trains, one spiked and one unspiked, 70-130 % recovery, field data adjusted to R value

Which Sampling Technique Should Be Used?

- Direct Interface: Excellent, provides real-time data if all analytes can be separated by one column/detector combination
- Dilution Interface: Same benefits as direct interface; excellent if high concentrations of target compounds are present in stack gas

Which Sampling Technique Should Be Used?

- Adsorbent Tube: Excellent if concentrations of target compounds are sub-ppm levels
- Bag Sampling: Everybody's favorite; cheap; excellent when more than one detector is needed; excellent for explosive environments

FRM 18
Adsorbent Tube Sampling

- Any commercially available adsorbent is allowed
- May use water knockout impinger before adsorbent

FRM 18
Adsorbent Tube Sampling

- Must perform dual sampling trains, one spiked and one unspiked
- Three dual-sampling trains constitutes a test

FRM 18
Adsorbent Tube Sampling

- Desorption/analysis usually performed in lab
- May perform solvent or thermal desorption
- If solvent desorption, analyze each in triplicate

FRM 18
Adsorbent Tube Sampling

- If thermal desorption,
  analyze each sample once
- Recovery of PE must be 70-130%

FRM 18
Adsorbent Tube Sampling

- Method applicable to most sampling programs when
  - 10 or less compounds
  - compounds are known
  - fairly high vapor pressure at room temperature

FRM 18
Adsorbent Tube Sampling

- ppb to ppm levels dependent on use of adsorbent or Tedlar® bag
- mass balance around system is required
- should not be used after combustion source unless compounds identifiable

FRM 18 Pre-survey Requirements

- A pre-survey shall be performed on each source to be tested to obtain all information necessary to design emission test
- Pre-survey optional if target compounds are known

FRM 18 Pre-survey Requirements

- Only place where canister sampling is allowed
- Typically grab sample, qualitative analysis, GC/MS for identification
- Canisters can be used during pre-survey

FRM 18 Pre-survey Requirements

- Obtain stack temperature and temperature range
- Obtain approximate particulate concentration
- Obtain static pressure and water vapor content

FRM 18 Pre-survey Sample Train Selection

- 250 mL double-ended glass sampling flask (specified cleaning procedures provided)
- Method 7 evacuated flask
- Tedlar® or aluminized Mylar flexible bag
- Adsorption tubes
- Specially-treated canisters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FRM 18 Pre-survey Sample Analysis

- Select GC columns based upon manufacturer's recommendation
- Select GC conditions for good resolution by varying conditions after 1st injection

FRM 18 Pre-survey Sample Analysis

- Heat pre-survey sample to duct temperature
- Analyze pre-survey samples using retention time (RT) compared to calibration standards

Criteria for Pre-survey and Sample Analysis

- Prepare calibration standards by proper technique
- Determine optimum GC settings
- Obtain retention times with repeatability of ±0.5 seconds

Criteria for Pre-survey and Sample Analysis

- Use smaller sample loop or dilution if necessary
- Identify all peaks > 5% of the total area (i.e., tentatively identified compounds [TICs])

Preparation of Calibration Standards

- Liquid standard in desorbing solution
- Direct analysis of NIST reference gases or commercial certified gas mixtures

Preparation of Calibration Standards

- Gas dilution from high concentration of gas cylinder
  using calibrated rotameters
- Direct syringe-bag dilution for known quantity volatile liquid material

Preparation of Calibration Standards

- Indirect syringe-bag dilution for known quantity of less volatile liquid materials

FRM 18 Final Sampling and Analysis Procedure

- Consider safety and source conditions, select appropriate sampling and analysis procedures (use direct interface if source < 100°C and organics suitable for detection)

FRM 18 Final Sampling and Analysis Procedure

- If source has high concentration (> 100 ppm), then select direct dilution interface technique

FRM 18 Compliance Test Direct/Dilution Interface

- On-line, on-site GC
- Real-time analysis
- Triplicate injections, three concentrations of each target compound for generation of calibration curve

FRM 18 Compliance Test Direct/Dilution Interface

- Calibration gas must be certified to 2% accuracy by manufacturer
- Method 205 allowed

FRM 18 Compliance Test Direct/Dilution Interface

- Recovery study basically leak check, 70-130% recovery
- Five consecutive samples equals a run

FRM 18 Compliance Test Direct/Dilution Interface

- Post-test calibration check
  - If > 5% difference, use both curves
  - If < 5% difference, use first curve generated

FRM 18 Summary

- Source has great flexibility in choosing sampling/analytical methodology (as long as recovery criteria are met)
- Encourage direct/dilution interface: real-time data, less chance of sampling loss

FRM 18 Summary

- Any detector, including mass spectrometer, may be used
- Any adsorbent is allowed as long as recovery met
- Analyte recovery performed once per source
- Canisters are not allowed as a compliance test technique

FRM 18 Reporting Results

- Reported Results = (Measured concentration, ppm)/ R
- R = Recovery = $(m_v)(V_s)/S$
  - S = Theoretical mass

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 25: TGNMOs as C



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1 FRM 2 FRM 3 FRM 4 FRM 5 FRM 25

Family of Method 25s

- FRM 25: Total VOCs
- FRM 25A: Instrumental FID
- FRM 25B: Instrumental NDIR
- FRM 25C: Landfill Gases
- FRM 25D: VOC Waste Sample
- FRM 25E: VOC Waste Sample

Applicability

- Method 25 applies to the measurement of volatile organic compounds (VOCs) as total gaseous nonmethane organics (TGNMO), condensable and non-condensable, as carbon in source emissions
- This method is not applicable for the determination of speciated VOCs or organic particulate matter

Method 25

- Applicability
  - Originally developed for determining the percent reduction of VOC emissions achieved by emission control devices for automobile and light-duty truck surface coating operations
- Concerns
  - Complex method
  - Use as last resort
  - Use FRM 18 first as survey tool

FRM 25 Timeline

- Original Proposed 10/05/79
- Promulgated 10/03/80
- Amendment 11/07/86
  - Added filter heating system
  - Redesigned condensate trap
  - Specified oxidation catalyst
  - Specified new separation column
- Corrections 04/07/88

Method 25 Applicability

- Concerns
  - Not applicable for measuring concentrations of VOCs or mass emissions of VOCs from sources whose concentrations are < 50 ppm
  - Possible bias when:
    - % CO_2 X % H_2O > 100
  - As water freezes in the trap, CO_2 is trapped out prematurely. The CO_2, when reduced to methane, is counted as VOCs in the analytical system

Method 25 Applicability

- Concerns
  - Not applicable for measuring emissions from sources whose principle solvents are chlorinated hydrocarbons
  - Generally, for any situation where a more simpler procedure is more accurate
  - High organic droplets in gas stream can cause high bias or data variability

Method 25 Applicability

- Concerns
  - Source which has a complex flue gas flow
  - Moisture content of the exhaust gas is much higher than what is found in the audit sample
  - The presence of organic and inorganic particulates in concentrations larger than those found in the audit sample
  - Presence of droplets, tar, and wax aerosols

Historical Method 25 Common Problems

- High gas sample moisture content and freezing of trap
- Probe exit and filter temperatures not within specifications
- Non-constant sample flow rate
- Use of Method 25 for measuring low levels of VOCs from source
- Measurement in ducts containing organic droplets


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Method 25 Principle

- A gas sample is withdrawn from the stack at a constant rate through a chilled condensate trap (dry ice temperature) by means of an evacuated sample tank (> 4 L)
- Condensate trap is 3/8 " stainless steel packed with glass wool
- TGNMO are determined by combining the analytical results obtained from independent analysis of the condensate trap and sample tank fraction

Method 25 Applicability

- Applicable to all sources where VOC emissions are to be expressed as carbon (C)
  - To be used where there are too many solvents being emitted simultaneously
  - No speciation required

Method 25 Applicability

- After a combustion source where compound conversion takes place and identification is difficult
- A mass balance is not required (i.e., capture efficiency is not determined)

Method 25 Interference

- Organic particulate matter will interfere with the analysis; therefore, a particulate filter may be required (i.e., in-stack or out-of-stack)

Method 25 Advantages

- Gives constant results from source to source whether sample composition is known or not
- Sample train does require heated probe and filter, but is less complicated than FRM 5 hardware

Method 25 Disadvantages

- Will not yield true mass emission rate nor instantaneous results
- No real time data (sample must be returned to laboratory for analysis)
- High moisture and CO_2 together can cause interference
  - $(\%CO_2)(\%H_2O)>100$ gives potential high bias (EPA Guidelines)

Method 25 Summary

- Withdraw emission sample from stack through chilled condensate trap (dry ice) into evacuated cylinder
- Analyze contents of trap and cylinder separately
- Oxidize organic content of trap to CO_2
- Reduce to methane, measure with FID

Method 25 Summary

- Inject portion of cylinder sample into GC to separate non-methane organics, oxidize NMO to CO_2, reduce to methane, and measure with FID
- Combine results (condensable and non-condensable) and report as total gaseous nonmethane organics (TGNMO)

Method 25 Apparatus

- Sampling System
  - Probe (260 °C)
  - Filter (250 °C +/- 5 °C)
  - Condensate trap (-78 °C) for condensables
  - Flow control system
  - Sample tank for non-condensables


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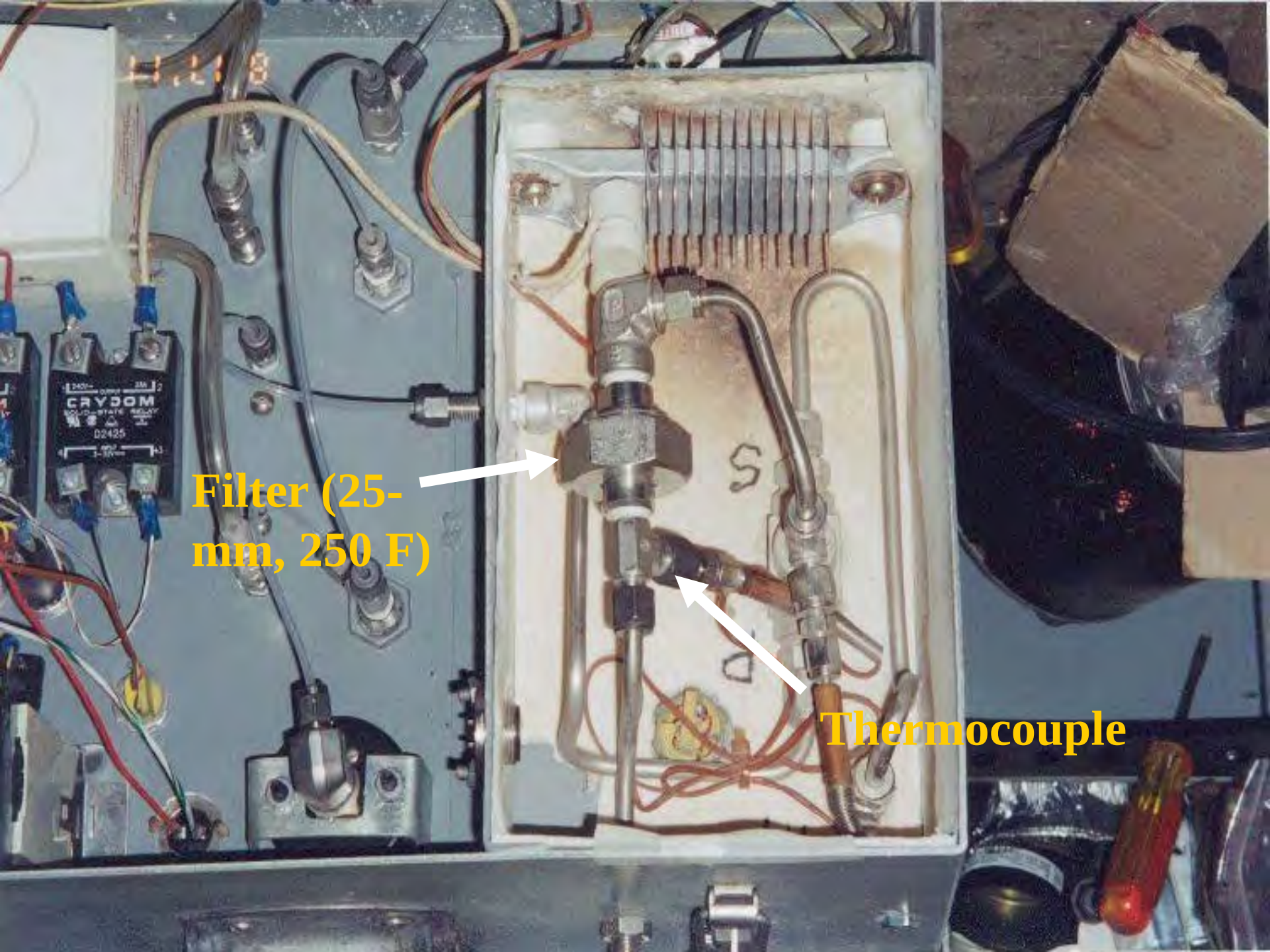
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Thermocouple
CRYDOM
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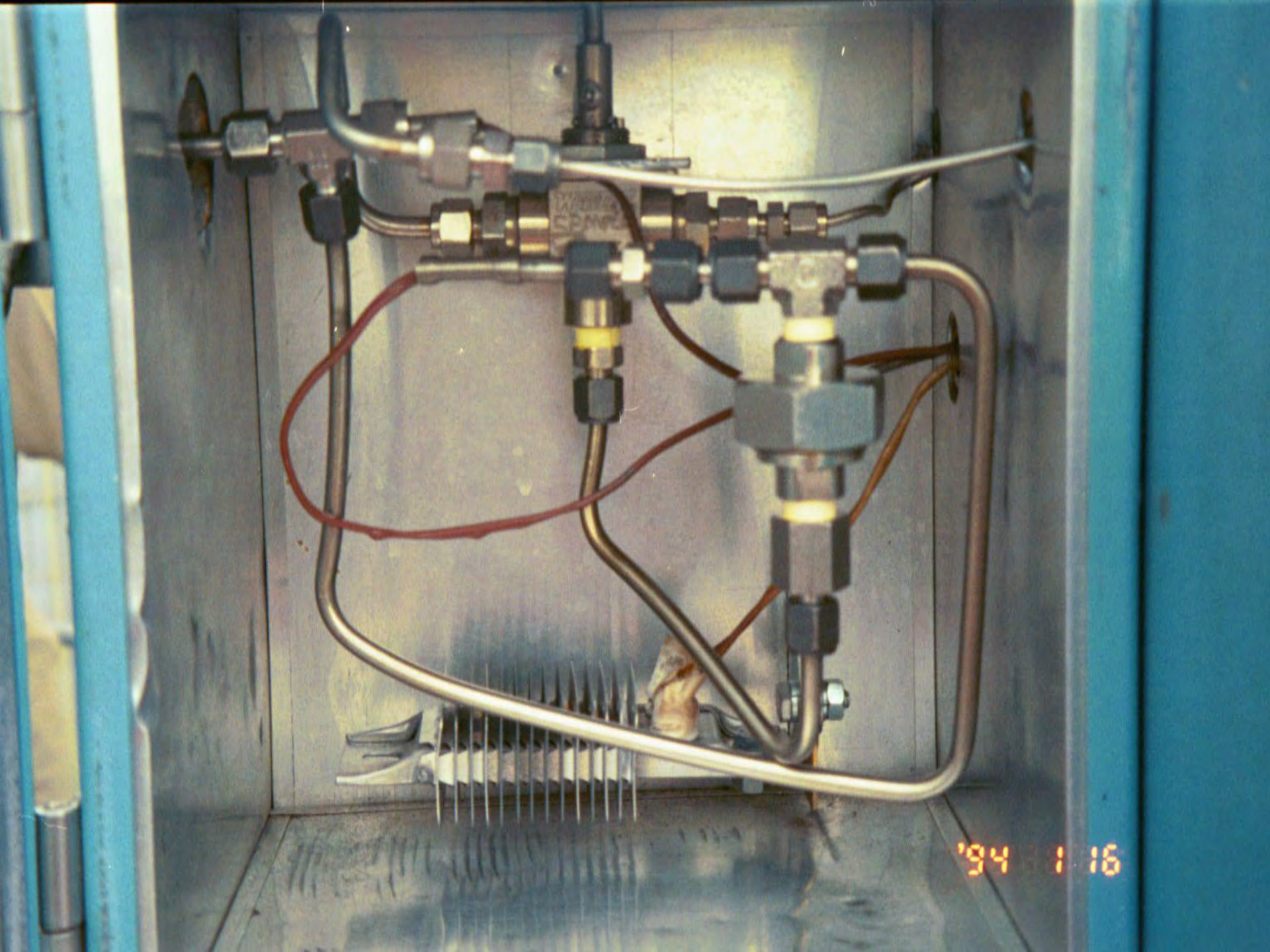
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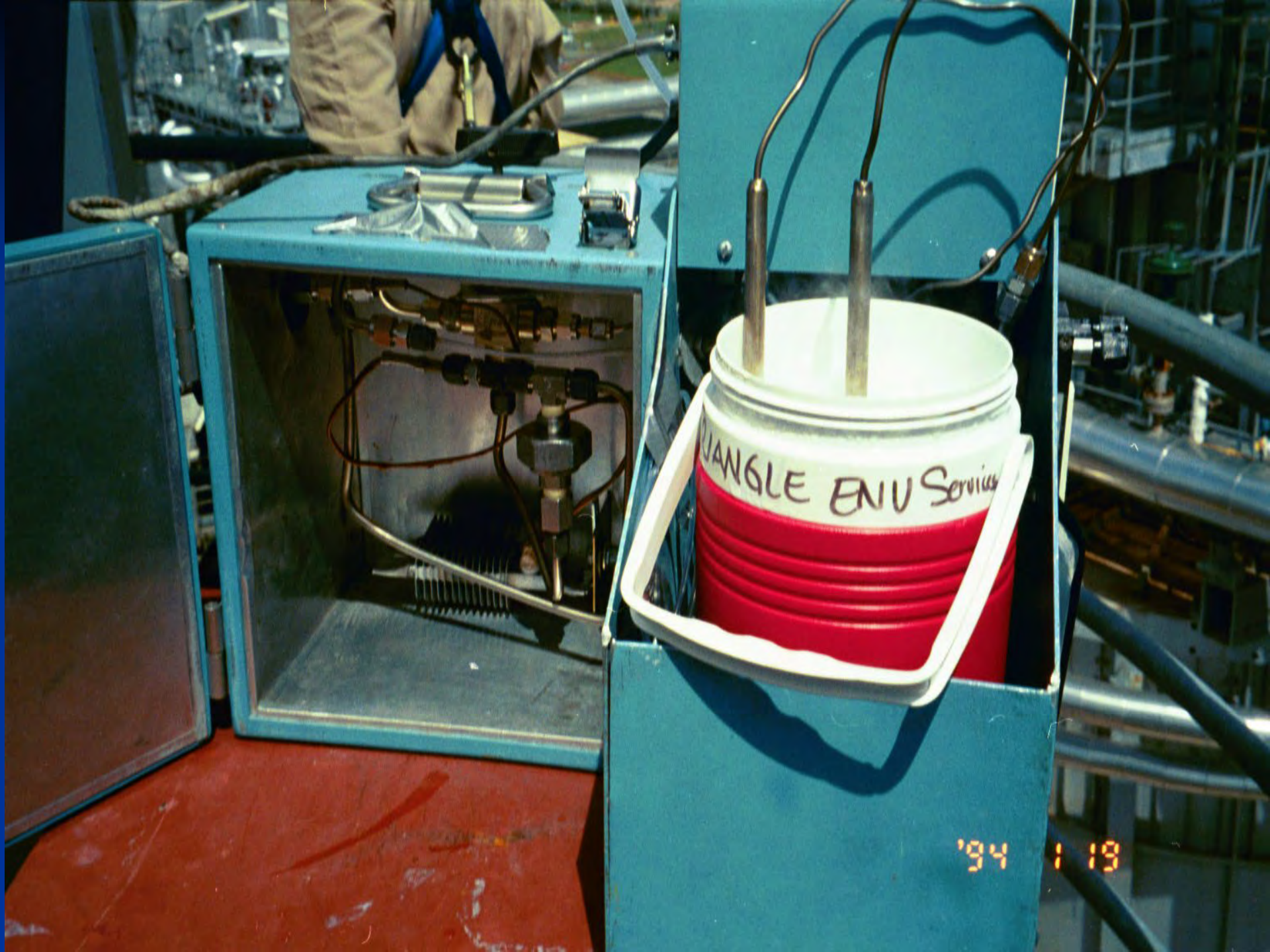
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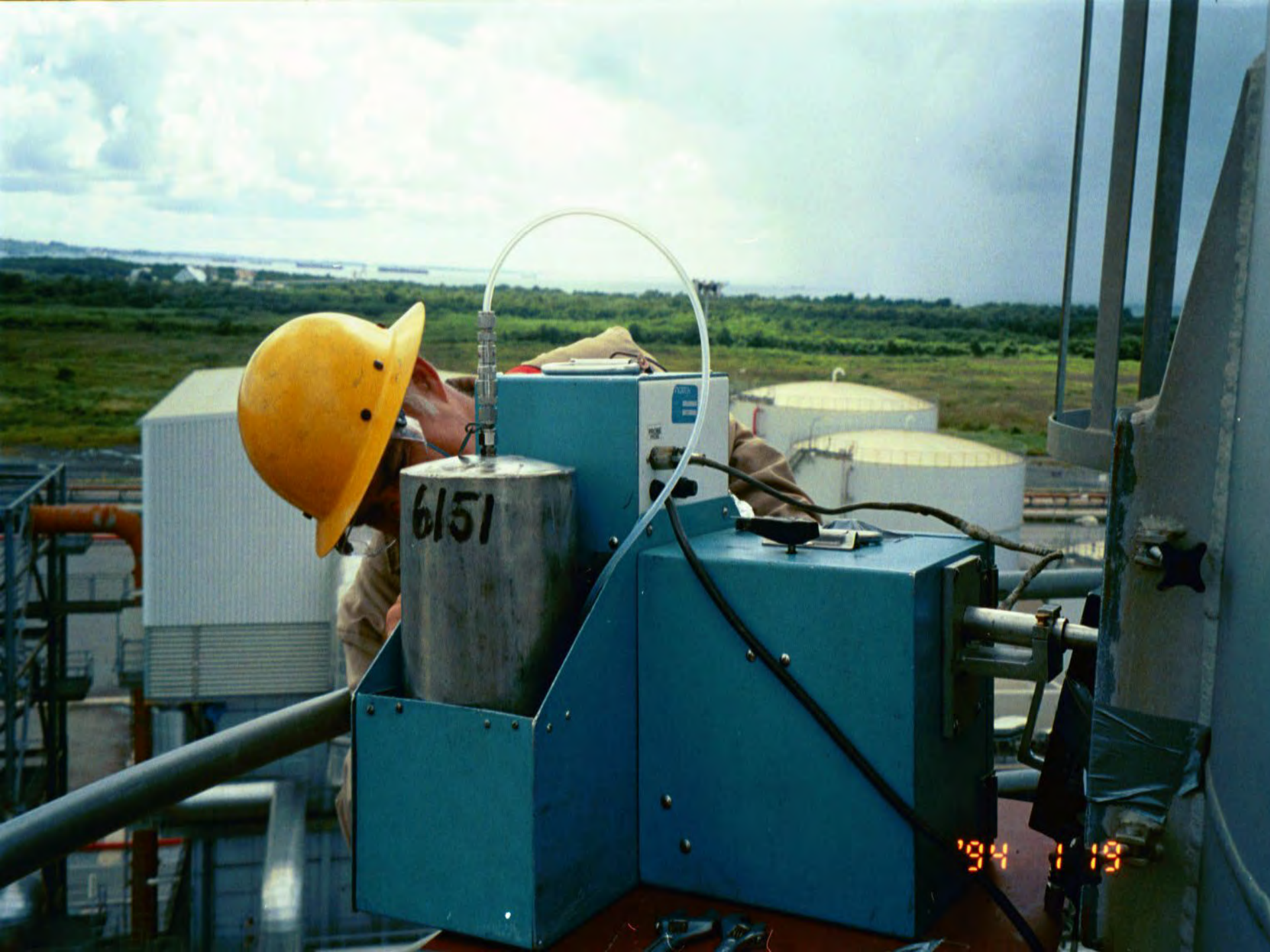
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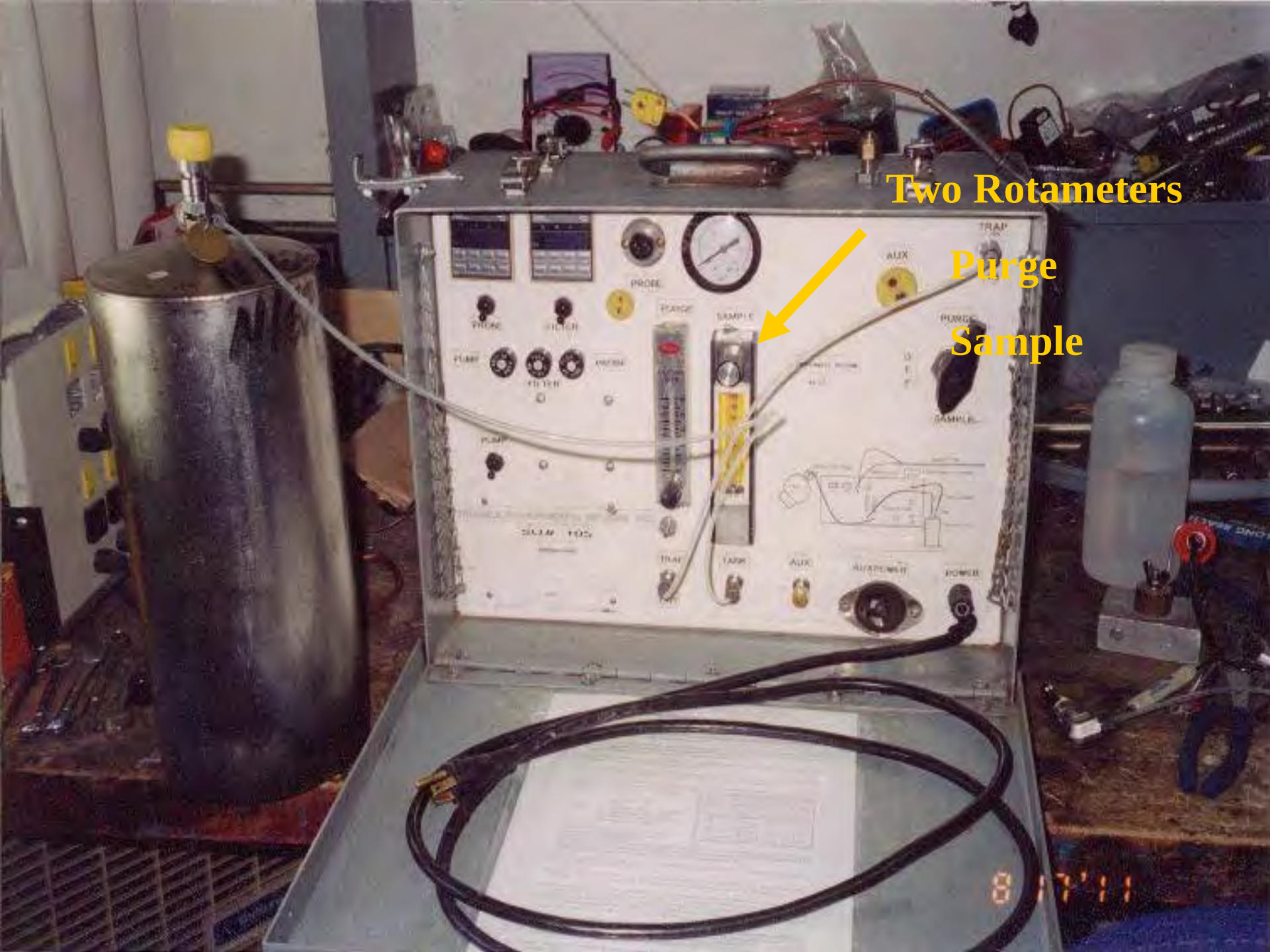
Two Rotameters
Purge
Sample


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EMISSIONS-VELOCITY PROBE
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Calibration of Sampling System

- Sample tank volume (Measure to nearest 5 mL or 5 g)
- Volume of sampling train from probe tip to sample tank valve (This volume maximum should be 100 mL)

Calibration of Sampling System

- Sample tank: Within 5 g or 5 mL
- Sample train volume: No limits (< 100 mL)
- Rotameter: Not calibrated
- Thermometers: Within 3°C of true value
- Barometer: Within 0.1 in. Hg of mercury-in-glass barometer

Method 25
Sampling Train Preparation

- Leak check the tank (#1)
- Assemble the sampling train
- Leak check the entire sampling train

Method 25
Train Preparation

- Evacuate sample tank to 10 mm Hg. Record on field test data sheet (FTDS). Set aside and recheck within 1 hour. Should be within 2 mm of previous reading
- Just before train assembly, measure tank vacuum

Method 25
Train Preparation

- Assemble sampling system; immerse condensate trap in dry ice ~ 30 minutes before sampling
- Plug probe tip

Method 25
Train Preparation

- Evacuate sampling system from probe tip to valve to 10 mm Hg
- Close purge valve, turn off pump, wait 10 minutes
- Record Δ P. Vacuum should not change more than 2 mm to be acceptable

Method 25
Train Preparation

- Calculate maximum allowable pressure change based on leak
  rate of 1% and compare to measured Δ P
- Record findings on FTDS

Method 25 Sampling

- Mark probe for point of average stack gas velocity (probe ≤ 36 in. as specificed in FRM 25)
- Check dry ice level (Maintain as high level as possible)
- Calculate flow rate, record time, set flow rate, probe temp, and filter

Method 25 Sampling

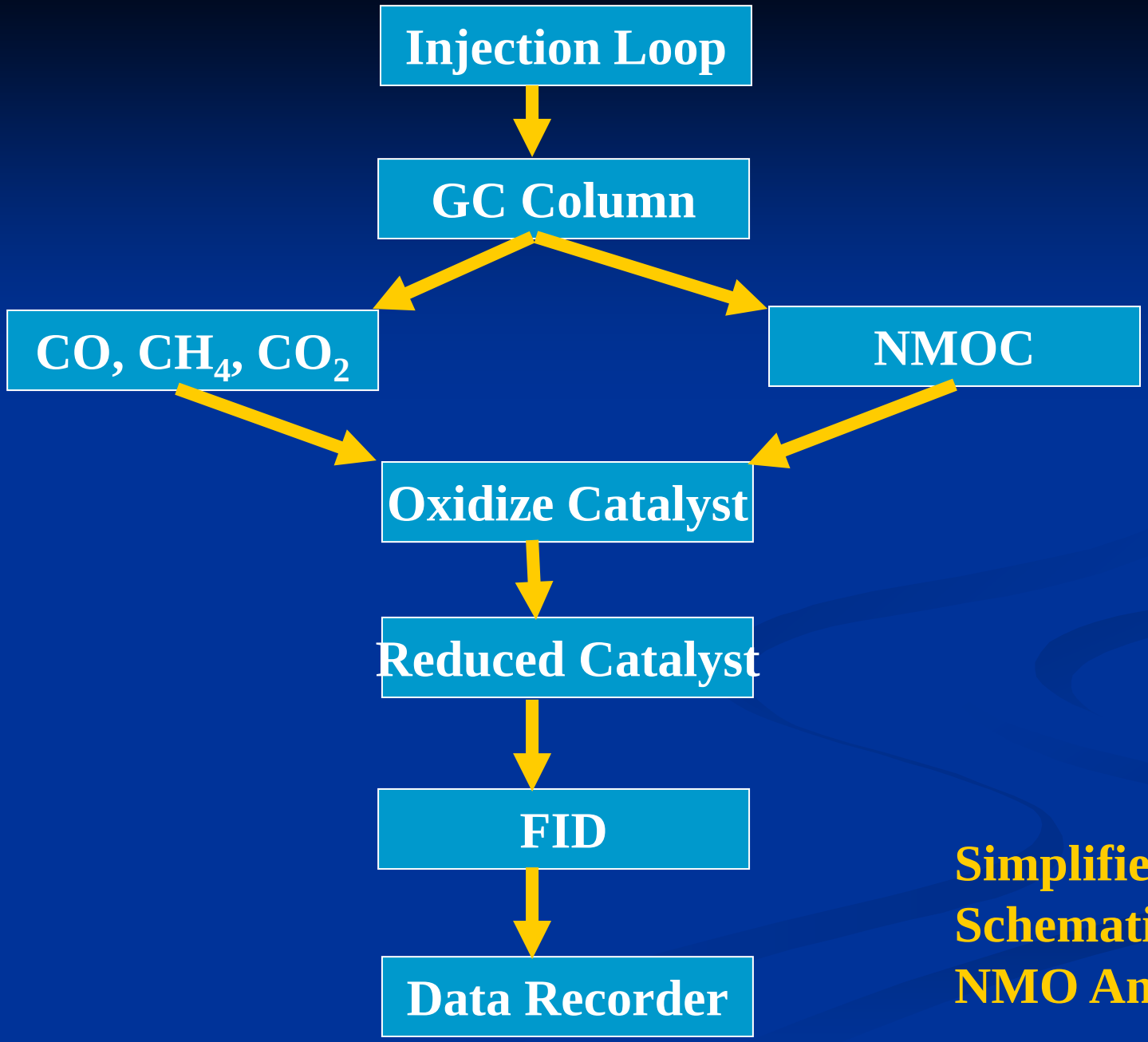
- Attach trap to sampling train
- Position probe tip perpendicular to stack gas flow (Take plug off end)
- Purge sampling train, then adjust flow rate

Method 25 Sampling

- Record sample tank vacuum, flow meter settings, and temperatures at 5 - minute intervals on FTDS
- Sampling must be ±10% over duration of sampling rate between 60-100 mL/min (i.e., 3.6 to 6.0 L of total sample acquired)
- After sampling, record final readings

Method 25 Sampling

- Recover components, disconnect sample tank, record tank vacuum
- Disconnect condensate trap, seal both ends with brass fittings
- Record final readings on FTDS and chain-of-custody
- Pack trap in dry ice during storage and shipping



Simplified Schematic of NMO Analyzer

Method 25 Sample Analysis

- Condensables in the trap are vaporized and oxidized to CO_2
  and collected in a separate (#2) evacuated tank
- The CO_2 (which are the original condensable organics from sampling) in #2 tank is then injected into the NMO analyzer, reduced to methane, and detected with an FID

Method 25 Sample Analysis

- Non Condensables
  - The non-condensables sample in the original field sample tank (#1) is injected into the analyzer
  - Methane, CO, CO_2, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO_2, reduced to methane and detected with an FID

Method 25 Apparatus

- Analytical System
  - Oxidation system for recovery and conditioning of condensate trap contents
    - Heat source
    - Oxidation catalyst (chromia@ 650 C)
    - Non-dispersive infrared analyzer (NDIR)
    - Intermediate evacuated canister (#2)

Method 25 Apparatus

- NMO Analyzer
  - GC with back-flush capability
  - Oxidizing/reducing catalyst (Ni @ 400 C)
  - FID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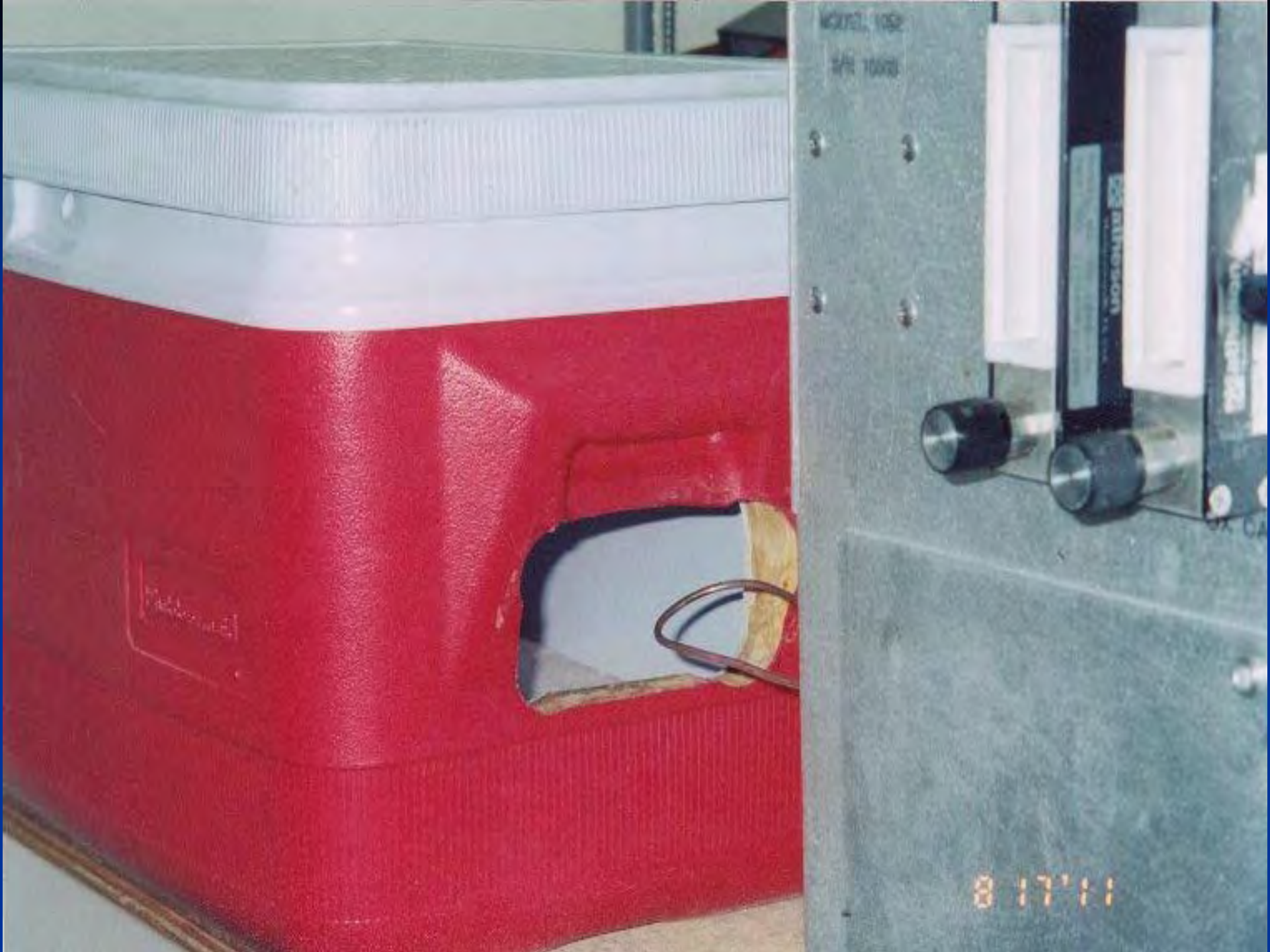
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FLOW
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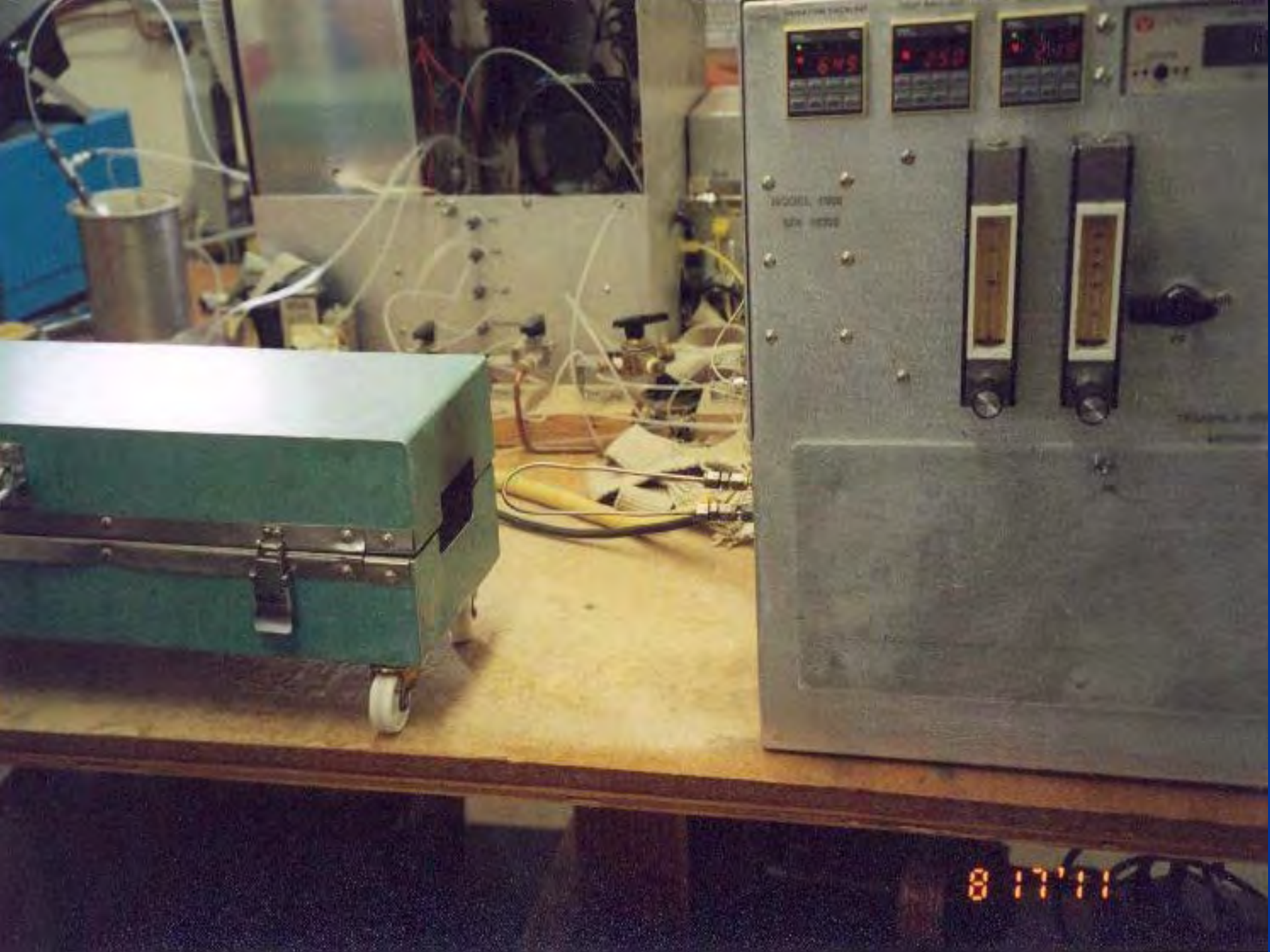
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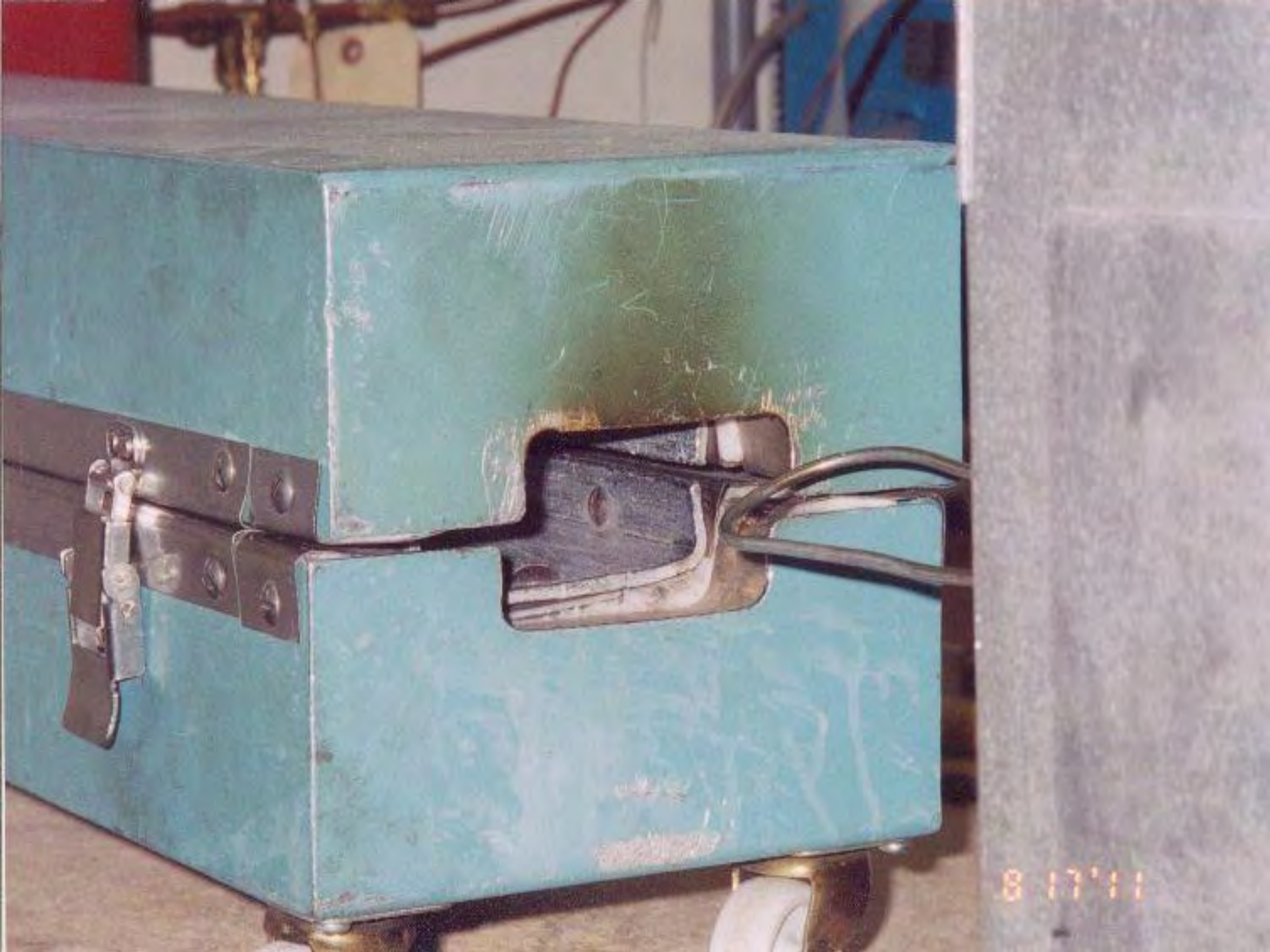
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Initial Performance Check of Condensate Recovery and Conditioning Apparatus

- Carrier gas and auxiliary oxygen blank (< 5 ppm contaminants)
- Catalyst efficiency check with 1% methane (+/- 2%)
- System performance check
  - Hexane, toluene, methanol (+/- 5%)

Daily Performance Tests

- Condensable organic recovery system
  - Leak test
  - System background test
  - Oxidation catalyst efficiency test
- NMO analyzer daily calibration
  - CO_2 response calibration (CO_2/methane)
  - NMO response calibration (Propane)

Condensable Organic Fraction Recovery

- Recovery of condensable organics is accomplished in two stages
  - Condensate trap is purged of CO_2 (< 5ppm) while cooling the trap in dry ice and put into original field tank (#1)
  - Condensate organics are volatilized and converted catalytically to CO_2 which is collected in an intermediate collection vessel (ICV or #2) for analysis

Condensable Organic Fraction Recovery

- Trap purge and sample tank pressurization
  - Obtain sample tank and condensate trap
  - Set zero air flow to 100 mL/min
  - Attach the sample tank (#1) to the condensate trap recovery system

Condensable Organic Fraction Recovery

- Measure sample tank pressure
- Immerse the condensate trap in crushed dry ice
- Observe IR response to CO_2 to minimum level of < 5 ppm
- Pressurize sample tank (#1) to 1060 mm Hg absolute pressure and detach

Condensable Organic Fraction Recovery

- Recovery of condensible organics
  - Attach an ICV (i.e., #2 tank) to the trap recovery system and evacuate to 10 mm Hg
  - Set auxiliary oxygen flow to 150 mL/min
  - Switch 4-port valve to collect position

Condensable Organic Fraction Recovery

- Remove condensate trap from dry ice and allow to warm to room temperature
- Heat trap by placing it in a furnace at 200˚C

Condensable Organic Fraction Recovery

- Recovery of condensable organics
  - After NDIR analyzer indicates a CO_2 concentration of < 10,000 ppm, begin heating the tubing that connects the condensate trap to the oxidation catalyst with a heat gun

Condensable Organic Fraction Recovery

- Continue trap heating and purging until the CO_2 concentration is below 10 ppm
- Pressurize the ICV (i.e., #2) to approximately 1060 mm Hg


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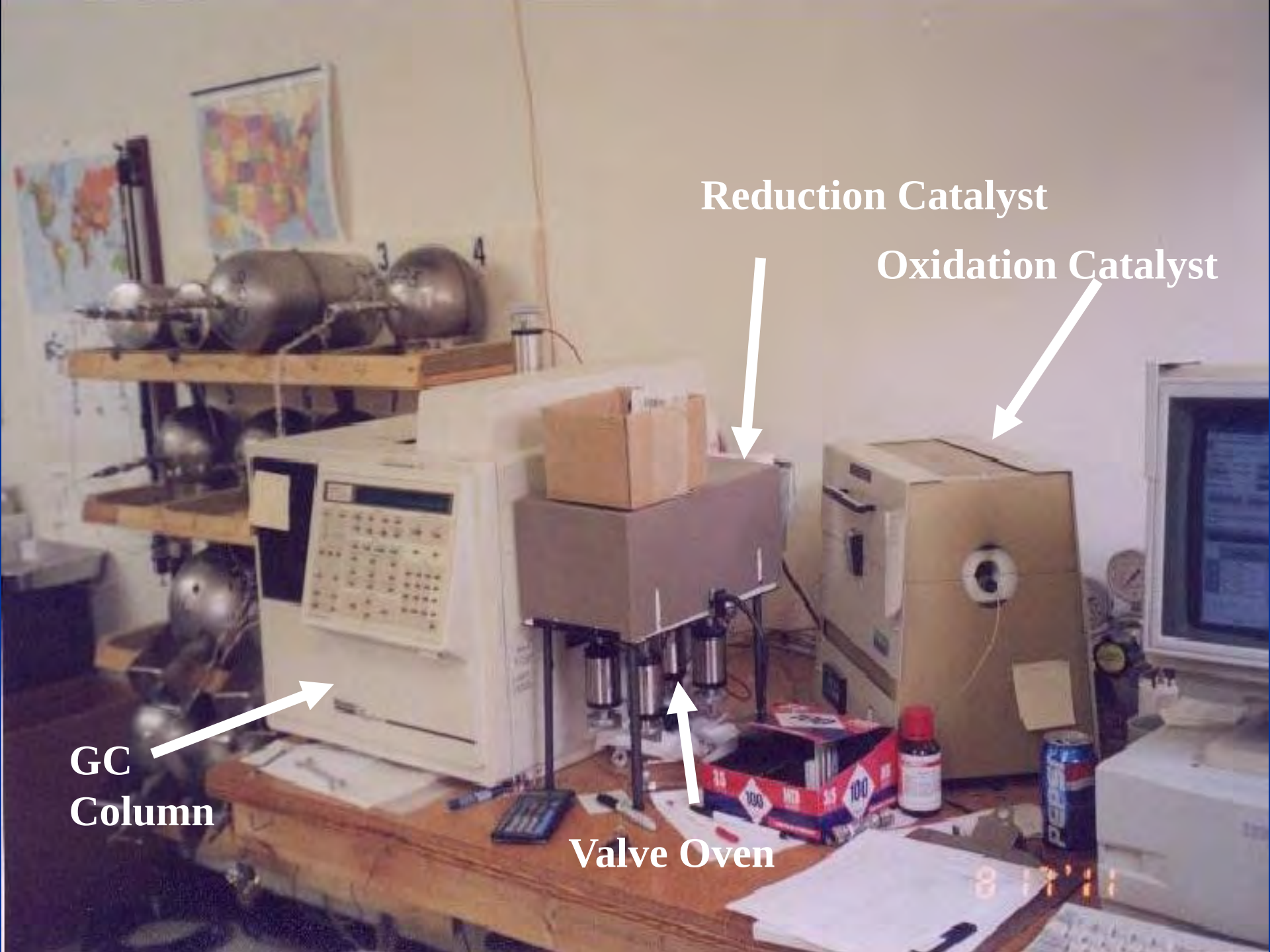
Reduction Catalyst
Oxidation Catalyst
GC
Column
Valve Oven


3.5
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HD
PEPSI


400 C Reduction Catalyst
3.5
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HD
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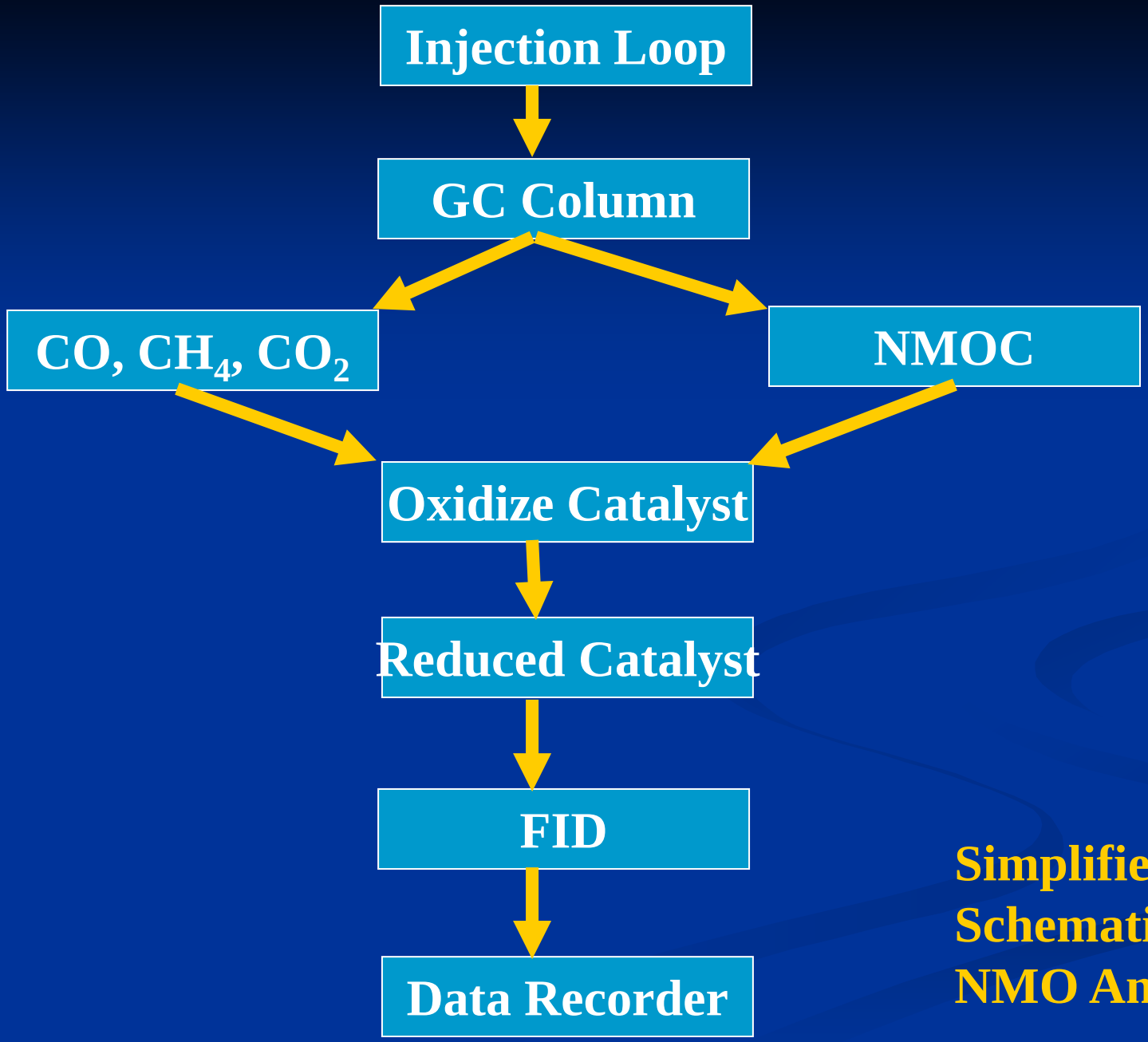
Method 25 Apparatus

- Method 25 NMO Analyzer Apparatus
  - GC with back-flush capability
  - Oxidizing catalyst (19 % chromia on alumina @ 650 C)
  - Reducing catalyst (Ni @ 400 C)
  - FID

Method 25 Sample Analysis

- Both Tanks (#1: Sample) and #2 (ICV)
  - Sample in both tanks (#1 and #2) are injected into the NMO analyzer
  - Methane, CO, CO_2, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO_2, reduced to methane, and detected with an FID
  - Original tank (#1) only NMO quantified



Simplified Schematic of NMO Analyzer

Method 25 Analysis

- ICV (i.e., #2) Analysis
  - Attach the ICV (#2) to the 10-port gas sampling valve
  - Purge sample loop
  - When detector response returns to near baseline after CO_2 peak, back-flush and increase column oven temperature

Method 25 Analysis

- After detection of any NMOC, return column oven temperature to 85˚C
- Record the CO_2 peak area and NMO peak area
- Repeat analysis two additional times

Method 25 Analysis

- Sample Tank (#1): Same as ICV (#2)
  - Inject triplicate samples from the sample tank and record the values obtained for nonmethane organics only
  - Perform three analyses and average the NMO values

Method 25 Calculations

- Sample volume
- Noncondensable organics
- Condensable organics
- Total gaseous nonmethane organics
- Percent recovery
- Relative standard deviation
- EPA provides audit sample

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Method 25 QC Checks

1. Oxidation Catalyst Efficiency Test
   - 1 % CH_4
     - Oxid/Red. Cat. Unheated (R1)
     - Oxid Cat. Heated (R2)
     - Oxid. Cat. Eff. = R1 - R2/R1 X 100

Method 25 QC Checks

2. Reduction Catalyst Efficiency Test

   1 % CH_4

      Oxid. Cat. Unheated + Red. Cat. Heated (R4)

      Oxid./Red. Cat. Heated (R3)

      Red. Cat. Eff. = R4/R3 X 100

Method 25 QC Checks

3. NMO Response Linearity Test
   - 20, 200, 3000 ppm propane standard
     - Response Factor (RF) within 2.5 % over range, then linear response

Method 25 QC Checks

4. CO_2 Response Linearity Test and Initial Calibration
   - 50, 500, 10,000 ppm CO_2 standard
     - Response Factor (RF) within 10 % over range, then linear response

Method 25 QC Checks

5. NMO Analyzer Performance (ppmC)

   Std #1: 50 ppm CO, 50 ppm CH_4, 2 % CO_2, 20 ppm Propane

   Std #2: 50 ppm Hexane

   Std #3: 20 ppm Toluene

   Std #4: 100 ppm Methanol\

   Criteria: +/- 5%

Method 25 QC Checks

6. Condensible Organic Recovery System Check
   - Stage #1: Carrier Blank Check (< 5 ppm)
   - Stage #2: Oxidizing Catalyst
   - Stage #3: Known Organic Concentration

Method 25 Daily QC Checks

1. Leak test of condensable recovery system (< 10 mm Hg for 10 minutes)
2. System background check (Syringe of gas < 10 ppm CO_2)
3. Oxidation catalyst efficiency check
4. CO_2 analyzer response
5. NMO response check

Method 25 Guide

- Make sure tanks, traps, and sample trains are clean (< 1 ppm)
- Analyze confirmation preferred
- Leak check sampling trains in the field, even though they are checked in the lab

Method 25 QC Checks

EPA Audit Sample (2)

- Between 50 % below standard and 100 % above standard
- +/- 20% of known concentration

Method 25 Guide

- Leak check cold (minimize heating/re-cooling system)
- Leak check before adding trap
- Leak check canisters before use in field
- Leak check with rotameter completely open

Method 25 Guide

- Setup sampling train properly
- DO NOT over-tighten the filter or the swage fittings
- If there is a leak, go to last fitting disturbed
  - Use logical approach to find leak
  - Isolate specific areas in the sample train

Method 25 Guide

- Get most accurate pre-test and post-test barometric pressures, tank vacuums, and temperature possible
- Used in sample volume

Method 25 Guide

- Use small pellets of dry ice around the trap to increase contact to trap organics
  - This will generate better results (esp. oxygenated organics)

Method 25 Guide

- Monitor both sample flow and tank vacuum with the rotameter and gauge on the unit
- Vacuum gauge is not accurate, but used as an indicator of proper sampling

Method 25 Guide

- Take care that the brass caps from the traps don't come into contact with pump oil, vacuum grease, or other contaminants
- Use tags to identify the tank/trap pairing, as well as noting the pairings on the sample data sheet

Method 25 Guide

- Seal both arms of the trap with the brass caps and pack the cooler with sufficient dry ice to ensure the temperature is maintained until receipt at the labs

Method 25 Guide

- Perform Method 25 gas audits prior to field sampling to minimize carryover of contaminants from a dirty sampling train (Audit through sample train)
- If sampling blanks are part of the program, a preferred method is to collect a clean air sample over a one hour period using the project sampling train components (i.e., blank train)

Method 25 Guide

- If high concentrations are expected, then collect only
  3.5 L sample
- If low concentrations are expected, then collect larger volume of gas (Increase trapped sample volume)

Method 25 Guide

- If very high moisture is expected, then add an ice water second trap in front of the cryogenic trap to prevent freezing water from plugging the sample flow

Method 25 Guide

- However, this increases analytical cost and may increase the positive bias from trapping CO_2
- This approach does appear to limit sampling problems

Observations

- Obtain the most accurate pre-test and post-test barometric pressure, tank vacuums, and temperatures. This data determines the volume of gas sampled. Don't use gauge on control box for tank vacuum measurement…it isn't accurate enough and effects final volume sampled
- Do not over tighten swage-lock fittings as part of the sample train

Observations

- A pre-test leak check is required. I suggest set-up everything and leak check without the dry ice and condensate trap. This limits the number of components that might leak
- Method suggest purge the probe for 10 minutes at 60-100 cc/min. If the source has high moisture, then purge only for 5 minutes to minimize possible freezing of trap

Observations

- FRM 25 requires you to evacuate the sample tank to <1o mm Hg absolute. Need laboratory pump and may take several attempts and 5 minutes to reach that value
- Purchase dry ice in small pellets. Pack the condensate trap to top of weld and cover dry ice during sampling with aluminum foil

Observations

- Make sure that the sample canister and condensate trap are both labelled properly with the same sample run. The VOCs are determined from both components for that single sample run
- If sampling a high particulate source, then change the filter after each run to minimize potential biases in the analysis

Observations

- If you are sampling a source with high moisture (> 20%) and high CO2 (>20%), then there is a real possibility that your trap will freeze at the very top of the trap.
  - Use hair dryer to unfreeze trap
  - Remove foil and let the sun melt the plug at the top of the trap
  - Add a dry water impinger in front of the condensate trap. However, must analyze content of that trap also


'94 1 18

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 25A: TGOCs Using FID



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment

FRM 1
FRM 2
FRM 3
FRM 4
FRM 5
FRM 25A

Family of Method 25s

- FRM 25: Total VOCs
- FRM 25A: Instrumental FID
- FRM 25B: Instrumental NDIR
- FRM 25C: Landfill Gases
- FRM 25D: VOC Waste Sample
- FRM 25E: VOC Waste Sample



Method 25A Timeline

- Proposed 12/17/80
- Promulgated 08/18/83

FRM 25A

- Originally developed to determine compliance with VOC emission standards for bulk gasoline terminals
- FRM 25A not recommended for high moisture (> 40 % by volume)
- High organic droplets in gas stream can cause high bias or data variability

FRM 25A Uses

- Incinerators
- Carbon Adsorption Units
- Coating and Printing Operations
- Web Offset Presses
- Method 25A measures total hydrocarbons (THCs) (i.e., non-compound specific)

Applicability

- This method is applicable to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons)
- Only measures C-H bond very well and analytes that can generate a response factor (RF)

Applicability

- Results from the use of FRM 25A are expressed in terms of volume concentration of propane (or other appropriate organic calibration gas) or in terms of carbon
- Results from FRM 25A are measured on a wet basis and the concentration must be adjusted for the percent moisture in the sample gas stream for the purpose of emission calculations

Applicability

- FRM 25A "*…can only be used where an appropriate response factor for the stack gas can be determined*"

Instrument Response Factors (RF)

- The instrument response factor for the compound of interest is determined by:
  - Response Factor (RF) = (Act. Conc.) / (Instru. Observ. Conc.)
  - Typical RF:
    - Benzene: 0.29
    - Chloroform: 9.28
  - M25A requires RF determination

Agency Example RF Application
(Surface Coating Operation)

- Four analytes which you know % of solvent used in mixture
- Standard prepared with that same percent ratio in mixture in gas std.
- Response of analyzer in ppm as carbon
- Concentration of gas stream is determined by dividing by RF

Applicability

- The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon
- Measurement is made on a wet bases and emissions must be adjusted accordingly to dry bases
- Span value of the analyzer is usually 1.5 to 2.5 times the applicable emission limit

FRM 25A Items

- Calibration for FRM 25A should be done using EPA Traceability Protocol gas standards, preferably propane
- The entire sampling system prior to the flame ionization detector (FID) should be heated to the higher temperature of 248 +/- 25 F or stack temperature. Heating above 400 F is not required

FRM 25A Items

- A system bias check is required and is performed by introducing the bias check standard directly into the FID and then through the entire sampling system, excluding the probe. Results must agree within 5 % to be acceptable
- The bias check standard must be representative of the effluent (i.e., boiling point, solubility, chemical reactivity etc.). Propane may be used if effluent is unknown.

FRM 25A Items

- For the bias test, propane should be used at the following processes:
  - Incinerators, boilers, asphalt plants, cement plants and resource recovery facilities.
- For the bias test, propane should NOT be used at the following processes:
  - Bakeries (using yeast),ethylene oxide sterilizers, chemical manufacturing facilities (HON/SOCMI), surface coating operations, and graphic arts operations

FRM 25A Items

- Calibration error test must be performed within 2 hours of start of testing
  - Introduce zero and high level standard, adjust
  - Introduce low and mid level standard, no adjustment. Criteria of 5 %
- Perform response time test at same time as calibration error test for zero and high level standard. Repeat 3 times and record. Typically < 1 minute

FRM 25A Items

- Drift determination is determined each hour during the test
  - Introduce zero and mid-level gas standards
  - Criteria: < 3 %
- FRM 25A sampling system must be leak checked prior to monitoring
- Location of sampling point can be a single point (> 1.5 meters from inside wall of stack) or racked probe (16.7, 50, 83.3 %)

Wet Bases to Dry Bases

- Wet bases measurement emissions to dry bases measurement emissions:
  - $C_{s(dry)} = C_{s(wet)}/(1-B_{ws})$
  - $C_{s(dry, STP)} = [C_{s(wet)}/(1-B_{ws})]\ [(T_s)(P_{std})/(T_{std})(P_s)]$

Principle

- A gas sample is extracted from the source through a heated sample line and filter to a total hydrocarbon analyzer (THC) containing a flame ionization detector (FID)
- All components kept at 250 F (121 C)

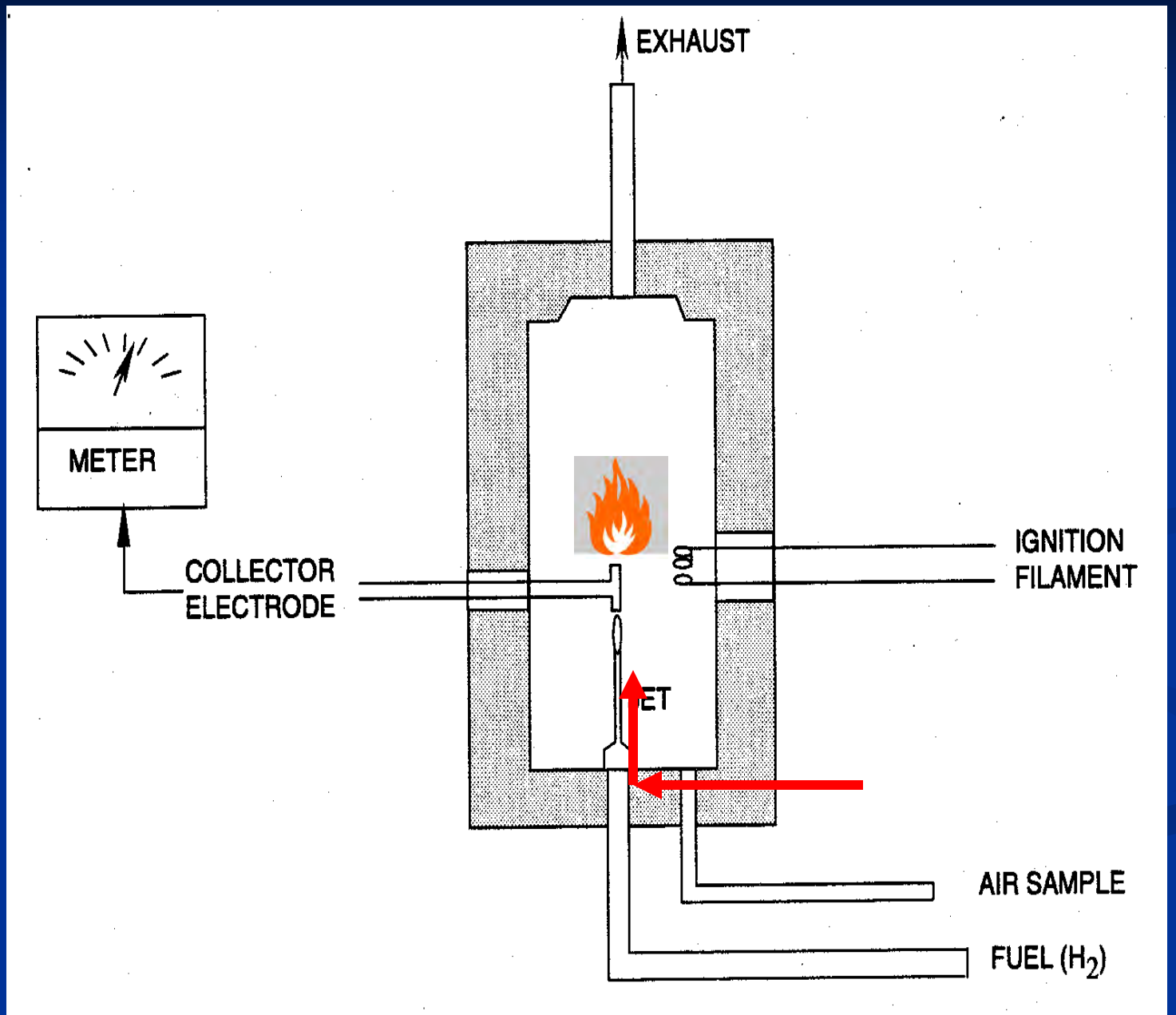
Principle

- Sampling is performed on a continuous, real-time basis with results proportional to the carbon content of the sample stream passing through the detector on a wet bases
- FID is linear from 0-10,000 ppm (If higher concentrations, then use dilution system)
- Method 25A is good up to about 40 % moisture in the stack gas

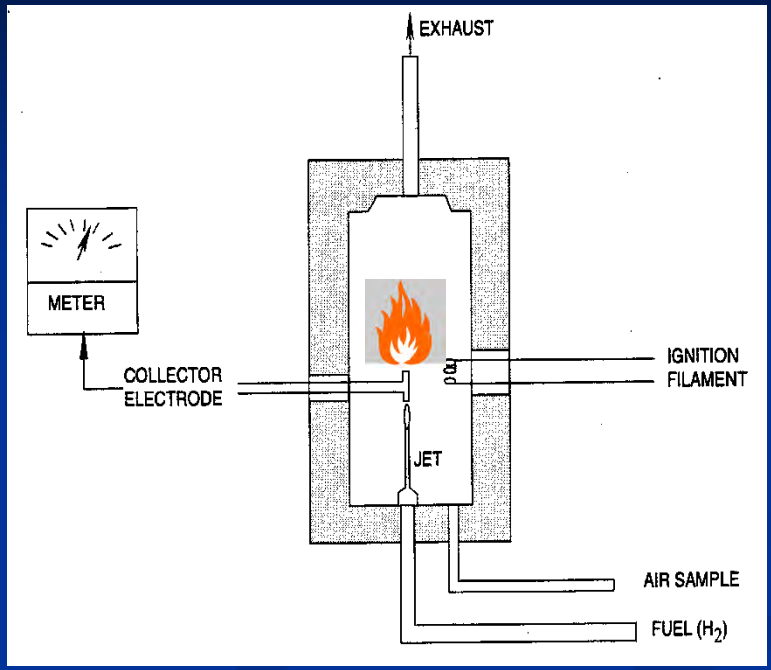
FID Theory

- Basic Theory:
  - Sample is introduced into an ionization chamber and burned
  - Process separates free ions
  - Free ions are attracted to a collecting electrode
  - Collection of the ions results in an increased current which is proportional to the concentration of the compound
  - By-products are H_2O and CO_2

Diagram of FID

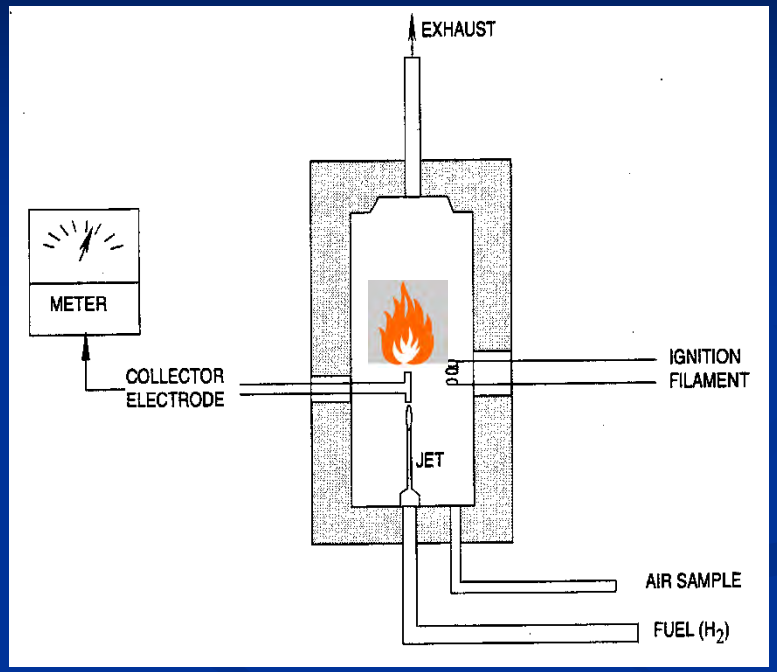


Flame Ionization Detection



- Advantages
  - Wide dynamic and linear range (0-10,000 ppm)
  - Highly sensitive to hydrocarbon vapors
  - Very stable and repeatable
  - Unaffected by ambient levels of CO, CO_2 vapor

Flame Ionization Detection



- Disadvantages
  - Requires oxygen > 16% to operate
  - Total hydrocarbon detector - not specific

Principle

- FRM 25A results are measured on a wet basis and the concentration must be adjusted for the percent moisture in the sample gas stream for purposes of emission calculations

Principle

- In general alkanes, alkenes, and aromatics are the most appropriate compound groups for FRM 25A sampling and analysis
- May also be used on C,H & O compounds. Ethanol gives ~ 60% signal to that of propane, but can still be used for ethanol

FRM 25A Limitations

- Sensitivity greatest for the alkane, alkene, and aromatic organic compounds
- FRM 25A can only be used in situations where an appropriate response factor for the stack gas constituents can be determined

FRM 25A Limitations

- Gas streams with high moisture (> 40%) can effect response of the FID
- Limitations of the FID. FID response is different for different analytes
- Large quantities of methane present gives questionable results
- Sample gas needs O_2 (> 16 %) for combustion in the FID

FRM 25A Sampling System

- Sample Probe: A heated (> 250°F) stainless steel, three-hole rake type probe. Holes should be 4 mm diameter or smaller and located at 16.7, 50, and 83.3% of the equivalent stack diameter
  - Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10% area of the stack cross-section

Options for Sampling Point

- Single point in centroid of stack
- Single point at average velocity of stack gas
- Rake probe (i.e., 16.7%, 50%, and 83.3% of the equivalent stack diameter
  - Therefore, FRM 2 needed to determine cyclonic flow and velocity of stack gas

FRM 25A Sampling System

- Sample Line: Heated (> 250°F) stainless steel or Teflon® tubing
- All components must be heated > 250 F so moisture and organics don't drop out of the gas stream
  - Check unions for cold spots
  - Check for unheated transfer line
  - Check for sudden spiking at steady state conditions
  - Check for unheated filter

Sampling System

- Calibration Valve Assembly:
  A heated (> 250°F) three-way valve at exit of probe assembly to direct the zero and calibration gases to the analyzer
- Particulate Filter: An in-stack or an out-of-stack heated (> 250°F) glass fiber filter assembly
- Pump: A heated (> 250°F) leak-free diaphragm type

Sampling System

- Organic Concentration Analyzer:
  A heated (> 250°F) total hydrocarbon analyzer (THC) with
  a flame ionization detector (FID)
- Recorder: A strip-chart, digital recorder, or computer for recording measurement data

FRM 25A Gases

- Fuel: 40% H_2/60% He or 40% H_2/60% N_2
- Zero Air: High purity air with less than 0.1 ppmv of organic material (propane or carbon equivalent)
  - Most systems use 100% H_2 as the fuel which makes for a hotter flame

Gases

- Calibration Gases (i.e., propane in air/N_2)
  - Low-level calibration gas: An organic calibration gas with a concentration equivalent to 25 to 35% of the applicable span value
  - Mid-level calibration gas: An organic calibration gas with a concentration equivalent to 45 to 55% of the applicable span value

Gases

- High-level calibration gas: An organic calibration gas with a concentration equivalent to 80 to 90% of the applicable span value
  - Note: Use hydrocarbon/air standards; Propane/N_2 may yield inaccurate results!

Steps to Perform An Analysis

- Analysis of PE sample not mandatory, but suggested, due to calibration gases are NIST traceable!
- Leak Check System not mandatory, but suggested!
- Calibration Error Test (With Propane): +/- 5% of calibration gas value

Steps to Perform An Analysis

- Response Time Test: 1-2 minutes; traditionally < 1 min; No specifications in FRM 25A
- Calibration Drift (Zero/Mid-span Gas)Test (No adjustments allowed to analyzer): +/- 3% of span value

Pre-test Requirements

- Sampling Site: Located as required by the specific regulations
  (i.e., exhaust stack, inlet line etc.)
  - At a minimum, 1.5 to 2 equivalent stack diameters upstream of the gas discharge to the atmosphere

Pre-test Requirements

- Assemble the sampling system following manufacturer's specification
- Prepare sample interface from stack to extraction system
- Make system operable

Pre-test Requirements

- All delivery pressures of the gases to the THC/FID system must be maintained at the same value used during calibration and sampling

First Step To Perform An Analysis

- Leak Test of System: Perform both positive and negative leak check of sampling and analytical system
  - 1. Vacuum: Attach manometer to probe inlet, pull 2 in. of Hg vacuum; no leak for 1 minute
  - 2. Pressure: After pump, apply pressure and use soapy water to determine leaks at all joints/connections

Pre-test Requirements

- After leak test of system, place probe at centroid of stack,
  pipe, or duct and is sealed tightly

Remember Sampling Point Options!

- Single point in centroid of stack
- Single point at average velocity of stack gas
- Rake probe (i.e., 16.7%, 50%, and 83.3% of the equivalent stack diameter
  - Therefore, FRM 2 needed to determine cyclonic flow and velocity of stack gas

Calibration of M25A

- Calibration of THC/FID Analytical System: Generate a series of high, mid, and low range calibration gases of known concentrations spanning the linear range of the FID and introduce at the calibration valve assembly to the THC/FID
  - The analytical range must be chosen so that the source THC limit is 10 to 100% of the range
  - Calibration must be done on-site to determine RFs

Second Step To Perform An Analysis

- Calibration Error Test (Response to True Value):
  Perform a calibration error test (within 2 hours of the start of the test) by introducing the zero and high level calibration gases to the analyzer

Pre-test Calibration Error

- Calibration
  - The calibration gases are usually propane in air, propane in nitrogen, or methane in air or nitrogen
  - Perform three injections each of the calibration gases
  - Calibration gases must be NIST traceable; Therefore, no method does not require a PE sample

Pre-test Calibration Error

- Calibration
  - Generate calibration curve from the three injections performed in the calibration of the analytical system
  - Develop a "calibration factor" for each level of the injected calibration gases (the calibration factor should fall between 0.95 and 1.05 to be acceptable)

Pre-test Calibration Error

- Inject zero and high level (80-90 % of span value) at the calibration valve
- Adjust the analyzer output to the appropriate levels
- Introduce the mid and low level calibration gases
- Make no adjustments to the analyzer
- If system is linear, differences should be < 5%

Pre-test Calibration Error

- If can't meet < 5% of the calibration gas concentration value, then system must be replaced or repaired
- No adjustments can be made to the system after the calibration error test and before the calibration drift test
  - If adjustments are required, perform the calibration drift test prior to the adjustments and repeat the calibration drift test after the adjustments

Third Step To Perform An Analysis

- Response Time Test: Response time test is used to document response of gases by the THC/FID analytical system
  - Introduce zero gas at the calibration valve assembly
  - When the system output has stabilized, switch quickly to the high level calibration gas

Pre-test Requirements

- Record the time from the concentration change to the measurement system (no limit specified, just determine)
- Repeat the test three times
  - Just record results
- Response time should be < 1 minute, but can be 1-2 minutes
  - FRM 25A does not specify limit

Fourth Step To Perform An Analysis: Sampling

- Purge the sample system for a period of time longer than the response time of the system
- Mark the start time on the data recorder after purging. Remember, all delivery pressures of the gases to the THC/FID system must be maintained at the same value used during calibration and sampling
- Begin sampling!!!

Fifth Step To Perform An Analysis: Post-test

- Calibration Drift Determination: Immediately following completion of the test period (and hourly during the test), perform a calibration drift test
  - Reintroduce the zero and mid level calibration gases, one at a time, to the measurement system at the calibration valve

Post-Test Procedures

- Make no adjustments to the instrument, just record response
- If drift exceeds 3% (span value) for either gases, invalidate the test results preceding the check
  - If you fail drift test during run, then void sample to that point from the last acceptable drift test, recalibrate, and then continue!

Organic Concentration Calculations

- Calculated as ppm_v as carbon

$$C_c = K\,C_{meas}$$

Where:

K = 1 for methane
K = 2 for ethane
K = 3 for propane
K = 4 for butane
K = Appropriate response factor for other organic calibration gases

Agency Bias Check

- Agency bias check is not required by FRM 25A
- Bias check procedure:
  - Introduce bias gas standard at back of analyzer
  - Introduce bias gas standard through entire sampling system
  - If results agree within 5% of bias gas standard concentration, then PASS!

Agency Bias Check

- Bias gas standard must be representative of the effluent as a whole with regard to BP, water solubility, and chemical reactivity
- Propane may not be used for the following facilities:
  - Bakeries, ethylene oxide sterilizers, chemical manufacturing facilities, surface coating operations and graphic arts operation



Method 25A Notes

- The use of Method 25A usually must be justified to regulatory agencies instead of using Method 25. Key points would be:
  - Expected concentration < 50 ppm
  - VOCs known to consist of C and H
  - $(CO_2)(H_2O)$ > 100 %
- Set-up instrument in environmentally controlled room to minimize instrument drift

Method 25A Notes (Contd)

- To minimize condensation of VOCs in the analytical system, keep at least 10 F hotter than rest of system
- Protocol 1 standard should be used for calibration, but other standards allowed if manufacturer certified accurate is 2 %
- Void test run if using expired standards….but!

Method 25A Notes (Contd)

- The entire sampling system (probe, heated sample lines, valves and manifolds) must be maintained at stack temperature or 250 F (May go hotter/Web Offset Presses..350 F)
  - Actual temperature of each component may want to be recorded every 15 minutes and included in final test report

Method 25A Notes (Contd)

- Agency may require a system bias check conducted with a certified standard that has properties (boiling point, water solubility, and reactivity) similar to the effluent as a whole. *Propane is not normally acceptable by regulatory agencies!*
  - Concentration of the system bias check standard must be similar to the concentration of the stack

Method 25A Notes (Contd)

- The analyzer temperature and pressure must be the same during sampling as it was during calibration
- Pollutant concentration must be measured on a wet basis and reported on a dry bases
- Any run in which the average VOC concentration exceeds the span must be voided

Method 25A Notes (Contd)

- For Destruction Efficiency (DE) Testing:
  - The same sampling method should be used; The outlet test location determines the method (i.e., concentration, % H_2O etc.)
  - The results (lbs/hour) at both the inlet and outlet must be on the same bases (as propane or as VOCs)

Method 25A Notes (Contd)

- The actual emissions should be determined if at a VOC coating source:

Emission Rate = {(Coating Usage)(VOC Content)(1-DE)(CE)} + {(Coating Usage)(VOC Content)(1-CE)}

FRM 25B

Determination of Total Gaseous Organic Concentration Using A Non-dispersive Infrared Analyzer

Applicability

- This method is applicable to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes (other organic materials may be measured as long as appropriate calibration procedures have been implemented)

Applicability

- The concentration is expressed in terms of propane or in terms of carbon

Principle

- A gas sample is extracted from the source through a heated sample line, heated calibration valve, heated particulate filter assembly, heated pump, and total hydrocarbon analyzer (THC) containing a non-dispersive infrared (NDIR) detector

Principle

- All components are heated and follow the same configuration of FRM 25A replacing the FID with a NDIR
- NDIR is usually used where concentrations of VOCs are extremely high (> 10,000 ppm) or where gas dilution is implemented

U.S. EPA APTI Compliance Test and Source Test Observation EPA's Conditional Test Method (CTM) 035



Introduction

- Emission standards lower in recent years
- Employs a trap and tank approach designed for low concentrations
- Method 25.3 intended to fill void in existing VOC method applicability

VOC Test Methods

- **EPA Method 25**
  - less precise at low concentrations
- **EPA Methods 25A, 25B**
  - for Alkanes, Alkenes, and Aromatics only
- **EPA Method 18 - not for total VOC**
- **SCAQMD Method 25.1**
  - similar to EPA Method 25

VOC Test Methods

- SCAQMD Former Draft Method 25.2 - removed from consideration
- SCAQMD Method 25.3
  - for low concentrations only
- EPA's Conditional Test Method (CTM)-035

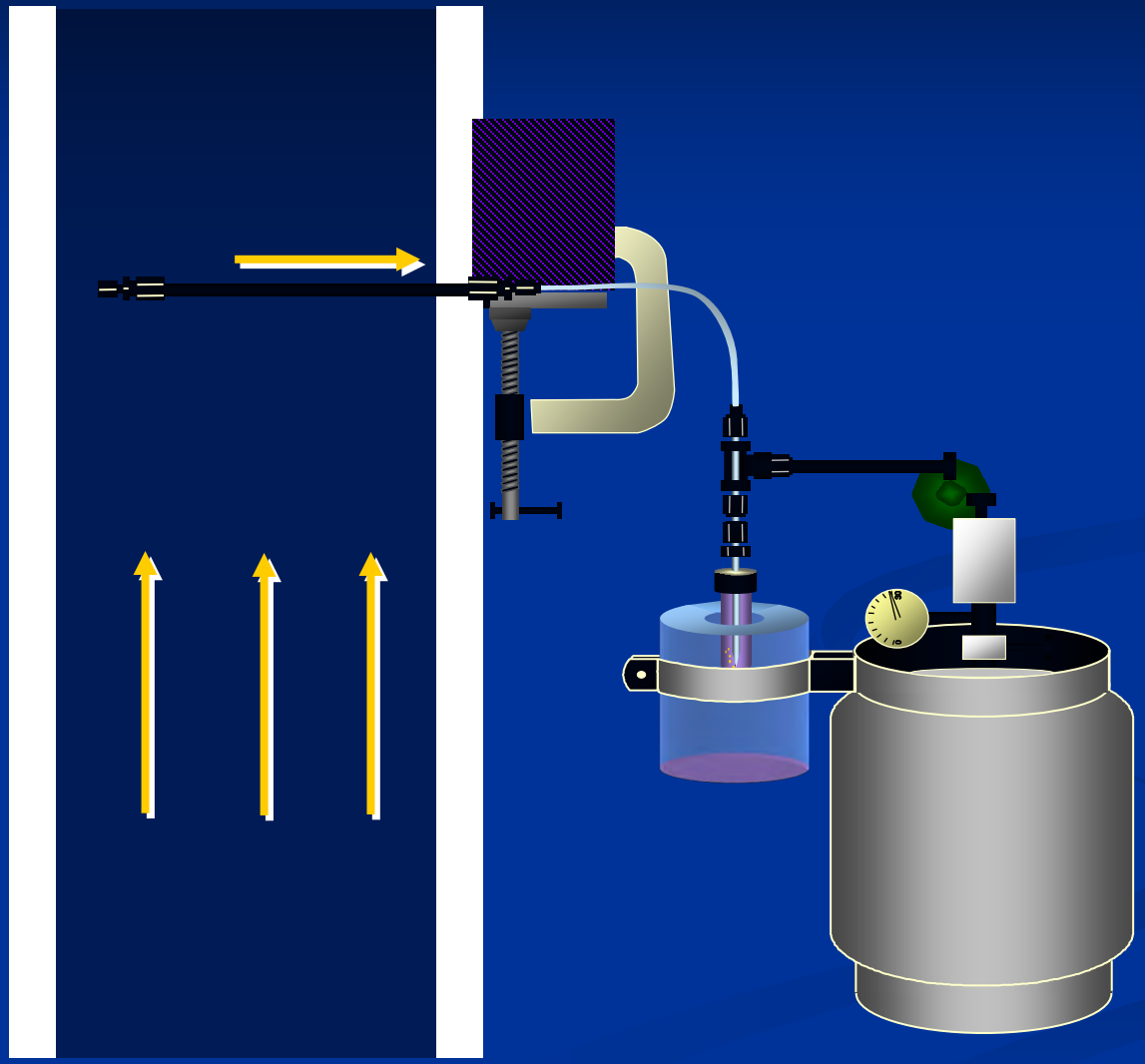
Applicability

- EPA's CTM-035 for combustion exhausts < 50 ppmC
- Continue to use FRM on inlets or higher concentrations (> 50 ppm)
- SCAQMD M25.3 replaces former draft M25.2
- Has a provision for deleting trap when no elevated moisture present (ambient)

EPA's CTM-035 Sampling

- Simple self contained sampler
  - No power, no heaters, no adjustments
  - Analysis is completed off-site
- Duplicate sampling
  - Probes are placed flush with port entrance

Sampling Apparatus



Duplicate Samplers



Trap Assembly



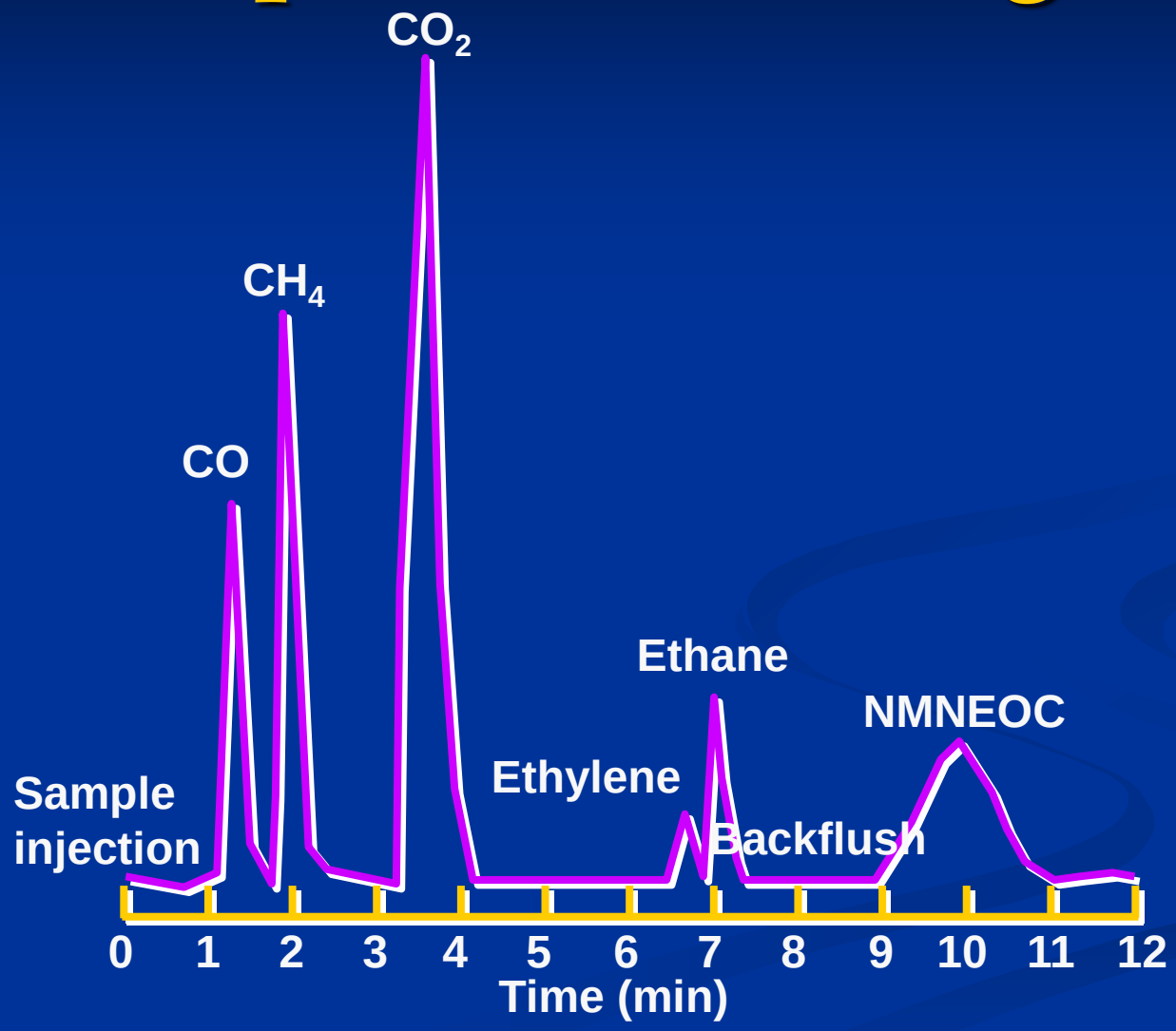
Condensate Trap



Analysis

- Condensate by infrared total organic carbon analyzer
  - Lower detection limit 1 ppmC
- Canister by Method 25.1 modified for low concentration
  - GC/oxidation/reduction/FID
  - Lower detection limit 1 ppmC

Example Chromatogram








01:11:2







0
5
10
15
20
25
30
PSI



Method Development

- **Various improvements made**
  - **Trap volume, connector line recovery, trap purge for CO_2, cleaning and handling**
- **EPA Method 301 validation needed however**
- **Recent test indicate 92% spike recovery, 20% COV (0.5 ppm)**
- **Deemed validated by EPA giving CTM status**

Implementation Issues

- **In interim, distributing CTM-035 for comments**
- **Have been allowing use of draft method subject to protocol review**
- **Requires determination for MW/C ratio**
  - **Draft method contains guidelines for MW/C**

Rental Cost

- CTM-035
  - Canister, impinger, flow controller, and probe……$ 120
  - Analysis (water trap and canister)
    - Speciated……..$ 250
    - Total VOCs……$ 65

Rental Cost

- FRM 25
  - Canister, cryogenic trap, metering box, and probe…….$ 295
  - Analysis (Cryo trap and canister)
    - Total VOCs……..……$ 295

Conclusions

- Method is thought to have superior accuracy and precision than existing methods (i.e., FRM 25 or FRM 25A)
  - Next phase – comparison to Method 25A
- Well received by industry and source test firms
- Not accurate above 50 ppmC

NCASI Impinger and Canister Method

- National Council for Air and Stream Improvement (NCASI)
  - IM/CAN/WP-99.01
  - "Impinger/Canister Source Sampling Method for HAPs at Wood Products Facilities
  - Publications@ncasi.org

NCASI Impinger and Canister Method

- Sampling train consist of three chilled impingers/pump/canister
- Flow through impingers is ~ 400 cc/mL
- Single point sampling for 60 minutes

NCASI Impinger and Canister Method

- Ketones/phenols-Water Impinger: GC/FID
  - Acetaldeyde
  - Acrolein
  - Methanol
  - Methyl Ethyl Ketone
  - Methyl Isobutyl Ketone
  - Propionaldehyde
  - Phenol

NCASI Impinger and Canister Method

- Formaldehyde-Water Impinger: Acetylacetone Reagent
  - Measure absorption at 412 nm

NCASI Impinger and Canister Method

- Organic Analysis-Canister: Cryogenic trapping followed by GC/MSD EPA's Compendium Method TO-14
  - Acetaldehyde
  - Acetone
  - Acrolein
  - Methanol
  - Methyl Ethyl Ketone (2-Butanone)
  - Methyl Isobutyl Ketone
  - Propionaldehyde
  - Phenol

NCASI Impinger and Canister Method

- Terpene Analysis-Canister: Direct Injection GC/FID
  - Camphene
  - p-Mentha-1,5-Diene
  - 3-Carene
  - p-Cymene
  - Limonene
  - α-Pinene
  - β-Pinee

NCASI Impinger and Canister Method

- Total Hydrocarbons-Canister: Direct Injection GC/FID
- Bacharach Gas Analyzer For $CO/O_2/CO_2$-Canister: Direct Analysis By Bacharach Gas Analyzer

U.S. EPA APTI
Compliance Test and Source Test Observation
Comparison FRMs 18, 25, and 25A



Lecture Objectives

- Compare the Methods
- Discuss Their Advantages and Disadvantages
- Describe Current EPA Guidance on Their Use

Background

- FRM 25 - measures total VOC
- FRM 25A - measures total hydrocarbons (THC)
- FRM 18 - measures individual organic compounds

Background

- Generally, “stack testing” is performed using FRM 25A or FRM 18
- FRM 25/25A were created in order to determine the removal efficiency of a control device

Background

- Typically, once a method is promulgated (and sometimes before it is) the method will be
  used for a variety of purposes including functions that it
  was not designed to perform
- FRM 25 and FRM 25A are not applicable to mass emission rate

Background

- FRM 25
  - Samples are time integrated
  - Analysis is completed off site
- FRM 25A
  - Sampling is continuous
  - Analysis is done on site

Background

- FRM 18
  - Samples can be time integrated or semi-continuous
  - Analysis can be on site or off site

Background

- FRM 25 - All compounds are converted to methane before measuring with an FID
- FRM 25A - All compounds are measured directly, as a whole, with an FID

Background

- FRM 18 - Each compound is separated and measured individually with an FID

FRM 25 & 25A

- The FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under any of the following limited conditions

FRM 25 & 25A

- Where only one compound is known to exist
- When the organic compounds consist of only hydrogen and carbon

FRM 25 & 25A

- Where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known

FRM 25 & 25A

- Where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed
- Where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example)

Advantages: FRM 25

- Measures only VOC (excludes Methane)
- Responds equally to all VOC

Disadvantages: FRM 25

- Potential positive bias that may vary according to source category
- Relatively poor precision

Advantages: FRM 25A

- Very good precision
- Real time analysis
- Relatively low detection limit

Disadvantages: FRM 25A

- Does not respond equally to all VOC
- Requires a separate measurement of Methane to convert THC to VOC

Advantages: FRM 18

- Good precision
- Low detection limits
- Can exclude methane

Disadvantages: FRM 18

- Measures individual organic compounds - not total VOC
- Requires calibration standards for all measured compounds

General Guidance

- Use FRM 25 for unknown mixtures with concentrations greater than 50 ppm
- Use FRM 25A for unknown mixtures with concentrations less than 50 ppm

General Guidance

- Use any of the methods for known mixtures with the following conditions
  - FRM 25 should only be used for concentrations greater than 50 ppm

General Guidance

- Use any of the methods for known mixtures with the following conditions
  - FRM 25A should be calibrated with the known mixture or the results mathematically corrected for varying response factors

General Guidance

- Use any of the methods for known mixtures with the following conditions
  - FRM 18 must be calibrated for each of the compounds in the mixture

Summary

- None of the existing methods for measuring VOCs are perfect
- Because their problems can be source specific, we may have to approve alternative methods for some sources
- We must continue to improve the existing methods

Reporting VOCs

- Many state agencies require reporting "as VOCs;" or as "carbon, methane; or propane" or "make up your own!"
- One must know how the state wants data reported for VOC emissions
- Volatile organic compounds as defined in 40 CFR 51.100

Reporting VOCs

- The reporting format of the data must be known prior to accepting test data
  - Mass emission rates - lb/hr as carbon, methane, or propane?
  - Mass emission rates - lb/hr “as VOC”

Case Study Molecular Weight - FRMs 25 & 25A

- Emissions testing was performed and submitted in support of a permit application
- Gas Stream consisted of ~ 100 VOCs
- Total VOCs per FRM 25A = 2.5 lb/hr as carbon

Case Study

- One speciated compound per a compound specific test was emitted at 5 lb/hr
- Outcome
  - Facility adjusted the reported VOC emission rate using a MW that was considered 'average' for the pollutant gas stream (avg MW of the VOCs)

Case Study

- Using the MW of carbon for mass emission rate calculation
- Consider Propylene Glycol ($CH_3CH(OH)CH_2OH$)
- Molecular Weight is 76.10
- Assume: Concentration = 100ppm
- Qsd of 100,000 dscfm

Case Study

- lb/hr “as carbon” (MW=12) = 18.7 lb/hr.
- lb/hr “as VOC” (MW=76.1/3) = 39.57 lb/hr.
- An error in excess of 100% due only to MW

Case Study

- Identification of a major concern with the reporting of VOCs when using FRMs 25 & 25A
- Propose using a molecular weight adjustment
- Every organic will weigh more than just carbon

Other Errors Involving FRM 25 & 25A

- "Response factor" error associated with FRM 25A
- The flame ionization detector (FID) used in FRM 25A does not give a 1:1 response with all organics

FRM 18 Reporting of VOCs

- FRM 18 measures specific VOCs
- Requires knowledge of the pollutant gas stream
- Can only measure VOCs for which the GC/specific detector has been calibrated

FRM 18 Reporting

- Difficulties
  - Sources claim that they only need to measure "total VOCs" - not speciated
  - What to do with a "soup" of VOCs?

Summary VOC Methods

- FRM 25 - Measures Total VOC (> 50 ppm)
- FRM 25A - Measures Total Hydrocarbons (THC) (10-100 ppm)
- FRM 18 - Measures Individual Organic Compounds (Sub-ppm)

U.S. EPA APTI
Compliance Test and Source Test Observation
VOC Midwest Scaling Protocol



Applicable Sources

This protocol is designed to determine the actual VOC mass emission rates from sources where significant amounts of oxygen-containing organic compounds are emitted from:

- Wet and Dry Grain Mills
- Ethanol Production Facilities

Sampling Methodology

- Either FRM 25 or FRM 25A is used to determine total organic compound concentration of the emission samples
- The concentration data are then converted to carbon mass (or propane mass) emission rate
- Simultaneously, the concentrations of the most significant individual organics are measure with FRM 18

Background

- FRM 25 - measures total VOC
- FRM 25A - measures total hydrocarbons (THC)
- FRM 18 - measures individual organic compounds
- However- measurement methods can't be compared adequately because of molecular weight and response factor considerations

Background

- Midwest Scaling Factor (MSF) protocol provides means for the quantitative measurements of air emissions of individual VOCs from sources at grain mills and ethanol production facilities
- MSF also serves as a reference for equations used to convert VOC concentration measurements reported "as carbon" or "as propane" to actual VOC mass emissions

Background

- MSF based upon Commonwealth of Pennsylvania Department of Environmental Protection, Bureau of Air Quality, Source Test Manual, Revision 3.3, November 2000 (www.dep.state.pa.us/dep/deputate/airwaste/aq/source/sts.htm)
  - Correction for different molecular weights
  - Correction for relative response factors (RRFs)

MSF Target Compound List

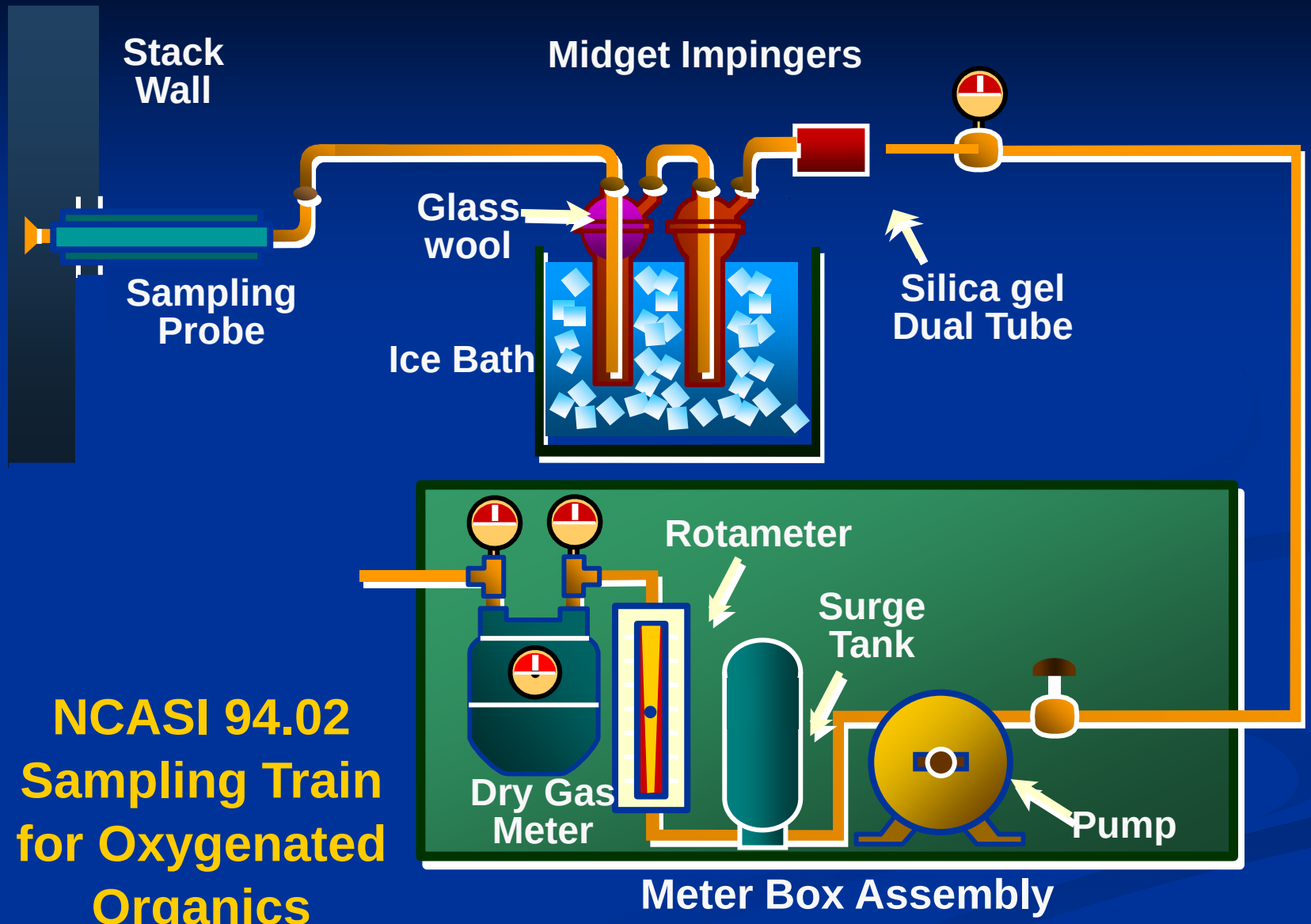
- Total Organic Compounds
- Acetaldehyde
- Acetic Acid
- Ethanol
- Formaldehyde
- Formic Acid
- 2-Furaldehyde
- Methanol

Reporting of Emissions Utilizing MSF Protocol

- Converts VOC results using FRM 25 (“as carbon”) or FRM 25A (“as propane”) to “as VOC” emission rate
  - Takes into account MW and RF
- Source may opt to use a standard scaling factor (SF) of 2.2 pounds of VOC per pound of VOC as carbon (Usually between 1.8-2.9)

Measurement of Oxygenated Organics in Using MSF Protocol

- Use of chilled impingers (i.e, FRM 18) to measure the individual oxygenated organic compounds as required by the MSF protocol
  - National Council for Air and Stream Improvement (NCASI) Chilled Impinger/Silica Gel Tube Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde (NCASI CI/SG/PULP-94.02)



NCASI 94.02 Sampling Train for Oxygenated Organics

Measurement of Oxygenated Organics in Using MSF Protocol

- NCASI Chilled Impinger/Silica Gel Tube Test Method Analytical Finish for Oxygenated Organics:
  - Impinger water analyzed by GC/FID
  - Silica gel desorbed with 3% solution of n-propanol, then direct injection to GC/FID
  - Formaldehyde analyzed by the acetylacetone derivatization/spectrophotometric analysis method

U.S. EPA APTI
Compliance Test and Source Test Observation
Agency Observer Method Specific Checklist for FRMs

