United States
Environmental Protection
Agency

Air Quality Planning and Standards
Education and Outreach Group
Air Pollution Training Institute
Research Triangle Park, NC 27711

EPA XXX/X-XX-XXX
December 2009

EPA APTI Course #468
Student Workbook
DRAFT

Monitoring Compliance Test And Source Test Observation

Notice

This is not an official policy and standards document. The opinions and selections are those of the author and not necessarily those of the Environmental Protection Agency. Every attempt has been made to represent the present state of the art as well as subject areas still under evaluation. Any mention of products or organizations does not constitute endorsement by the United States Environmental Protection Agency (USEPA).

Usage of This Manual

The Central States Air Resource Agencies Association (CenSARA) is one of several multi-jurisdictional organizations (MJOs) operating for the U.S. Environmental Protection Agency (USEPA), through the Air Pollution Training Institute (APTI), to update more of the frequently used APTI courses. The primary objectives of the MJOs are to:

- Promote the exchange of information between the States;
- Serve as a forum to discuss regional air quality issues of common concern;
- Share resources for the common benefit of the member states; and
- Provide training services to their member air pollution control agencies.

APTI provides courses on air pollution control technology, ambient air and source monitoring, and air quality management. Historically, APTI designed courses that meet the job training needs of governmental agency personnel and others in the field of air pollution. This requires a thorough examination of both the materials for instruction and the characteristics of the student audience. Based on studies conducted by APTI of those who have participated in the various training courses, courses were developed and revised to provide training that enables every student to achieve specific course objectives. A basic goal of APTI was to provide training that will enable a student to do specific jobs in his or her home environmental agency. However, recently APTI has taken a new direction and has given money to the various MJOs, of which CenSARA is one, to update needed training course for their member states.

CenSARA meets these training needs of its member states by identifying, designing, developing and delivering needed, cost-effective, responsive, and focused educational opportunities for state and local air agency staff. Agenda and course materials are obtained from a variety of sources including EPA, colleges and universities, regional training consortia, and individual instructors. Yet, due to changes in environmental regulations, the implementation of new policies, and the advancement of technologies, agendas and course materials become out-of-date. When this happens, staffs' ability to enhance skills, knowledge and abilities are constrained, limiting their ability to excel in the dynamic field of air pollution control. So by providing up-to-date, high quality educational opportunities for staff, their chances to greatly enhance their skills, knowledge and abilities is significantly improved.

Consequently, CenSARA announced a Request for Proposals (RFP) to the environmental training community to solicit technical proposals and cost bids to review current compliance test

and observation programs within the USEPA and to **update** as necessary the content title, agenda topics, course length, instructor and student manuals, lectures involving presentation slides, classroom and homework exercises, and other handouts and materials for EPA's APTI Course 468 entitled: *"Monitoring Compliance Test and Source Test Observation."* In response to CenSARA's RFP, EnviroTech Solutions, William T. "Jerry" Winberry, 1502 Laughridge Drive, Cary, North Carolina 27511, jwinberry@mindspring.com, 919-467-2785, was awarded the contract to update EPA's APTI Course #468. Mr. Winberry is the author of this Student Workbook and every attempt has been made to represent the most recent advances in sampling and analytical methodology

DISCLAIMER

This material has been developed and assembled to provide training associated with EPA's APTI Course #468 entitled: *"Monitoring Compliance Test and Source Test Observation."* It is not intended to be used for regulatory purposes, or to be a substitute for, nor interpreted as official Agency policy. Every attempt was made to reflect the technical state of art and regulatory information as of the date of this publication. This is not an official policy and standards document. The opinions and selections are those of the author and not necessarily those of the EPA. Any mention of produces or organizations does not constitute endorsement by the EPA.

U.S. Environmental Protection Agency
Air Pollution Training Institute
Course #468
Compliance Test and Source Test Observation

Student Workbook (SW)

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knowledge and abilities is significantly improved. Consequently, CenSARA has taken the initiative to update EPA's APTI Course #468.

The updated Course #468 is targeted primarily at agency personnel who have the responsibility to monitor compliance test and source test observation of various FRMs and SW-846 methodologies. The revised course materials provide the best available and most current information as well as relevant example exercises to improve the knowledge and expertise of agency observer personnel. The desired outcome of this effort is that agency staff be able to properly observe compliance test and perform source test observations to protect public health and the environment by developing an understanding of EPA's stack testing programs and strategy, various stack test methodologies for quantifying HAPs from industrial processes, and associated quality assurance/quality control activities and requirements.

The specific objectives of updating APTI Course #468 materials include:

- Explain why sampling of source emissions for PM and HAPs is important in air pollution control agency programs;
- Define symbols and common terms used in the application of FRMs 1-5 and SW-846 source sampling;
- Recognize, interpret and apply sections of the Code of Federal Regulations, Appendix A, pertinent to source sampling for particulate pollutants;
- Understand the construction, operation and calibration of the component parts of the FRM 5 particulate matter sampling train;
- Define "Isokinetic sampling" and illustrate why it is important in sampling for PM;
- Understanding the "working" isokinetic rate equation and its derivation
- Learn how to use specific software for determining isokinetic sampling rates;
- Apply FRMs 1 through 4 in preparation for applying FRM 5 at a source to characterize PM emissions;
- Understand how the "S-type" pitot tube is constructed and standardized and how it is applied in source sampling;
- Understand the difference between systematic error and precision as applied to source test measurements;
- Properly assemble and leak check a FRM 5 sampling train;
- Describe the operation of the VOST, Semi-VOST, Acid Gas and FRM 201/201A sampling trains;
- Describe what are "condensibles" and how the FRM 202 sampling train operates to measure condensibles; and
- Calculate the "% Isokinetic" value for a source test, and interpret the effect of over or under-isokinetic values on the source test results.

One of the products of the #468 update is the Student Workbook (SW). The SW provides copies of visuals presented in each technical lecture. Contained in this SW are the visuals for the each of the Sessions and lessons presented in APTI Course #468, as outlined in the Table of Content.

APTI Course #468
Compliance Test and Source Test Observation

Table of Content

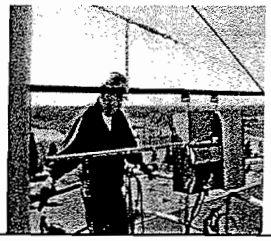
Session #4: Stack Testing for Hazardous Air Pollutants (HAPs) Utilizing SW-846 Methodology

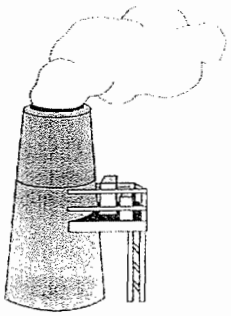
Session #5: Stack Testing for Sulfur-Based Compounds

Session #6: Stack Testing for Acid Gases, Sizing Particulate Matter (PM) and Special Topics

Session #7: Instrumental Monitoring for HAPs

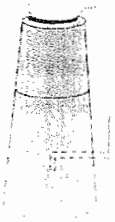
U.S. EPA APTI
Compliance Test and Source Test Observation
APTI Course #468 Introduction





Measurement of Source Pollutant Emissions

Manual Sampling



Extract samples from various points in stack.

Analyze samples in lab.

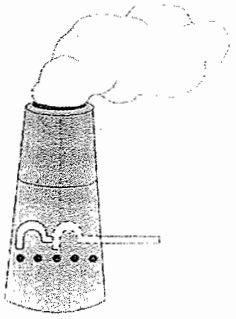
Procedures described by federal reference methods (FRMs)

Methods for Measuring Emissions

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

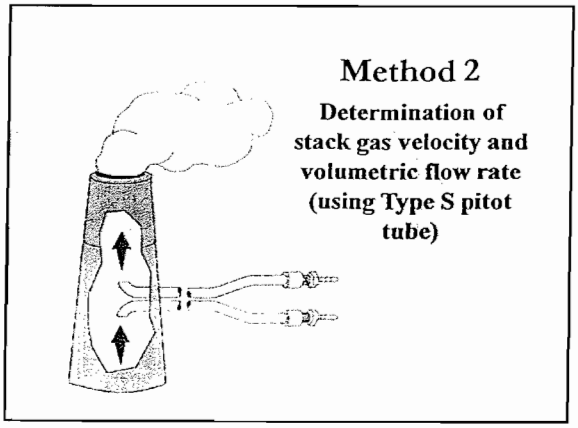
EPA Manual Federal Reference Methods (FRMs)

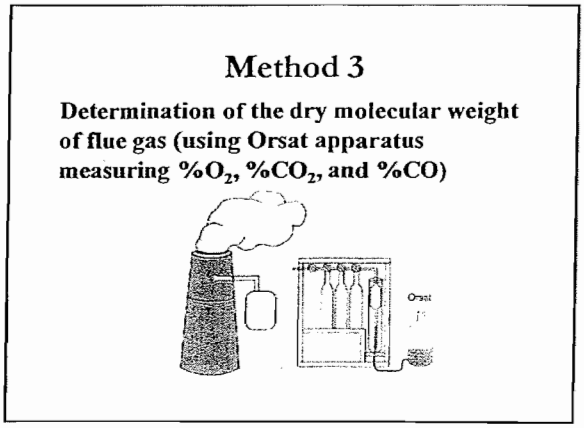
- Used for source compliance testing
- Describe actual testing procedure
- Found in Code of Federal Regulations

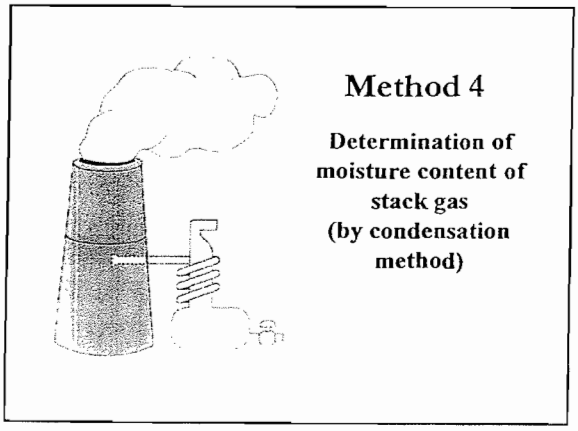


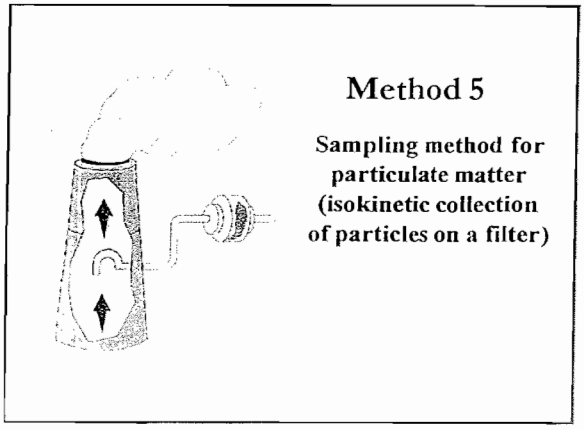
Method 1

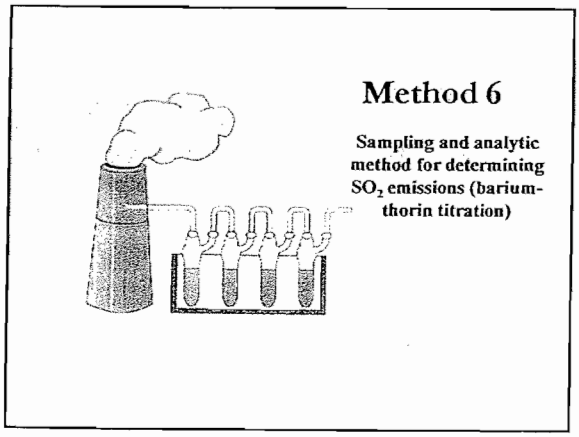
Selection of sampling traverse points

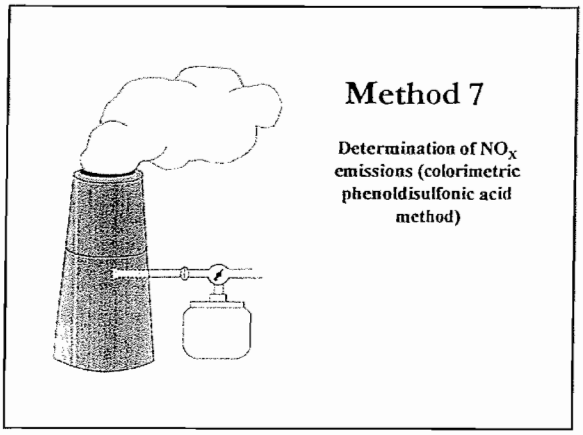

Method 2
Determination of stack gas velocity and volumetric flow rate (using Type S pitot tube)


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)

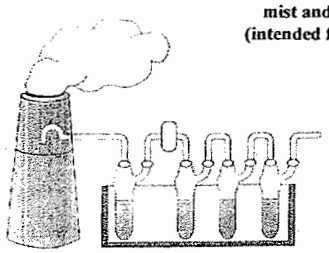

Method 5
Sampling method for particulate matter (isokinetic collection of particles on a filter)


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.

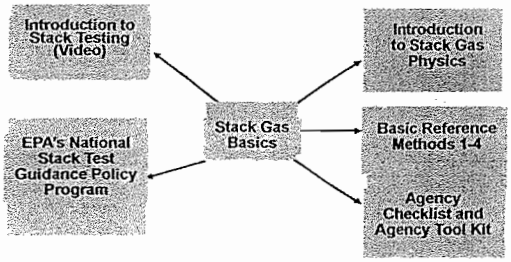
Objectives

- 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

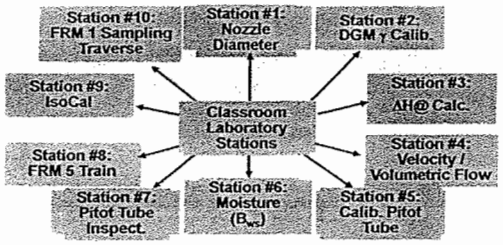
Objectives

- 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

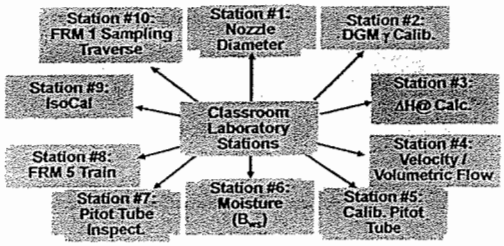
What We Will Cover Monday, Day 1



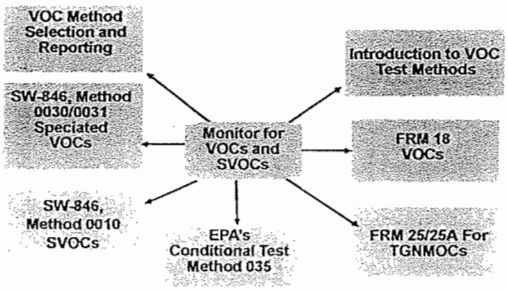
What We Will Cover Tuesday, Day 2



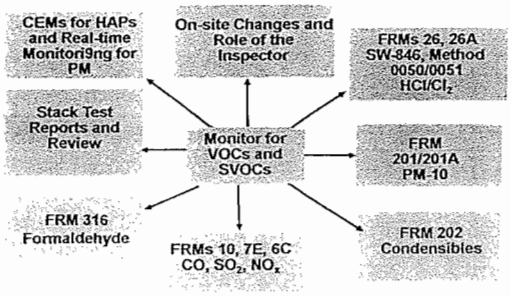
What We Will Cover Wednesday, Day 3



What We Will Cover Thursday, Day 4



What We Will Cover Friday, Day 5

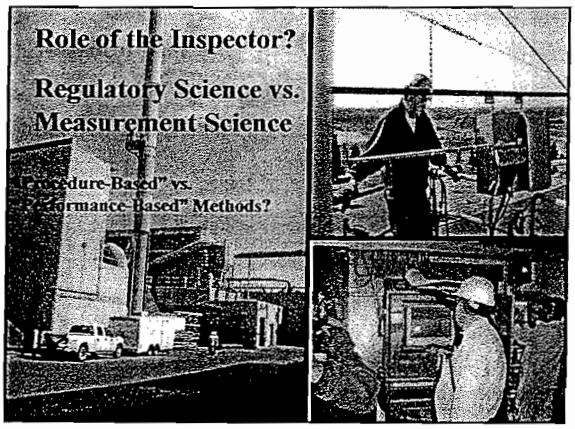


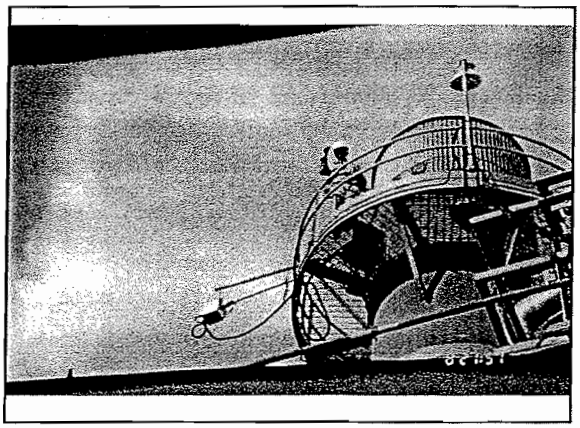
Course Materials

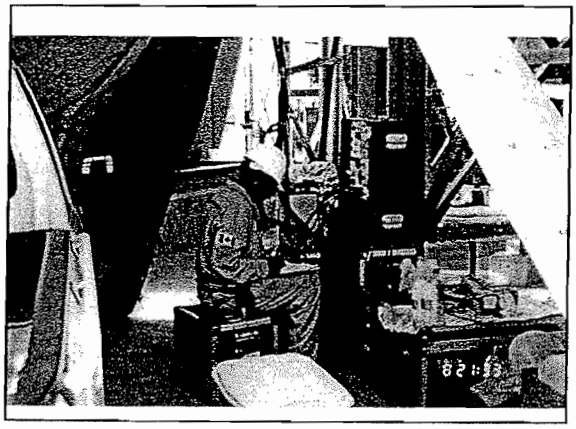
- Student Workbook
  - Contains the course agenda and copies of selected slides presented in each of the topic areas
- Student Manual
  - APTI Course #450 Manual and Checklist

Course Materials

- Federal Reference Method 5 Manual
  - Operating Manual
  - Agency observation checklist, and various reference materials
- Federal Register containing FRM 1-5
- Course CD- Contains Over 90 Stack Testing Entries
- Laboratory Guide Manual







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)?

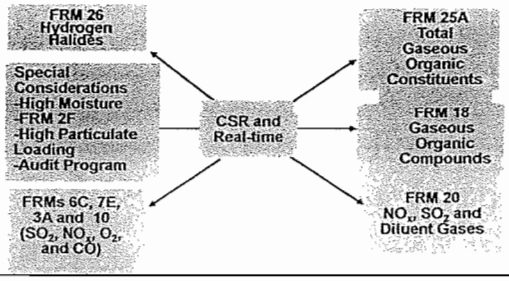
Historical Questions?

- 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?

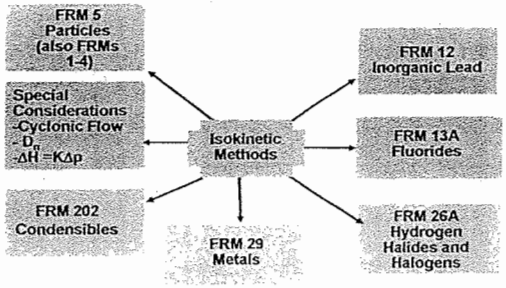
Historical Questions?

- 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?

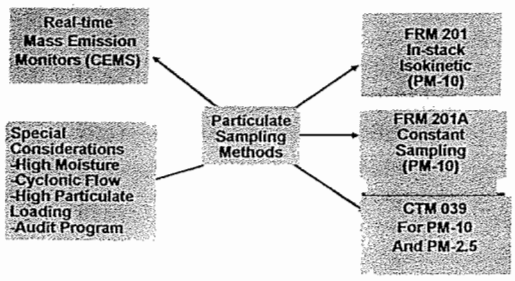
Constant Sampling Rate (CSR) and Real-time Methods



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

$PMR_s = c_s Q_s$

Q_s c_s

$v_s = v_n$

Isokinetics

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

Obtain C_p, T_p, Δp, M_s, P_s

Obtain $\Delta H@$, D_n, B_{ws}, P_m, T_m, ΔH

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

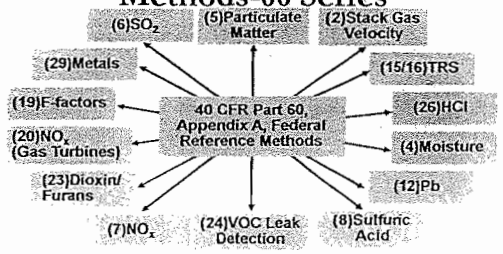
Where Do We Find the Test Methods?

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)

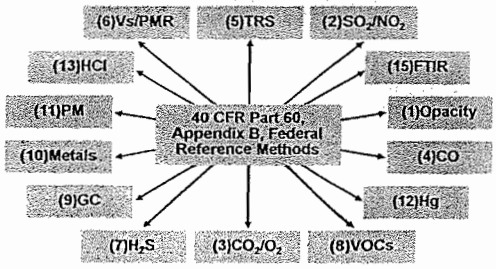
New Source Performance Standard (NSPS) Reference Methods-00 Series



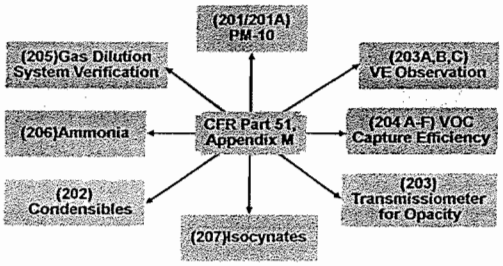
Regulations

- 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



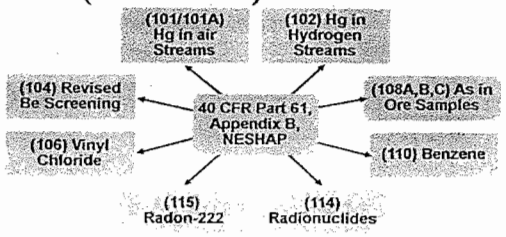
State Implementation Plan (SIP)- 200 Series



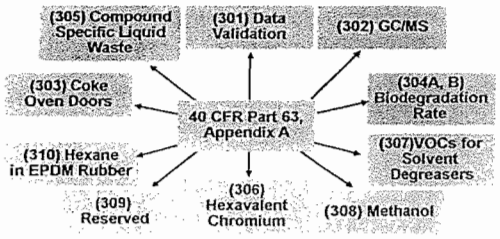
Clean Air Act and It's Amendments

- 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)

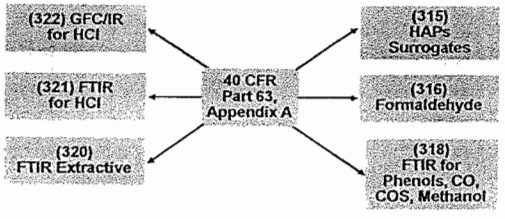
National Emission Standards For Hazardous Air Pollutants (NESHAPs)- 100 Series



Maximum Achievable Control Technology (MACT)-300 Series



Maximum Achievable Control Technology (MACT)-300 Series



Categories of Stack Test Methods by EPA

- 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 Methods"
  - Compliance Methods for specific applications with approval from EPA

Categories

- Category C: "Other Methods" evaluated by EPA; This category includes test methods which have not yet been subject to the Federal rulemaking process.

Categories

- Category D: Historical Conditional Methods which may be useful in limited applications until more supporting information is provided.

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 (Conditional): Particulate (PM Screening) Method; conditional test method for Acrylonitrile; halogenated organic method; Method for isocyanates

Example Category Stack Test Methods

- Category D (Preliminary Methods): PRE 5-Determination of oxides of nitrogen from stationary sources (UV Instrumental Analyzer)

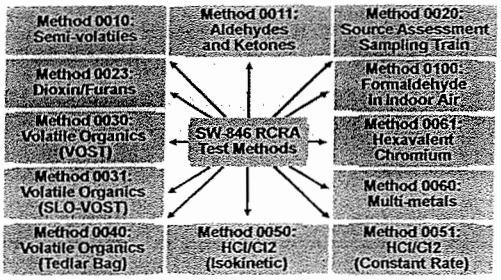
Where To Locate EPA's Test Method Categories

- All categories of methods found on
  - www.epa.gov/ttn/emc/tmethods.html

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



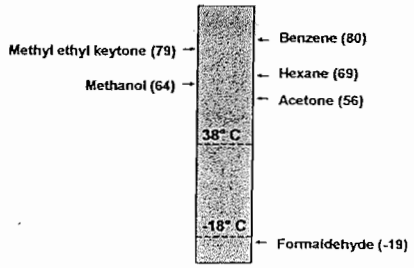
How Do We Define HAPs

- 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)

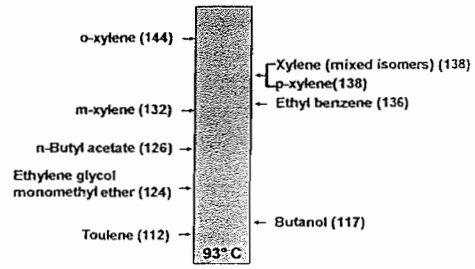
General Classification of VOCs

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

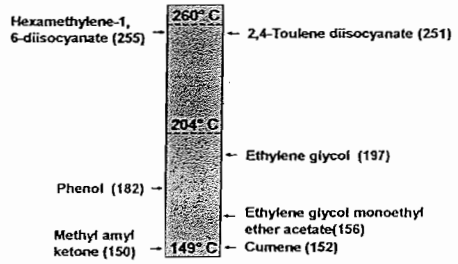
Boiling Points of Volatile Organic Compounds



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)	106
Semi-volatiles (SV)	65
Non-Volatile (NV) Particles	17
Total HAPs	188

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)

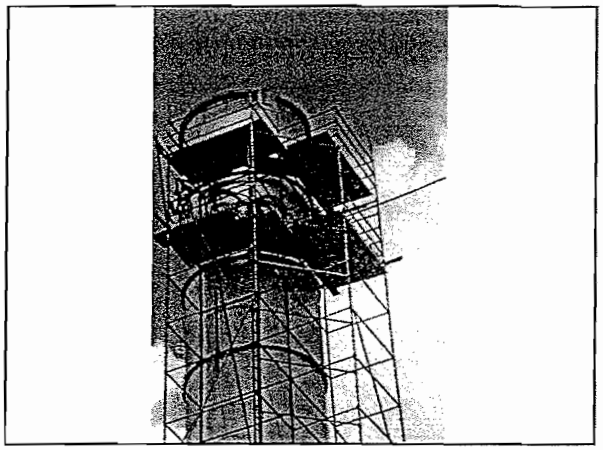
3,3'-Dimethoxybenzidine	10^{-13} mm Hg	458°C
Antimony	Very Low	656°C
Coronene	10^{-13} mm Hg	525°C

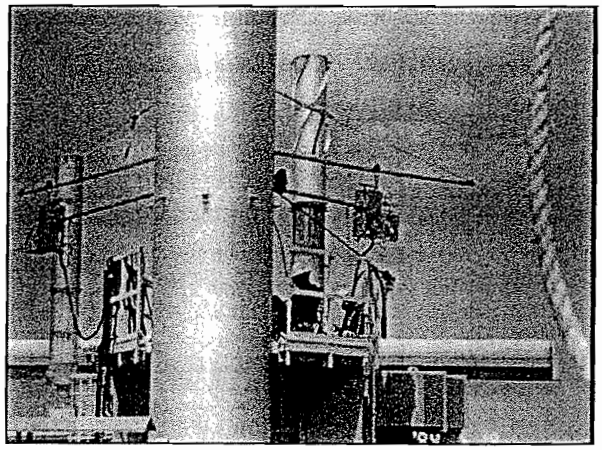
General Classification of VOCs

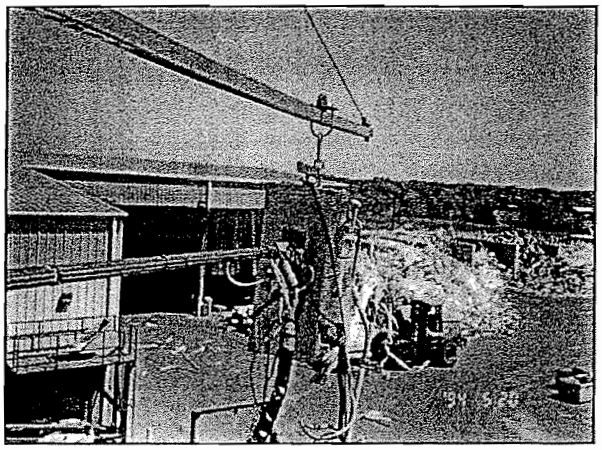
Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	> 10^{-1}	< 200°C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	200 - 500°C
Particles (NV)	< 10^{-7}	> 500°C

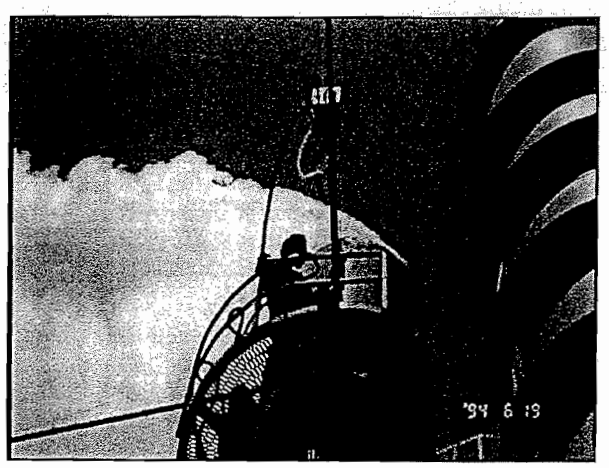
Compliance Test and Source Test Observation

EPA's National Stack Testing Guidance









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

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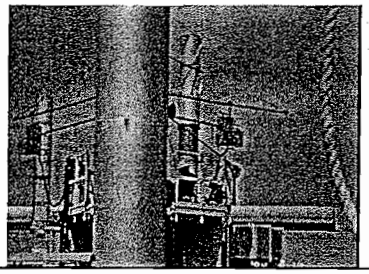
*States/EPA have until 12/1 to report FY '08 data

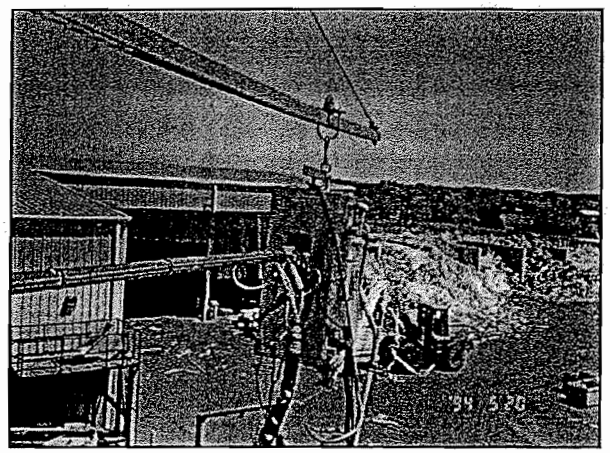
Additional Information

- 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)





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

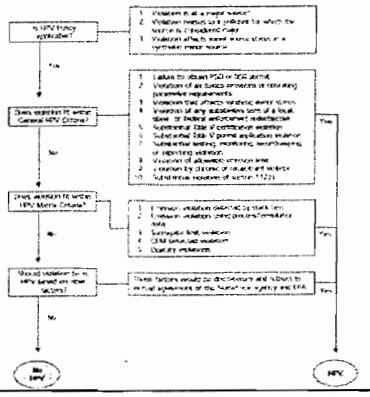
- December 22, 1998 Memo
  - This memo eliminates use of the terms "Significant Violator" and "Significant Violation" and substitutes the term "High Priority Violation" (HPV) in describing violations.
  - EPA expects that all violations of air pollution regulations, whether meeting the HPV criteria or 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

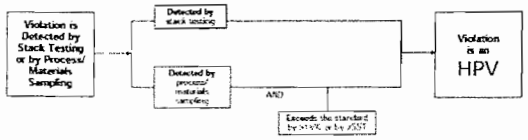
- Violation of Applicable Standards (non-opacity)
  - Continuous Emissions Monitoring (where the CEM is certified under federal performance specifications)
- Violation of Applicable Standards (opacity)
  - Continuous Opacity Monitoring or
  - Method 9 Visual Emissions Readings

Standards For Violation

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

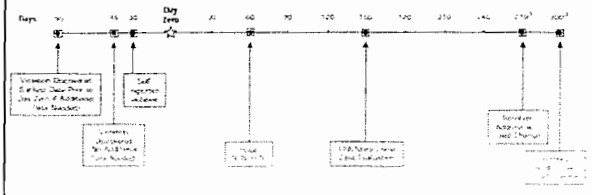
VIOLATION	DETECTION METHOD	STANDARD	SUPPLEM. THRESHOLD	% EXCESS REF. LIMITS
Allowable Emission Limits	Stack Test	Any Applicable Requirement		Any Violation of Standard
	Coating Analysis, Fuel Samples, Other Process Material Sampling	Any Applicable Requirement	CO 23 lb/hr NOx 9 lb/hr SO2 9 lb/hr VOC 9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

Logic Flow For Stack Testing Violation

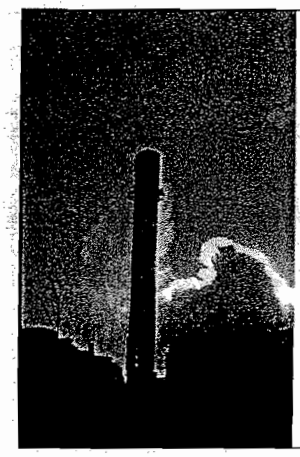


(See Resource CD, Session 1: EPA's HPV Workbook for Examples)

Timely and Appropriate Enforceable Timeline



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



Compliance Test and Source Test Observation

Role of the Agency Inspector/Observer

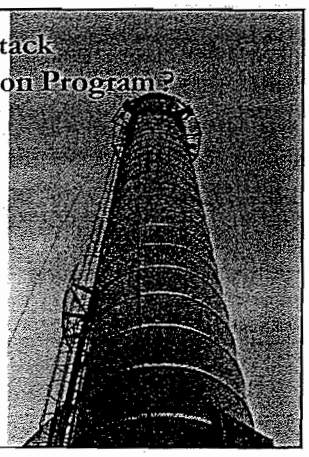
Why Compliance Stack Test and Observation Program?

Identify Air Pollutants

Evaluate

Evaluate Test Results

by prescribed EPA Federal Reference Methods (FRMs)



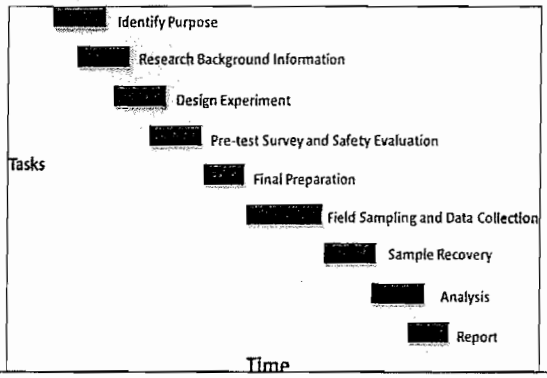
Example of Typical Industries

- Coal-fired Power Plants
- Asphalt Plants
- Gas Turbines
- Gasoline Terminals
- Coating and Printing Facilities
- Secondary Aluminum
- Cement Plants

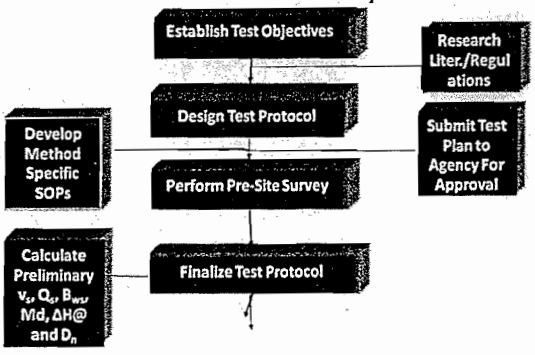
Groups Involved In A Compliance Test

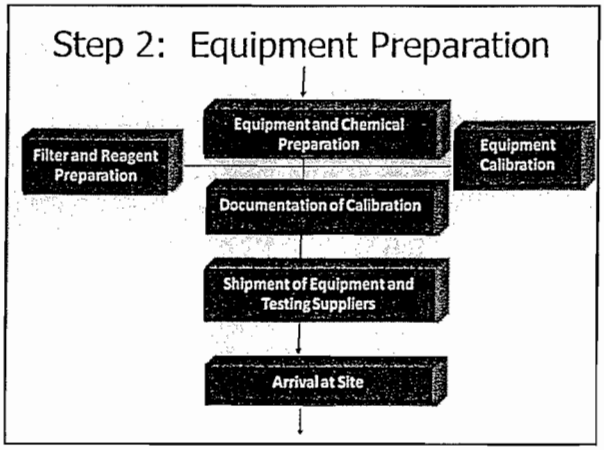
- Officials of the facility being tested
- Consulting stack testing team
- Agency officials in which the facility is located (i.e., State Air Quality Division)

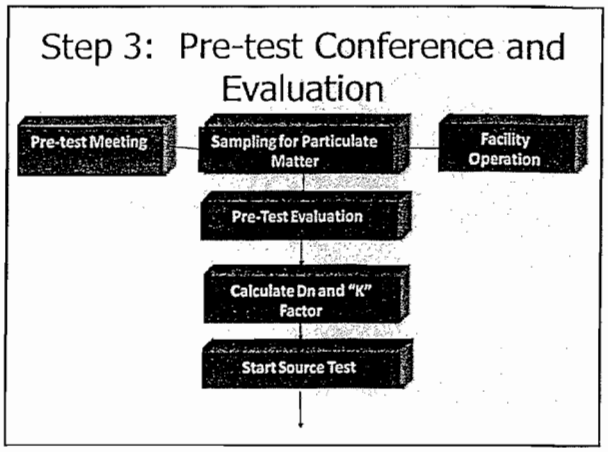
Source Test Time-line

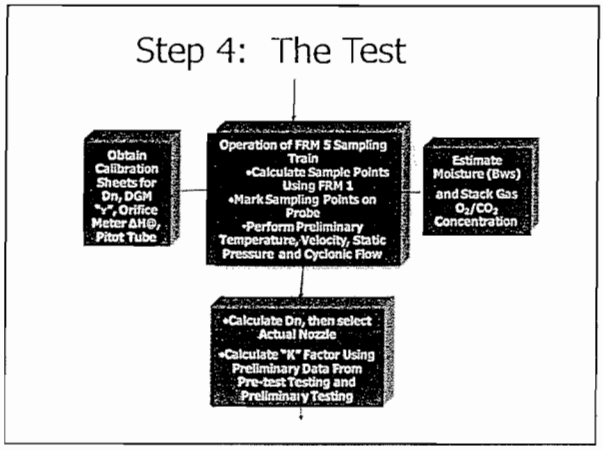


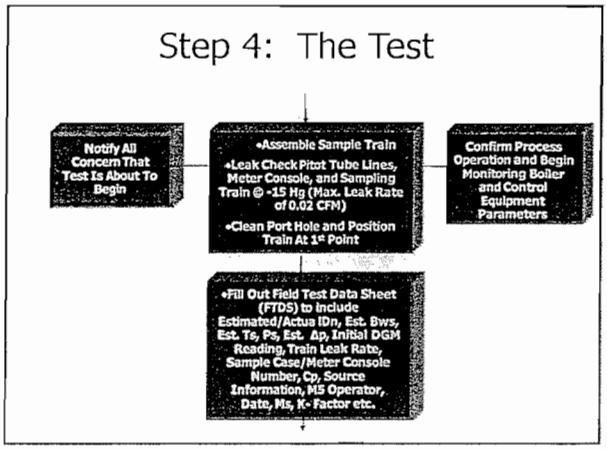
Step 1: Objectives, Protocols and Pre-site Survey

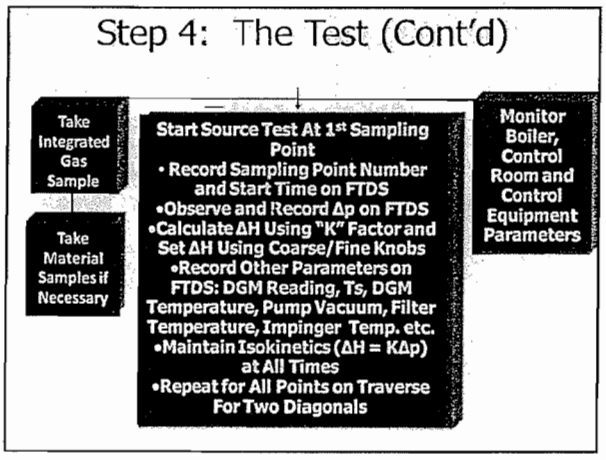


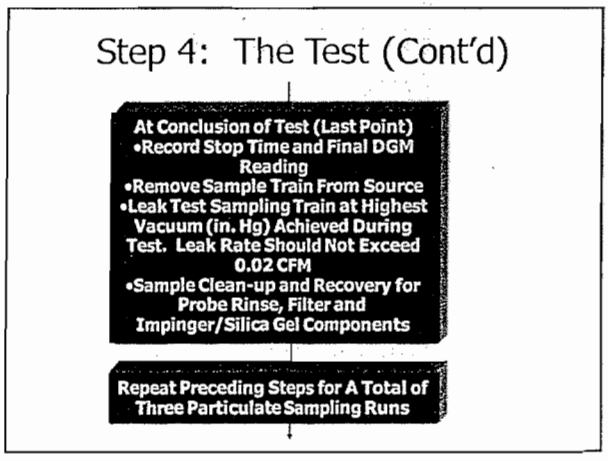

Step 2: Equipment Preparation
Filter and Reagent Preparation
Equipment and Chemical Preparation
Equipment Calibration
Documentation of Calibration
Shipment of Equipment and Testing Suppliers
Arrival at Site


Step 3: Pre-test Conference and Evaluation
Pre-test Meeting
Sampling for Particulate Matter
Facility Operation
Pre-Test Evaluation
Calculate Dn and "K" Factor
Start Source Test

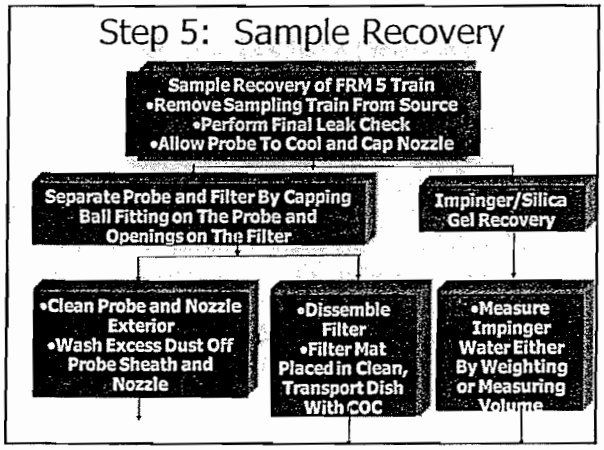

Step 4: The Test
Obtain Calibration Sheets for Dn, DGM "γ", Orifice Meter ΔH@, Pitot Tube
Operation of FRM 5 Sampling Train
•Calculate Sample Points Using FRM 1
•Mark Sampling Points on Probe
•Perform Preliminary Temperature, Velocity, Static Pressure and Cyclonic Flow
Estimate Moisture (Bws) and Stack Gas O_2/CO_2 Concentration
•Calculate Dn, then select Actual Nozzle
•Calculate "K" Factor Using Preliminary Data From Pre-test Testing and Preliminary Testing


Step 4: The Test
Notify All Concern That Test Is About To Begin
•Assemble Sample Train
•Leak Check Pitot Tube Lines, Meter Console, and Sampling Train @ ~15 Hg (Max. Leak Rate of 0.02 CFM)
•Clean Port Hole and Position Train At 1st Point
Confirm Process Operation and Begin Monitoring Boiler and Control Equipment Parameters
•Fill Out Field Test Data Sheet (FTDS) to include Estimated/Actua lDn, Est. Bws, Est. Ts, Ps, Est. Δp, Initial DGM Reading, Train Leak Rate, Sample Case/Meter Console Number, Cp, Source Information, MS Operator, Date, Ms, K- Factor etc.

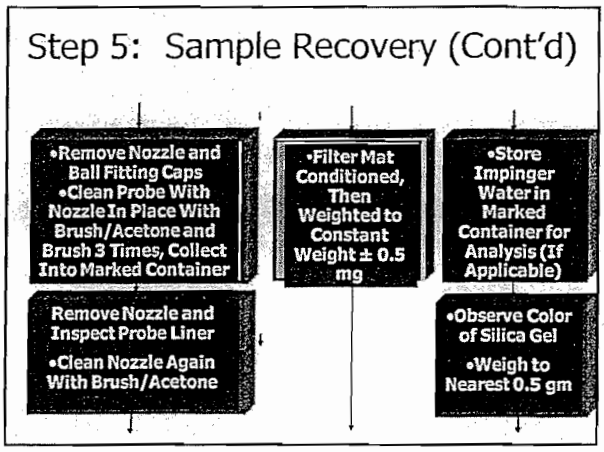

Step 4: The Test (Cont'd)
Take Integrated Gas Sample
Take Material Samples if Necessary
Start Source Test At 1st Sampling Point
• Record Sampling Point Number and Start Time on FTDS
•Observe and Record Δp on FTDS
•Calculate ΔH Using "K" Factor and Set ΔH Using Coarse/Fine Knobs
•Record Other Parameters on FTDS: DGM Reading, Ts, DGM Temperature, Pump Vacuum, Filter Temperature, Impinger Temp. etc.
•Maintain Isokinetics (ΔH = KΔp) at All Times
•Repeat for All Points on Traverse For Two Diagonals
Monitor Boiler, Control Room and Control Equipment Parameters


Step 4: The Test (Cont'd)
At Conclusion of Test (Last Point)
•Record Stop Time and Final DGM Reading
•Remove Sample Train From Source
•Leak Test Sampling Train at Highest Vacuum (in. Hg) Achieved During Test. Leak Rate Should Not Exceed 0.02 CFM
•Sample Clean-up and Recovery for Probe Rinse, Filter and Impinger/Silica Gel Components
Repeat Preceding Steps for A Total of Three Particulate Sampling Runs

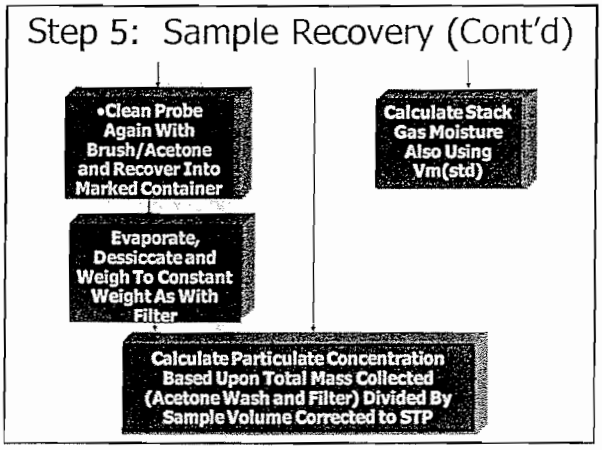
Step 5: Sample Recovery



Step 5: Sample Recovery (Cont'd)



Step 5: Sample Recovery (Cont'd)



Function of Stack Test Observer

- *"...the principle function of the stack test observer is to evaluate the representativeness of the compliance test in which emissions are sampled while the plant operates under typical conditions considered representative of day-to-day operations."*

The Inspector's/Observer's Role

- Be Present! (Phone insp. and windshield insp. are discouraged)
- Have a Plan, Follow the Plan!
- 3-Tier Inspection
- Observations – "familiar" with 40 CFR 60, App. A, Methods 1-4,5; 1.Velocity Profile, 2.Leak Check, 3.Clean-up 4. Observer Check-list
- Operations of facility
- Sample train recovery and data acquisition

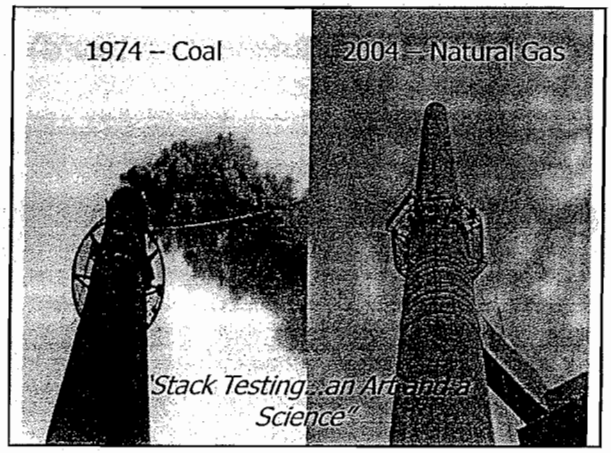
Inspectors Do's and Don'ts

DO

- Ask intelligent questions that add value
- Become "familiar" with test methods rules and test plans
- Show Up! Presence is critical
- Be critical but reasonable
- Reward "quality testing"

DON'T

- "Umpire" a test
- Challenge a test w/o good cause
- Be unresponsive to requests
- Hesitant to say "I don't have an answer"
- Be Careless



Seven Areas of Responsibility of Agency Personnel

- **Familiarize:** Agency observer establishes contact with the source and becomes familiar with operations, emissions, and applicable regulations.
- **Division of Air Quality Reviews Scheduled Source Test:** May be part of compliance test or annual test requirements
- **Division of Air Quality Establish Methodology:** Identify testing methodology as prescribed by regulations and receipt of testing plan from facility or contractor

Seven Areas of Responsibility of Agency Personnel

- **Division of Air Quality Reviews Final Test Plan:** Pre-test meeting between Division personnel, test team leader and facility to finalize test plan.
- **Actual Compliance Test:** The facility Operations Personnel and Division of Air Quality Test Personnel observe testing methodology.

Seven Areas of Responsibility of Agency Personnel

- **Review of Test Data: Division of Air Quality determines** compliance and official notification are determined.
- **Continuing Enforcement of Compliance:** Follow-up inspections are undertaken, using data generated from source test as a "baseline" for compliance purposes.

Compliance Evaluation In Terms of Five Criteria

- Process and control equipment must be operated in such a manner as to produce representative atmospheric emissions
- Location of the sample port and sample points must provide samples representative of the atmospheric emissions

Compliance Evaluation In Terms of Five Criteria

- The sample collected in the sample train must be representative of the sample points.
- The sample recovered and analyzed must be representative of the sample collected in the sample train
- The reported results must be representative of the sample recovered and analyzed

Division of Air Quality Personnel Involved In The Testing

- Phase 1: Preparation and planning
- Phase 2: Conducting the test
- Phase 3: Recovery, transport (Optional), and analysis of the samples (Optional)
- Phase 4: The observer's compliance test report

Role of The Observer

- Determine whether source test is required
- Coordinate process operation
- Coordinate control equipment operation
- Coordinate testing methodology
- Document all activities during the testing program
- Review test reports

Role of The Observer

- Specify Division requirements
- Make decisions regarding test methodology, process and control equipment operation and reporting requirements
- Determine representativeness of process and control equipment operation

Role of The Observer

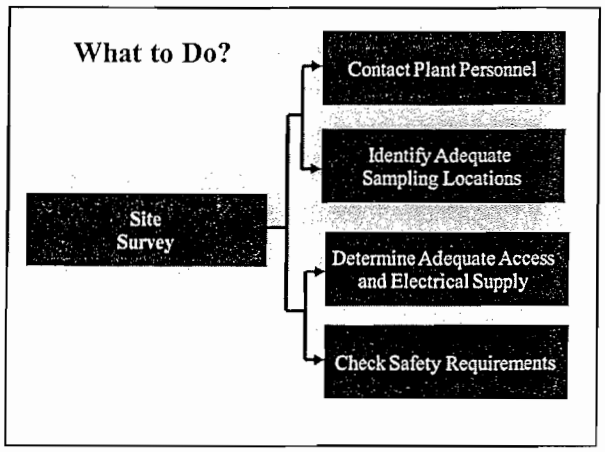
- Determine acceptability of testing methodology
- Compile summary report of test
- Review test report and make recommendation

Observer Behavior

- The observer should do all within his power to see that testing is successfully completed
- The observer should work cooperatively with the source and consultant
- The observer must be specific and forthright in his request
- The observer must be respectful of the positions of the other parties involved

Observer Techniques

- Do not write on process charts and graphs
- Do not turn knobs and dials
- Do not collect unnecessary data
- Do not touch or adjust testing equipment
- Do not question tester or interfere during critical times of the test
- Do not conceal unacceptable acts or procedures



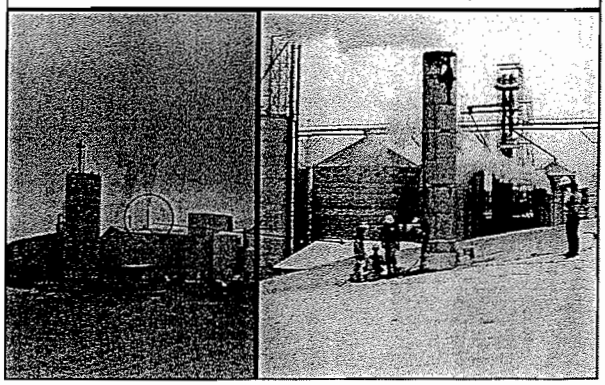
Phase 1: Preparation and Planning

- Division of Air Quality must clarify for the plant representative and stack test team leader procedures to be followed (i.e., compliance test guidelines)
  - Identification of Federal Reference Methods (FRMs): PM, Condensibles, Filter Temp, Inorganics, Organics etc.
  - Operation level of process during testing (i.e. "baselining" the control equipment/source)
  - Data acquisition and reporting of process and test methodology parameters

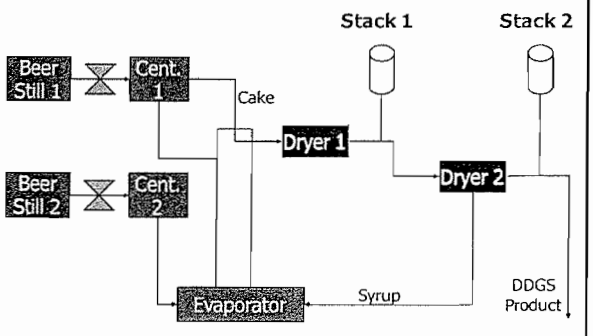
Phase 1: Preparing and Planning

- Block-style flowchart is adequate for our needs for "baselining"
- Do not need design-oriented piping and instrumentation (P&I) engineering drawings
- Only system components need to be block-style rather than actual drawing of equipment

Ethanol Plant – Methods 5, 25A



Ethanol Flowchart

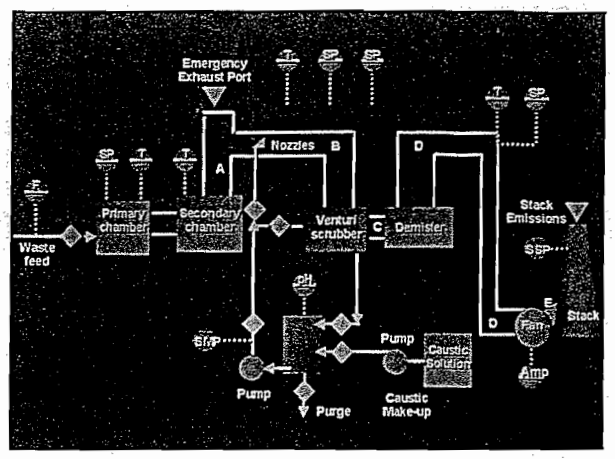


Utility of Preparing a Block-Style Flowchart

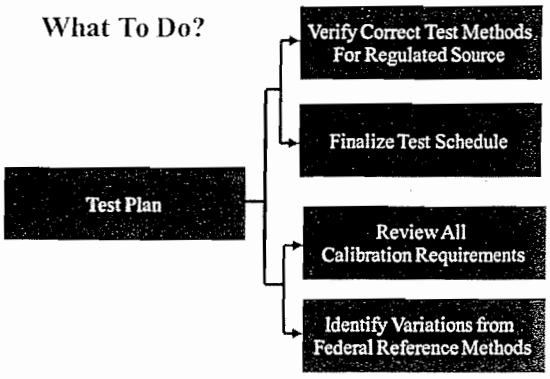
- Identifies health and safety hazards (i.e., high temperature, high positive pressure, fugitive leaks, slippery/wet surfaces etc.)
- Facilitates compliance evaluation
- Document operating conditions with reference to previous compliance test ("Baselining" the process!)
- Simplifies communications with plant personnel

Symbols Used in Block-Style Flowcharts

- Solid line……Solid or liquid stream
- Two Parallel Solid Lines…..Gas stream
- Square or Rectangle…….Major equipment
- Reverse Triangle…….Gas emission point
- Circles with "T" inside…Actual temper.
- Circles with "SP" inside….Static pressure



What To Do?



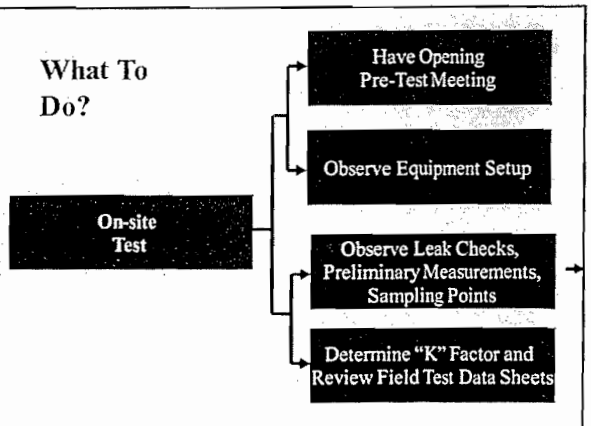
Phase 1: Preparing and Planning

- Division of Air Quality review of submitted test protocol
  - Deviation from standard sampling procedures
  - Operation of facility
  - Identification/discuss of test methods
  - Identification and discussion of sampling location
  - Calibration of all monitoring equipment

Phase 1: Preparing and Planning

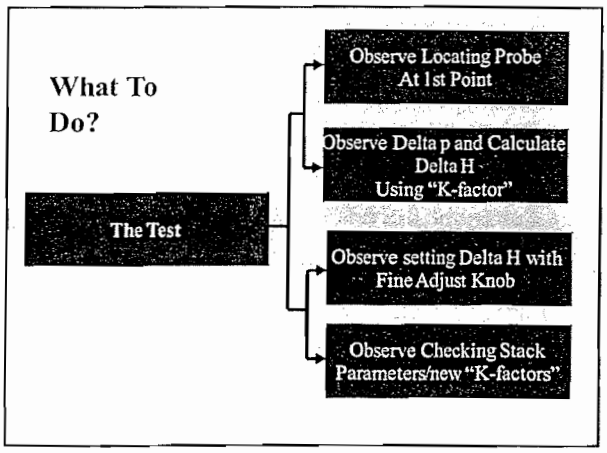
- Observer's Needed Documentation
  - Checklist for Federal Reference Methods (FRMs) and SW-846 Methods (See Resource CD)
  - Checklist for air pollution control equipment
  - Checklist for facility operation parameters
- Pretest Meeting
  - Finalize sampling plan
  - Establish "Baseline" conditions
  - Coordinate testing schedule
  - Checklist for pretest meeting

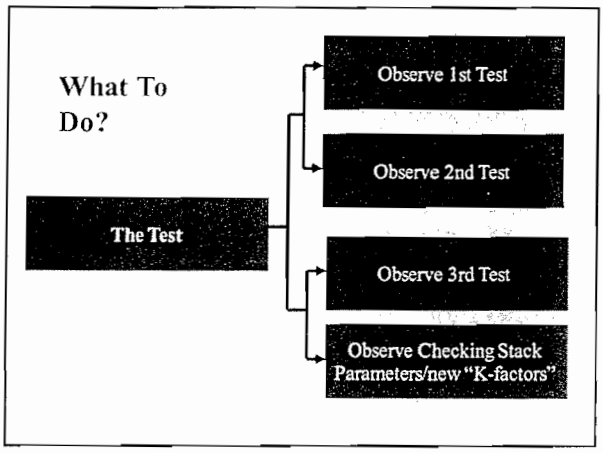
What To Do?



Observer Activities

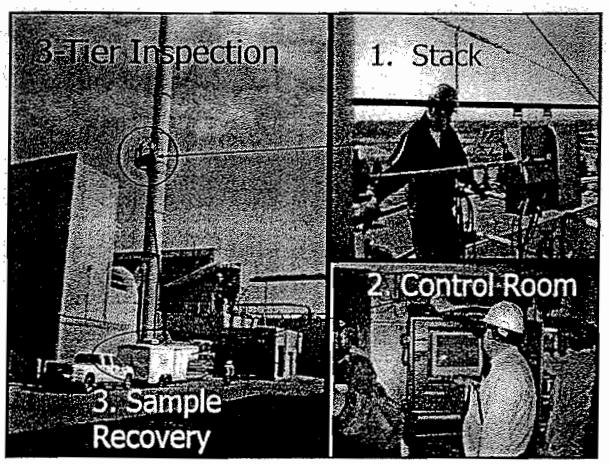
- Observe preliminary velocity traverse and cyclonic flow check
- Observe nozzle size determination
- Review approximate molecular weight and moisture determination
- Review "K-factor" determination





Phase 2: Conducting The Test

- Observer's Checklist (See Resource CD)
  - Health and safety requirements
  - Tentative testing schedule
  - Facility "baseline" conditions
  - Update stack test methodology checklist
  - Handling irregular situations, potential problems and their solutions
  - Calibration forms/checklist



What to Watch

- Review records of equipment calibration (pre-test/QC)
- Watch cyclonic flow check and preliminary flow traverse

Examine Probe Nozzle, Pitot, And Thermocouple Design

- Center of nozzle and pitot opening aligned
- Impact pressure sensor of pitot above nozzle opening

Examine

- Type-S pitot tube offset 3/4 inch to side of nozzle
- Thermocouple offset 3/4 inch to side of pitot or set back 2 inches from center of pitot opening

What to Watch

- Vacuum/pressure leak check
- Check traverse point marks, # is correct and within 1/2 inch

What to Watch

- Nozzle ID calibrated; 3 measurements within +/- 0.004 inch
- Check dry gas meter with restricted orifice: also a gamma check

What to Watch

- Pitot tube leak check; both (+) and (-) sides (check at pressure vacuum > 3 inches water and stable for at least 15 seconds)

Sample Train Leak Check

- Pre-test should be at 15 inches Hg
- Post test at vacuum >/= max. vacuum reached during the test

Sample Train Leak Check

- Leak rate < 0.02 cfm acceptable
- Leak rate > 0.02 cfm; either record leak rate and correct sample volume or void the test run

What to Watch

- Check sampling port is sealed
- Look to see that inclined manometer is level all the time
- Check that sampling train is being moved at the correct time and set at the correct traverse point

What to Watch

- Check that the operator is recording temperatures and setting sampling rate at the proper times
- Reagents stored properly; i.e., at correct temperature and protected from sunlight

What to Watch

- Sampling isokinetically; Is ΔH on meter box equal to ΔH on field data sheet?
- Check % Isokinetic rate equation at various points during the sampling scheme: $\Delta H = k \Delta P$

What to Watch

- Check that sampling system temperatures are within specifications:
  - Probe temperature
  - Filter temperature
  - Sorbent temperature
  - Impinger train temperature (iced?)

What to Watch

- Watch sample recovery
  - Nozzle rinse
  - Probe rinse
  - Front half filter housing rinse
  - Filter recovery
  - Resin recovery
  - Proper labeling/storage of recovered samples

What to Watch

- Samples properly identified and tied to specific sample runs
- Chain-of-custody properly prepared and maintained with samples

What to Watch

- Field and trip blanks prepared properly and shipped with field samples
- Documentation retrieved and signed

Phase 2: Conducting The Test

- Observe "First Test" Items
  - Configuration/preparation of train
  - Initial leak check
  - Positioning at 1st sampling point
  - Record initial data/operation meter box
  - Calculation of "K" factor
  - Verification of isokinetics
  - Movement of probe to other sampling points/ports
  - VE observations

Phase 2: Conducting The Test

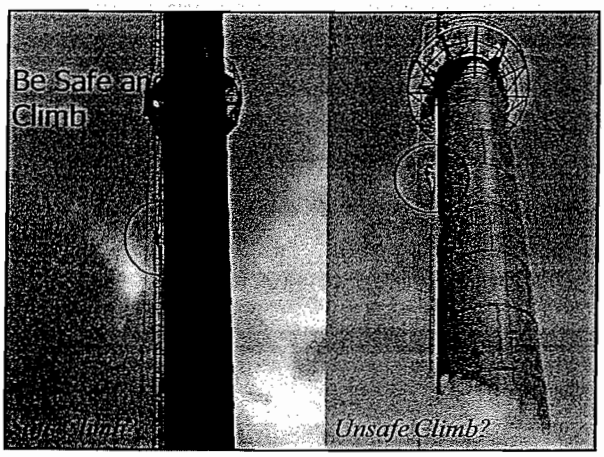
- Observe "First Test" Items
  - Facility Operation (i.e., "Baselining")
    - Fuel flow meters
    - Process monitors
    - Fuel consumption
    - Data from continuous emission monitors (CEMs)
    - Control equipment monitors
      - ESP (voltage, current, rapping rate etc.)
      - Bag houses (...p, bag failure logbook etc.)
      - Wet scrubbers (pH, flow rate etc.)

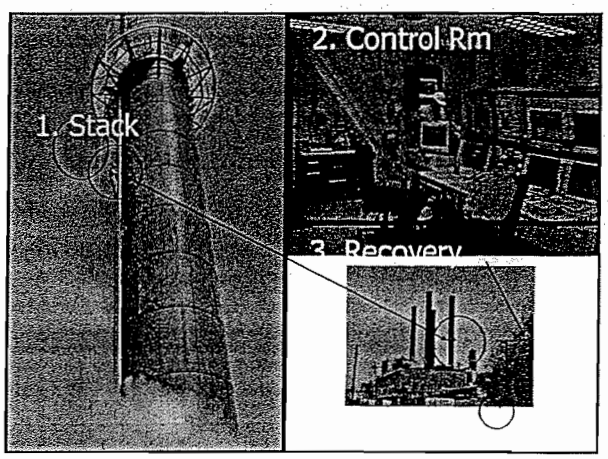
Phase 2: Conducting The Test

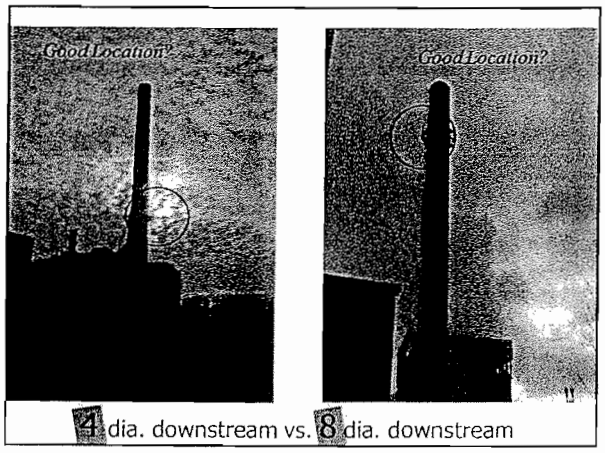
- Observe "Second Test" Items
  - During second test, record and observe process and pollution control equipment data/operation
  - Verification of operation of Method 5 train and recorded data
  - Movement of probe to final sampling points
  - Final leak check/observation of filter condition
  - Sample recovery and "chain-of-custody (COC)" documentation
  - Final VE observation

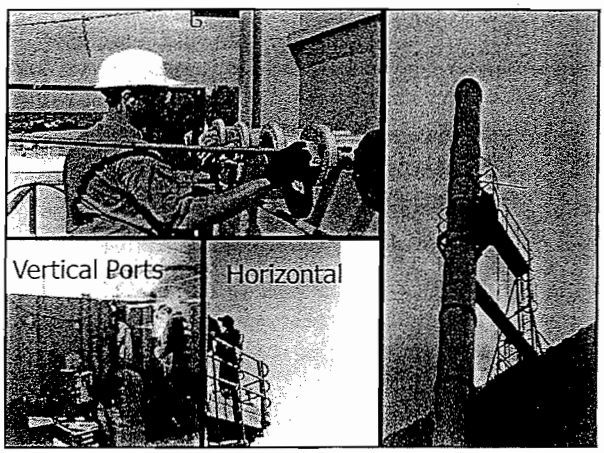
Phase 2: Conducting The Test

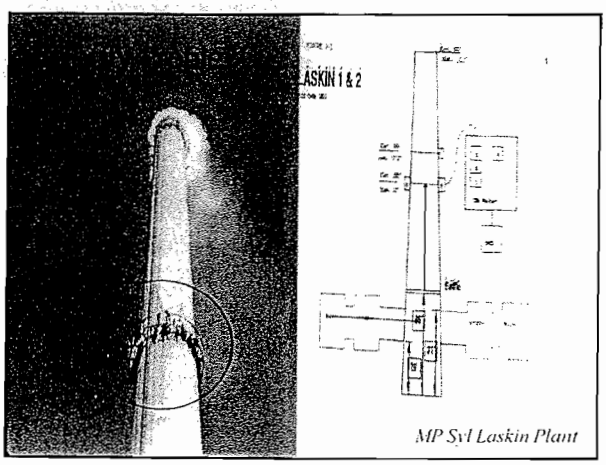
- Observe "Third Test" Items
  - During third test, record and observe process and pollution control equipment data/operation
  - Verification of operation of Method 5 and recorded data
  - Observation of continuous emission monitor systems (CEMs) and recorded information
  - Final leak check/train recovery of filter and impingers

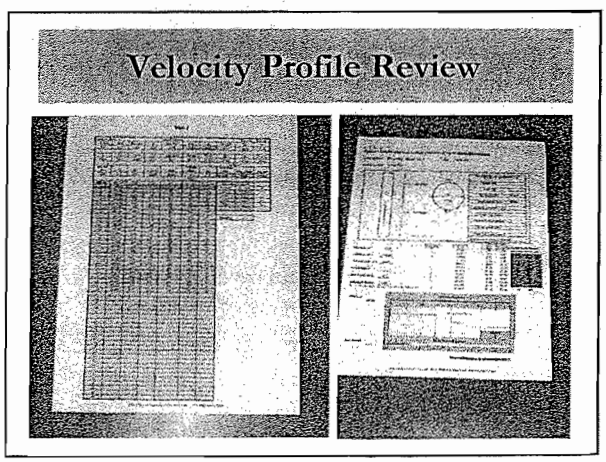

Be Safe an
Climb
Unsafe Climb?

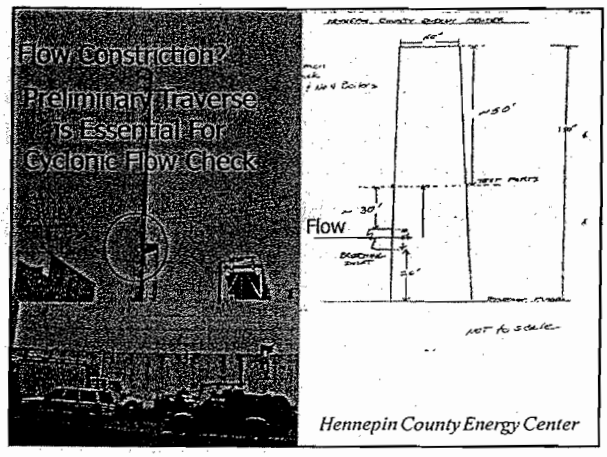

1. Stack
2. Control Rm
3. Recovery

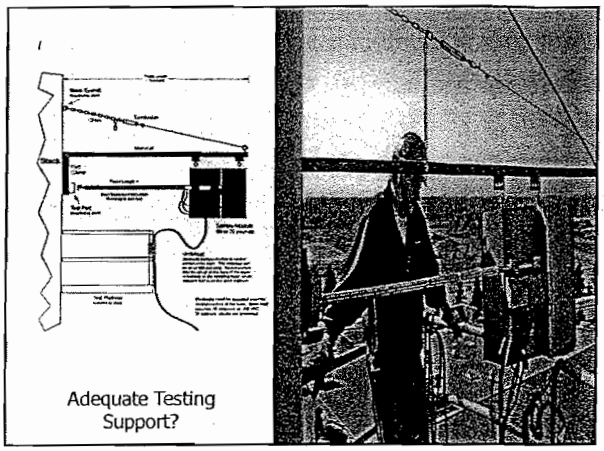

Good Location?
Good Location?
4 dia. downstream vs. 8 dia. downstream

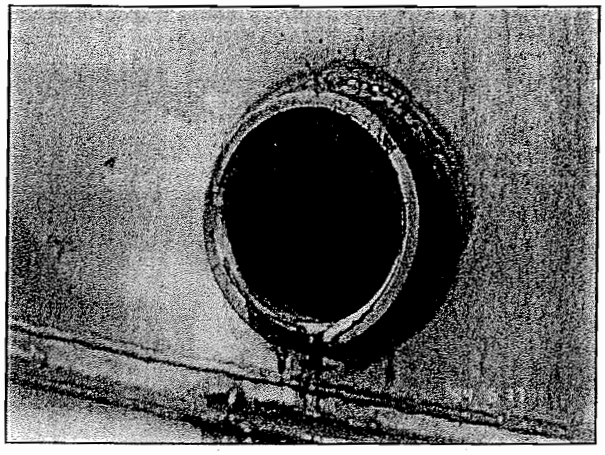

Vertical Ports
Horizontal

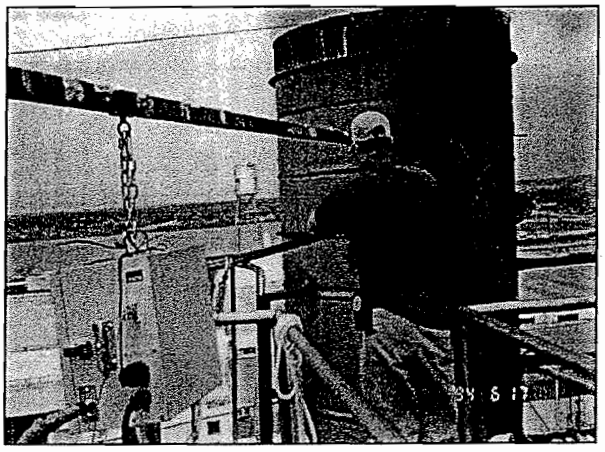

ASKIN 1 & 2
MP Syl Laskin Plant

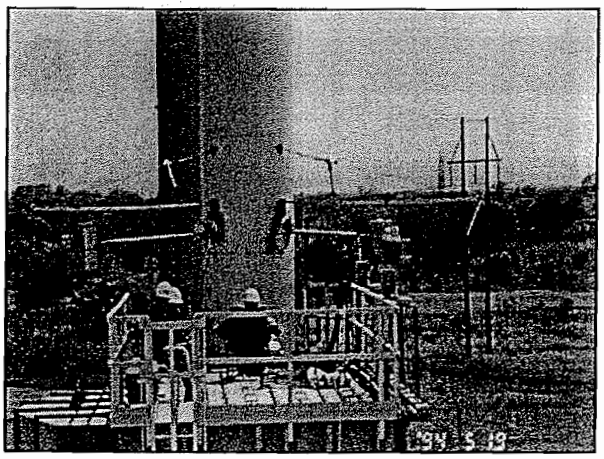

Velocity Profile Review

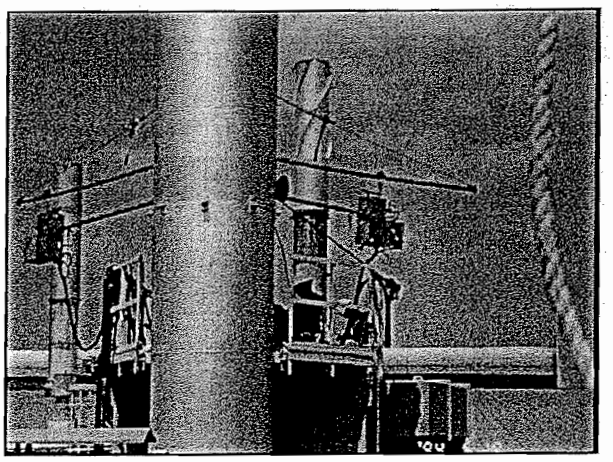

Flow Constriction?
Preliminary Traverse
Is Essential For
Cyclonic Flow Check
Flow
Hennepin County Energy Center

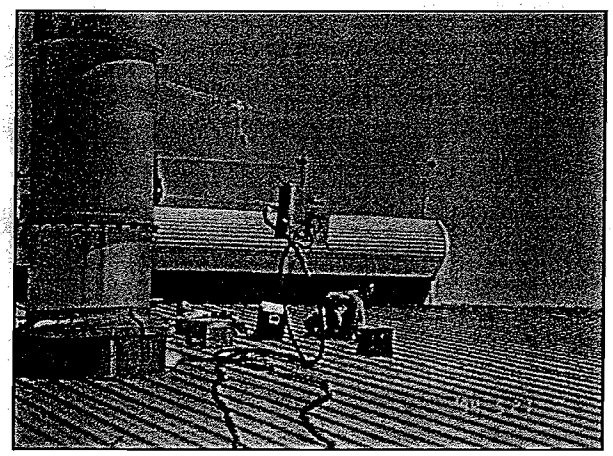

Adequate Testing
Support?

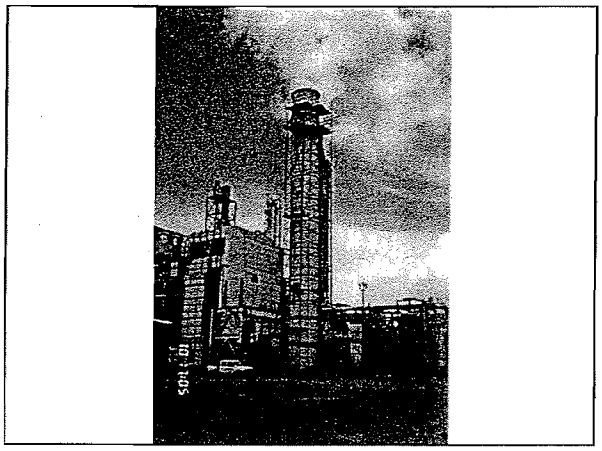


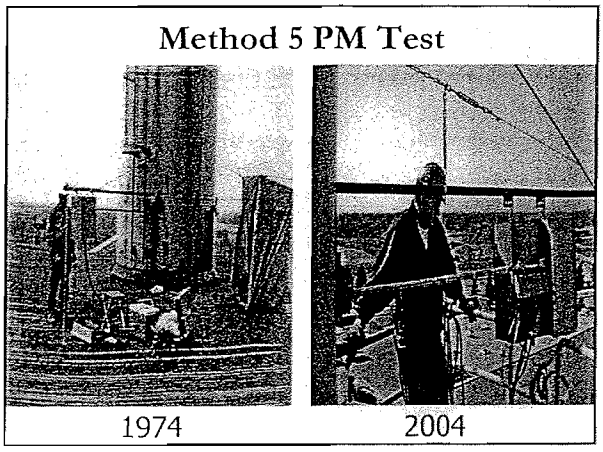


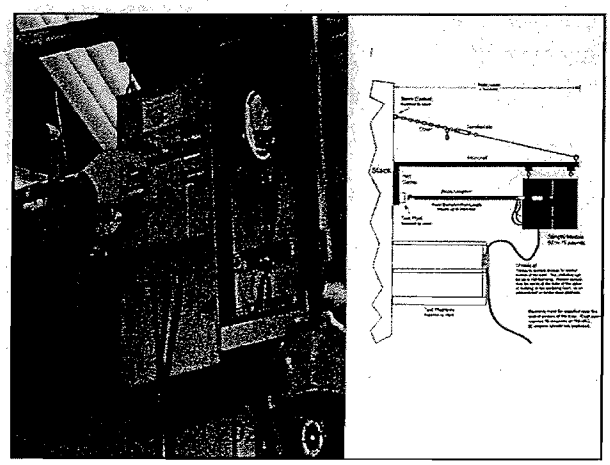


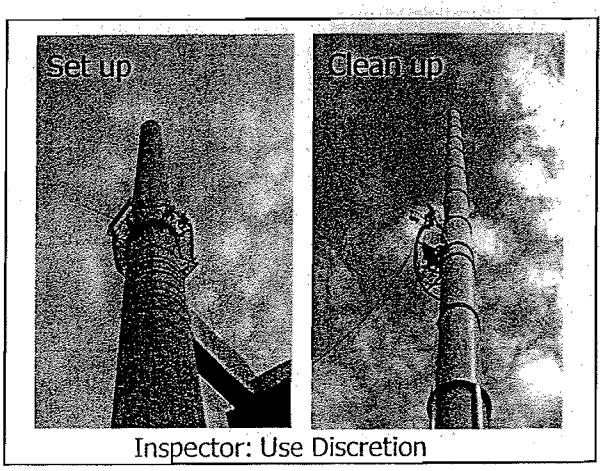


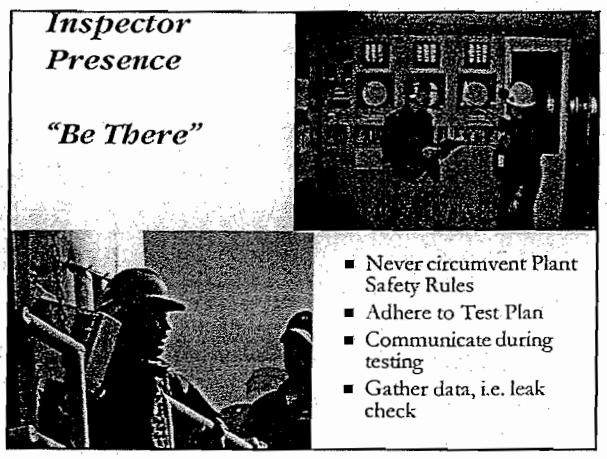


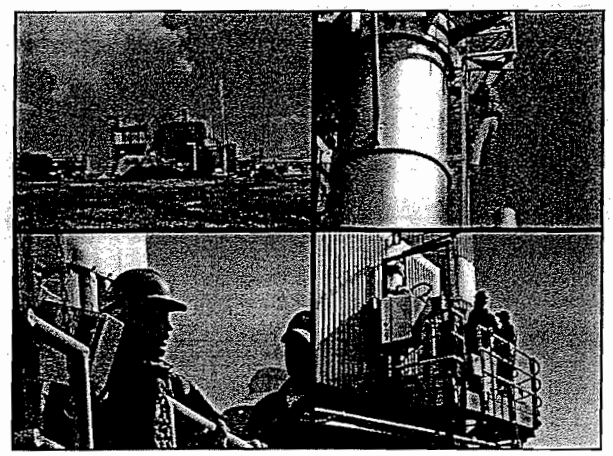


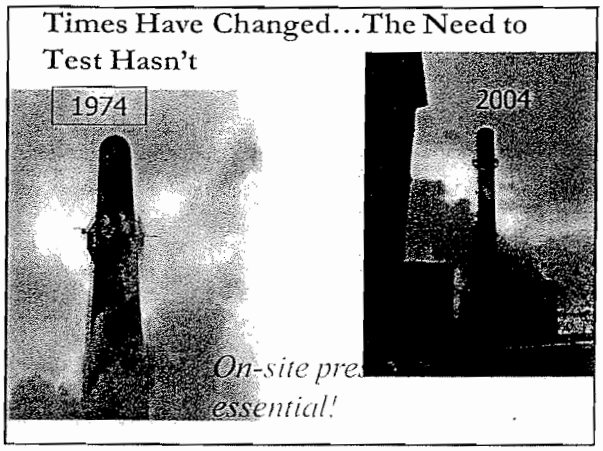

Method 5 PM Test
1974
2004

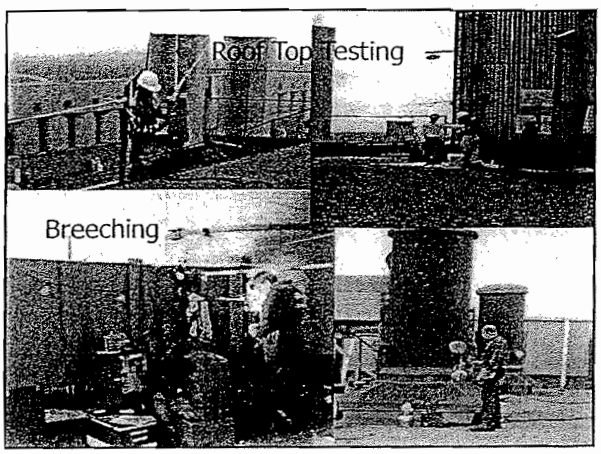


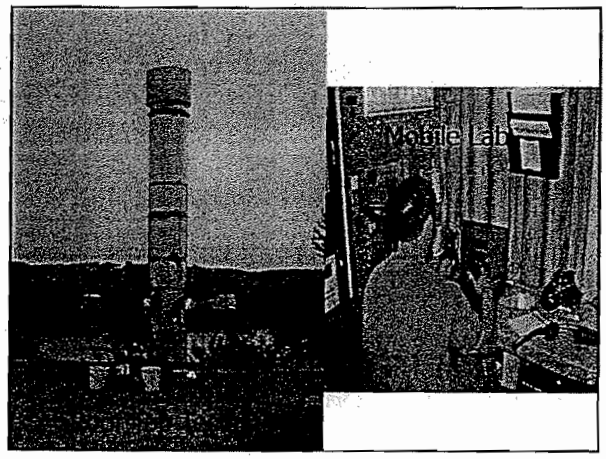

Set up
Clean up
Inspector: Use Discretion

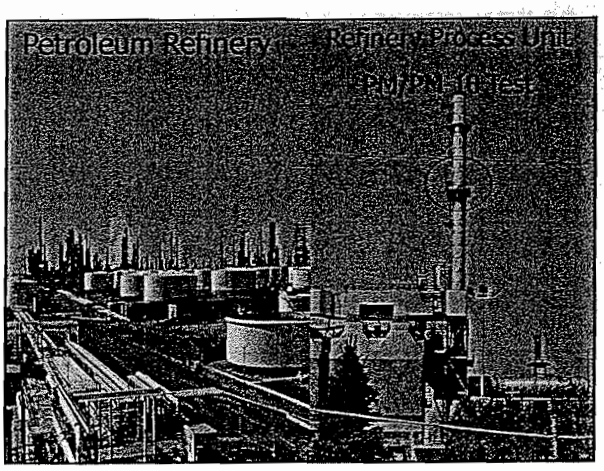

Inspector Presence
"Be There"
Never circumvent Plant Safety Rules
Adhere to Test Plan
Communicate during testing
Gather data, i.e. leak check

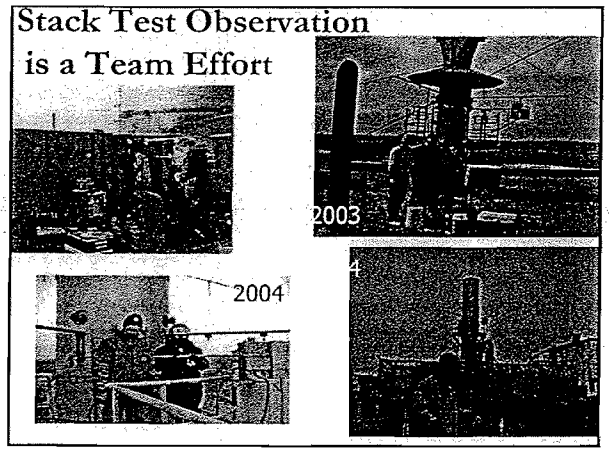


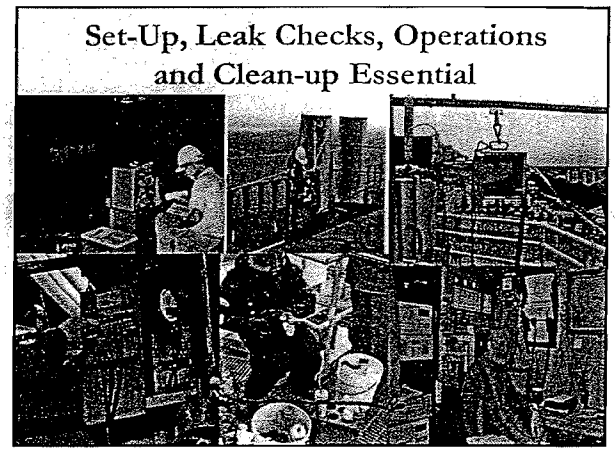

Times Have Changed...The Need to Test Hasn't
1974
2004
On-site pre
essential!

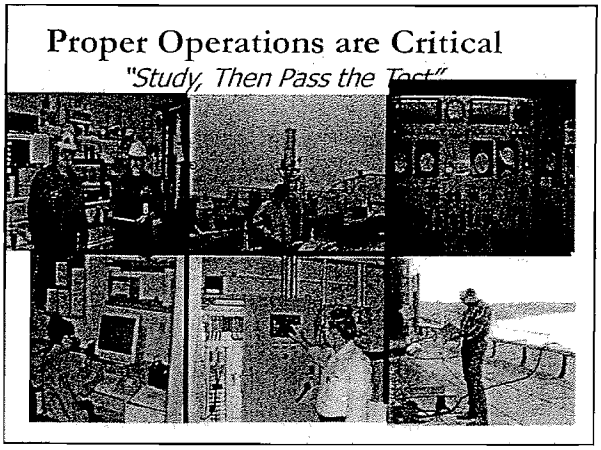

Roof Top Testing
Breeching

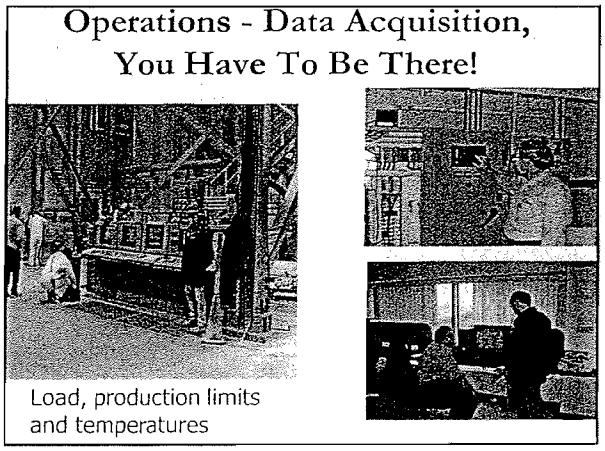

Mobile Lab

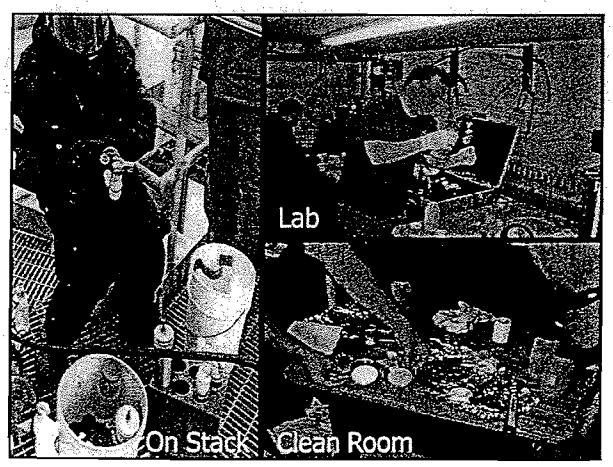

Petroleum Refinery

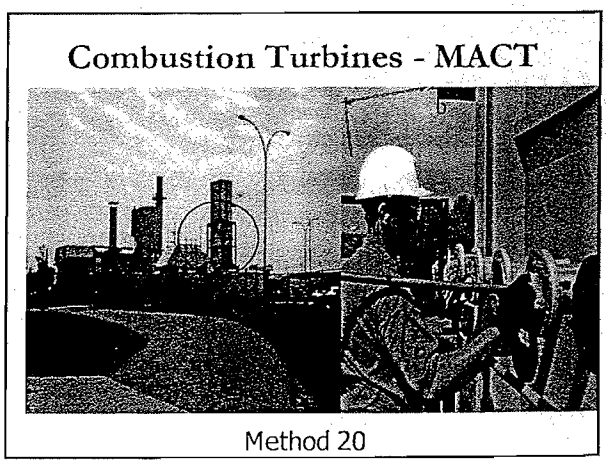

Stack Test Observation
is a Team Effort
2003
2004

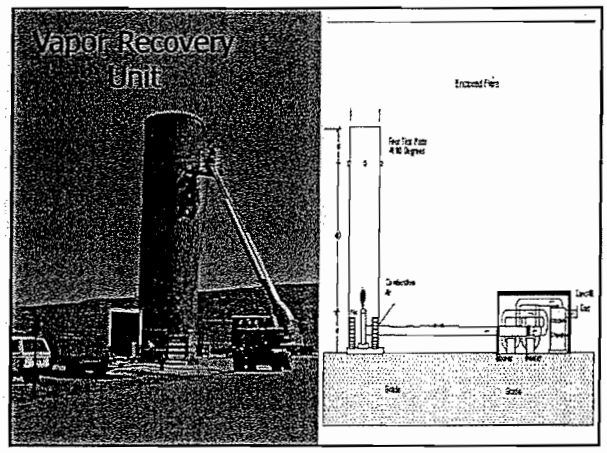

Set-Up, Leak Checks, Operations
and Clean-up Essential

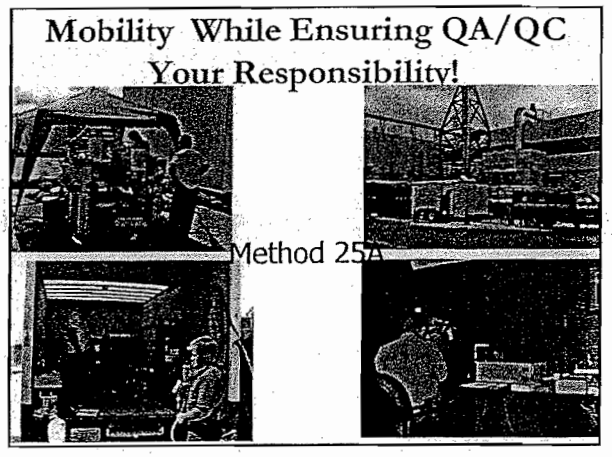

Proper Operations are Critical
"Study, Then Pass the Test"

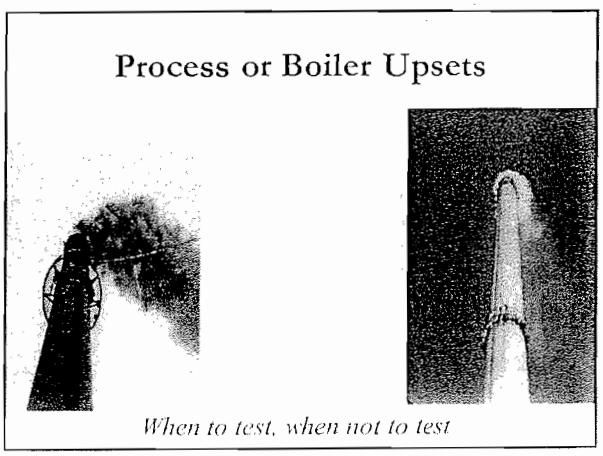

Operations - Data Acquisition,
You Have To Be There!
Load, production limits
and temperatures

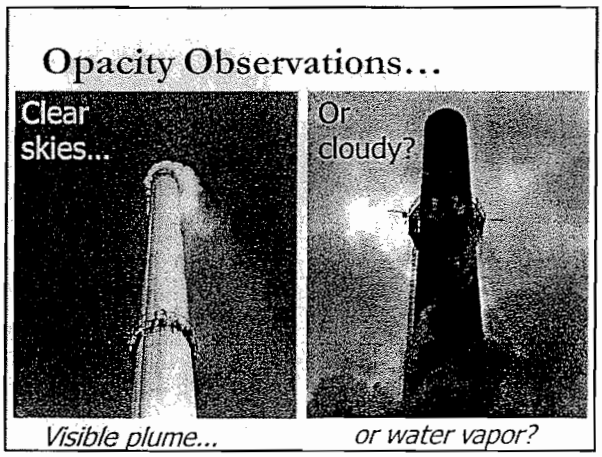

Lab
On Stack
Clean Room

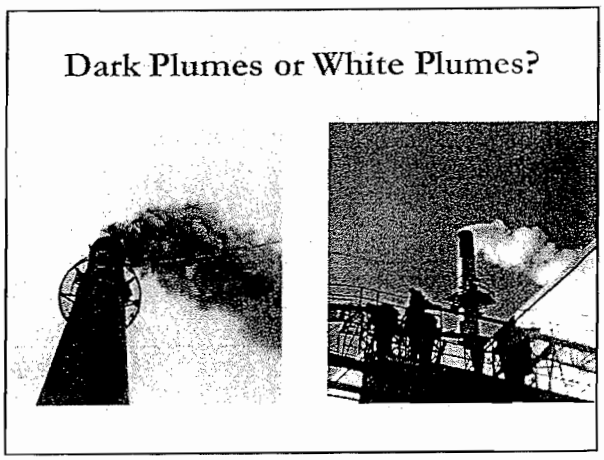

Combustion Turbines - MACT
Method 20

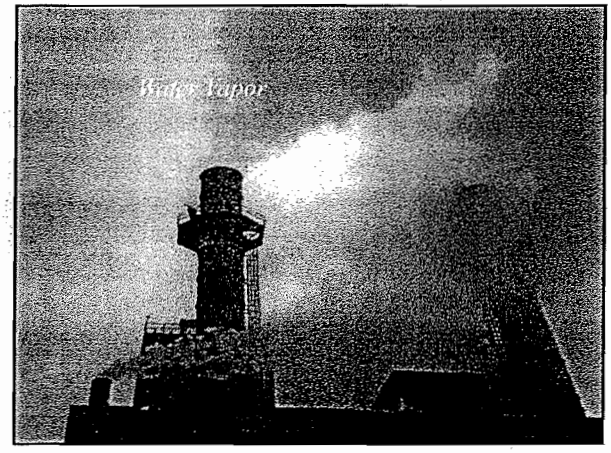

Vapor Recovery Unit


Mobility While Ensuring QA/QC Your Responsibility!
Method 25A


Process or Boiler Upsets
When to test, when not to test


Opacity Observations…
Clear skies...
Or cloudy?
Visible plume...
or water vapor?

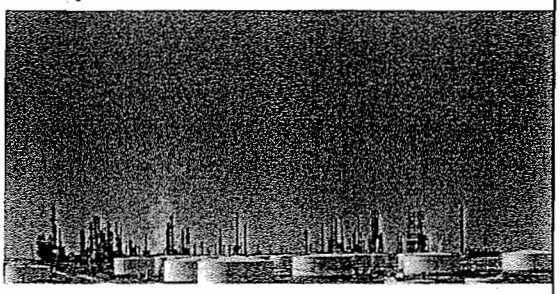

Dark Plumes or White Plumes?



Testing Issues

- Safety first – climbing, weather, platforms
- Port scrapping and stack liners
- Ethanol Plants – VOC Emissions
- Flow Disturbance (i.e. Cyclonic Flow)

Safety...



How do YOU stack up?

A hard hat?

Nomex suit?

Safety glasses?

Safety Shoes?

(OSHA 29 CFR 1910.23)

Distance up equals...

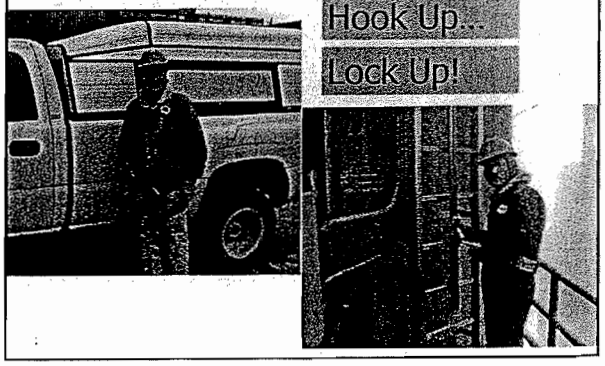
Distance down!

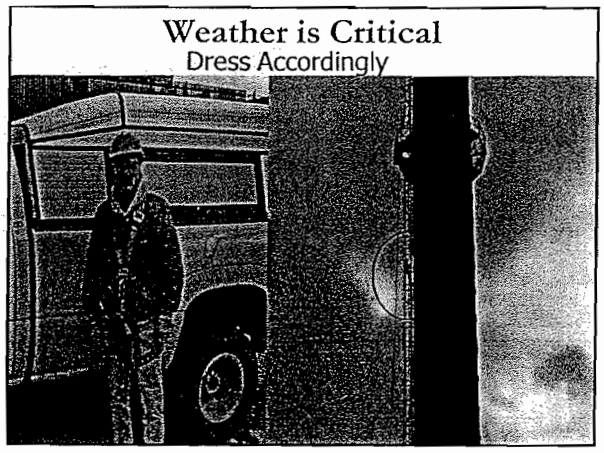
Be Prepared

Buckle Up...

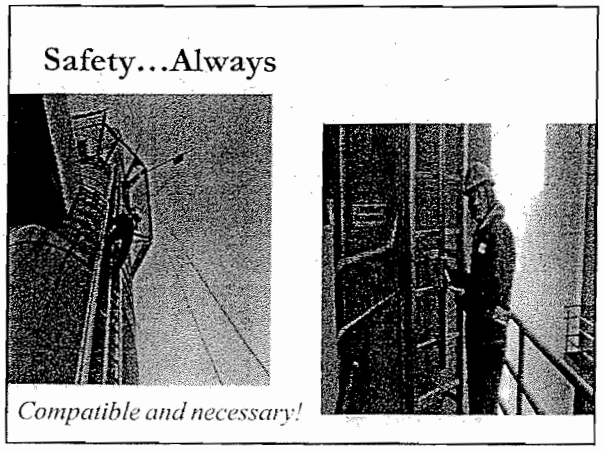
Hook Up...

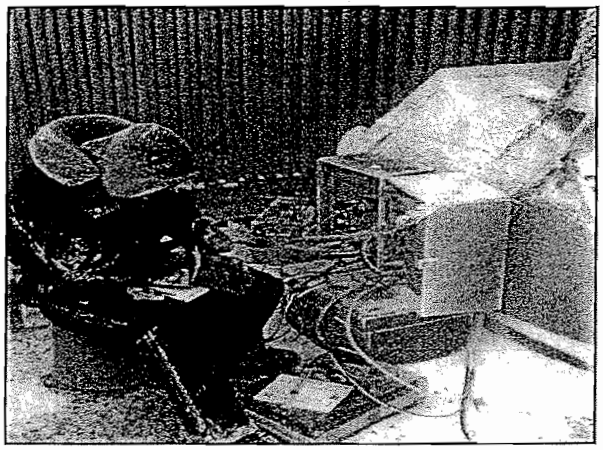
Lock Up!



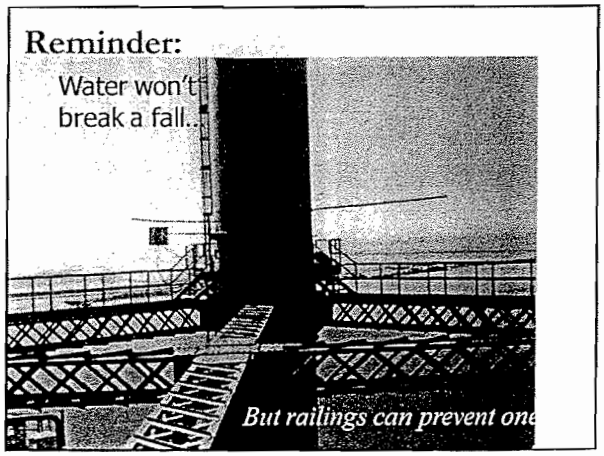

Weather is Critical
Dress Accordingly


Ladder + Cable + Cage
Be safe up there!
(OSHA 29 CFR 1910.23)

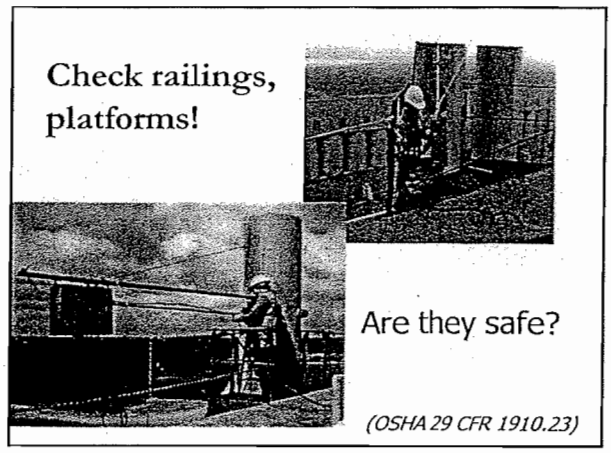

Safety…Always
Compatible and necessary!

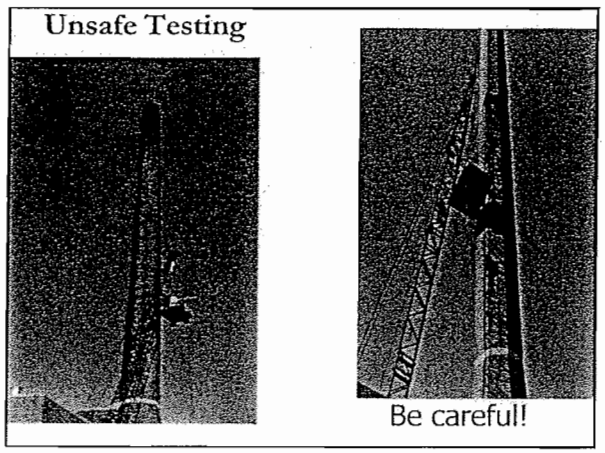


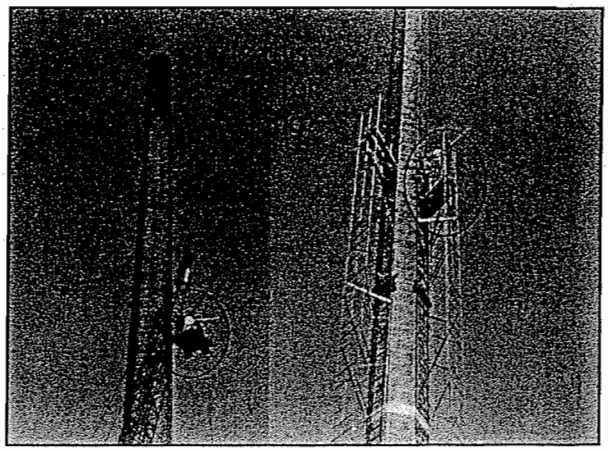

Cold Weather Testing
Dress for it!

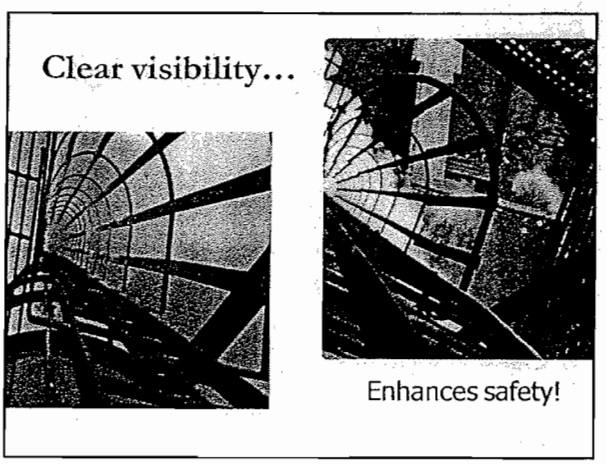

Reminder:
Water won't break a fall..
But railings can prevent one

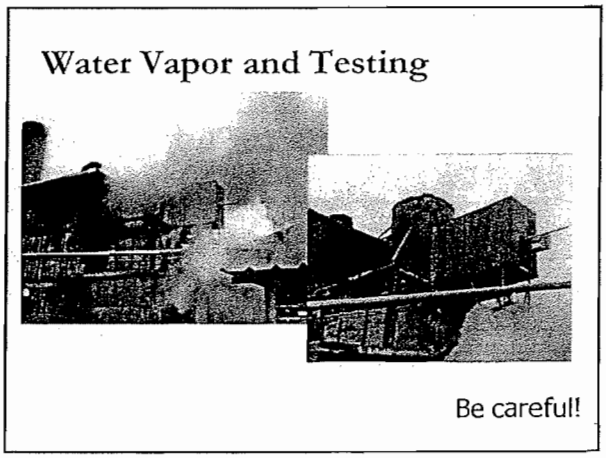

Weather conditions can vary!
Use good judgment during observation!


Check railings, platforms!
Are they safe?
(OSHA 29 CFR 1910.23)

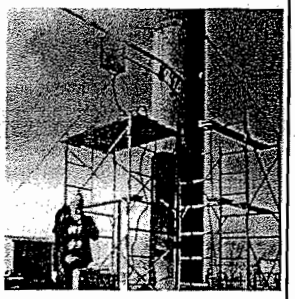

Unsafe Testing
Be careful!




Clear visibility...
Enhances safety!

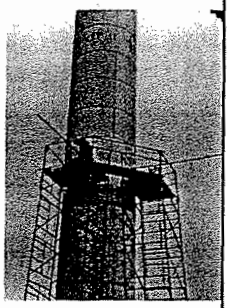

Water Vapor and Testing
Be careful!

Communications are Essential



Make time for *SAFETY!*

Testers use Harnesses!

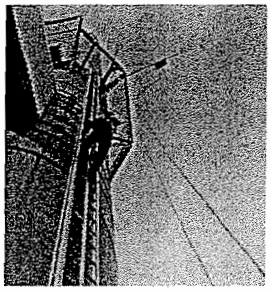


State inspectors should too!

Respirators...

Are helpful!

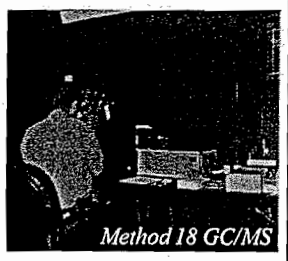
Scaffolding or Ladders



Always Buckle Up!

Ethanol 2000 - Method 18

DDGS Dryer No. 1 with Dan Deepen and Todd Potas overseeing stack testing personnel



Method 18 GC/MS

What To Do?

- The Test Recovery
  - Observe Recovery of Nozzle, Probe and Front Half of Filter Assembly
  - Observe Recovery of Filter
  - Observe Recovery of Impinger Solutions
  - Observe Labeling of Recovery Dishes and Completion of Chain-of-Custody

Phase 3: Recovering, Transporting, Analyzing Sample

- Observe final sample recovery and document (i.e., filter, impingers, silica gel)
- Observe properly marking of samples/containers
- Observe completion of Chain-of-Custody (COC)
- Observe sample analysis (i.e, FRM 3/4/6 etc.) if possible, and audit sample analysis

Phase 4: Observer's Compliance Test Report

- Use standard report format
- Cover all areas of responsibility
- Present information in logical manner
- Make determination of representativeness of the compliance test data
- Include field documentation and observer's checklist

Observer's Report Format

- Cover
  - Plant name and location
  - Source sampled
  - Data sampled
  - Testing firm
  - Control agency
- Certification
  - Certification by observer(s)
  - Certification by author if not observer
  - Certification by key agency personnel

Observer's Report Format

- Introduction
  - Agency name
  - Purpose for observer's report
  - Purpose for test
  - Plant name, location and process type
  - Test dates
  - Pollutants tested
  - Applicable regulations
  - Agency sections and personnel directly involved

Observer's Report Format

- Summary of Representativeness of Data
  - Compliance test protocol
  - Calibration of sampling equipment
  - process/control equipment data
  - Sampling/analytical procedures
  - Compliance test report

Observer's Report Format

- Facility Operation
  - Description of process and control device
  - "Baseline" conditions
  - Observer's facility data (Checklist)
  - Representativeness of process and control device
  - "Baseline" conditions for agency inspector
- Sampling Procedures
  - Acceptability of sample port and point locations
  - Compliance Test Protocol
  - Calibration of sampling equipment
  - Observer's checklist (pre-test, test, recovery)
  - COC review

Observer's Report Format

- Test Report
  - Introduction
  - Summary of results
  - Facility operation
  - Sampling procedures
  - Appendices
- Appendices
  - Copy of pertinent regulations
  - Related correspondence
  - Compliance test protocol
  - Observer's checklist
  - observer's test log
  - Other related material

Emission Test Problems Encountered by Agency Inspectors!

Typical Level of Resource Allocation by State Agencies (i.e., State of Pennsylvania)

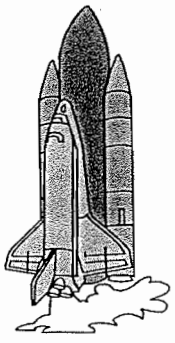
95 % of protocols are Agency reviewed
80 - 90 % of tests are Agency observed
95 % of reports are Agency reviewed

Typical Level of Resource Allocation by State Agencies (i.e., State of Pennsylvania)

Agency Hours Utilized in Effort

- 25 % of hours on Protocols
- 25 % of hours on Observations
- 38 % of hours on Reports

Protocols & Observations



This isn't rocket science!

Protocols & Observations

Protocols

- Goal - To minimize problems in the field
- Identify required sampling train components & procedures.
  - Filters, Nozzles, Purges, etc.
- Ensure method is properly tuned for the source.
  - Detection Limits, Interferences, etc.

Protocols & Observations (cont.)

Observations

- Ensure the methods and protocols are followed.

Frequency of Field Problems

Frequency of Field Problems

Internal Audit

- 1999 - 47% of the test observations resulted in significant corrections by State of Pennsylvania agency observers

Frequency of Problems (cont.)

EPA Inspector General Audit of 1999 tests

- Test Observations - Agency made significant corrections in 57 % of the test programs.
- Test Protocols - Agency found 86 % of the protocols to be deficient.
- Testing Programs - Agency required of the test programs to be repeated for at least one parameter.
- Test Reports - 26 % of the reports required significant correction, clarification or were rejected by Agency.

Frequency of Problems (cont.)

EPA Inspector General Audit of 1999 tests

- Testing Programs - Agency required of the test programs to be repeated for at least one parameter.
- Test Reports - 26 % of the reports required significant correction, clarification or were rejected by Agency.

And they know we're looking!!!

Types of Problems Found

Types of Problems Found

- Pre-site survey errors (?)
- Sample recovery & handling errors.
- Equipment errors
- Procedural errors
- Errors caused by inexperienced and/or frustrated testers.

Types of Problems Found (cont.)

Errors Attributable to the Pre-site Survey

(or lack thereof)

- Unacceptable Sample Locations
  - Port Locations Inadequate
  - Upstream & Downstream Measurements Wrong
  - Stack Diameters Measured Wrong

Types of Problems Found (cont.)

Errors Attributable to the Pre-site Survey

(or lack thereof)

- Equipment & Electrical Needs/Limitations
  Equipment Clearances
  - Port Diameters
  Traversing needs (vertical)

Types of Problems Found (cont.)

Sample Recovery and Handling Errors

- Unacceptable recovery locations
- Improper reagents and equipment
- Inadequate procedures
- Shipping errors

Types of Problems Found (cont.)

Equipment Errors

- Operating ranges/calibration gases
- Poor condition or not calibrated
- Incorrect train components
- Improper methods

Types of Problems Found (cont.)

Procedural Errors

- No cyclonic flow checks
- Failed pre-test leak checks
- Marked wrong traverse points
- Not maintaining isokinetics
- Temperatures not maintained
- Recovery procedures wrong

Types of Problems Found (cont.)

Inexperience or Frustration Errors

- You name it.
- End of Day Syndrome (EDS).

Favorite Follies

Favorite Follies

Method 25

- Everyone complained about the method.
- They claimed it didn't work.
- Couldn't pass the audits.
- Analysis was flawed.
- You name it, we heard it.

Favorite Follies (cont.)

Method 25 Requirements

- 1 hour tank leak checks
- 5 min. train leak checks @ 10 mm.
- 30 min heat-ups
- 10 min. purges
- Dry ice
- probe and filter @ temp.

Favorite Follies (cont.)

Method 25 Errors

- 1 hour tank leak checks not done.
- Could not calculate the allowable leak.
- Tried to quantify leak with a vacuum gauge.
- Attempts to skip the 30 min heat-ups and 10 min. purges
- Try to start before dry ice was on the traps.
- Didn't have dry ice and wanted to use H_2O ice.

Favorite Follies (cont.)

Method 25 Errors

- Attempts to skip the 30 min heat-ups and 10 min. purges
- Try to start before dry ice was on the traps.
- Didn't have dry ice and wanted to use H_2O ice.

Favorite Follies (cont.)

Pitot Problems

- Consultant didn't do the pitot tube leak check.
- The observer requested it be conducted prior to preliminary work.
- Consultant chose to leak check after preliminary work.
- Lost 1 hour on preliminary work, 2 hours finding & fixing the leak.

Favorite Follies (cont.)

Another Pitot Problem

- Asphalt Plant test initially not observed.
- Consultant called and reported cyclonic flow @ 80 degrees.
- We checked prior test report for indication of cyclonic flow.
- Report indicated no sign of cyclonic flow.

Favorite Follies (cont.)

Another Pitot Problem

- Two Agency people went to the site. Consultant claimed to be an ex-regulator.
- Pitot tube was in very poor condition.
- Very poor traverse procedure.
- Agency personnel determined cyclonic flow to be, on average, greater than 20 degrees.

Favorite Follies (cont.)

Paper Board Plant

- Protocol was approved with acceptable sampling locations.
- Three locations tested simultaneously (1 horizontal and 2 vertical)

Favorite Follies (cont.)

Paper Board Plant

- Protocol contained inaccurate information. The sampling locations were not acceptable and extensions were required. Testing delayed 1 week.

- The consultant was not traversing the vertical port location. Run voided. 2 hours wasted.

Favorite Follies (cont.)

Refinery Test

- Not observed
- Consultant believed ammonia was interfering with their NOx analyzer because their analyzer didn't agree with the facilities CEM.
- To fix the problem they placed an ammonia scrubber in-line.

Favorite Follies (cont.)

Refinery Test

- Agency identified the scrubber in the test report.
- Agency suspected that NOx would also be removed. Consultant disagreed.
- Agency conducted a converter efficiency test on their NOx analyzer while switching the same ammonia scrubber in and out.
- NOx was removed & the test was repeated.

Favorite Follies (cont.)

Sewage Treatment Plant Test

- H_2S test during which the consultant elected not to do the optional (but recommended) calibrations between runs.
- Consultant wanted to "save" time.
- Entire day scrapped due to failed post-calibration.

Favorite Follies (cont.)

Gypsum Plant Test

- Sampled while process was not operating.
- Sampling train took a dive!
- Improperly aligned probe and pitot assembly.
- Filter & impinger temps. above method criteria.
- Port locations not consistent with protocol. Tests postponed!

Favorite Follies (cont.)

Gypsum Plant Test

- Filter & impinger temps. above method criteria.
- Port locations not consistent with protocol. Tests postponed!

Favorite Follies (cont.)

General Source Test

- Incorrect impinger solutions for the HCl trains.
- Cascade impactor used instead of cyclone for PM-10 as identified in method
- Stainless steel filter support used when Teflon was required for the metals train.
- Particulate train was traversed incorrectly.

Solutions ???

Solutions ???

Possibilities

- Certification of individual testers and consultant companies (see Source Evaluation Society (SES) recommendations!)
- Facility awareness and communication
- Adequate regulatory oversight

Solutions ???

Certifications

- Would likely not solve the problem alone
- Must have a significant regulatory hammer to accomplish goal
- Would allow companies looking for a consultant to request a minimum level of expertise on their job and in their bid
- You must remember that there are significant dollars wrapped up in the collection of the samples.

Solutions ???

Facility Awareness & Communication

- Facilities could report their experiences to a "system" which could aid in the future selection of a qualified consultant
- Facilities should also pay close attention to delays in testing programs and their causes. Billing of "down-time" can then be easily quantified and confirmed

Solutions ???

Adequate Regulatory Oversight

- What % of errors is acceptable?
- We see about 50% and they know we're coming out to observe.
- At 80 - 90 % of the tests programs observed, only about 5 - 10 % of the test programs have unobserved errors. Some of those are found in the test report reviews

Solutions ???

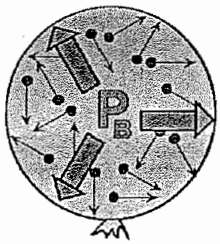
Adequate Regulatory Oversight

Training of facility personnel in stack testing issues may be required!!!

The Truth is "UP" There!

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 =

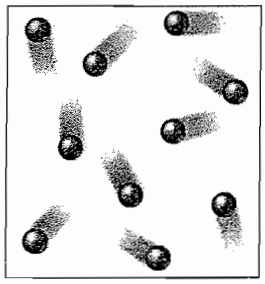
6.023 x 10^{23} molecules
(Avogrados's Number)

1 mole = Avogrado's Number worth of molecules
(6.023×10^{23})

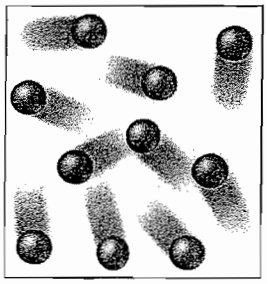
Occupies

22.4 L

At O° C and 1 atmosphere



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

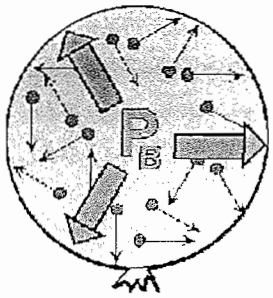


1 mol xenon at STP
Volume = 22.4 L
Mass = 131.3 g

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

Absolute Pressure

Absolute Temperature

$$PV = nRT$$

Volume

moles

Ideal Gas Law constant

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

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

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

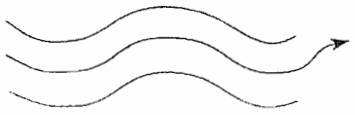
Dividing top by bottom gives

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

Properties of Moving Gases

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

Velocity



V_s = ft/sec or ft/hr

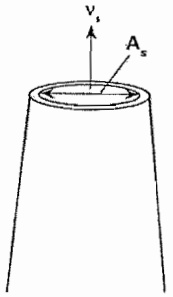
Velocity, v_s $\frac{ft}{sec}$ $\frac{ft}{hr}$

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

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

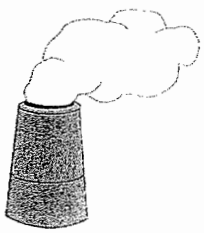
$$\%I_{final} = \frac{100\, T_{s(avg)} \left[K_3 V_{lc} + \left(\frac{V_{m(avg)}}{T_{m(avg)}} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60\, \theta\, V_{s(avg)} P_s A_n}$$

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

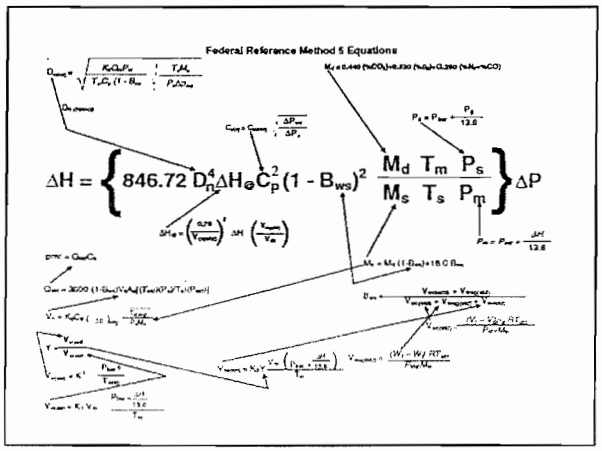
$$pmr_S = c_S Q_S$$

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

Emission Rate (Combustion Sources)

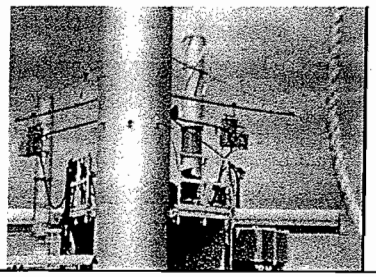
$$E = \frac{pmr_s}{Q_H}\left(\frac{lbs}{10^6\ \cancel{Btu}_{Q_H}}\right)$$

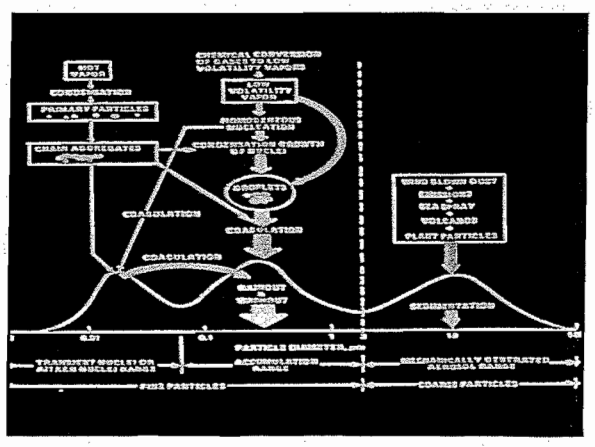
Where: Q_H = heat input rate in units of Btu/hr

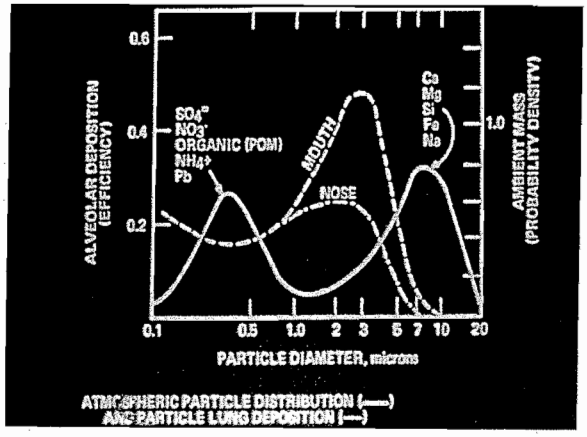


Compliance Test and Source Test Observation

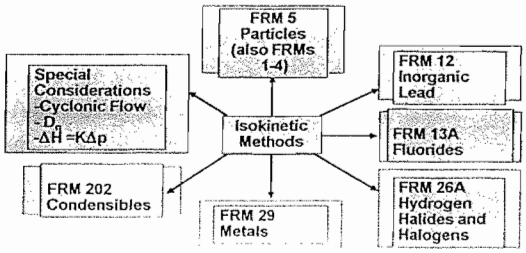
Stack Test Basics

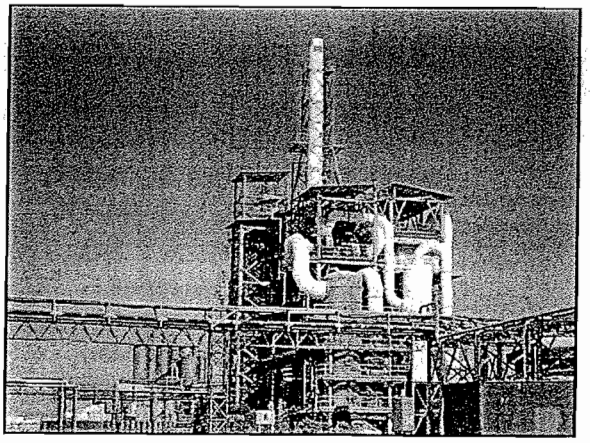






Isokinetic Sampling Methods

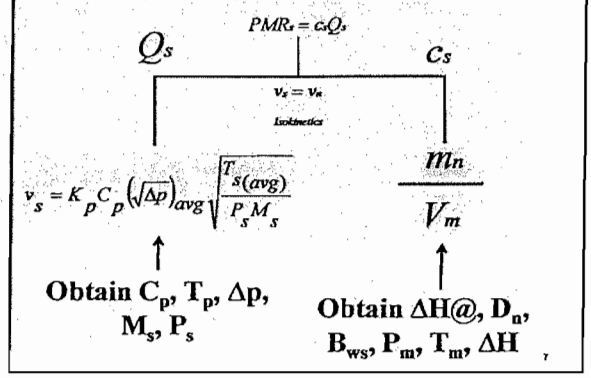




Basic Definitions

- 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



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

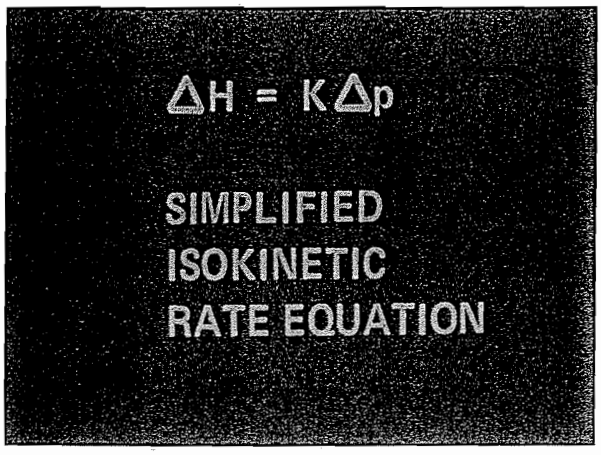
- Filterable (In-Stack) Particulate Matter PM-10 (FPM-I-PM10): Particulate matter with an aerodynamic diameter of < 10 micrometers as measured by FRM 201 or 201A
- Condensable Particulate Matter (CPM): Particulate matter captured in the back half of the FRM 5 sampling train, including water and organic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

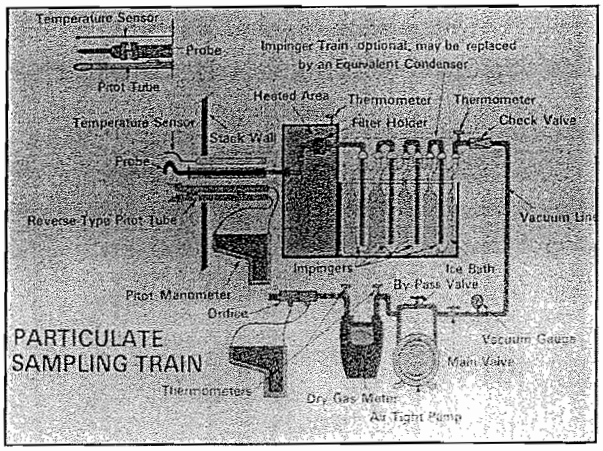
Definition of Extractable Particulate Matter

- 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

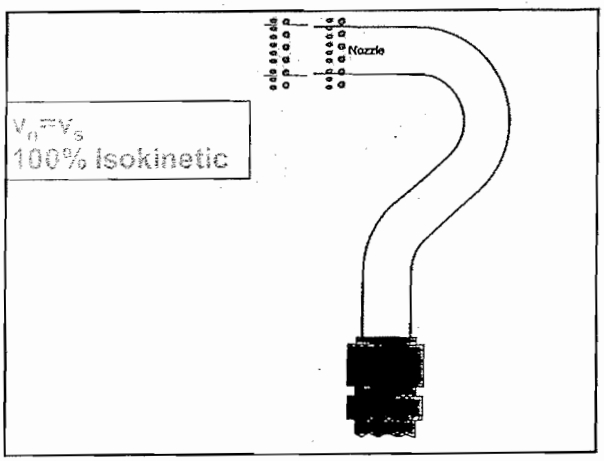
- Isokinetic Source Sampling
- "Iso" as denoting equality, similarity, uniformity. "Kinetic" is defined as of, pertaining to, or due to motion
  - $\Delta H = K \Delta p$



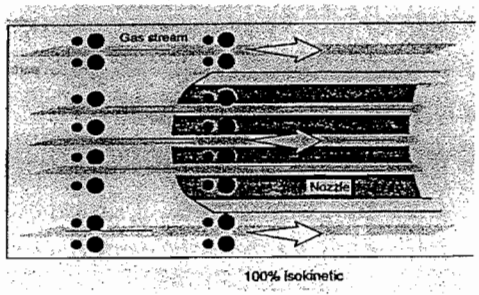


Isokinetic Sampling and Bias

- 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)

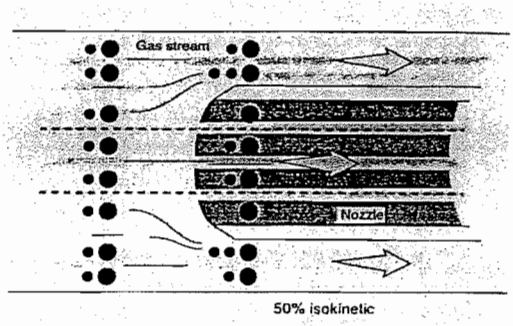


100 % Isokinetic



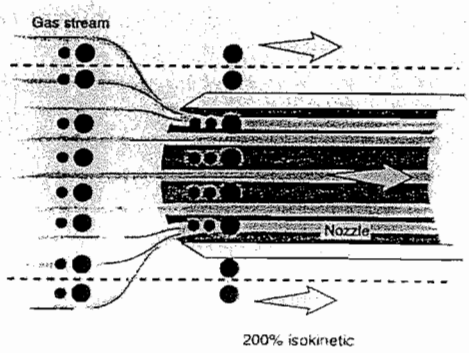
Vs=Vn

Sub-Isokinetic (50%)



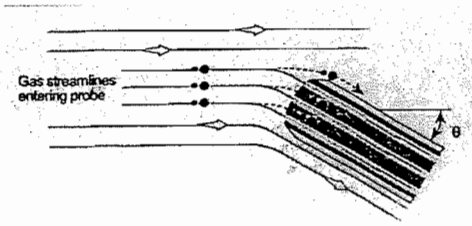
Vn=1/2Vs

Over-Isokinetic (200%)

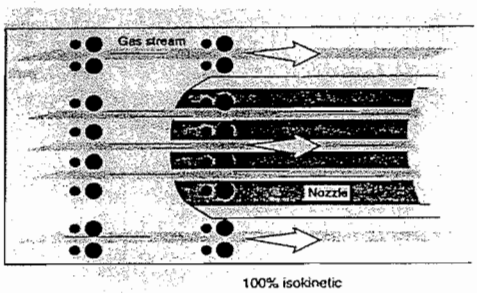


Vn=2Vs

Nozzle Misalignment



ΔH =KΔp



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

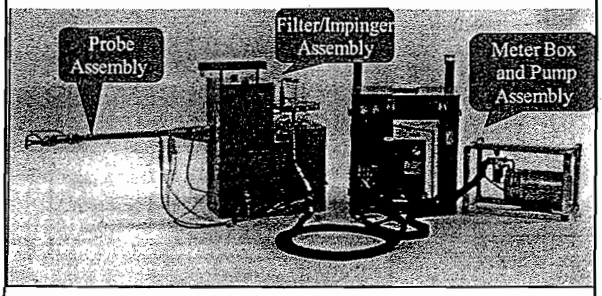
History of FRM 5

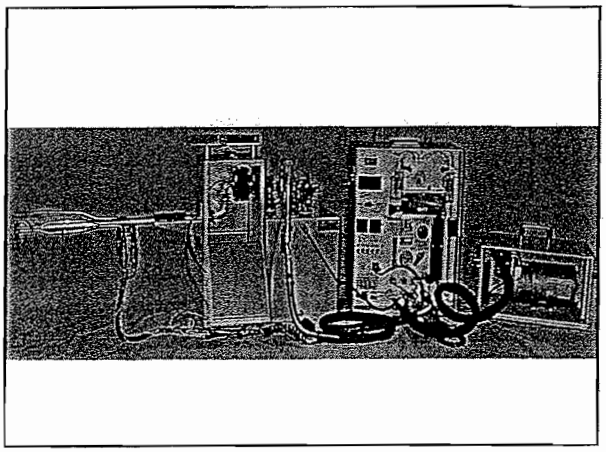
- 1985 FRM 5E: PM @ 248 F from Mineral Wool Plus Captured Condensible in 0.1 N NaOH (TOC)
  - Total Carbon @ 1740 F
  - Inorganic Carbon @ 300 F
  - $C_t = C_s + C_c$
- 1986 FRM 5F: Non-sulfuric acid PM @ 320 F with water rinse and ammonium sulfate substraction

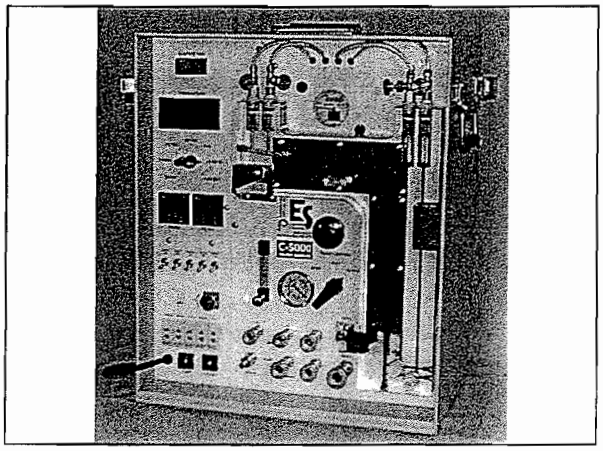
History of FRM 5

- 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







Errors in pmr Calculations Using FRM 5

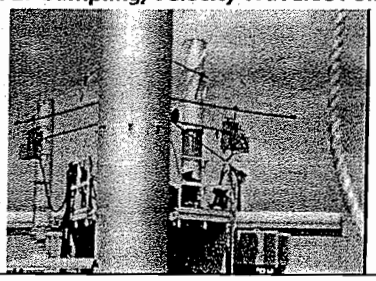
- T_s: 1.4 %
- DGM: 1.0 %
- P_s: 0.4 %
- P_m: 0.4 %
- P_b: 0.2 %
- B_{ws}: 1.0 % Affects % Iso
- Δ H: 5.0 %
- D_n: 1.0 %
- Delta $H_{@}$: 1.5 %

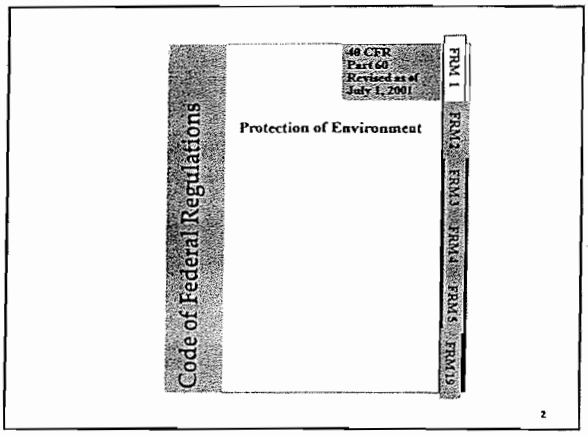
Federal Reference Methods (FRMs) 1 through 4

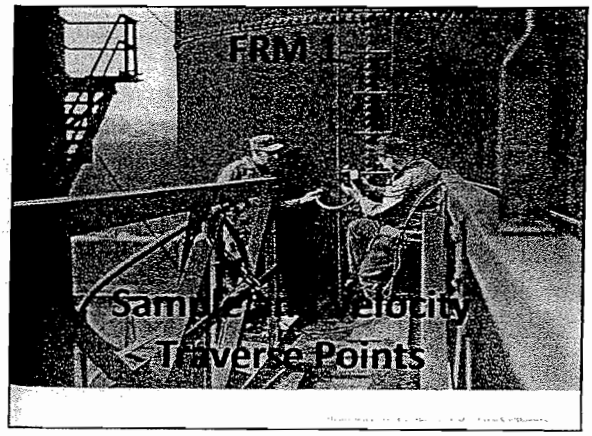
- Used in other reference methods
- Used to determine
  - Number of sampling points (FRM 1)
  - Stack gas velocity (FRM 2)
  - Stack gas molecular weight (FRM 3)
  - Stack gas moisture content (FRM 4)
  - Stack gas particulate matter (FRM 5)
- All have available checklist

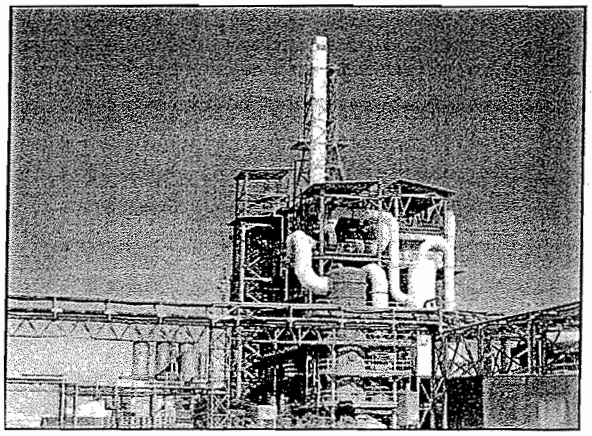
Compliance Test and Source Test Observation

FRM 1: Sampling/Velocity Traverse Points









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

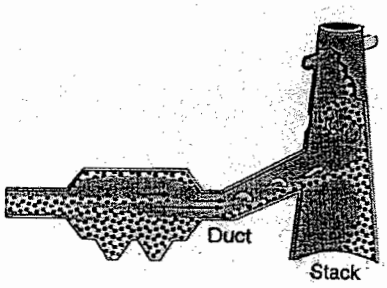
FRM 1

- 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

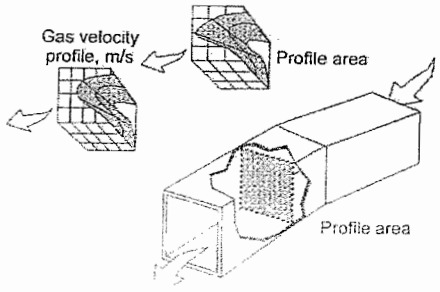
FRM 1 Basic Principle

- "...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

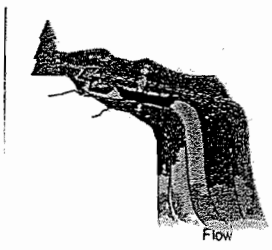


Particle mass concentration profile, mg/m³



Source: Adapted from Sunne, 1977

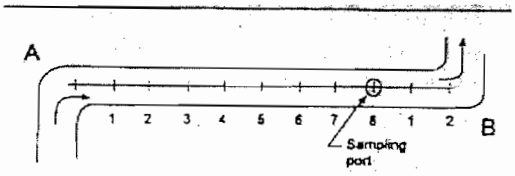
FRM 1 Siting Criteria



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



Port is downstream of A
Port is upstream of B

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

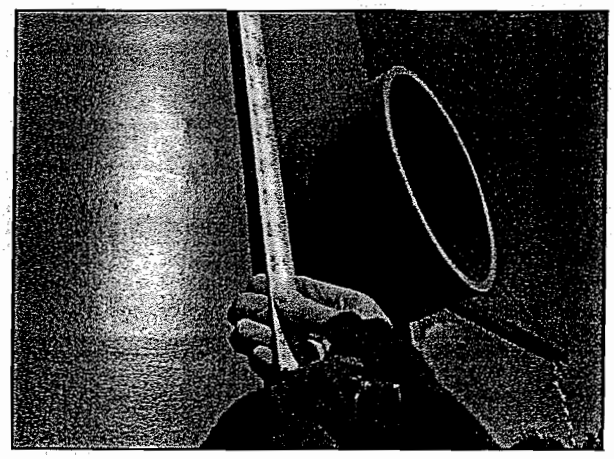
- Bend in duct
- Expansion or contraction in the duct
- Visible flame

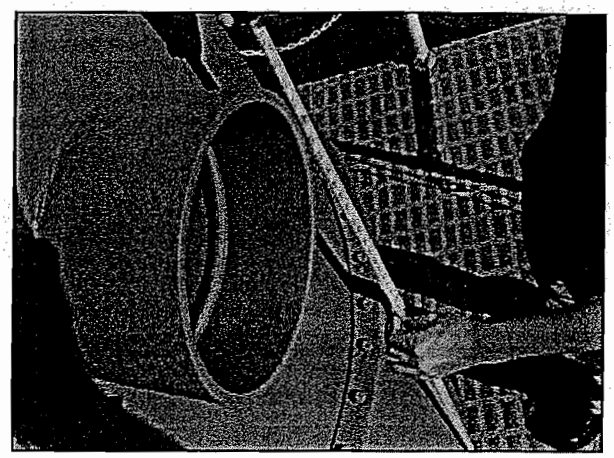
Stack Extensions Required

- 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

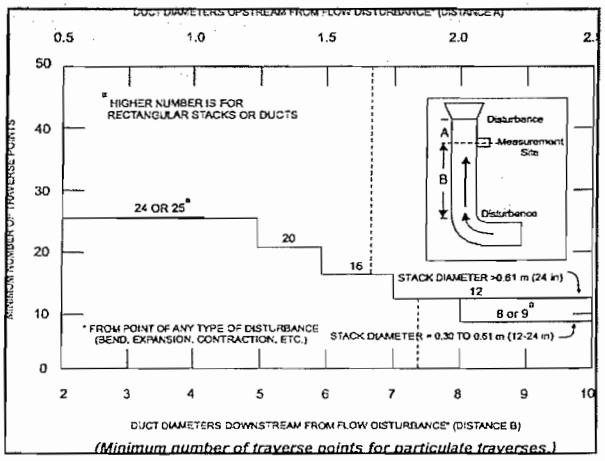
- At 8 duct diameters downstream and 2 duct diameters upstream of a flow disturbance, the siting criteria states
  - Velocity head profile is assumed to resemble laminar flow

FRM 1 Siting Criteria

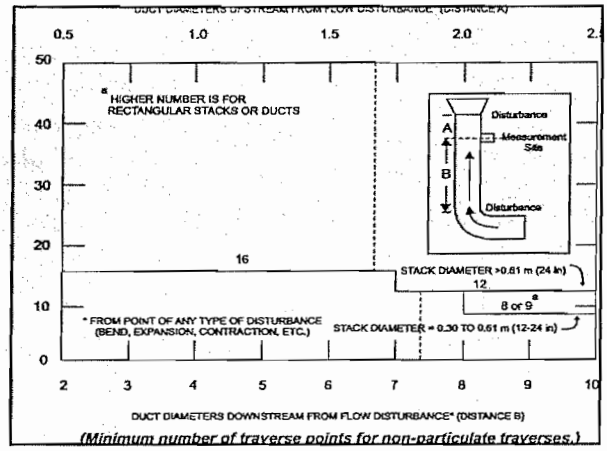
- The minimum number of sampling points can be used
  - 8 or 9 for 12-24 in. stacks
  - 12 for > 24 in. stacks

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."

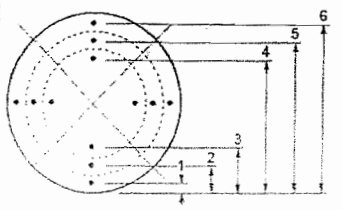
Table 1 - 2 Location of Traverse Points in Circular Stacks
(Percent of stack diameter from inside wall to traverse point)

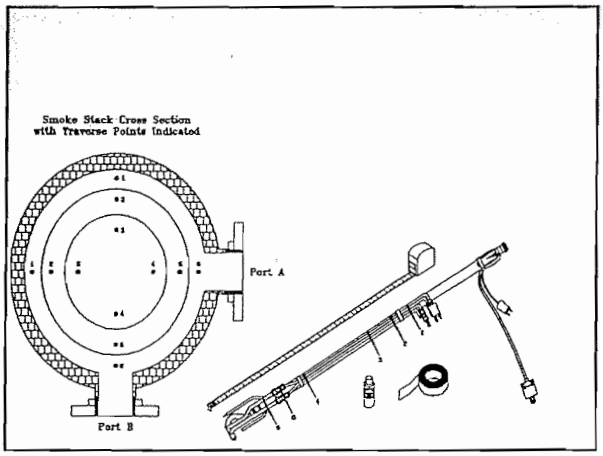
Traverse point on a diameter	Number of traverse points on a diameter											
	2	4	5	6	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.6	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	5.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	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	11.5	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	30.5	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	79.0	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	79.5	73.8	67.7
15								95.1	88.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									96.5	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.2	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.8	94.5
23												96.6
24												98.9

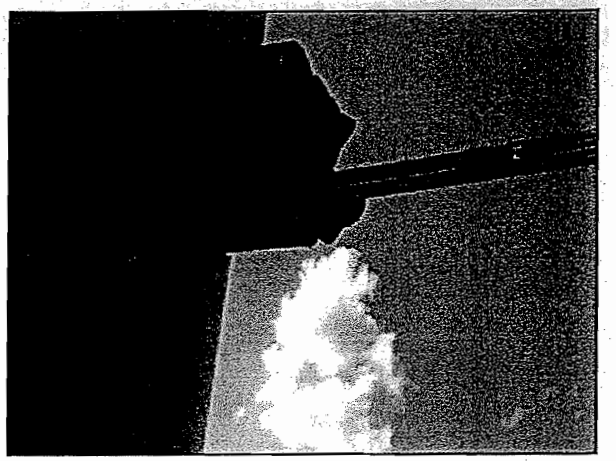
Pt. 60, App. Meth. 1

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

40 CFR Ch. 1 (7-1-89 Edition)

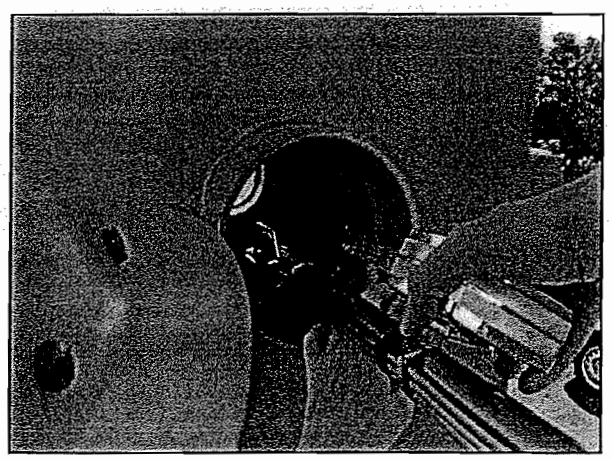






FRM 1 Location of Traverse Points

- 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

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

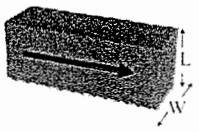
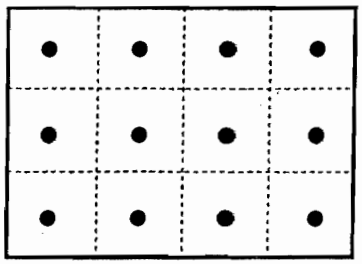


Table 1-1 Cross-Section Layout for Rectangular Stacks

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.)

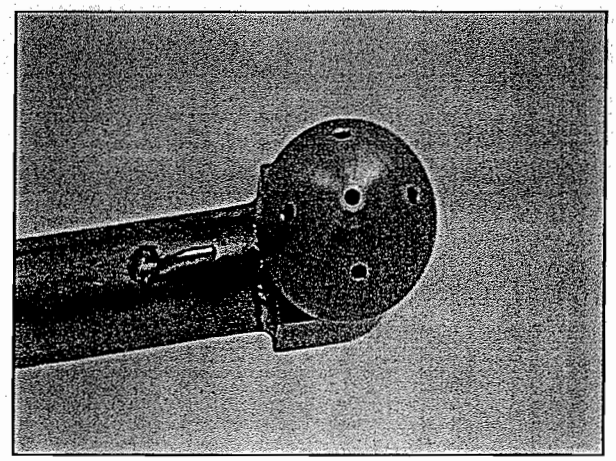
- Equipment
  - Manometer
  - Type S pitot tube/level indicator
- Procedure
  - "Null" reading; O.K.
  - Determine delta p if not "null"
  - Acceptance avg. $\Delta p < 20$ degrees

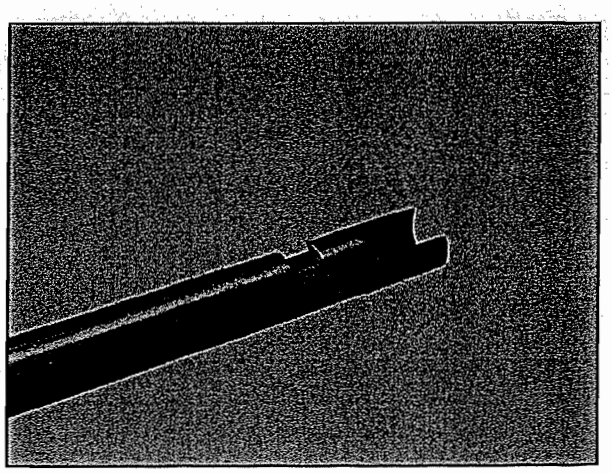
FRM 1 Alternative Measurement Site Selection Procedure

- 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

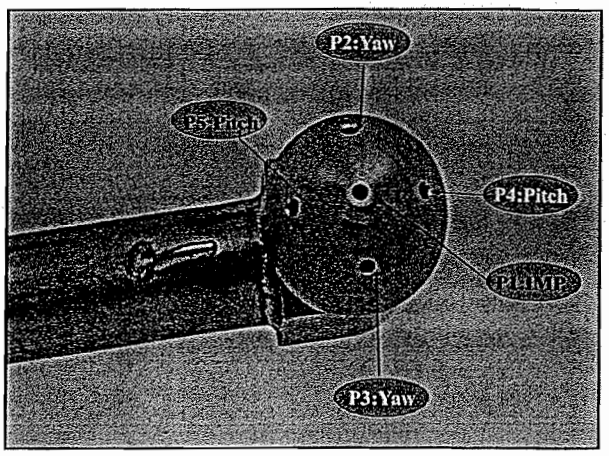
- 3D Probes
  - Spherical
    - Easy Leak Check
    - More Sensitive
    - Less Costly
  - Prism (DAT)





3-D Probe Measurements

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



3-D Probe Measurement

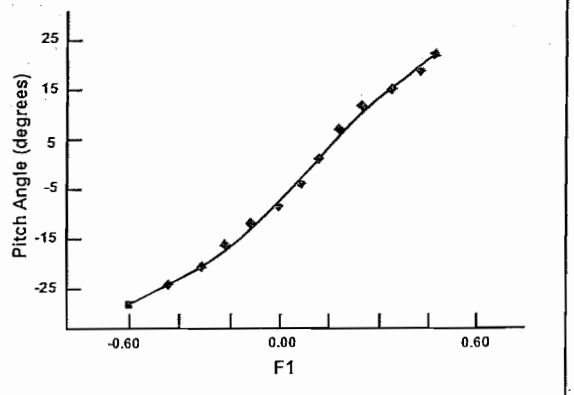
- Position probe at traverse point and verify position of "scribe line."
- Pre leak check
- Record yaw and pitch angles at each traverse point
- Calculate resultant angle
- Post leak check

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)



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

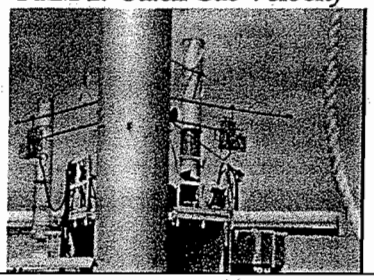
- Add first and last traverse points together to get internal stack diameter and compare to calculated value
- Don't forget to add nipple diameter to calculated traverse points
- "White-out" is an excellent tool for marking probe

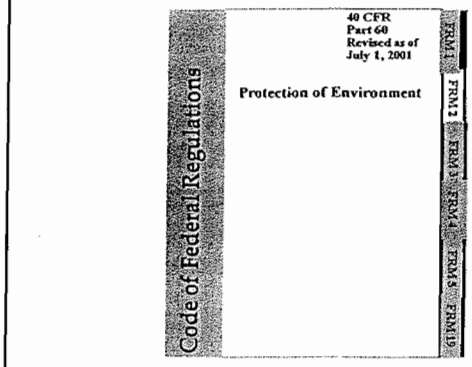
Dismiss Stack Test FRM 1

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

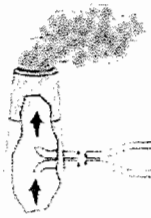
Compliance Test and Source Test Observation

FRM 2: Stack Gas Velocity





FRM 2 Method



Method 2

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

Pollutant Mass Rate

$$PMR_s = c_s Q_s$$

Q_s — c_s

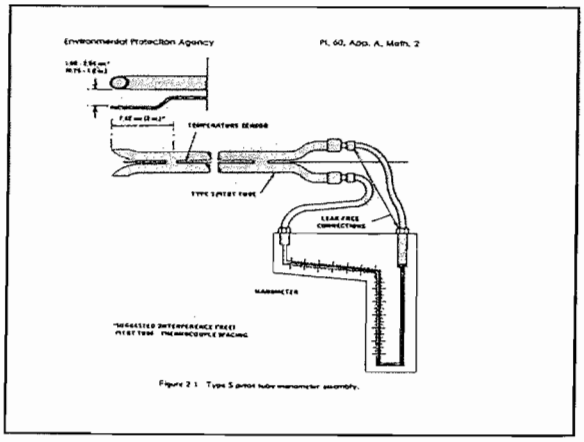
$v_s = v_n$

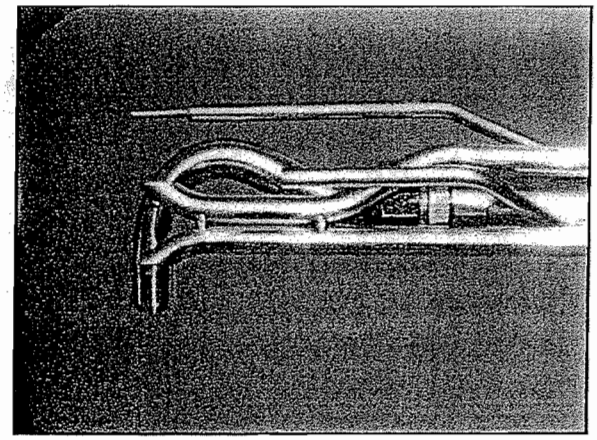
Isokinetics

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

Obtain C_p, T_p, Δp, M_s, P_s

Obtain $\Delta H@$, D_n, B_{ws}, P_m, T_m, ΔH





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

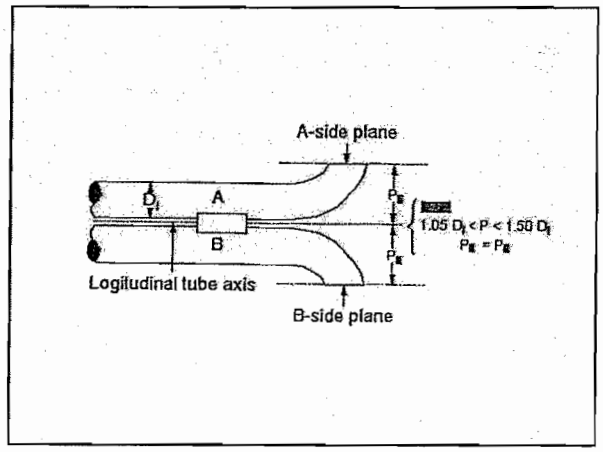
Interference-Free Component Arrangement

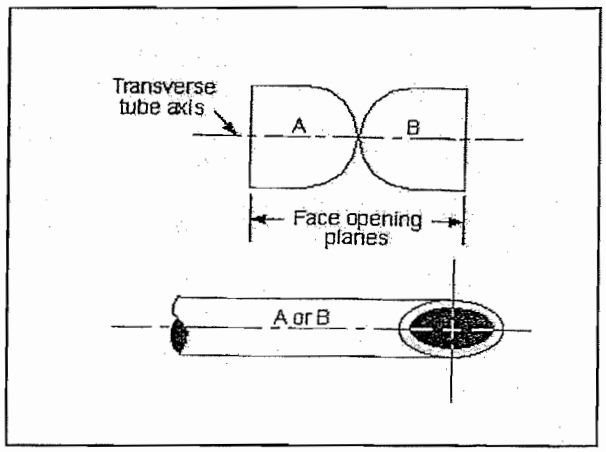
- Pitot tube distance to nozzle: >3/4 inches for ½ nozzles
- Center of nozzle and pitot tube opening aligned
- Thermocouple location to pitot tube > ¾ inch for 3 inches
- Back-recess thermo. > 2 inches
- Gas sampling assembly > 3 inches from pitot tube

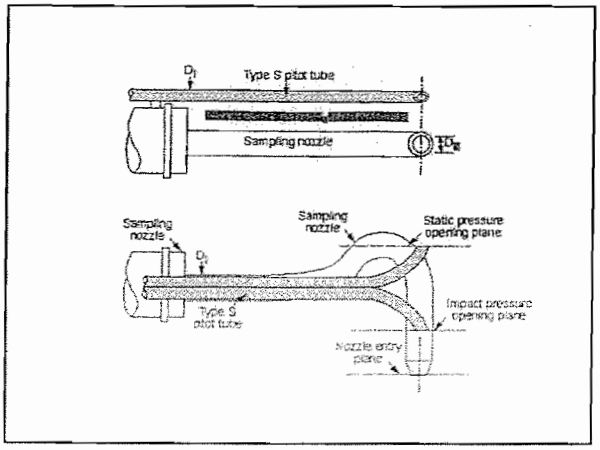
Type S Pitot Tube

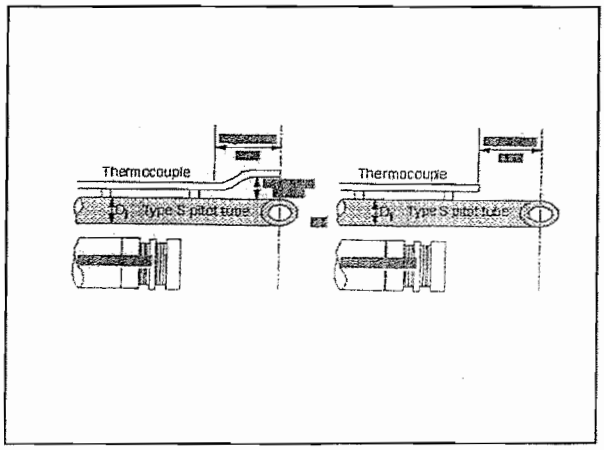
Design criteria for assigning

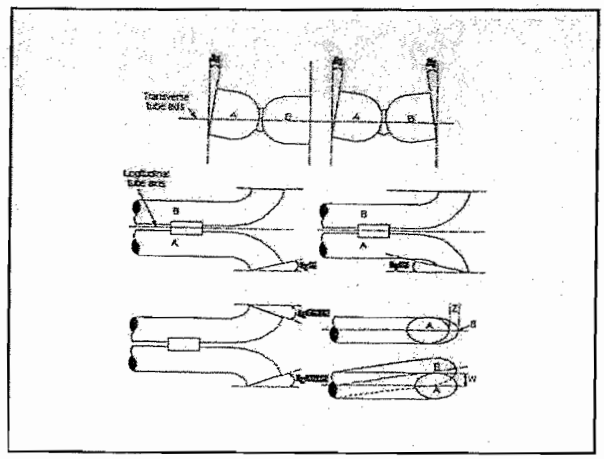
$C_p = 0.84$





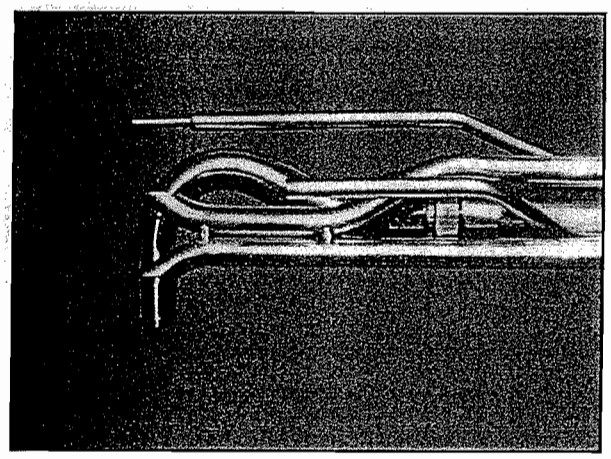


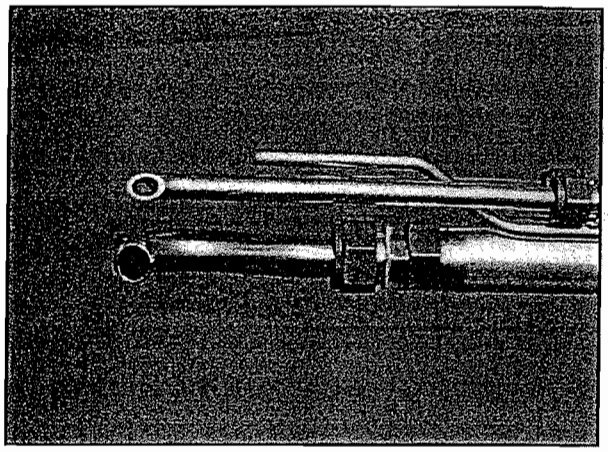


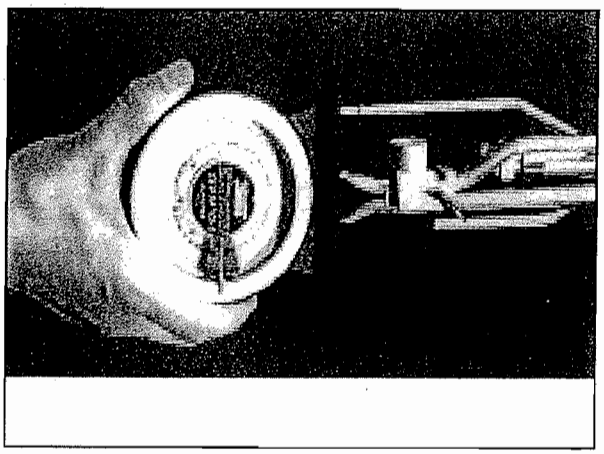


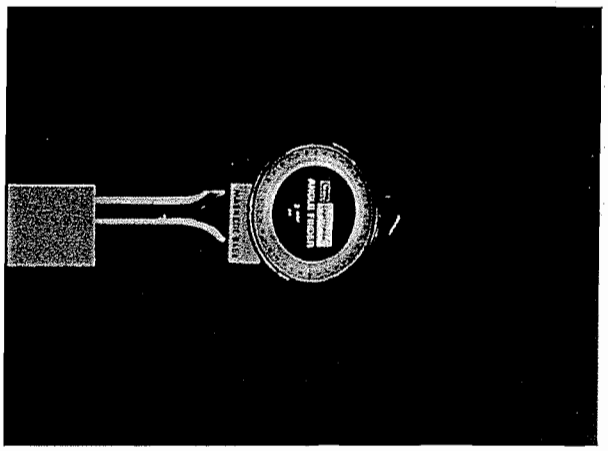
Verification of Geometry of Type S Pitot Tube To Assign 0.84

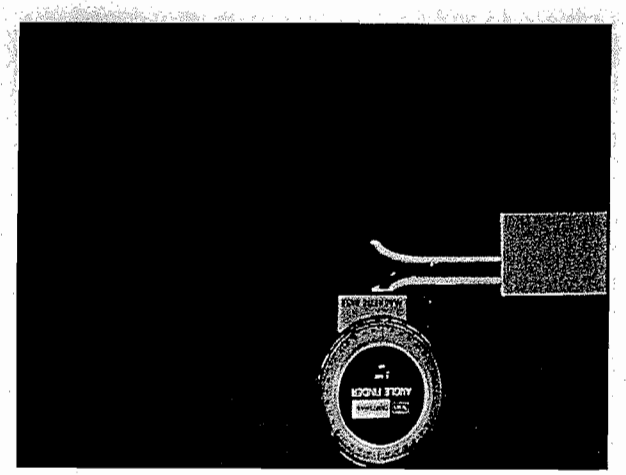
- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375

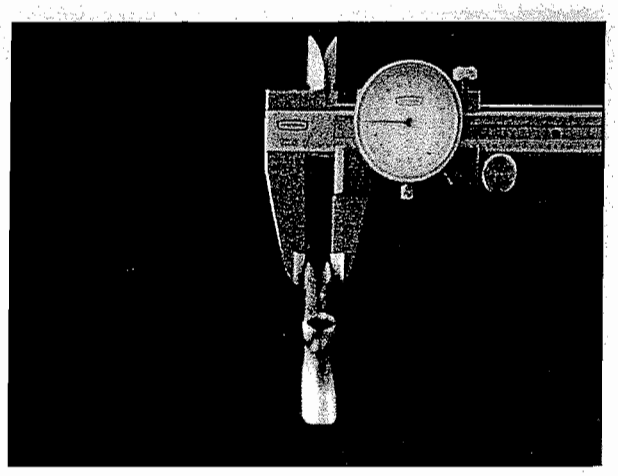


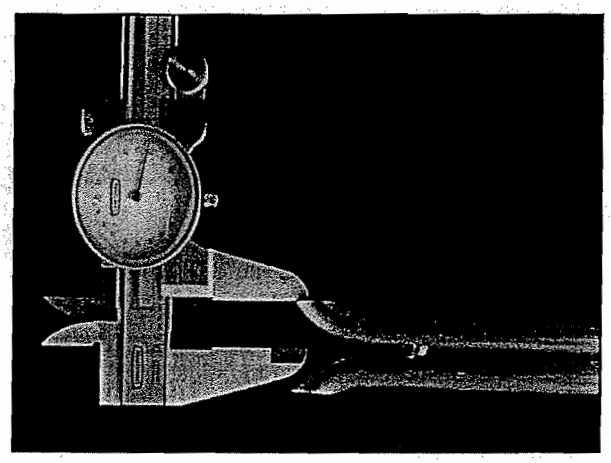




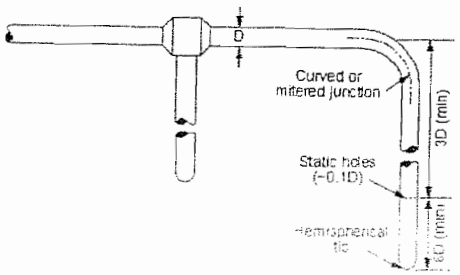


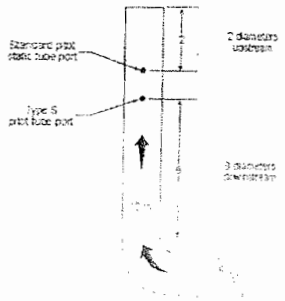






Type S Pitot Tube
Calibrate Using a
Standard Pitot Tube
and
Wind Tunnel

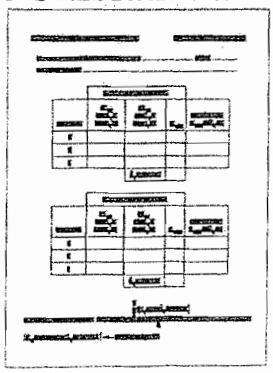




Pitot Tube Calibration Equation

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

Pitot Tube Calibration Data Sheet



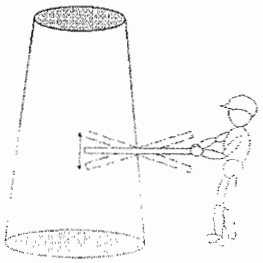
Velocity Measurement Procedures

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.

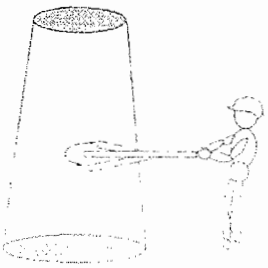
Velocity *(cont.)*

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.

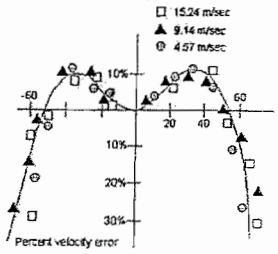
Pitch Angle



Yaw Angle



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



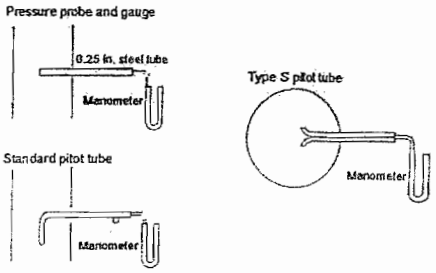
Federal Reference Method 2 Average Velocity Over Cross-Section

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

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

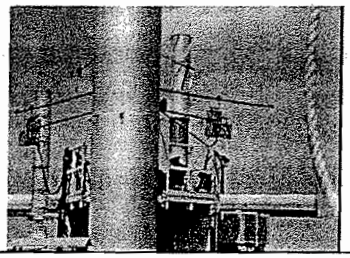
- Method 2F: calculates axial velocity (3-D Probes)
- Method 2G: calculates "near-axial" velocity (Type S or 3-D probes)
- Method 2H: Wall effects (Type S or 3-D probes or default wall effects adjustment factor)

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

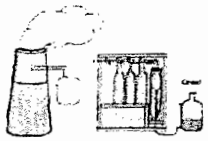
FRM 3: Gas Analysis Molecular Weight

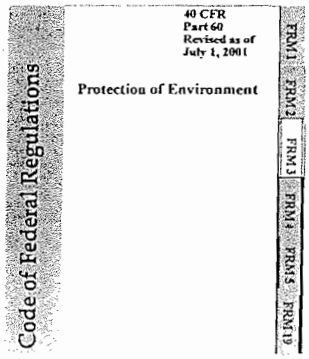


FRM 3

Method 3

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





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)

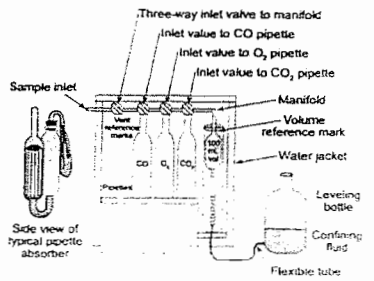
Federal Reference Method 3 History

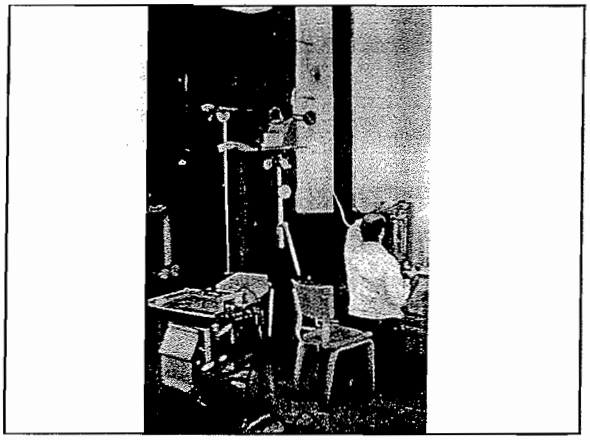
- 1970 FRM 3 Promulgated
- 1986 FRM 3A Instrumental
- 1990 FRM 3B Orsat for Correction Factor and Excess Air (F_o-Factor)
- 1996 FRM 3C Landfill Gas

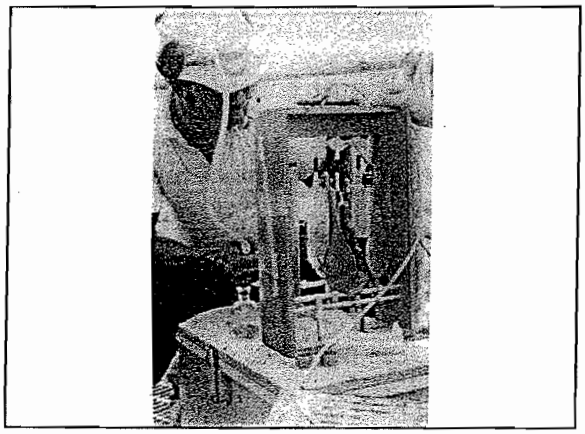
Federal Reference Method 3

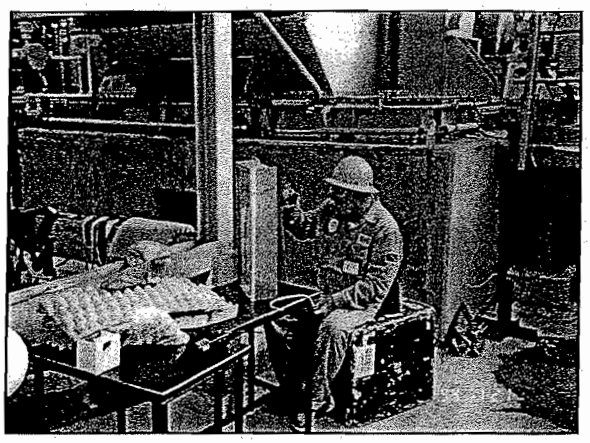
- Gas analysis: measuring percent of O_2 and percent of CO_2 to determine the dry molecular weight of the flue gas (using Orsat Apparatus)

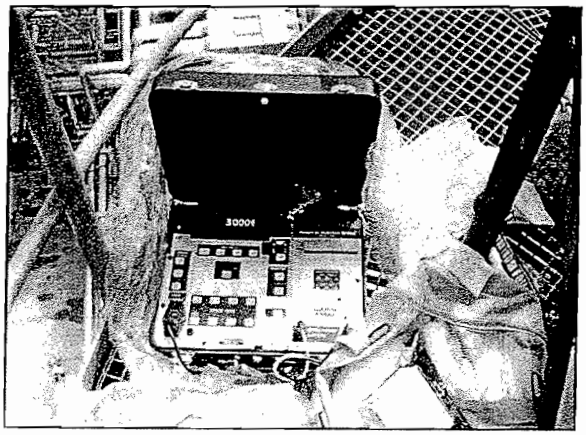
Orsat Analyser











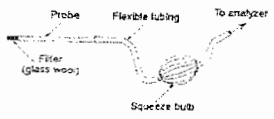
FRM 3 Sampling Techniques

- 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

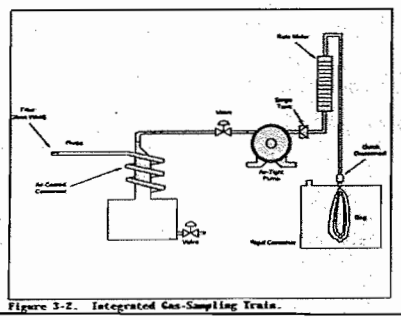


Figure 3-2. Integrated Gas-Sampling Train.

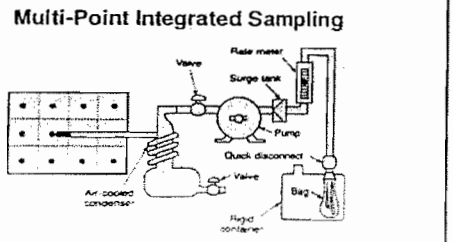
Single-Point Integrated Sampling

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



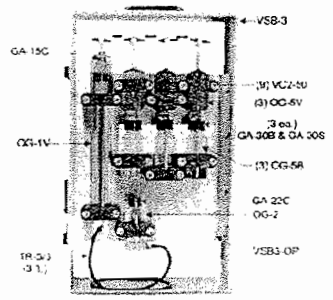
Multi-point Integrated Sampling

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.

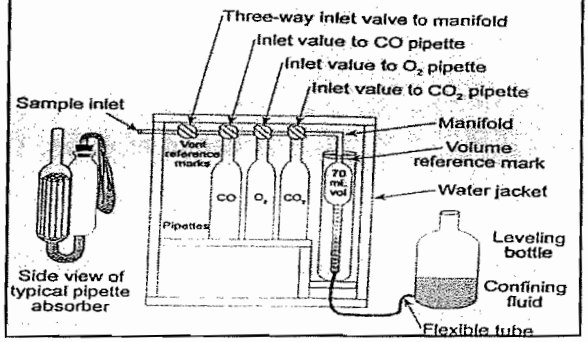
Multi-Point Continuous Integrated Sampling

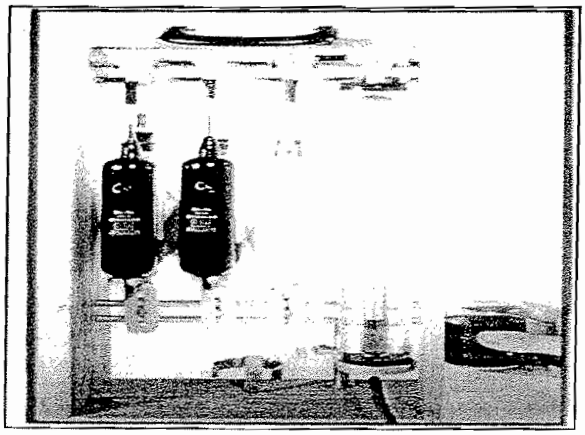
- Particulate sample and variations
- Modified Method 5 sampling
- VOST sampling
- For concentrations given to specific conditions (i.e., 12 % CO_2, 6 % O_2)
- For emission rate calculations (F-factor)
- For molecular weight determination

Orsat Analyzer



Orsat Analyzer





Orsat Analyzer Reagents

Reagent: Gas Confining Solution
A solution containing sodium sulfate, sulfuric acid and methyl orange

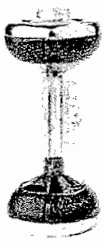
Reagent: Carbon Dioxide Absorbent
A solution of potassium or sodium hydroxide

Orsat Analyzer Reagents

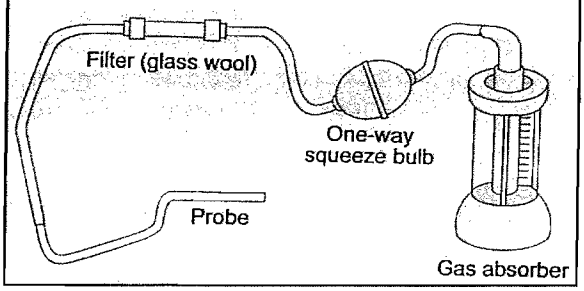
Reagent: Oxygen Absorbent
A solution of alkaline pyrogallic acid or chromous chloride

Reagent: Carbon Monoxide Absorbent
A solution of cuprous chloride or a sulfate solution

Fyrite Analyzer



Fyrite Analyzer



Dry Molecular Weight Equation

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

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

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

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

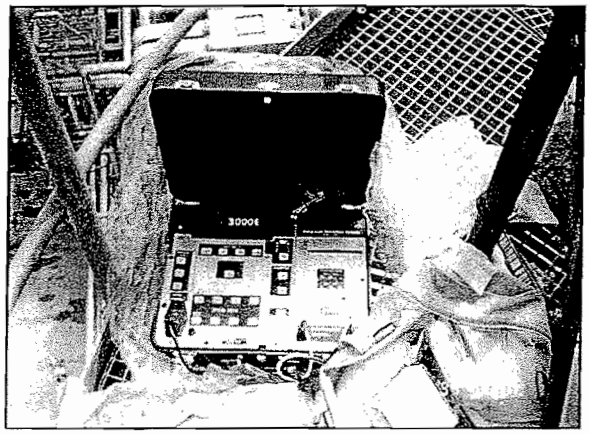
Principle

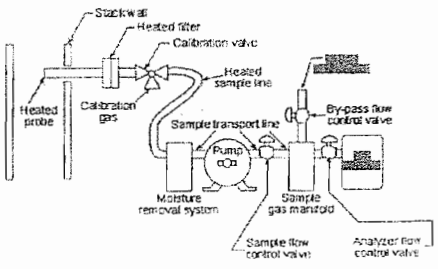
A sample is continuously extracted from the effluent stream. A portion of the sample stream is sent to an instrumental analyzer(s) for the determination of O_2 and CO_2 concentrations.

Analyzer Operating Principles

CO_2 Analyzers
- Nondispersive infra-red
- Polarography

O_2 Analyzers
- Paramagnetism
- Polarography
- Electrocatalysis





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

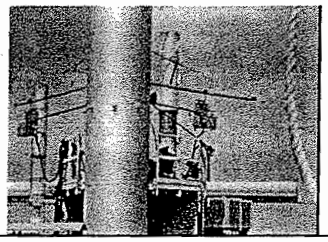
- Analyze bag sample within 4 hours
- No more than 20 separate analysis for a given set of reagents
- Three separate analysis for each bag
  - $\pm 0.3\%$ if $CO_2 > 4\%$
  - $O_2 < 15\%$
  - then $\pm 0.2\%$

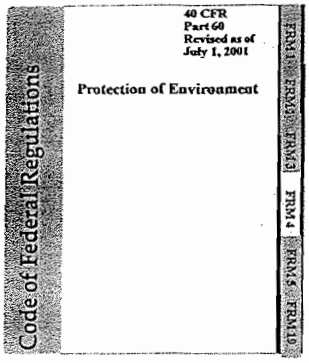
Dismiss FRM 3 Stack Test

- 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





FRM Method 4

Method 4

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

Applicability

For determining moisture content of stack gas.

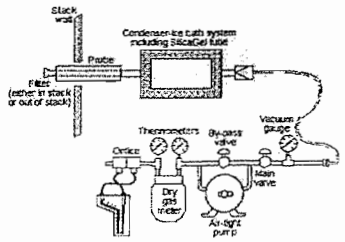
Two Methods in FRM 4

- 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)

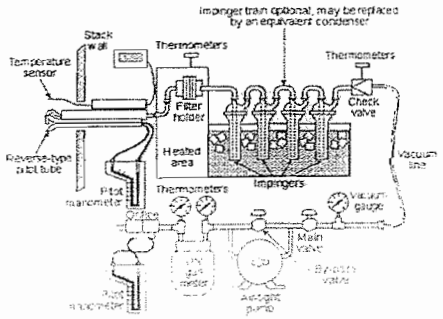


Procedure

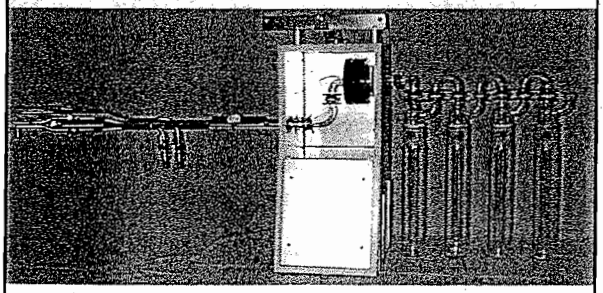
1. Determine traverse points using Method 1.
2. Select sampling time such that minimum gas volume of 21 scf will be collected at rate no greater than 0.75 cfm.
3. Leak-check sampling train (optional).

Procedure

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



Federal Reference Method 4



Volume of Water Vapor Condensed

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

$$= K_1 (V_f - V_i)$$

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

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

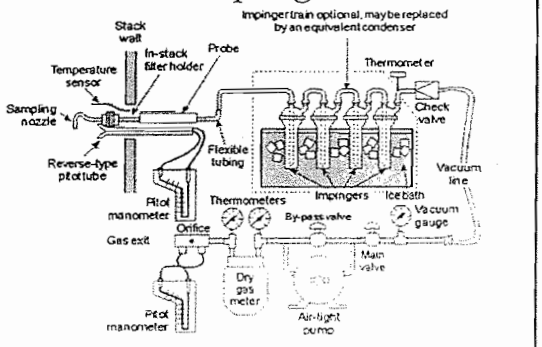
$$= K_3 Y \frac{V_m P_m}{T_m}$$

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

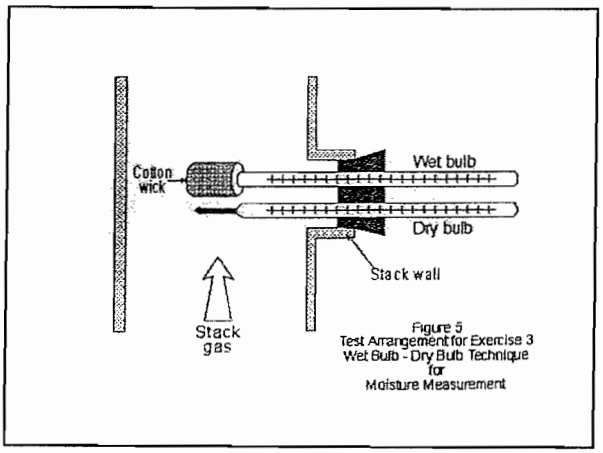
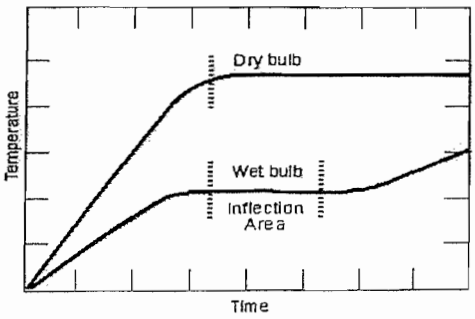
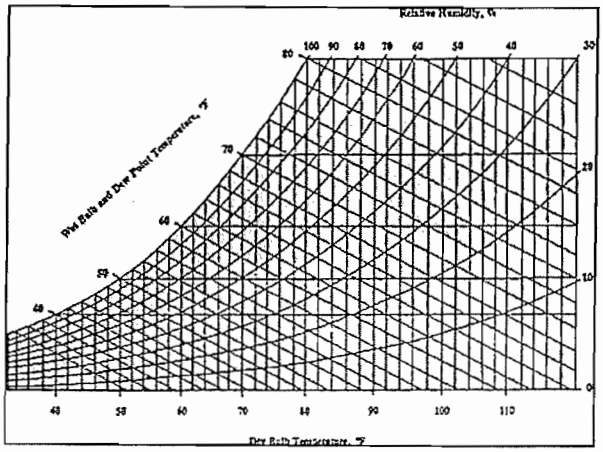


Figure 5
Test Arrangement for Exercise 3
Wet Bulb - Dry Bulb Technique
for
Moisture Measurement





Moisture Equation (Wet Bulb – Dry Bulb)

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

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

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

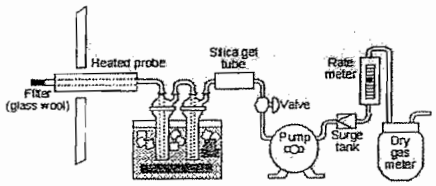
- Assume saturation.
- Attach temperature sensor to reference method probe.
- Measure stack gas temperature at each traverse point.
- Calculate the average stack gas temperature.
- Determine moisture fraction using saturation vapor pressure table.

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

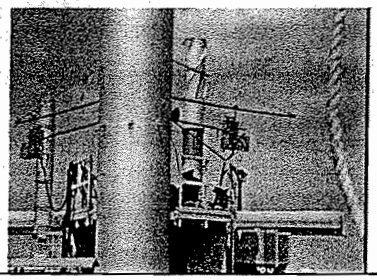
- Don't forget to wipe moisture from the outside of each impinger before weighing
- Do not weigh U-tube connectors
- Condensibles other than water leads to positive bias in results (i.e., acid aerosols and condensable organics)
- Stack gases that are supersaturated or no demisting

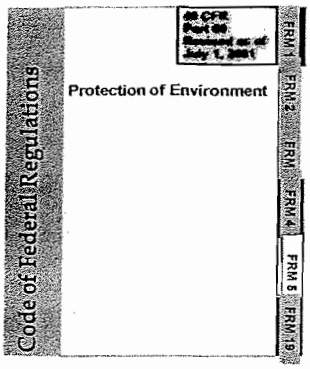
FRM 4 Tips

- 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

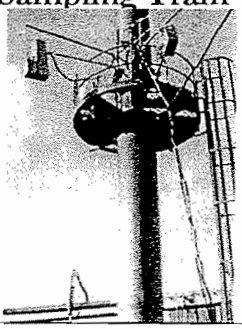
Compliance Test and Source Test Observation

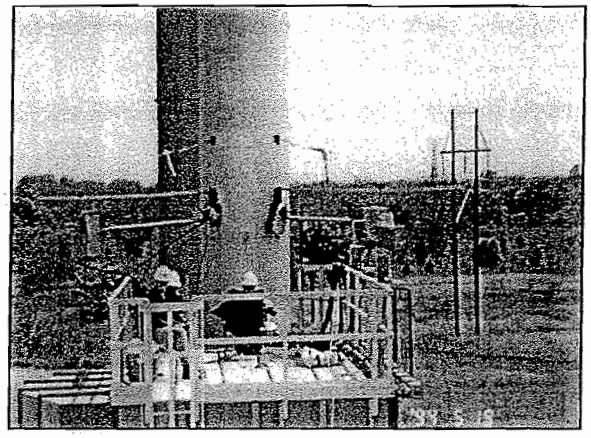
FRM 5: Particulate Emissions

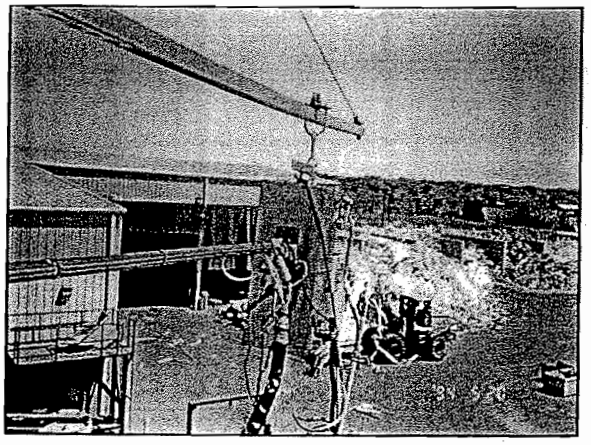


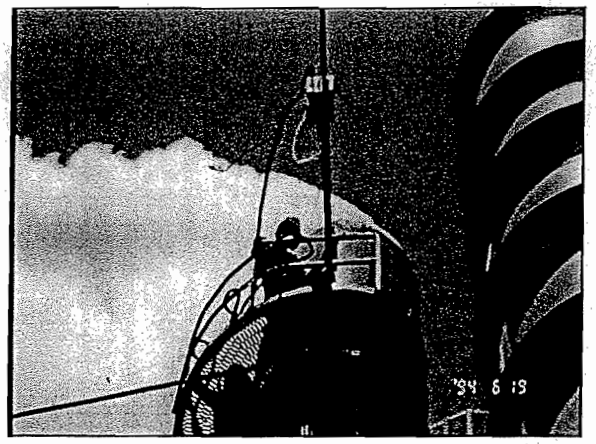


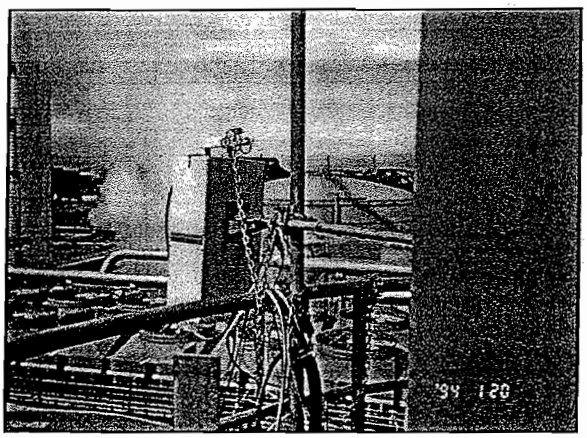
Federal Reference Method 5 Sampling Train

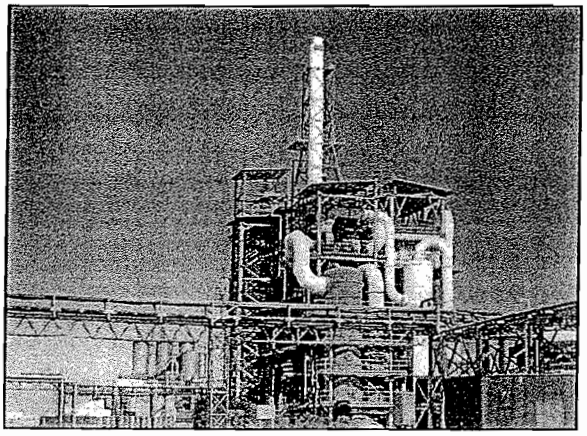


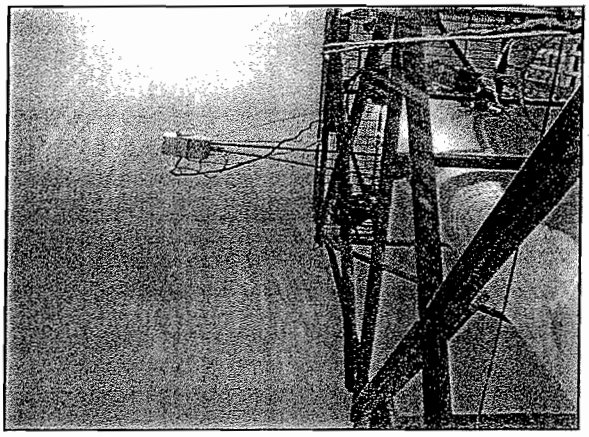


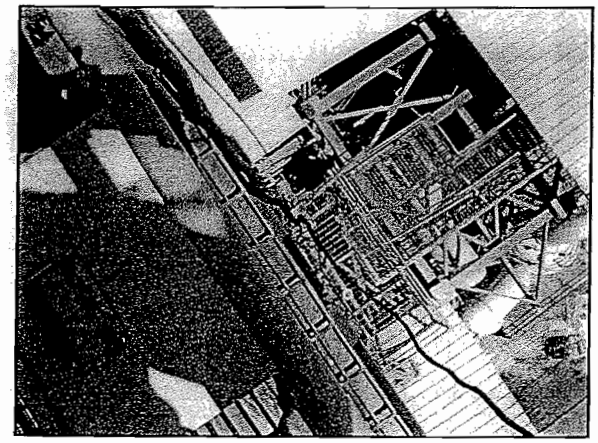




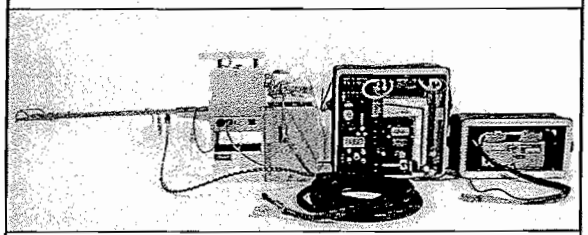








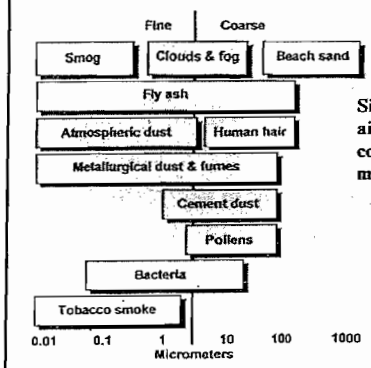
FRM 5 Sampling Train



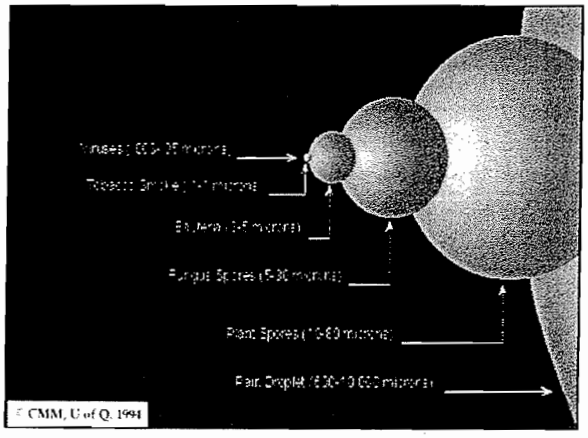
Particles

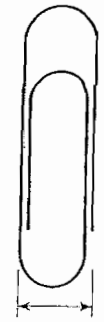
Small, Discrete masses of solid or liquid matter

Examples: dust, smoke, mist, and fly ash

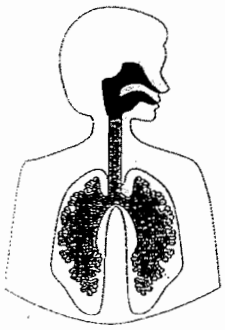


Sizes of typical airborne particles compared to common materials

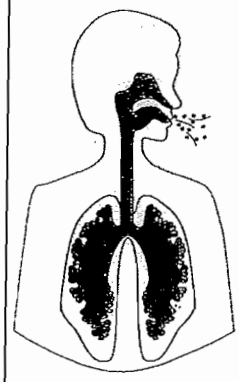




It would take 10,000 particles, each 1 micrometer (µm) in diameter, laid end to end, to stretch across the width of a small paper clip.

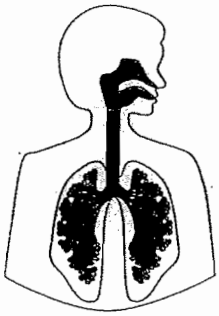


Collect in upper part of respiratory system



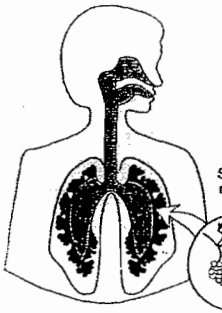
Particles collect moisture as they move through moist air of upper respiratory region, making them heavier and causing them to strike walls of throat, nose, etc.

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

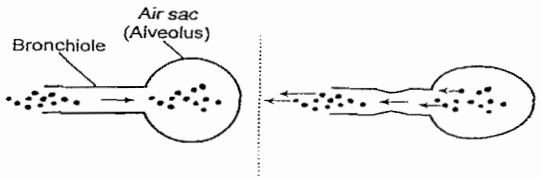


Particles 1-10 μm

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 μg/m³	Effect
2000 μg/m³ with 0.4 ppm SO_2 (24-hr avg) episodes of several days duration	Increase in deaths due to bronchitis
1000 μg/m³ with 0.25 ppm SO_2 (24-hr avg) during episodes	Increase in mortality from all causes including respiratory and cardiac disease
300 μg/m³ with 0.21 ppm SO_2 (annual avg)	Significant increase in bronchitis symptoms
130 μg/m³ with SO_2 (annual avg)	Increase in frequency and severity of lower respiratory illness
100-200 μg/m³ 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

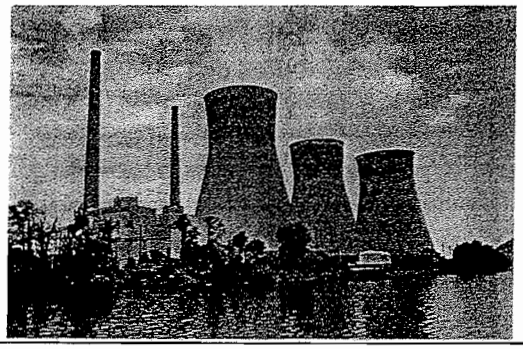
History of FRM 5

- 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

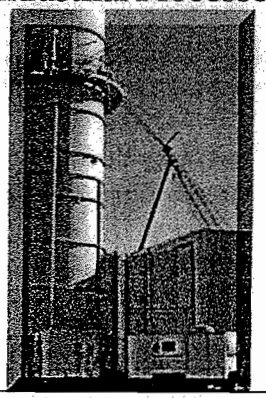


Stationary Combustion Sources

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

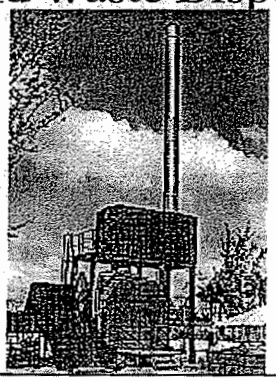


Industrial Processes

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

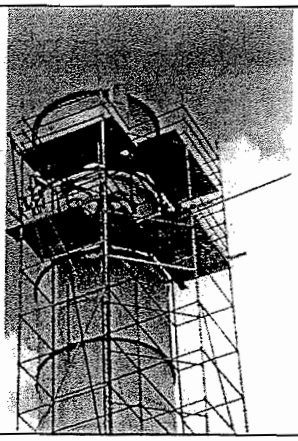


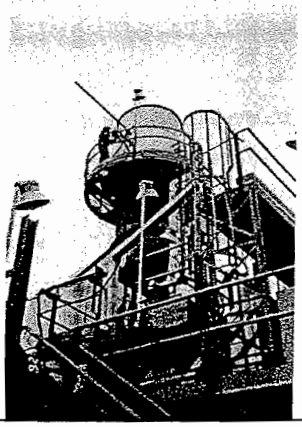
Solid Waste Disposal

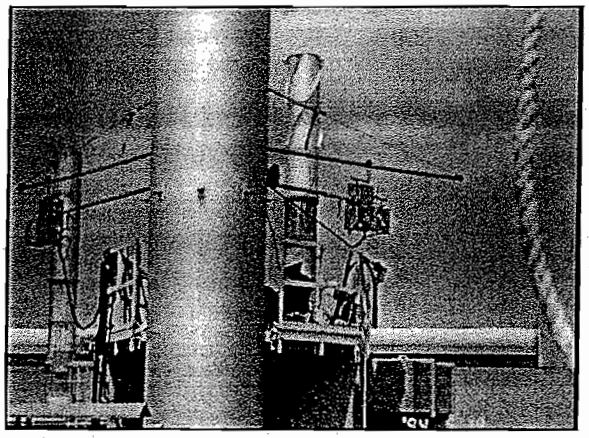
Facilities that dispose of unwanted products and by-products.
Emissions result from the disposal process
--usually burning.

Emission Generation Categories

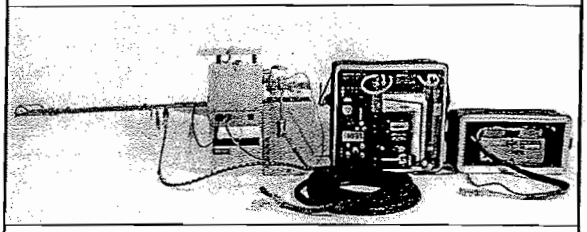
- Transportation
- Stationary source fuel combustion
- Industrial processes
- Solid waste disposal
- Miscellaneous





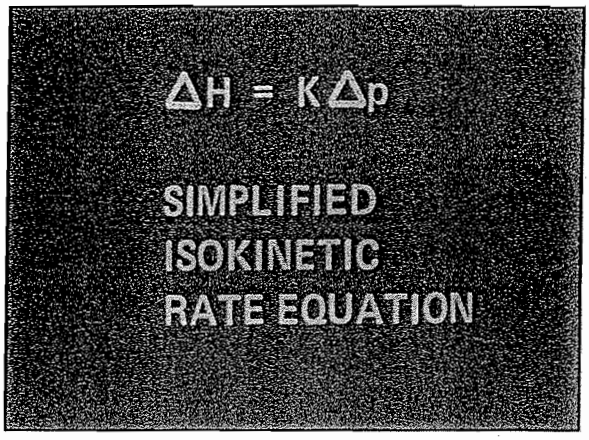


FRM 5 Sampling Train



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
  - $\Delta H = K \Delta p$

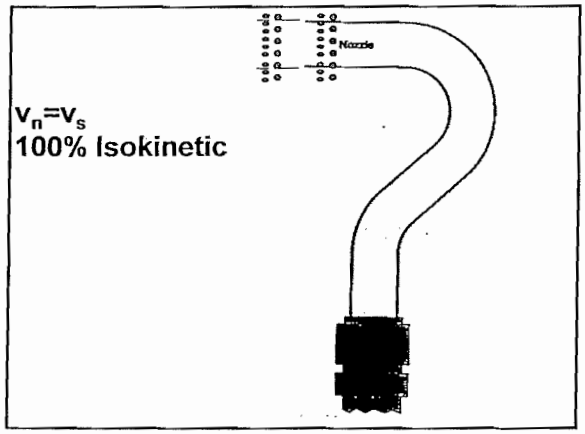


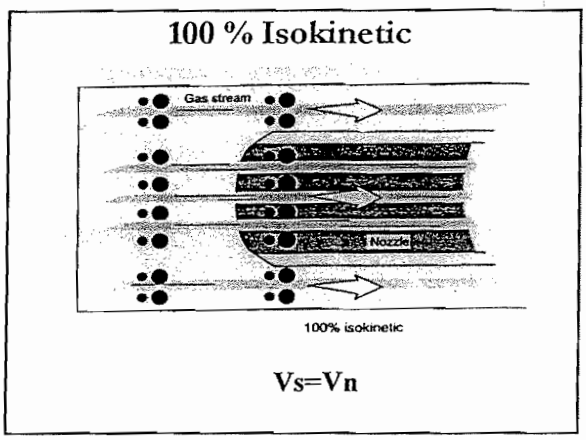
Isokinetic Sampling and Bias

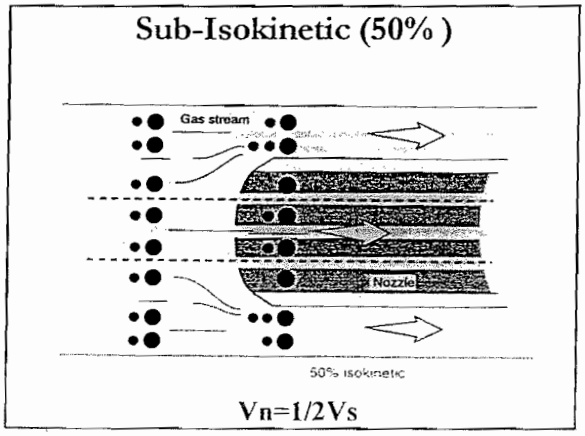
- To obtain average pollutant concentration, need parameters:
  - Quantity of mass emitted from stack
  - Total quantity of volume from stack

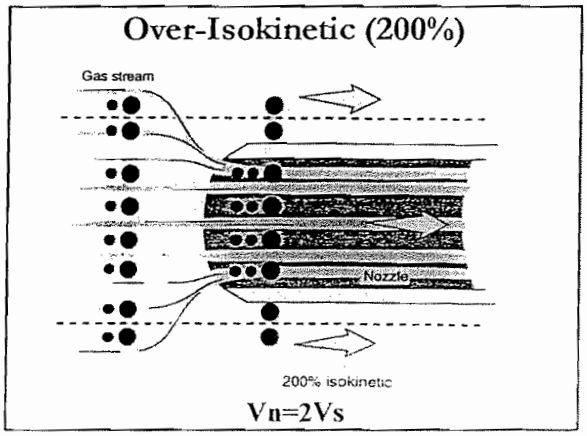
Isokinetic Sampling and Bias

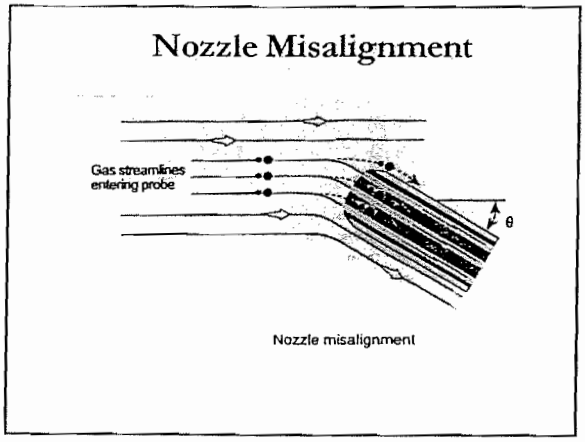
- Isokinetic sampling provides best approach for accurate data
- Pollutant mass rate (pmr)
  - pmr_a (Ratio-of-areas: A_n ratio A_s)
  - pmr_c (Ratio-of-conc.: m_n ratio A_n)

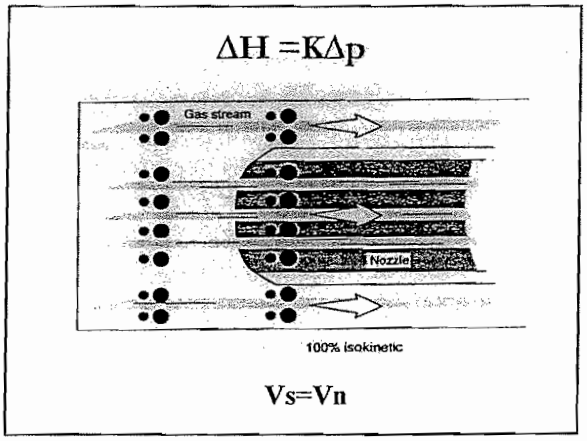

$V_n=V_s$
100% Isokinetic
Nozzle


100 % Isokinetic
Gas stream
Nozzle
100% isokinetic
Vs=Vn


Sub-Isokinetic (50%)
Gas stream
Nozzle
50% isokinetic
Vn=1/2Vs


Over-Isokinetic (200%)
Gas stream
Nozzle
200% isokinetic
Vn=2Vs


Nozzle Misalignment
Gas streamlines entering probe
θ
Nozzle misalignment


ΔH =KΔp
Gas stream
Nozzle
100% isokinetic
Vs=Vn

Isokinetic Sampling

% Isokinetic = —— ×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

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

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

FRM 5 Isokinetic Rate Equation (Simplified)

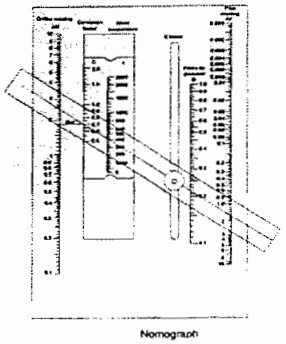
$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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

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



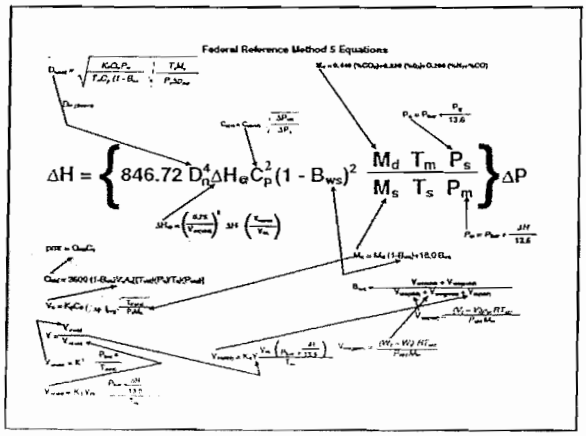
FRM 5 Isokinetic Rate Equation

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

FRM 5 Operation

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

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



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

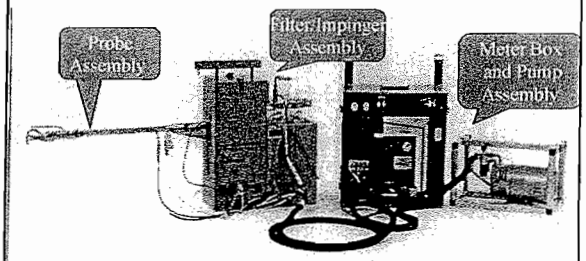
Difficulty in Maintaining Isokinetics

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

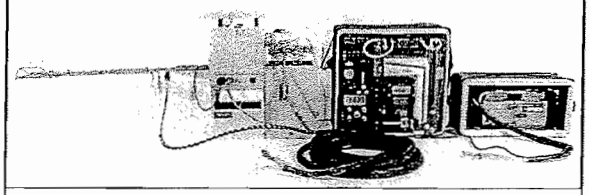
Difficulty in Maintaining Isokinetics

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

FRM 5 Sampling Train

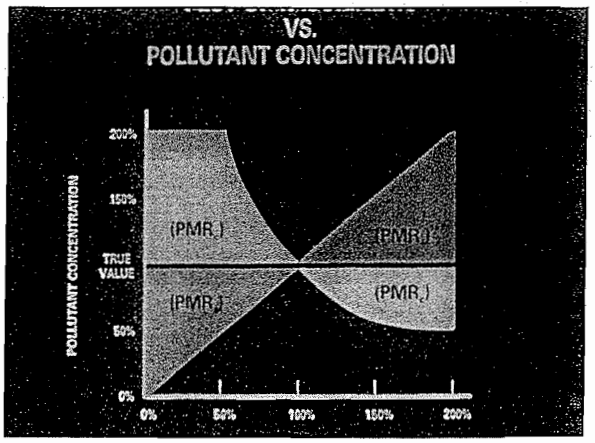


FRM 5 Sampling Train



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)



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
  - $Velocity_{nozzle} = Velocity_{stack}$
  - 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

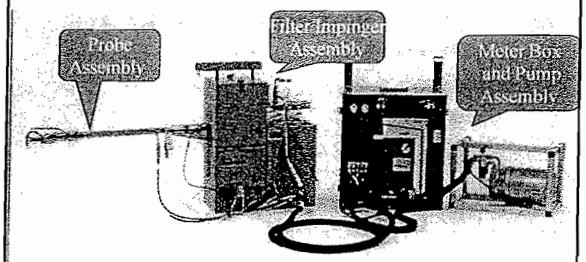
$\Delta H = K\Delta p$

SIMPLIFIED
ISOKINETIC
RATE EQUATION

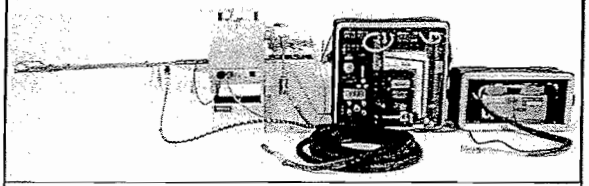
Sampling Train Components

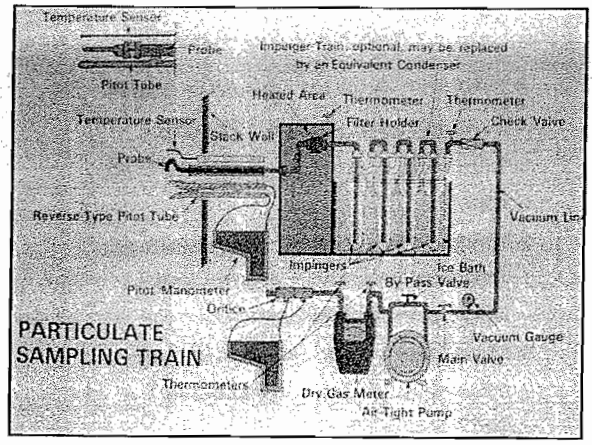
- The probe assembly
- The sample box
- The umbilical
- The meter box

FRM 5 Sampling Train

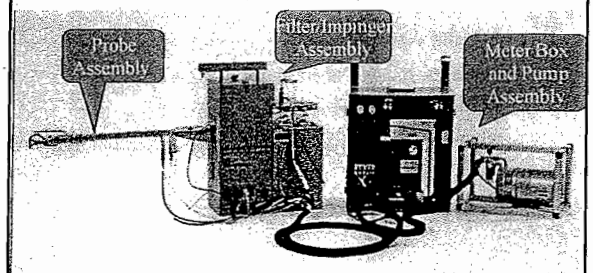


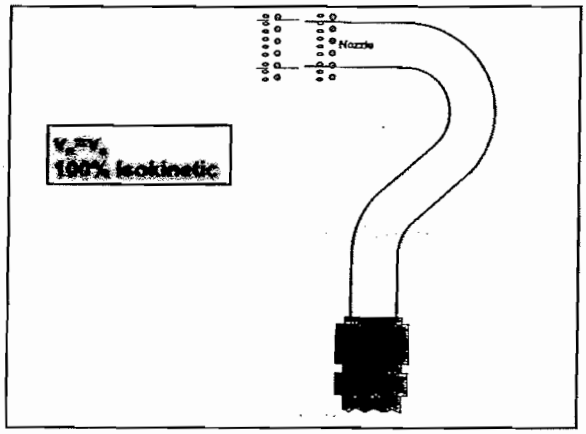
FRM 5 Sampling Train

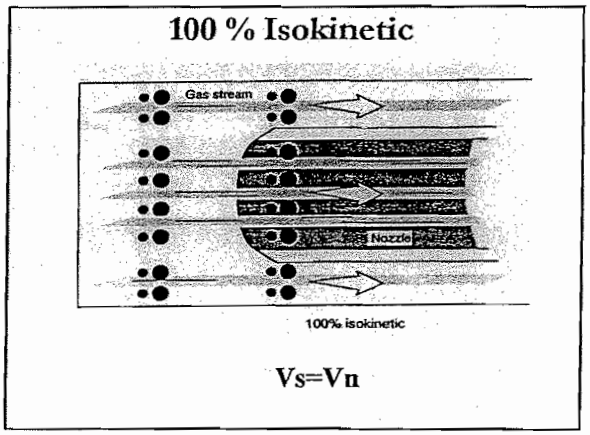


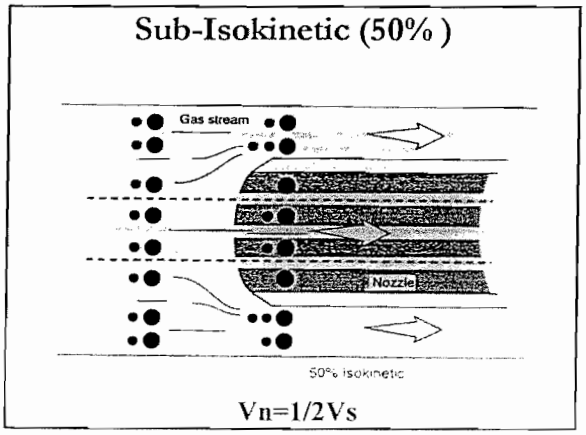


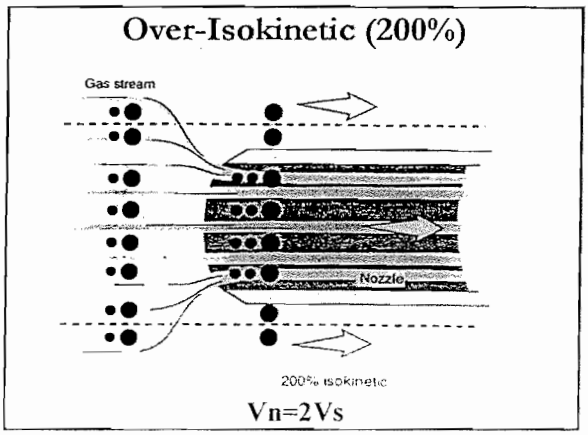
FRM 5 Sampling Train

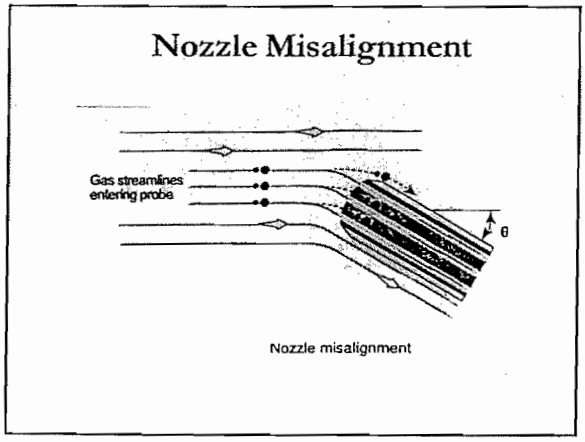


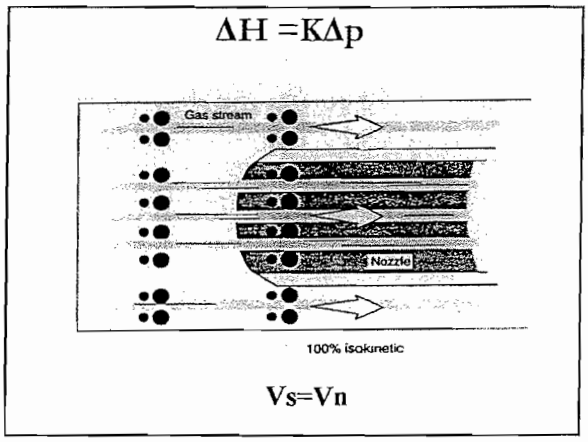

Nozzle
100% Isokinetic


100 % Isokinetic
Gas stream
Nozzle
100% isokinetic
Vs=Vn


Sub-Isokinetic (50%)
Gas stream
Nozzle
50% isokinetic
Vn=1/2Vs


Over-Isokinetic (200%)
Gas stream
Nozzle
200% isokinetic
Vn=2Vs


Nozzle Misalignment
Gas streamlines entering probe
θ
Nozzle misalignment


ΔH =KΔp
Gas stream
Nozzle
100% isokinetic
Vs=Vn

$\Delta H = K\Delta p$

SIMPLIFIED ISOKINETIC RATE EQUATION

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)

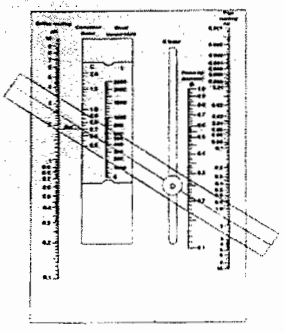
$$D_{n(est)} \sqrt{\frac{0.0358\ Q_m P_m}{T_m C_p (1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s \Delta p_{est}}}$$

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

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

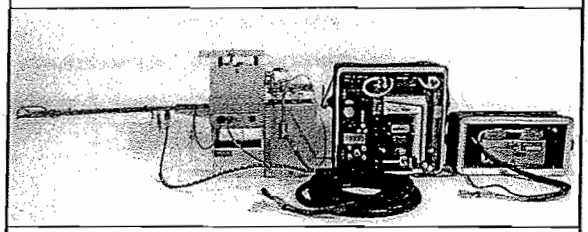


Nomograph

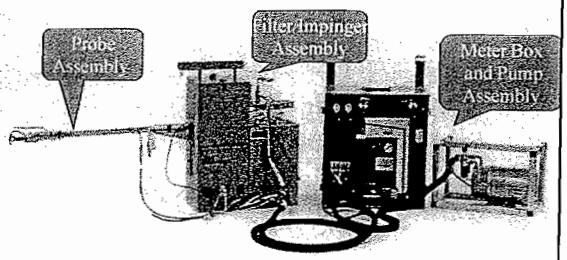
Federal Reference Method 5 Equations

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

FRM 5 Sampling Train



FRM 5 Sampling Train



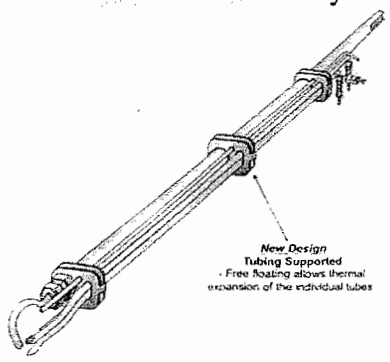
Sampling Train Components

- 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**

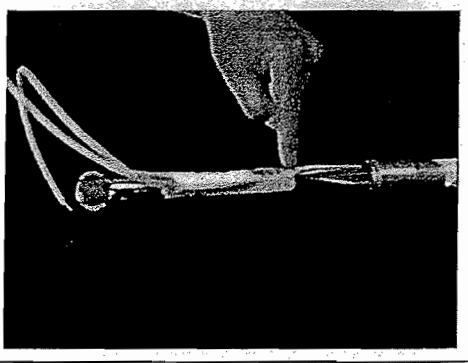
FRM 5 Sampling Probe

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

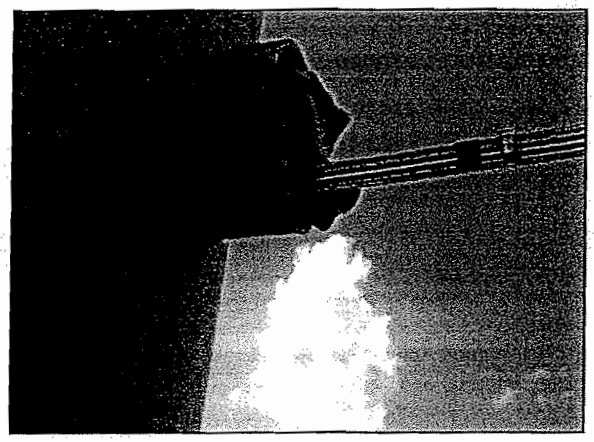
Probe Sheath

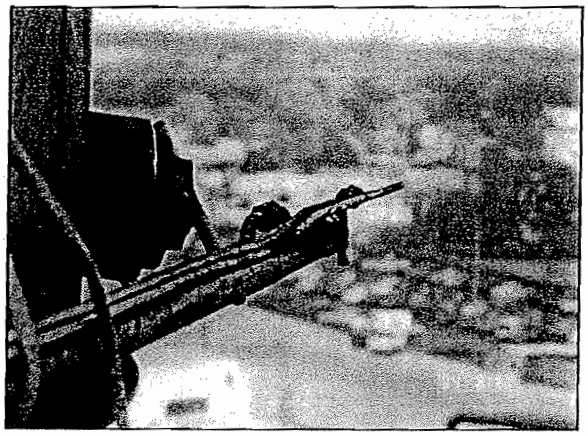
- Usually stainless steel
- Pitot tube welded to sheath to prevent misalignment
- Protects liner from breakage

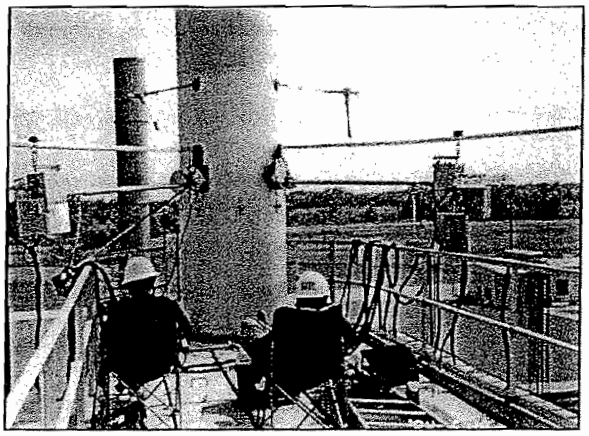
Probe liner and sheath



FRM 5 Ceramic Probe Heater





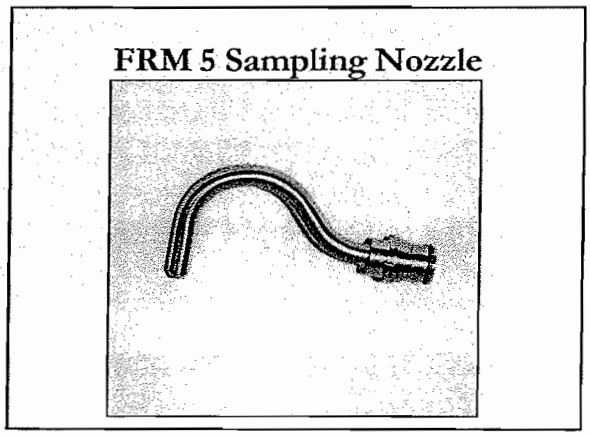


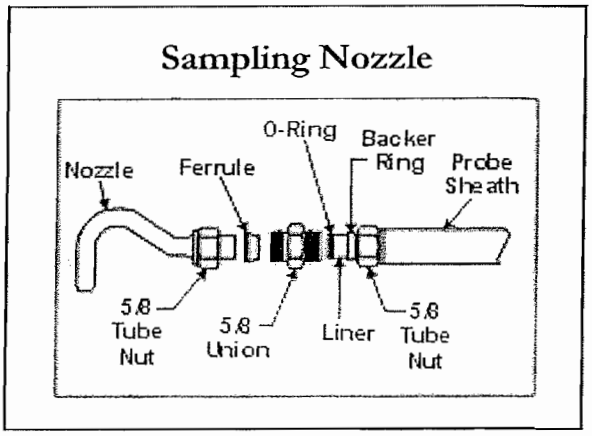
FRM 5 Sample Nozzle

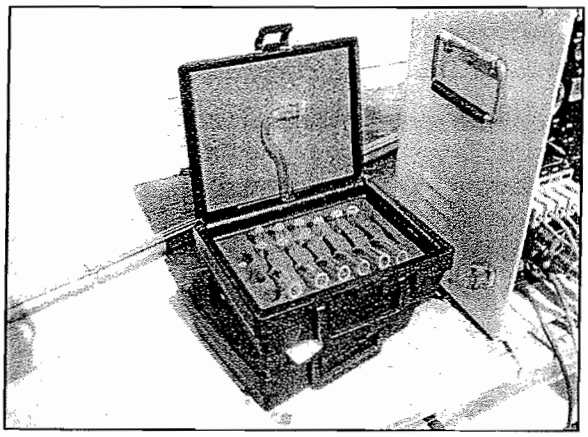
- Seamless stainless steel tubing or glass or Teflon
- Other materials approved by administrator
- Button-hook/elbow design
  - Sharp/tapered leading edge (<30 angle)
  - Constant internal diameter

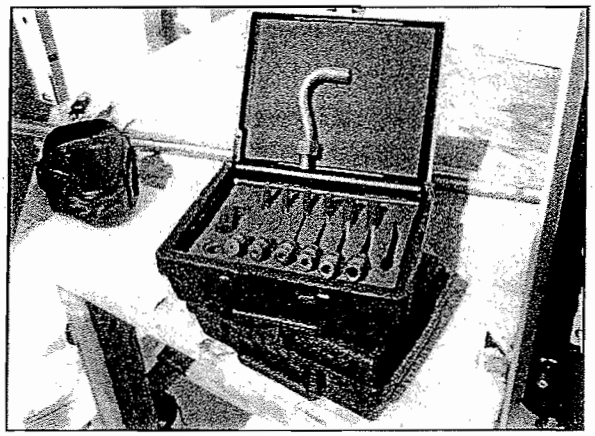
FRM 5 Sample Nozzle

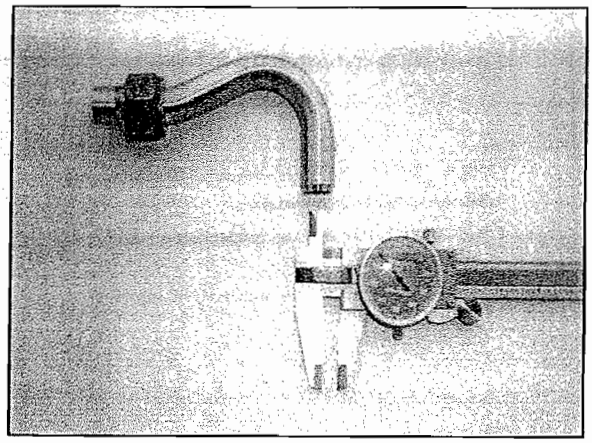
- Range of nozzles (0.32-1.27 cm ID)
  - Nozzle must be calibrated
  - Measure 3 readings using micrometer (take average)
  - Low/high readings not exceed 0.004 inches

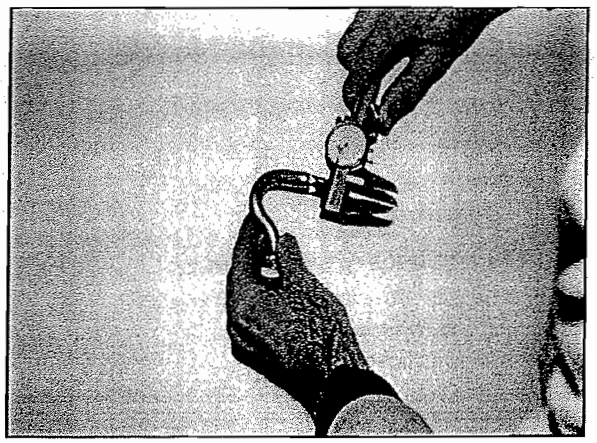

FRM 5 Sampling Nozzle

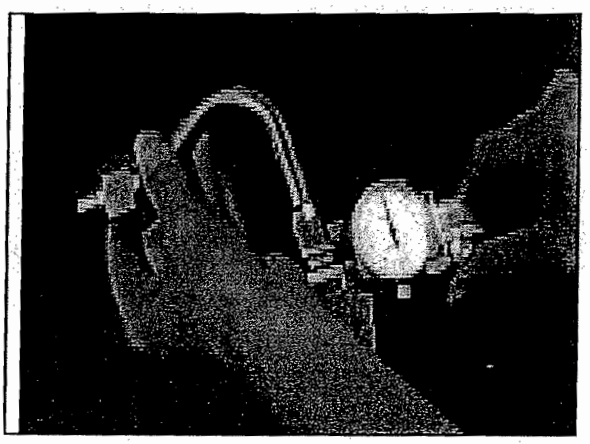

Sampling Nozzle
Nozzle
Ferrule
O-Ring
Backer Ring
Probe Sheath
5/8 Tube Nut
5/8 Union
Liner
5/8 Tube Nut











FRM 5 Sample Nozzle

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

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

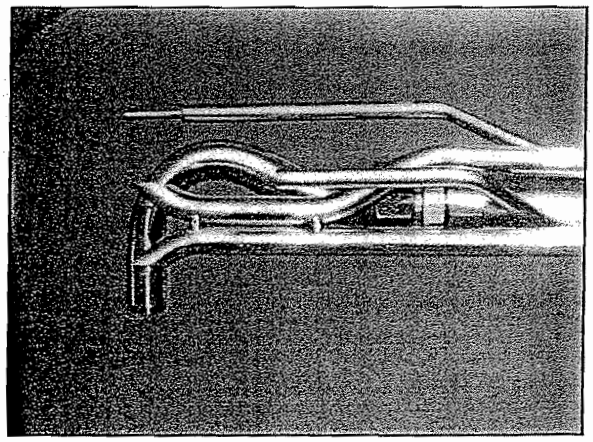
FRM 5 Isokinetic Rate Equation (Simplified)

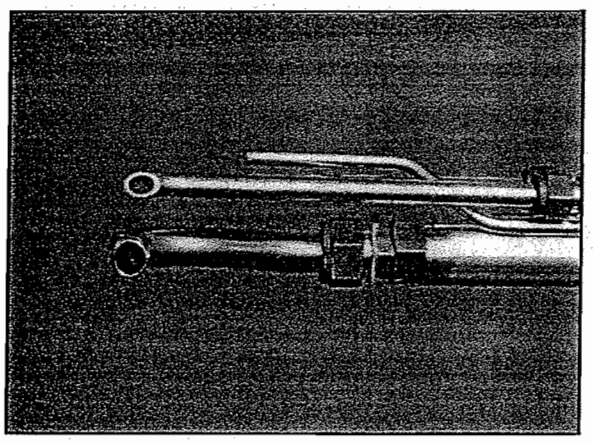
$$D_{n(est)} \sqrt{\frac{0.0358\, Q_m P_m}{T_m C_p\,(1 - B_{ws(est)})}} \sqrt{\frac{T_s M_s}{P_s\, \Delta p_{est}}}$$

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

FRM 5 Nozzle/Pitot Tube/Thermocouple Orientation

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

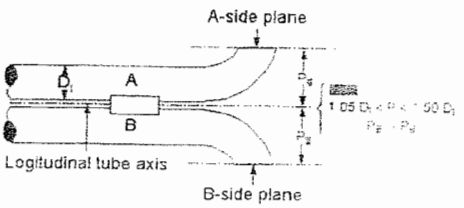


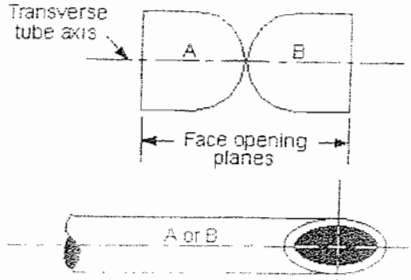


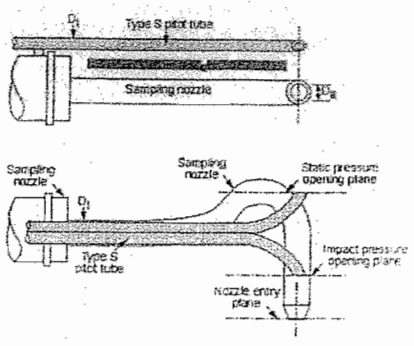
Type S Pitot Tube

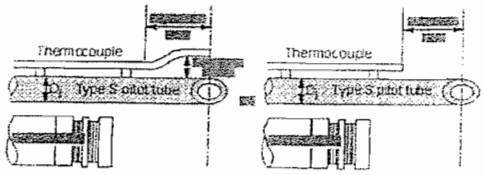
Design criteria for assigning

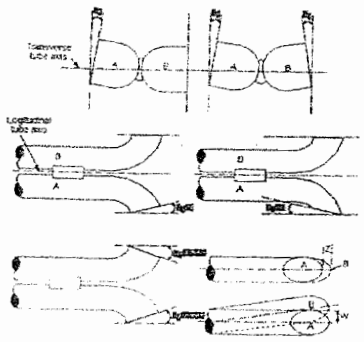
$C_p = 0.84$











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

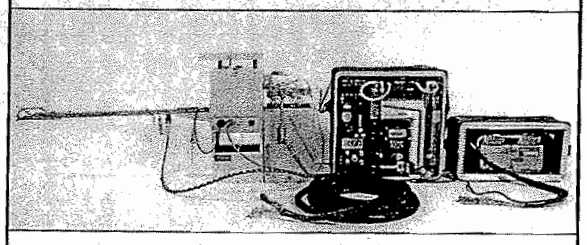
Type S Pitot Tube Inspection Data Sheet

- 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

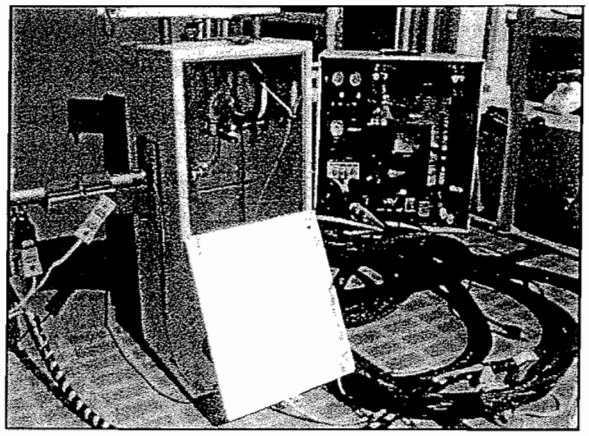
- Heating element to maintain filter temperature of 120° C
- Filter Holder
- Flexibility for vertical and horizontal traverses
- Insulated

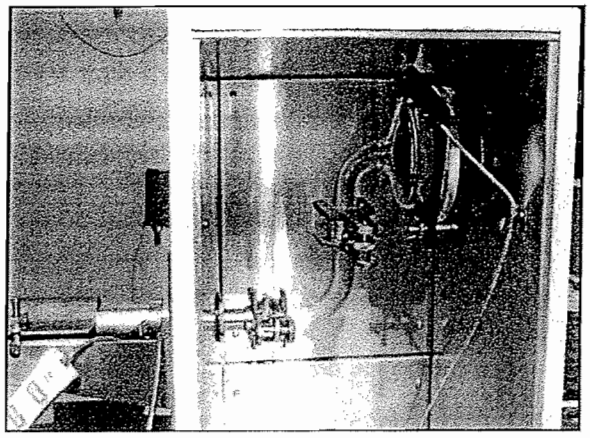
Impinger Box

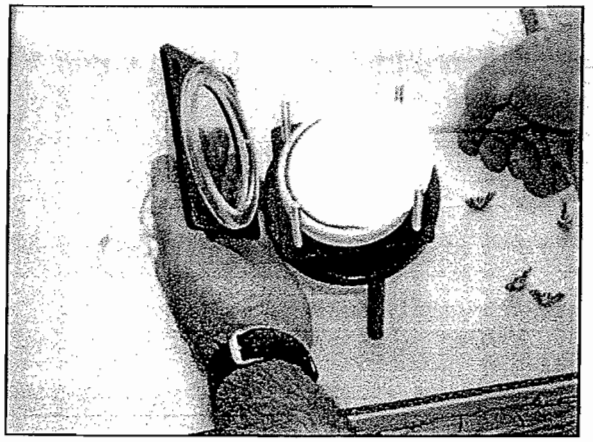
- Provide support and protection for glassware
- Insulated
- Holding container for ice to cool impingers

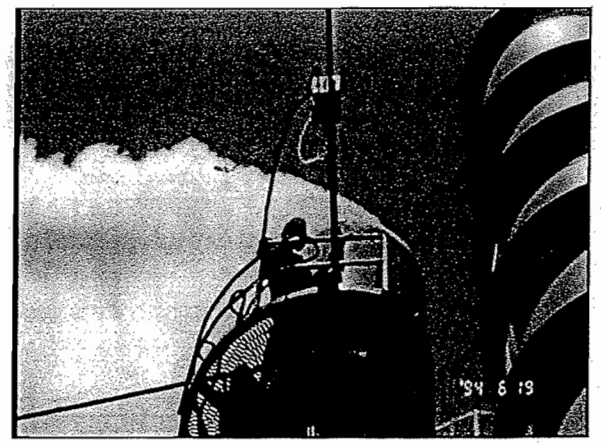
FRM 5 Heated Filter Box

- 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









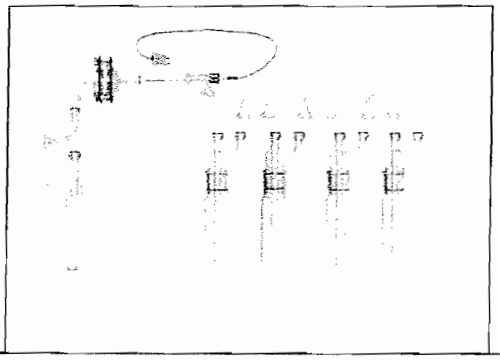
FRM 5 Heated Filter Box Desired Features

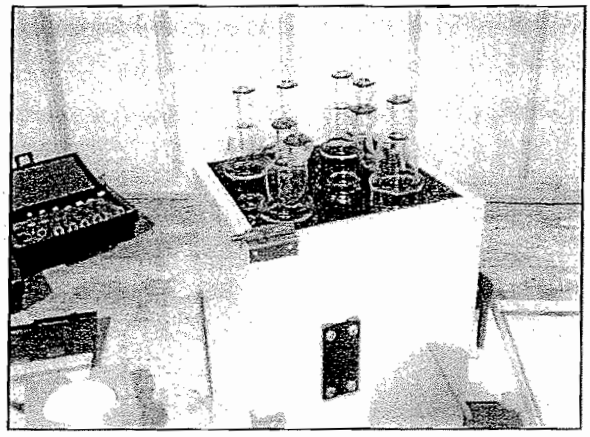
- Light weight, good insulation
- Positive probe alignment locking system
- Easy accessibility to all parts
- Good electrical system
- Durability/flexibility for vertical and horizontal stacks

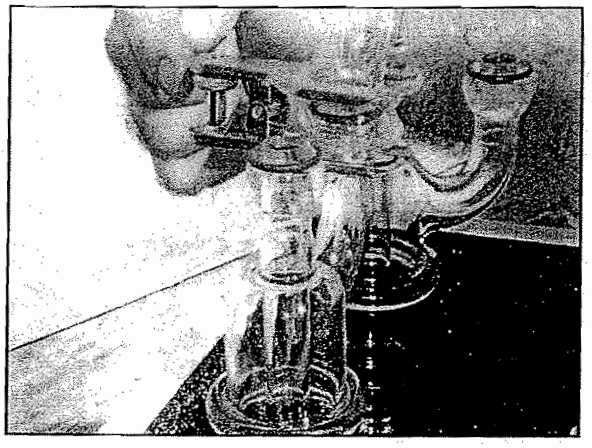
FRM 5 Impinger System

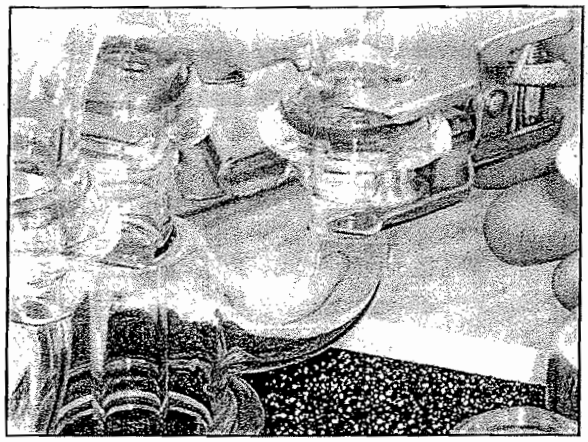
- Material of construction depends upon compounds being tested
  - Glass, Teflon, stainless steel
- Design should allow for additional space for impingers beyond FRM 5 requirements
- Need for water drain tap

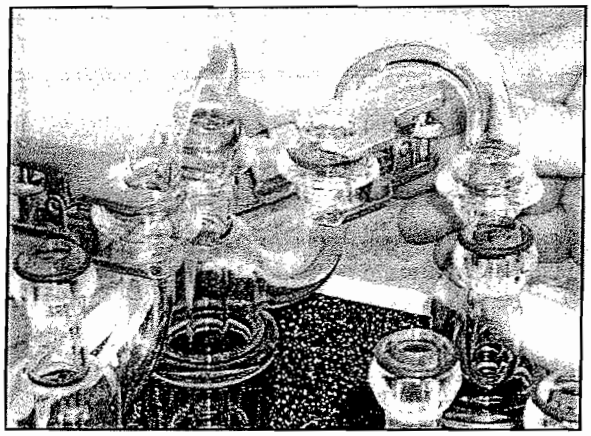
FRM 5 Impinger Assembly

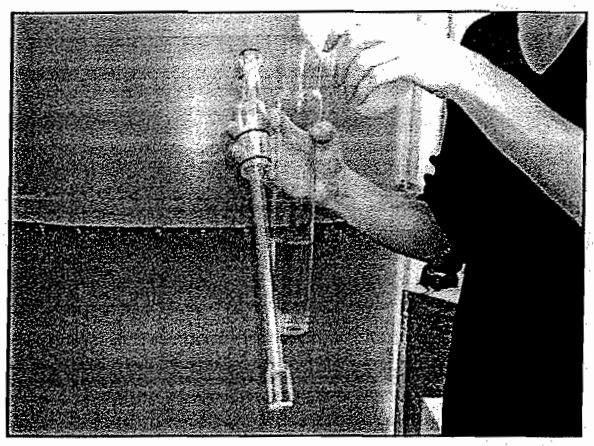


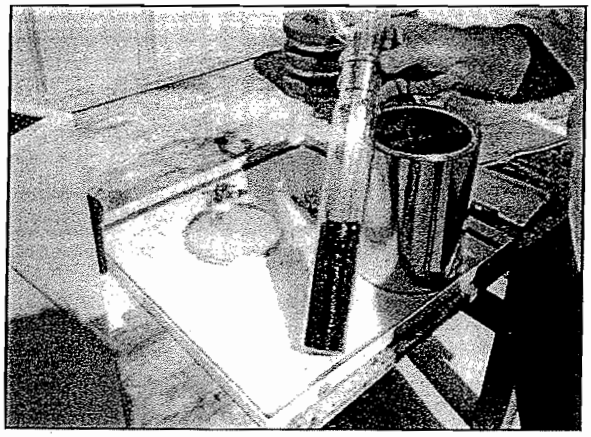




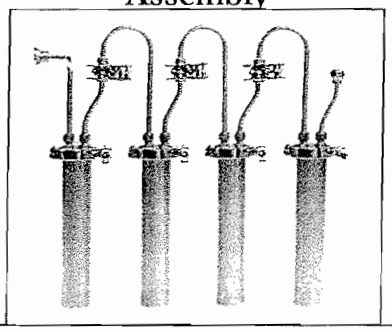




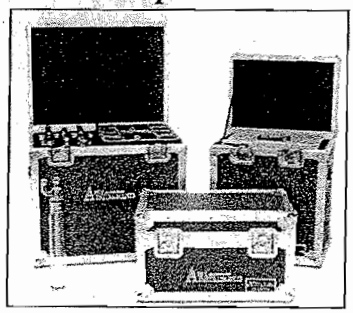




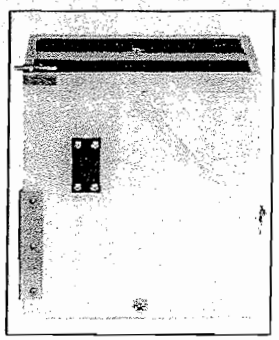
FRM 5 Stainless Steel Impinger Assembly



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%

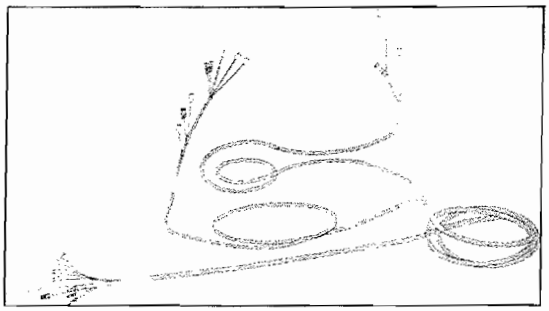
Sampling Train Components

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

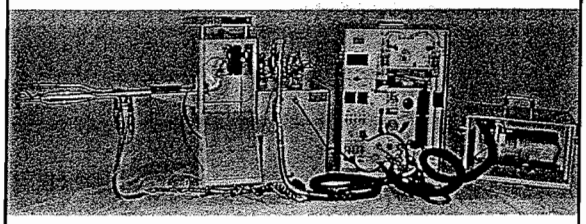
The Umbilical Line

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

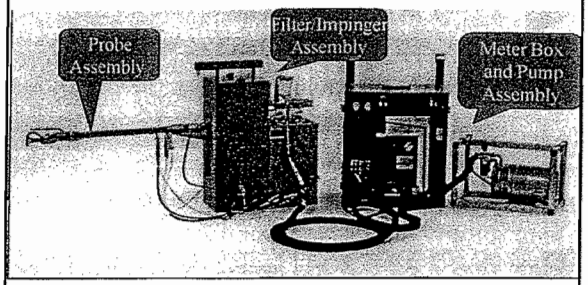
FRM 5 Transfer Line



FRM 5 Sampling Train



FRM 5 Sampling Train



The Meter Box

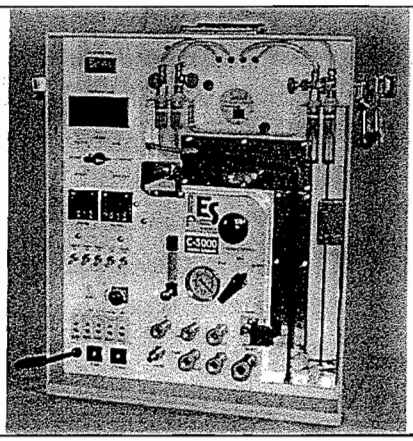
- Pump
- Dry gas meter
- Inclined manometer for Δp and ΔH readings
- Flow control valves
- Ports for integrated gas sampling

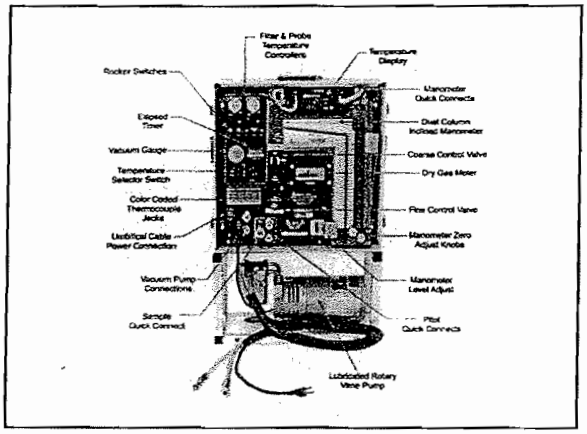
FRM 5 Meter Console Desirable Features

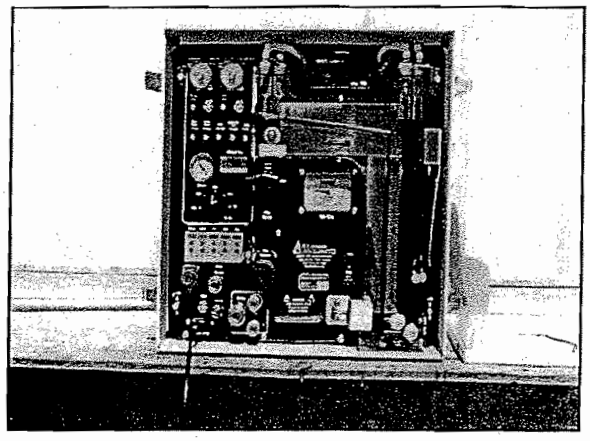
- Light weight
- Reliable leak free pump
- Good temperature controls
- Rugged construction/ good carrying handles

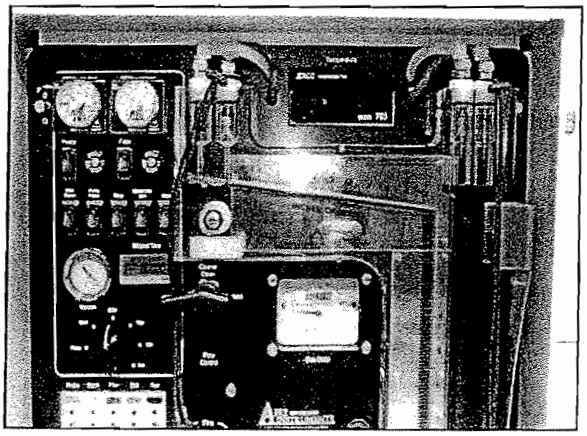
FRM 5 Meter Console Desirable Features

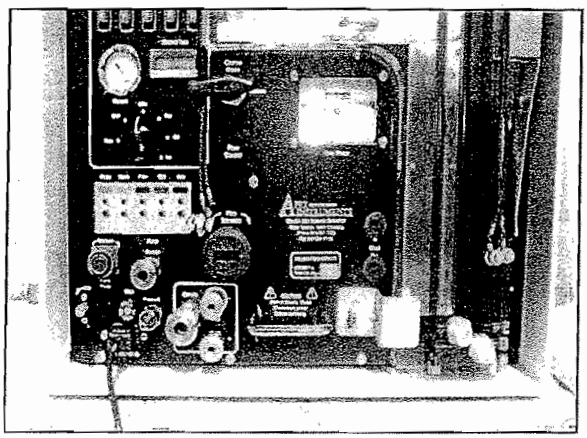
- Accessibility to components and fuse compartment
- Communication system
- Easy to read digital readouts



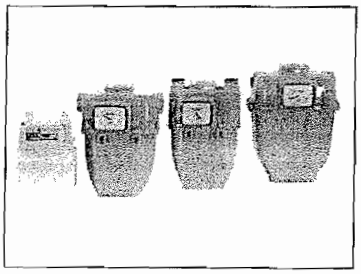


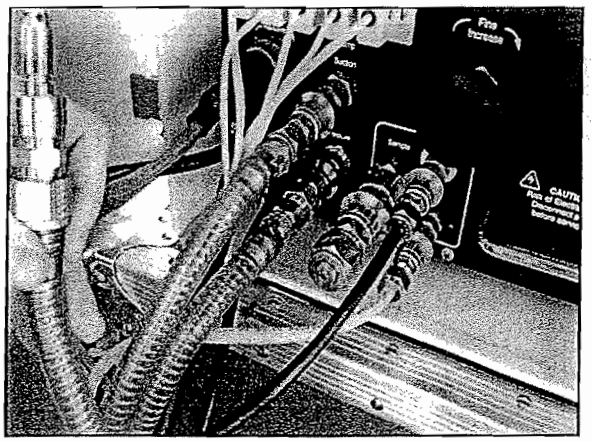


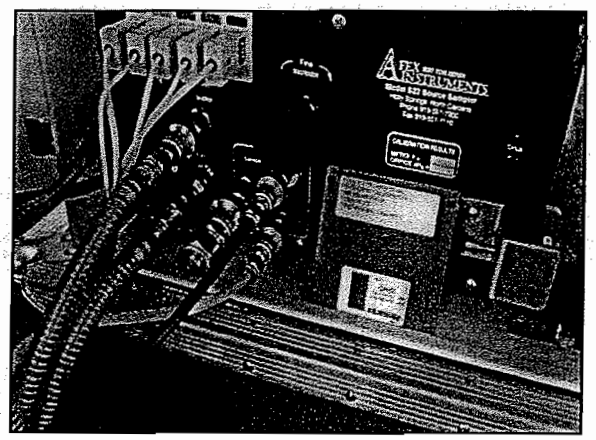




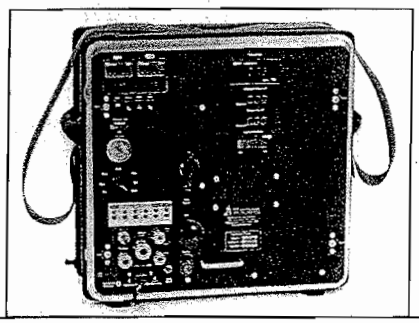
FRM 5 Dry Gas Meter



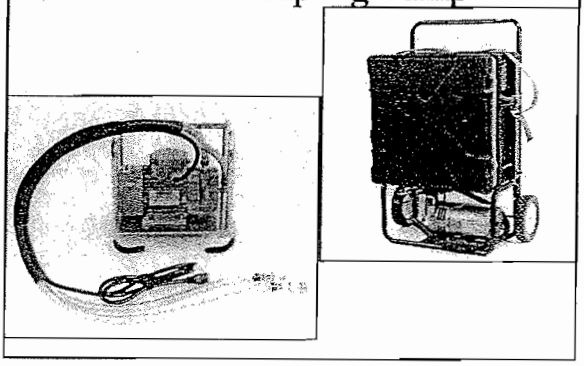




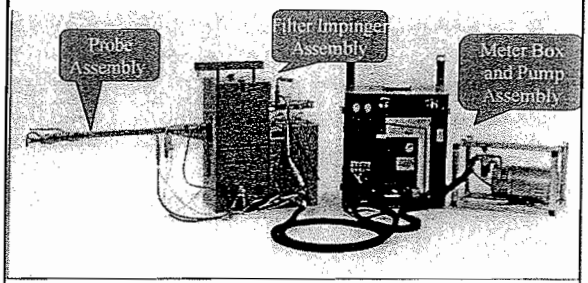
FRM 5 Digital Meter Box



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?

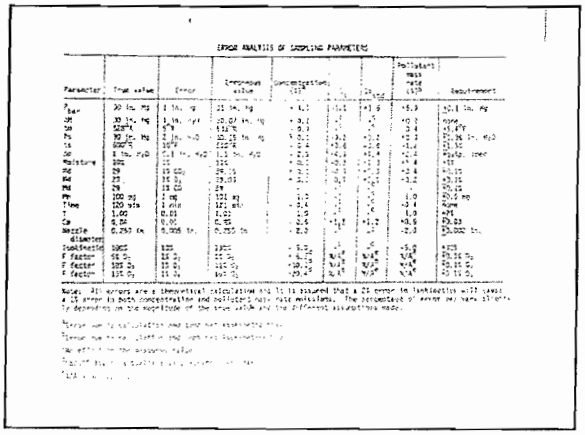
- Before obtaining the answer, the tester or observer needs to know three things to determine what is important in significant errors with FRM 5:
  - What is the data to be used for (i.e., proof of compliance, proof of violation, engineering evaluation etc.)?

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)



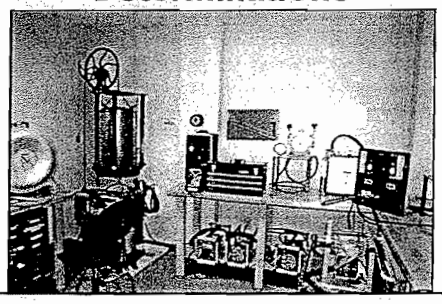
Example #1 (Stack Temperature)

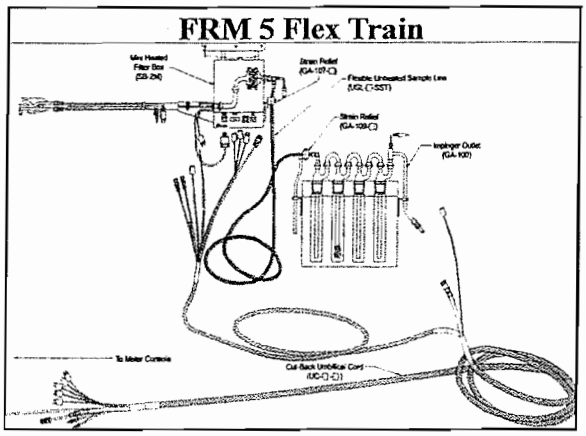
- Asphalt plant with concentration standard of 0.04 g/scf
- Team measured stack temperature at 350 F, but correct temperature was 320 F
- Question: How much error?
  - From Table, -0.4 %/10 F
  - Therefore, -1.2 % total error
  - Little effect!

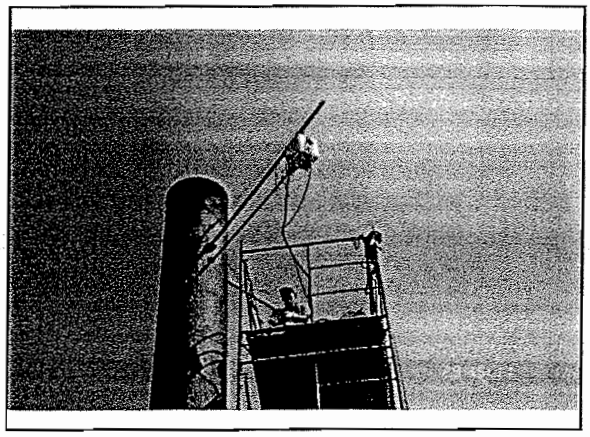
Example #2 (Orifice Meter)

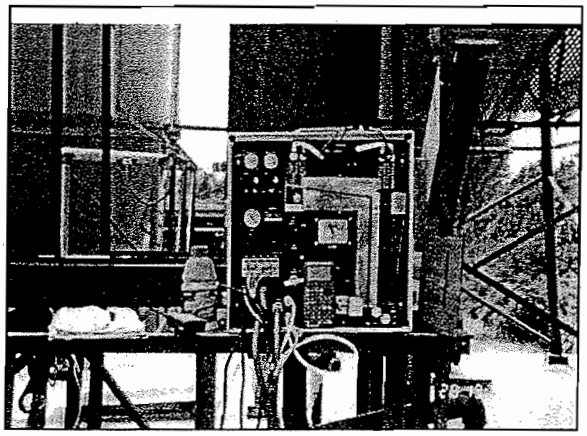
- Dry dog food plant
- Allowable mass emissions 5 lbs/hr
- DGM "Y" determined to be 0.91, but tester using 0.97
  - From Table, 1.0 % error for each 0.10
  - Therefore, 6 % bias high error
  - May want to reject test!

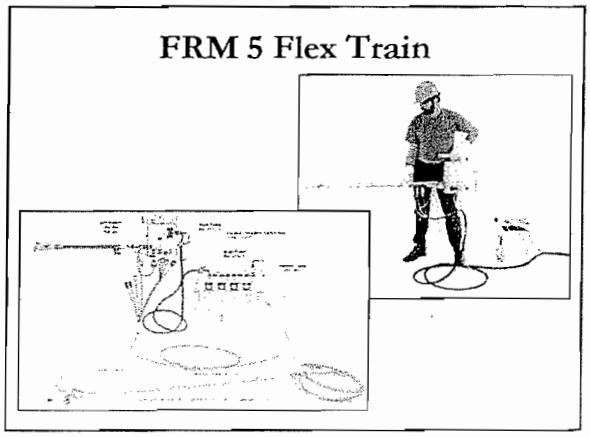
Calibration Laboratory for DGM "Y" and Orifice Meter "ΔH@" Determinations

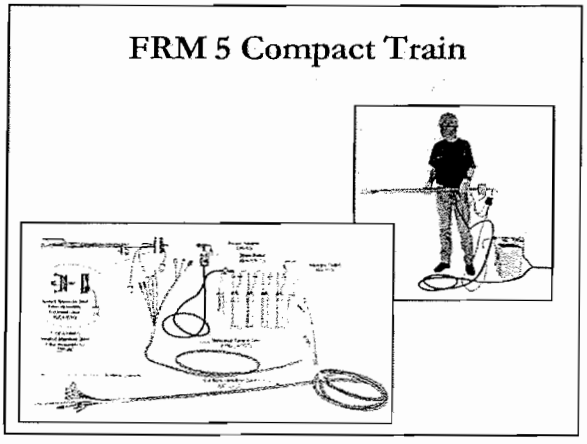












FRM 5 Recovery

- 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

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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

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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

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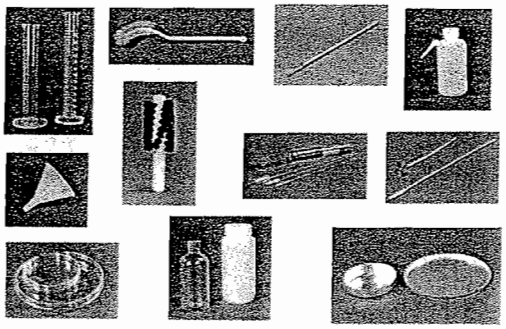
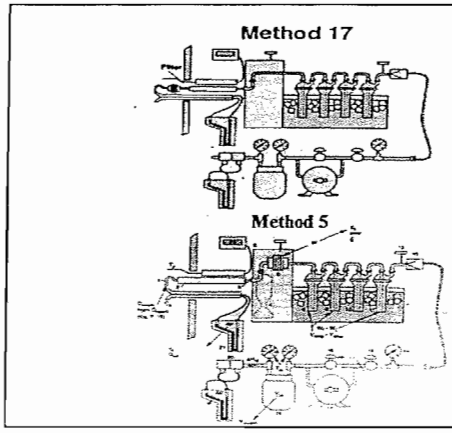
FRM 5 Sample Recovery Items



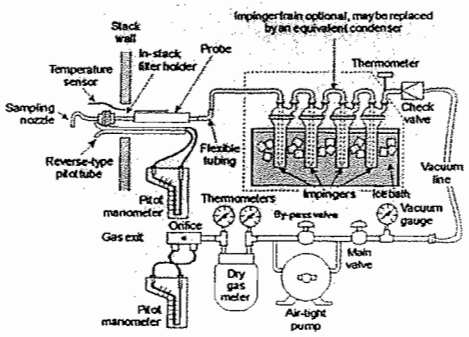


Method 17

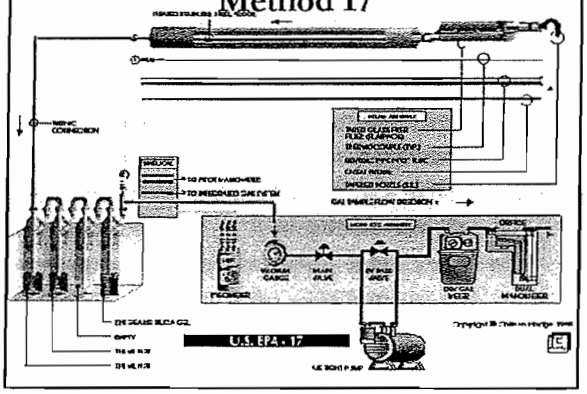
In-stack Filter
Applicability

In sources where particulate matter concentration is independent of temperature

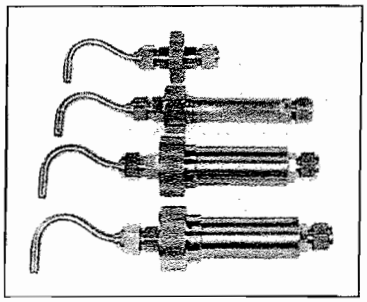
FRM 17



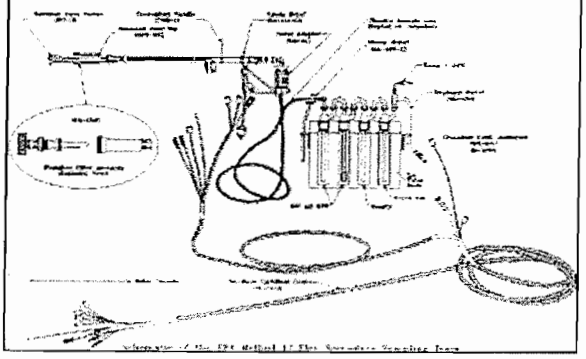
Method 17



FRM 17 In-stack Filters

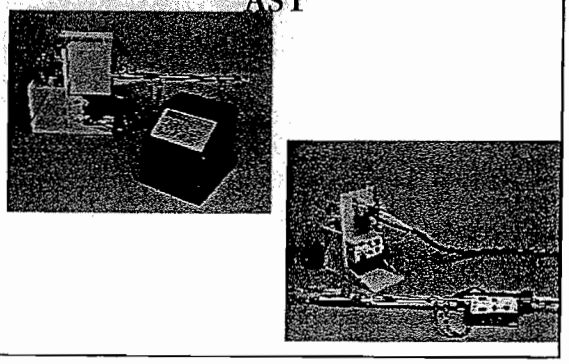


FRM 17 Flex Train



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

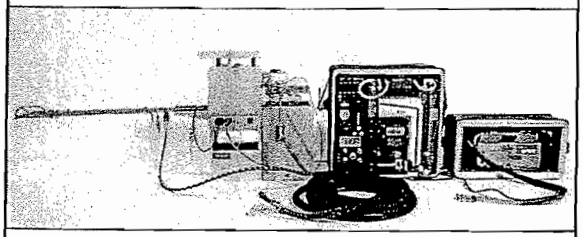
FRM Method 5I Potential Interferences

- 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

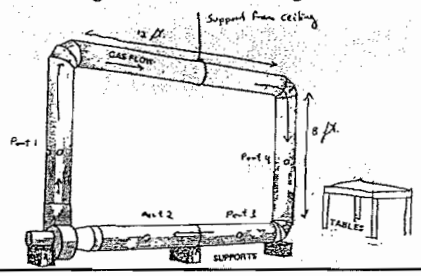
FRM Method 5I Quality Control (QC) Requirements

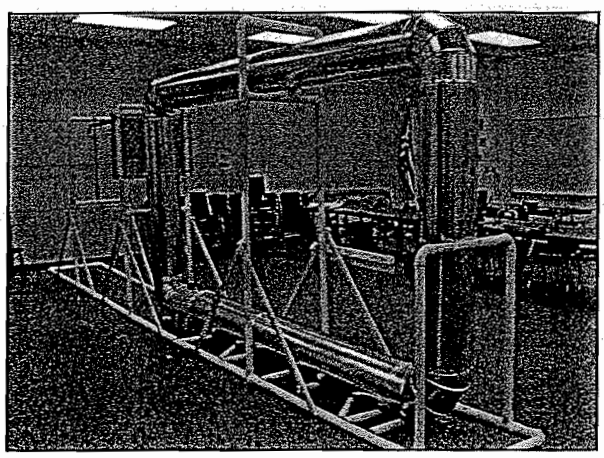
- Same as FRM 5
- Recommended field bias blank train. Similar train, taken to field, prepared, leak checked, and recovered but no sampling of source emissions
- Relative standard deviation
  - RSD=100% | $(C_a - C_b)$ | / $(C_a + C_b)$
  - Acceptable limits of < 10%

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°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

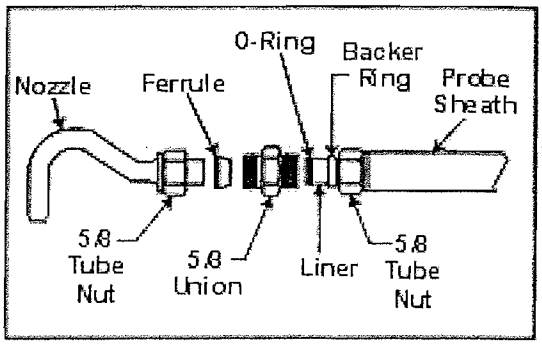
Ten (10) Laboratory Stations

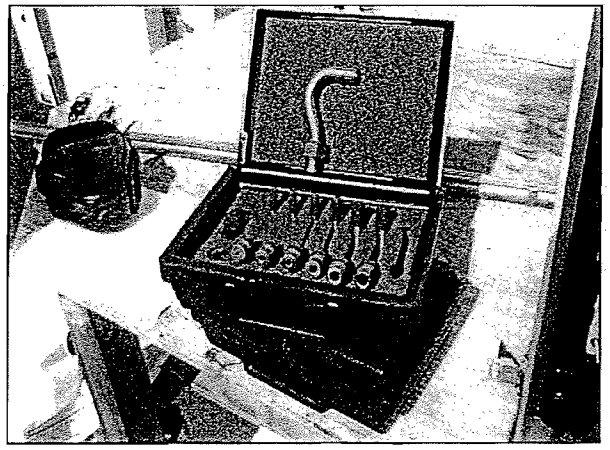
- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: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

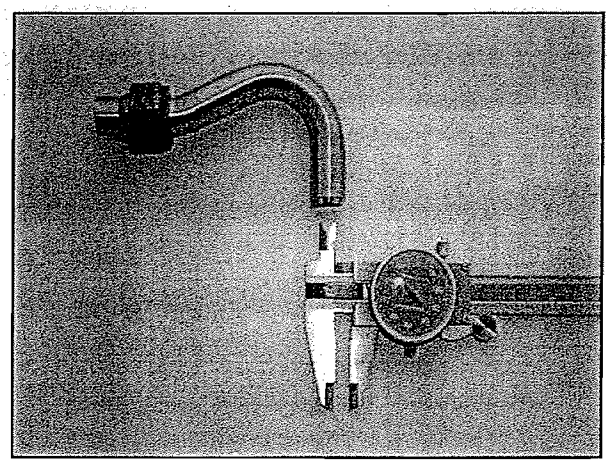
Classroom Stations

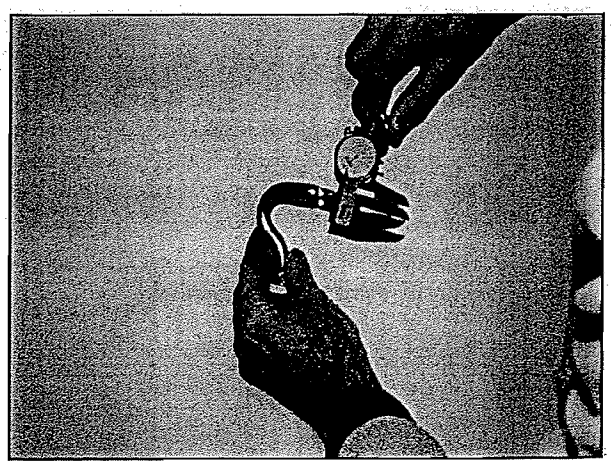
- Station #1: Nozzle Diameters
  - All readings within 0.004 inches
- Station #2: DGM γ Determination
  - Temperature ° R
- Station #3: Orifice ΔH@ Determination
  - Temperature ° R

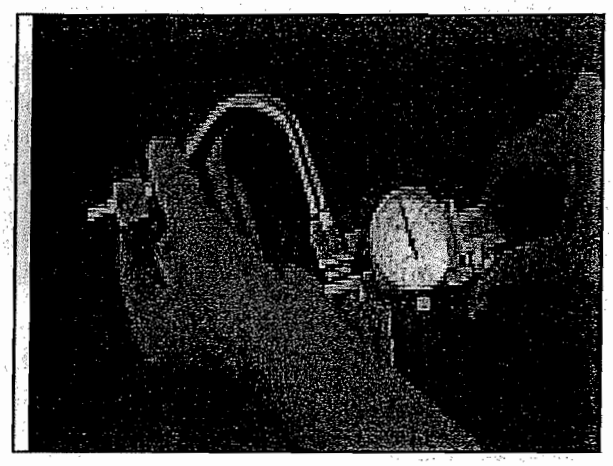
Sampling Nozzle











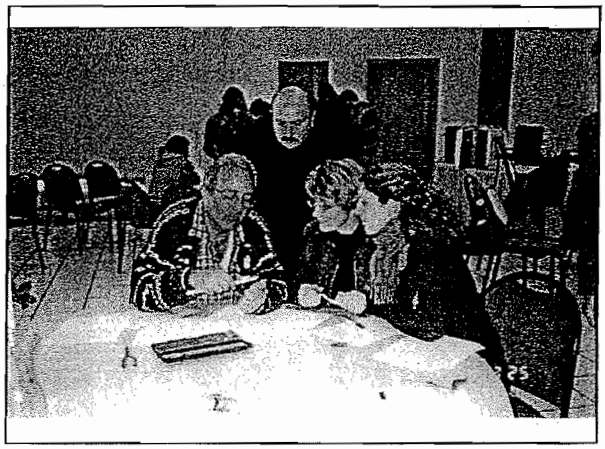
FRM 5 Sample Nozzle

- 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)

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

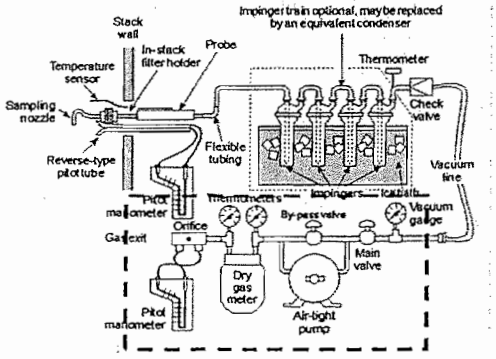
$$\Delta H = \left\{ 846.72\, D_n^4\, \Delta H_@\, C_p^2\, (1 - B_{ws})^2 \quad \frac{M_d}{M_s} \frac{T_m}{T_s} \frac{P_s}{P_m} \right\} \Delta P$$

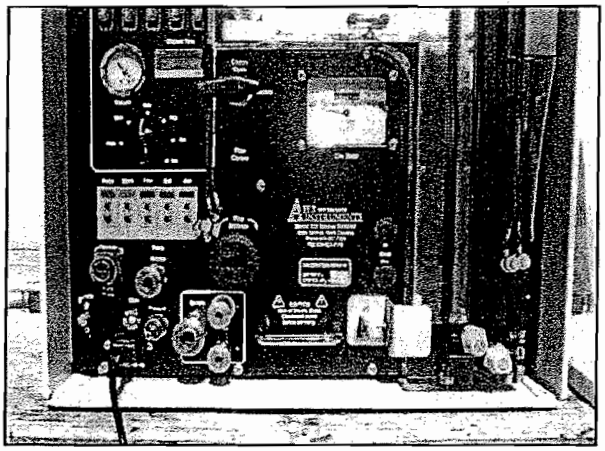


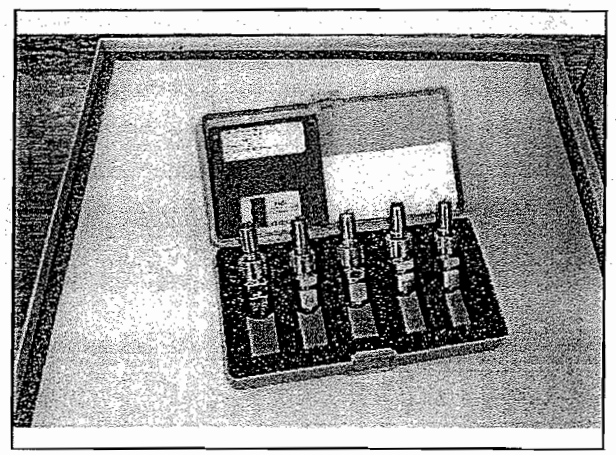
Classroom Stations

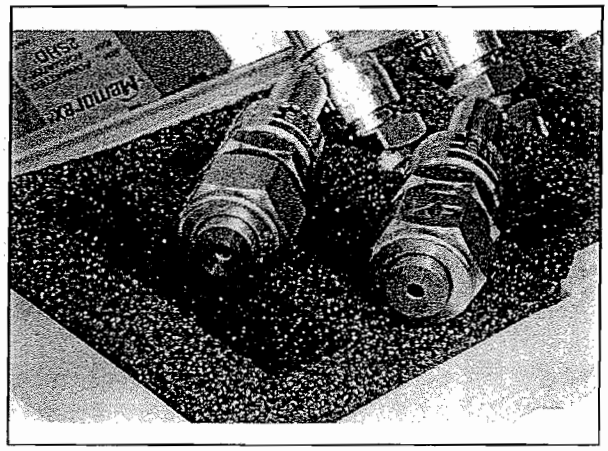
- Station #1: Nozzle Diameters
  - All readings within 0.004 inches
- Station #2: DGM γ Determination
  - Temperature ° R
- Station #3: Orifice ΔH@ Determination
  - Temperature ° R

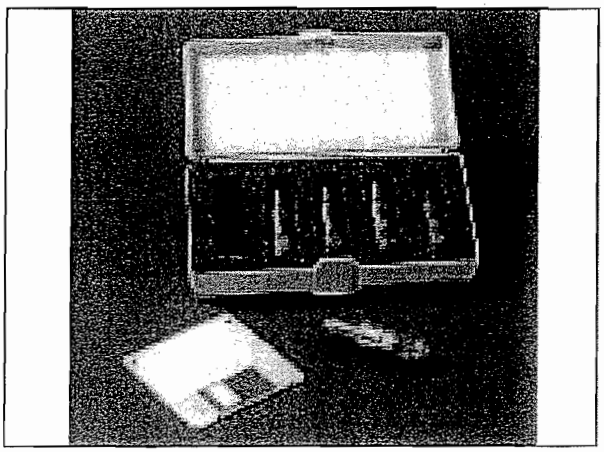
Meter Box

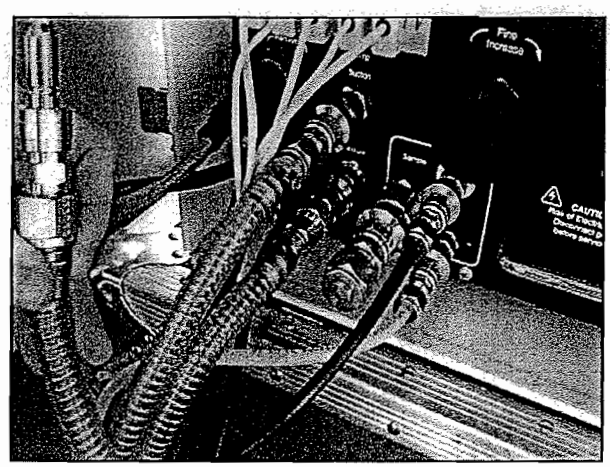


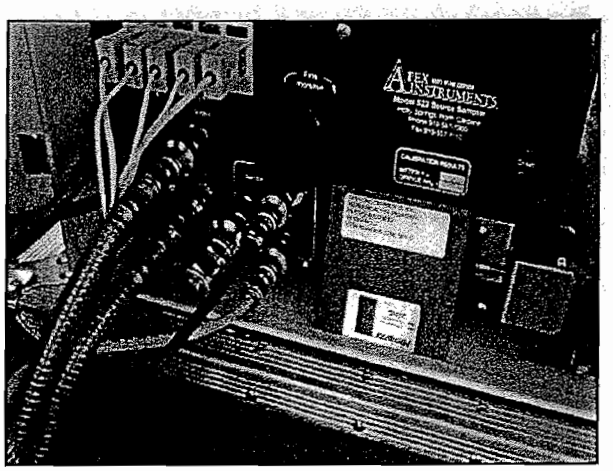






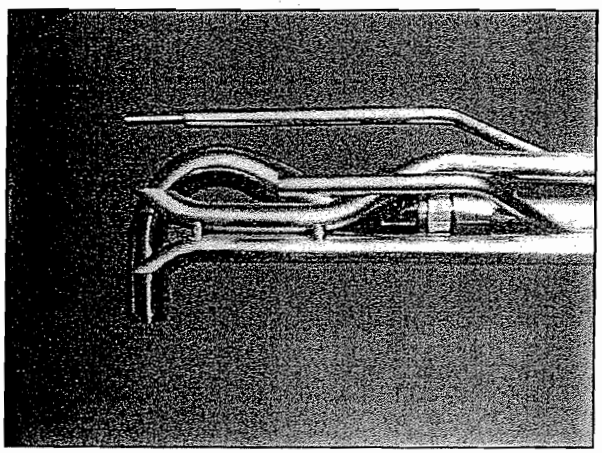


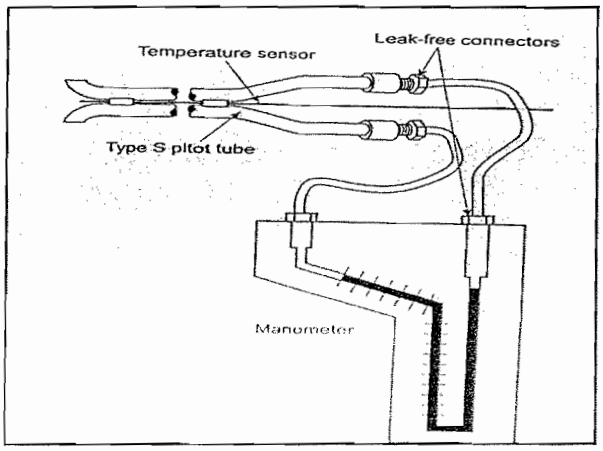




Classroom Stations

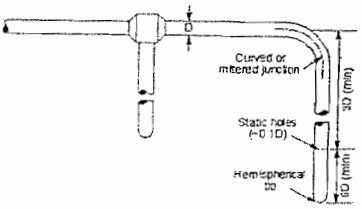
- Station #4: Stack Gas Velocity and Volumetric Flow Rate
  - Assume Traverse Points from Station # 10
  - Assume Bws = 3 %, Md = 30, Ts = 75°F
- Station #5: Pitot Tube Calibration
  - Sample point is 6 inches into duct



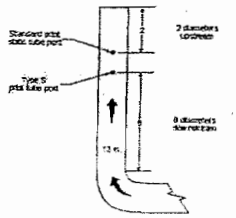


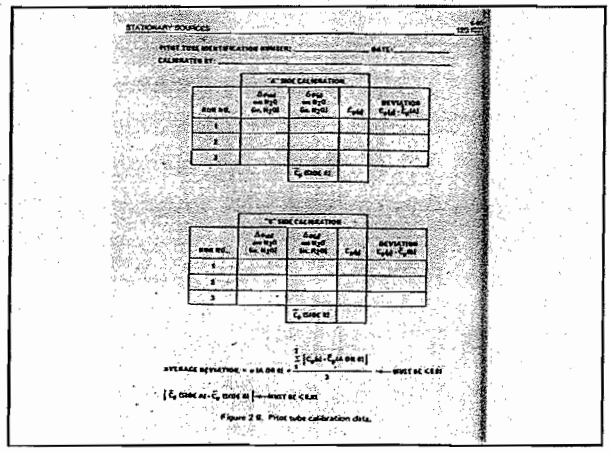
Pitot Tube Calibration

Calibrate in wind tunnel against standard pitot tube



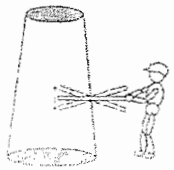
Calibration Duct

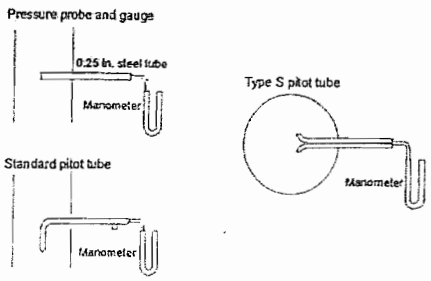




$$C_{p(s)} = \left[\frac{\Delta p_{std}}{\Delta p_s}\right]^{1/2} C_{p(std)}$$

Careful of Pitch Angle





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

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

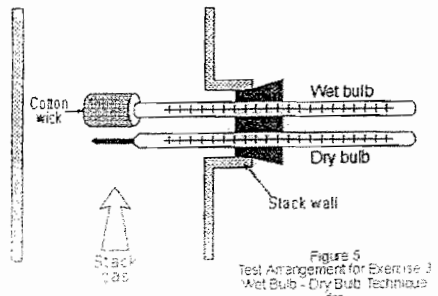
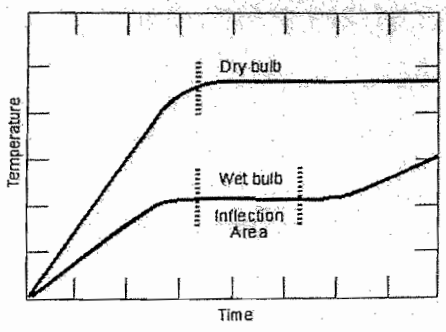
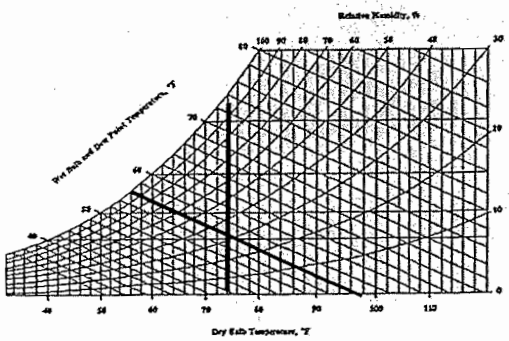


Figure 5
Test Arrangement for Exercise 3
Wet Bulb - Dry Bulb Technique
for
Moisture Measurement

Wet Bulb – Dry Bulb Method

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





Moisture Equation (Partial Pressure Method)

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

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

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

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

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

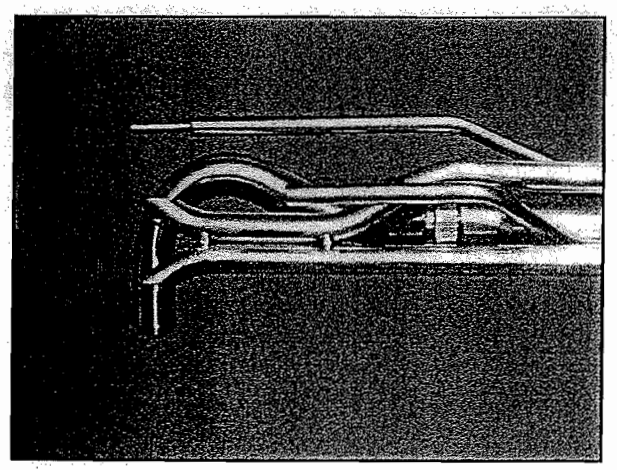
Where: B_{ws} = proportion (by volume) of water vapor in a gas mixture

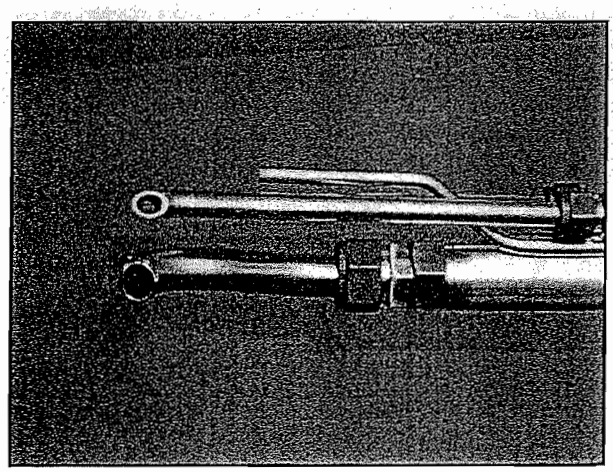
s.v.p. = saturated vapor pressure of water at average stack temperature

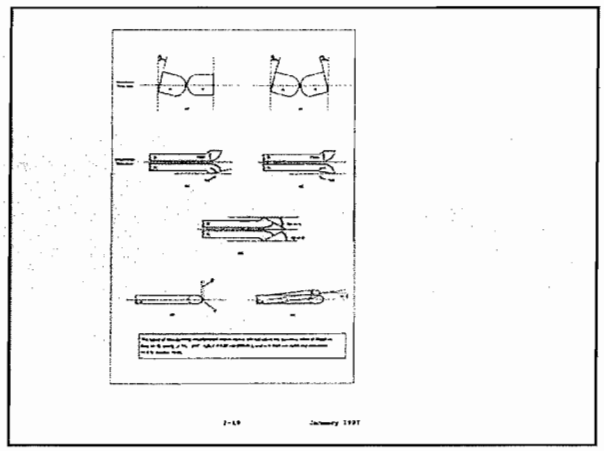
P_s = absolute pressure of the stack

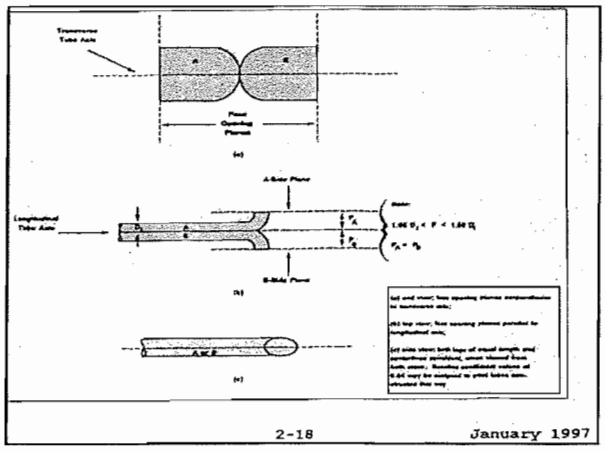
Classroom Stations

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







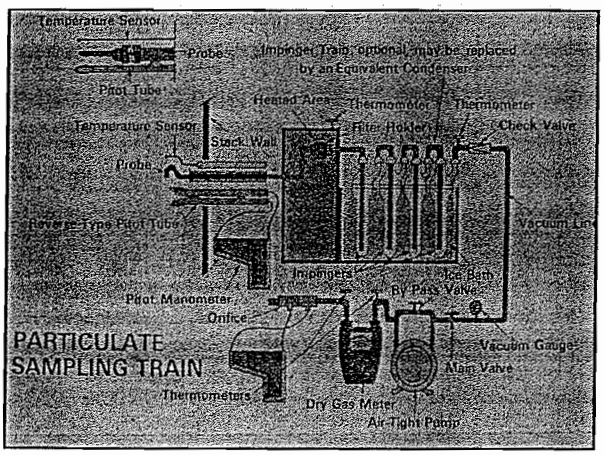


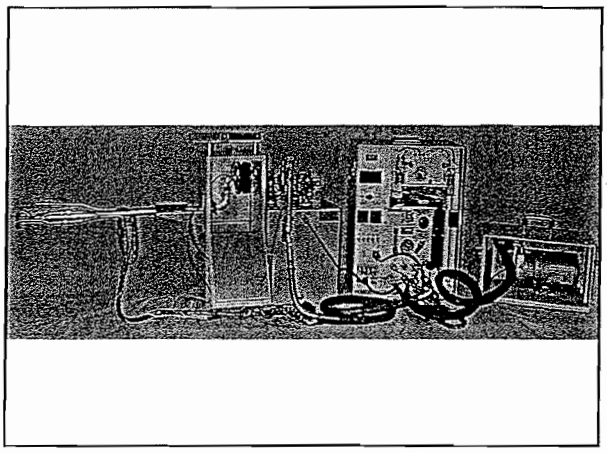
Verification of Geometry of Type S Pitot Tube To Assign 0.84

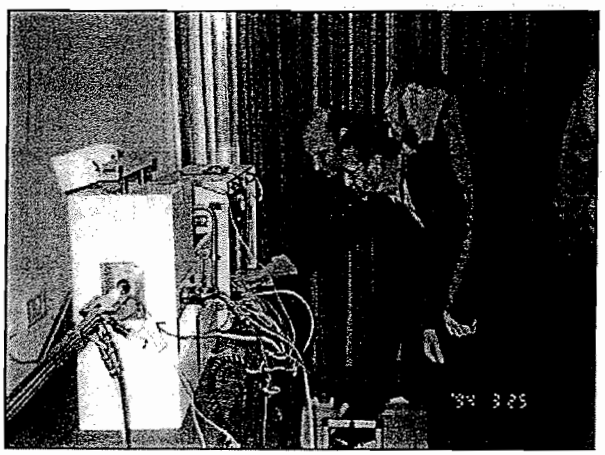
- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375

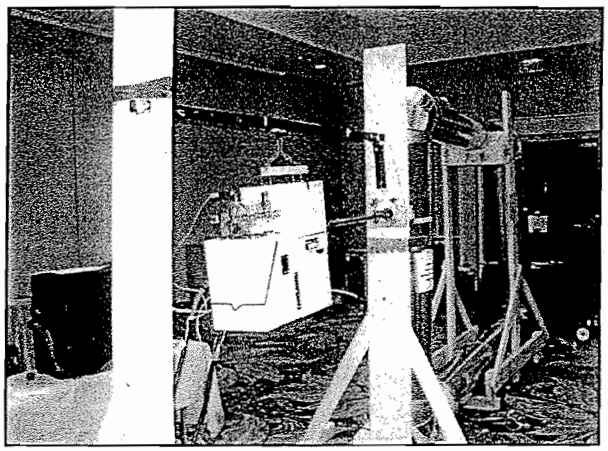
Laboratory Stations

- 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



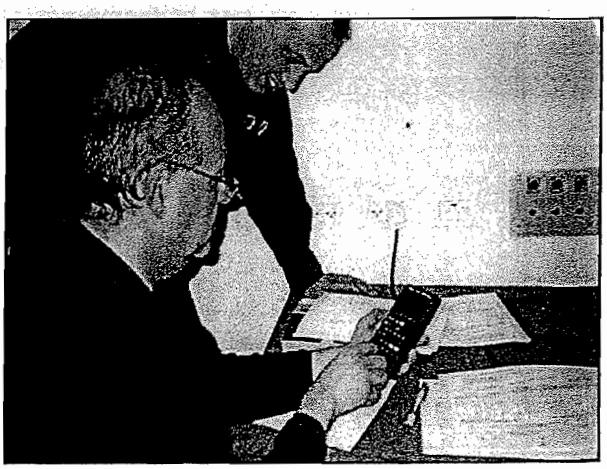






Laboratory Stations

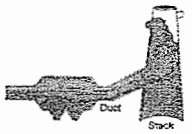
- Station # 8: Method 5 Sampling Train
  - Leak Checking with Fine/Coarse Valve
  - Leak Check to < 0.02 cfm
  - Sample Source Simulator for PM
- Station # 9: Isokinetic Rate Equation Using Isocal Spread Sheet
  - Enter all required data in "Bright Yellow Boxes"
  - Assume Bws of 5 %
- Station # 10: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



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

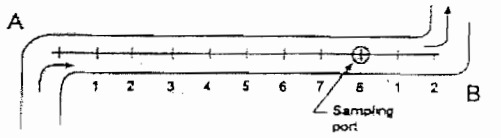
Determine the Number and location of sampling points



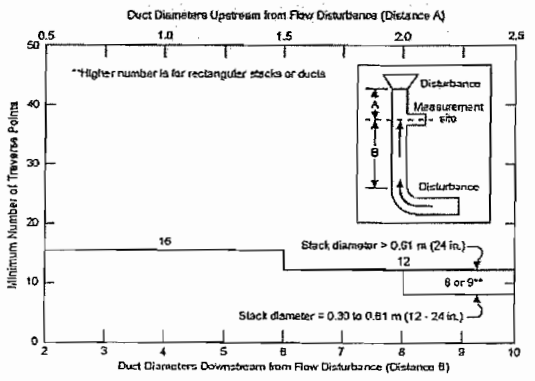
1 ft diameter duct

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

Ideal Siting Criteria



Port is downstream of A
Port is upstream of B



QUESTION?

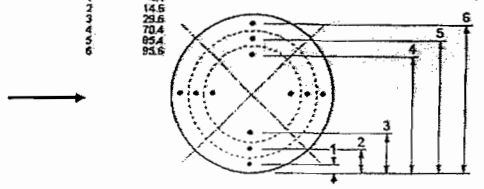
- How many points need to be sampled ?

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

40 CFR Ch. 1 (7-1-89 Edition)

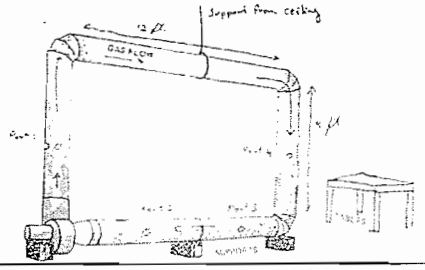


Traverse Point Location

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	26.0	20.1	16.9	14.8	12.9	11.6	10.5
6			95.6	80.6	65.8	26.9	20.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.9	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.9	25.9	21.8	19.4
9					91.8	82.3	72.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	78.9	71.7	61.8	39.8	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	79.0	73.0	67.7
15								95.1	89.1	83.5	78.0	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	86.4	80.5
18									98.5	93.3	90.4	83.9
19										96.1	91.3	86.9
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.

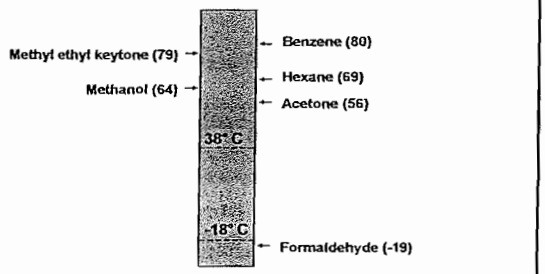
Historical Definition of VOCs

- 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)

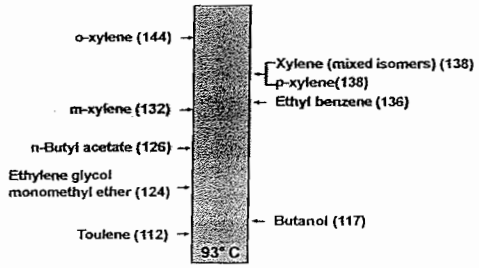
General Classification of VOCs

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

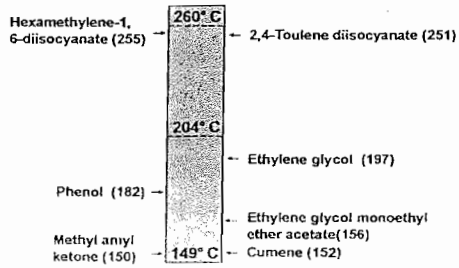
Boiling Points of Volatile Organic Compounds



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 °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

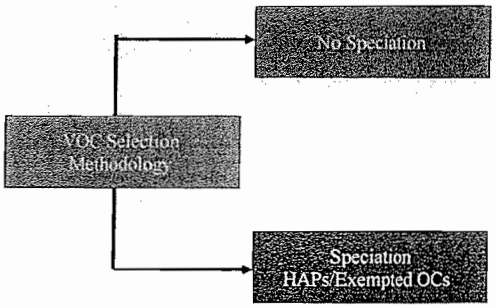
FRM	Conc. Range
FRM 25 B	0.5-10 %
FRM 25	50 ppm-10 %
FRM 18	1 ppm – 1 %
FRM 25 A	50 ppm – 1 %
Method 25.3 (CTM 035)	< 1 ppm

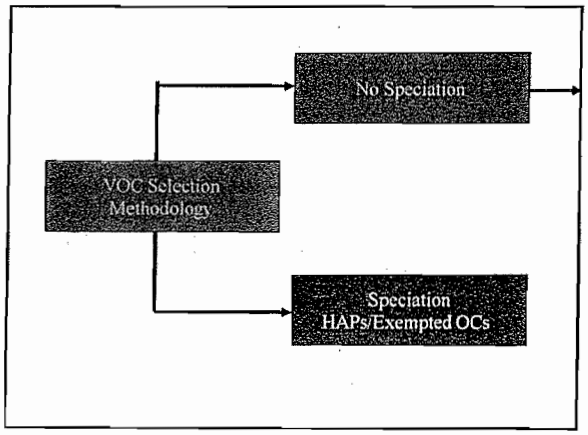
Applicability of Methods

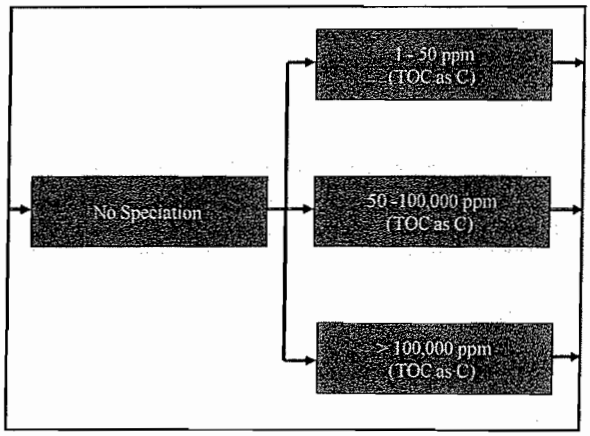
	FRM 18	FRM 25	FRM 25A
Measures...	VOCs	TGNMO	THC
Principle...	GC/MD	GC/FID	FID
Carbon Resp...	1:1	1:1	Var.
Results Exp As..	VOC	As C	Cal Gas

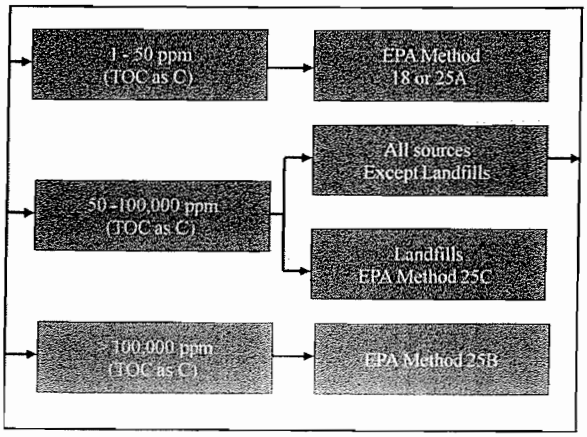
Applicability of Methods

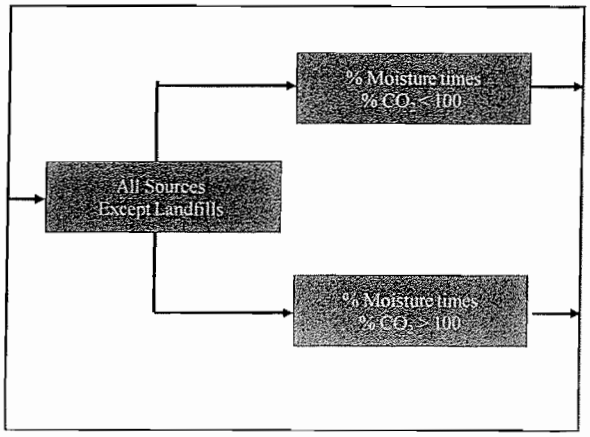
Nature of Emission	Report Emission As	Affected Facility
VOCs unknown/variable	Propane	Asphalt Plants Cement Plants Resource Rec
Single VOC > 75 %	That single VOC	Bakeries SOCMI
Single VOC < 75 %	Surrogate	Surface Coat Graphite Art

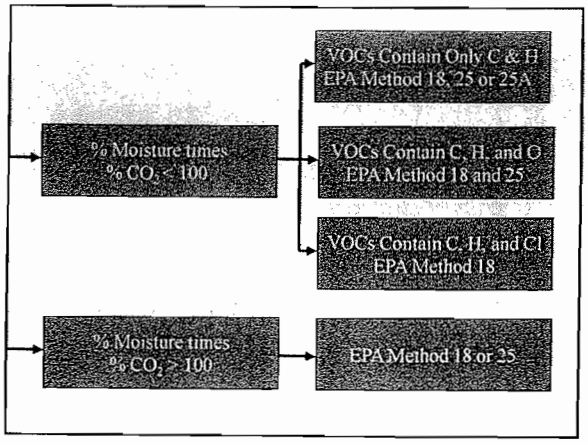


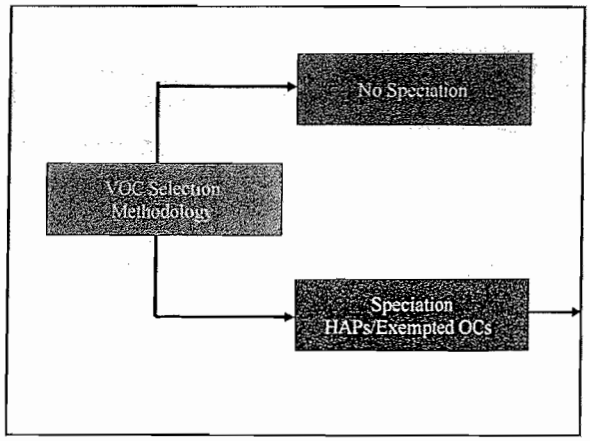

No Speciation
VOC Selection Methodology
Speciation HAPs/Exempted OCs

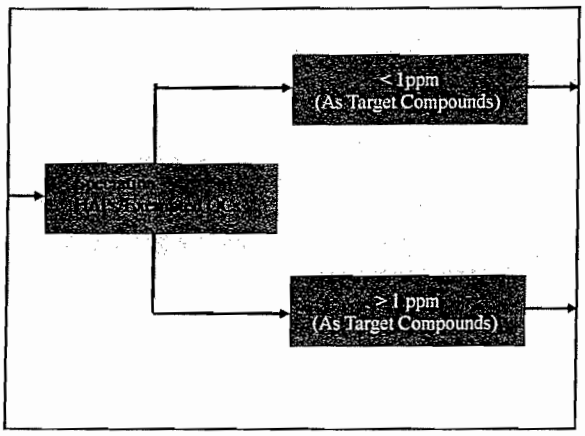

1 - 50 ppm (TOC as C)
No Speciation
50 -100,000 ppm (TOC as C)
> 100,000 ppm (TOC as C)

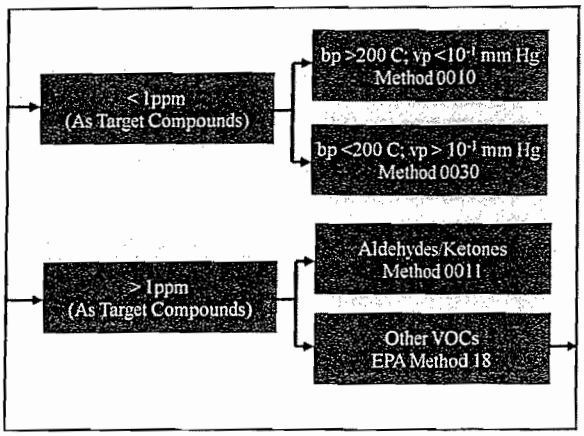

1 - 50 ppm (TOC as C)
EPA Method 18 or 25A
All sources Except Landfills
50 -100,000 ppm (TOC as C)
Landfills EPA Method 25C
> 100,000 ppm (TOC as C)
EPA Method 25B

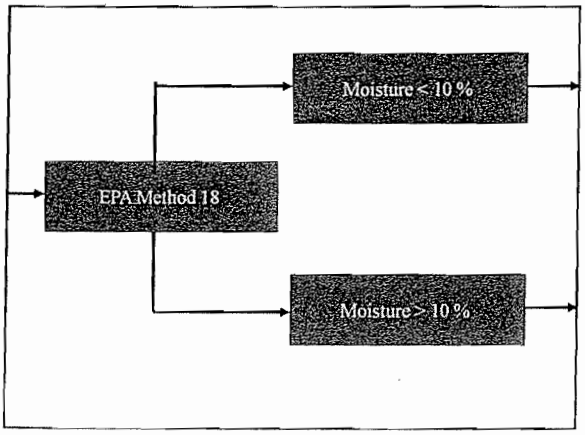

% Moisture times % CO_2 < 100
All Sources Except Landfills
% Moisture times % CO_2 > 100

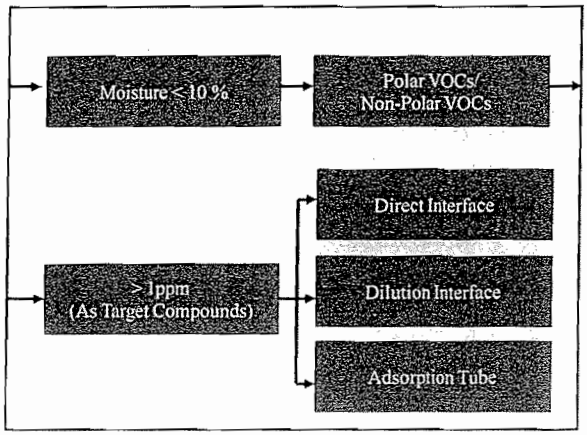

VOCs Contain Only C & H EPA Method 18, 25 or 25A
% Moisture times % CO_2 < 100
VOCs Contain C, H, and O EPA Method 18 and 25
VOCs Contain C, H, and Cl EPA Method 18
% Moisture times % CO_2 > 100
EPA Method 18 or 25

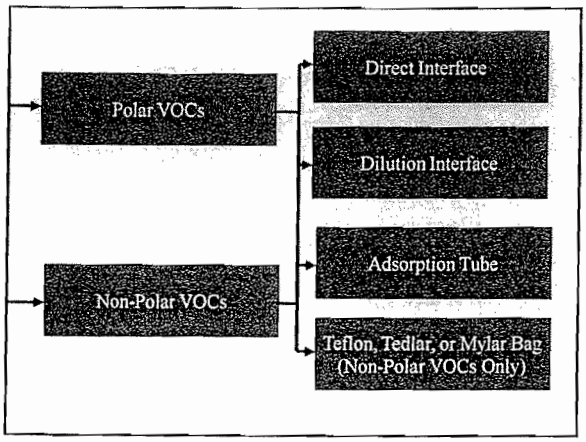

No Speciation
VOC Selection Methodology
Speciation HAPs/Exempted OCs











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 nonmethane 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…

$$\left(\frac{\text{ppmvw as } C_3H_8}{(1-B_{ws})}\right)\left(K_{mw}\right)\left(MW_c\right)\left(Q_{sd}\right)\left\{\frac{MW_{C_xH_yO_z}}{\left(\#C\text{ atoms}_{C_xH_yO_z}\right)\left(MW_c\right)}\right\}\left\{\frac{RRF_{C_xH_yO_z}}{RRF_{C_3H_8}}\right\} = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

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

$$385.3\times10^{6}$$

Reporting of Emissions

Example Calculation 2

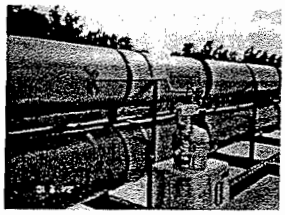
Calculating the VOC mass emission rate from a source emitting mostly ethanol (C_2H_5OH) using EPA Method 25 data in terms of carbon…

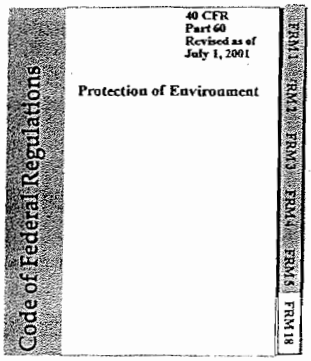
$$\left(\frac{\text{ppmvw as C}}{(1-B_{ws})}\right)\left(MW_c\right)\left(Q_{sd}\right)\left\{\frac{MW_{C_xH_yO_z}}{\left(\#C\text{ atoms}_{C_xH_yO_z}\right)\left(MW_c\right)}\right\} = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

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

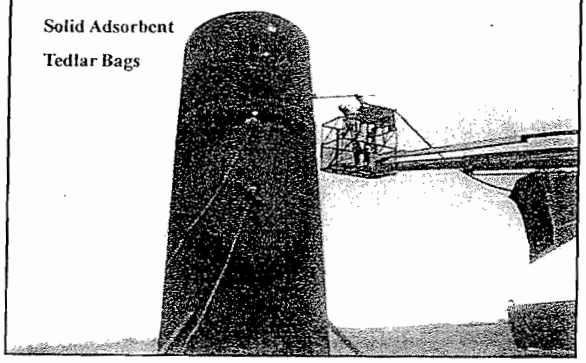
$$385.3\times10^{6}$$

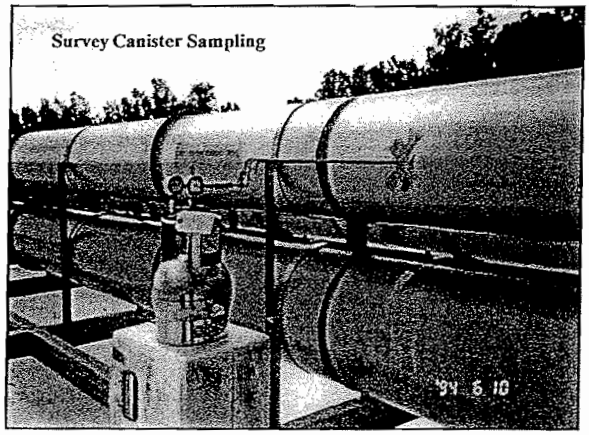
U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 18





Direct Interface
Direct Interface/Dilution
Solid Adsorbent
Tedlar Bags





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

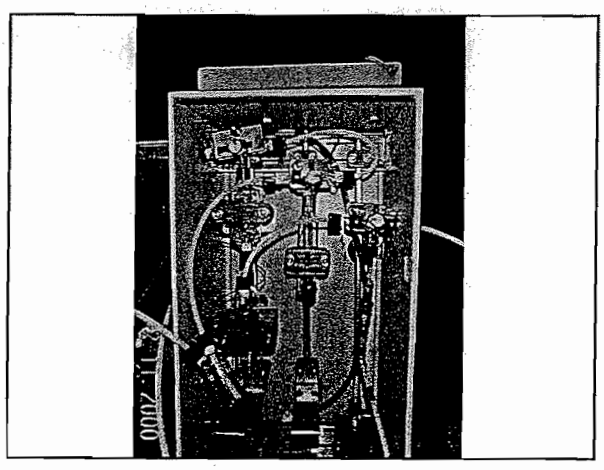
- Pre-survey samples collected in Tedlar® or aluminized Mylar flexible bags
- Flexible bag certification
  - Use new bag
  - Leak check all bags

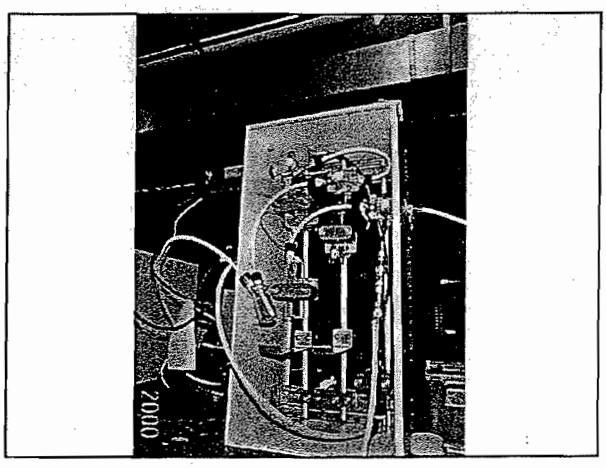
Flexible Bag Sampling Procedure

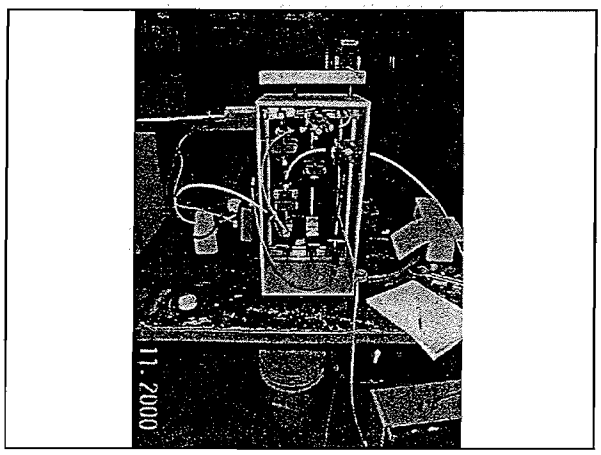
- Check for contamination by filling with nitrogen
- Analyze 24 hours later with GC

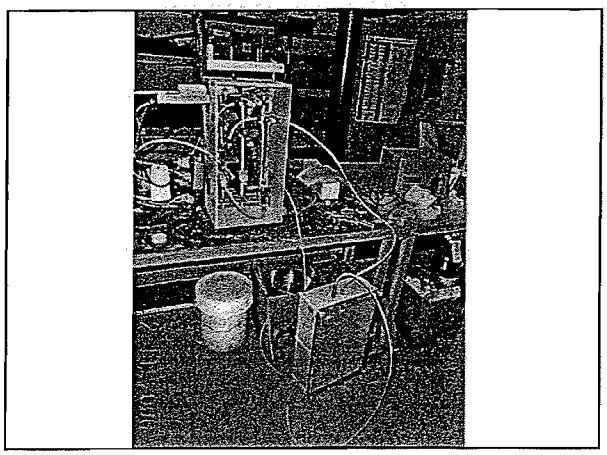
Bag Sampling

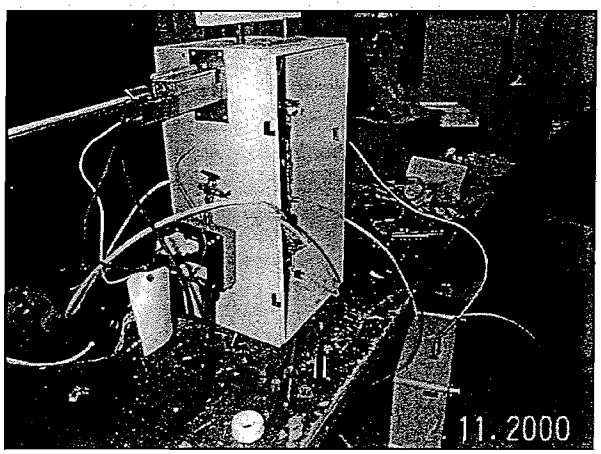
- Assemble sampling train
- Leak check both the bag and container
- Place probe > 1 meter from inside wall
- Purge probe line
- Evacuate container containing flexible bag





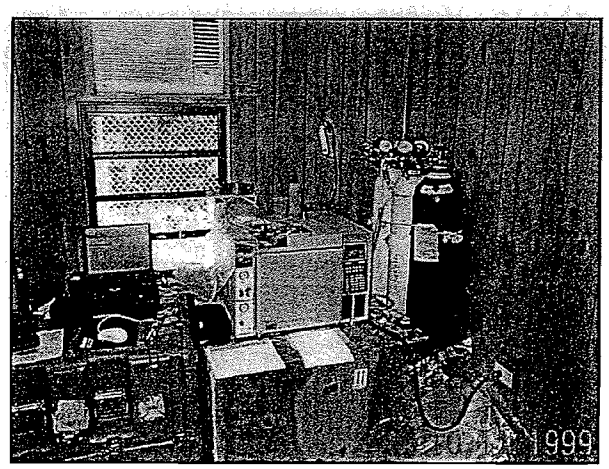






Bag Sampling

- 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



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

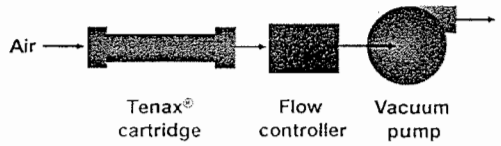
Adsorbent Recovery Solvent Extraction

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

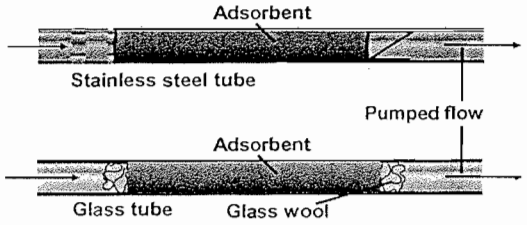
Adsorbent Tube Sampling Train

- 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

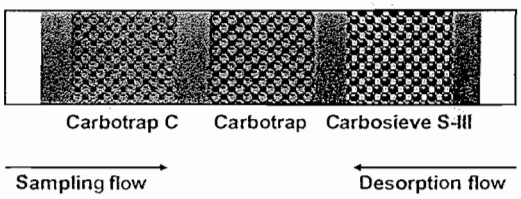
Active Sampling System Utilizing Solid Adsorbents

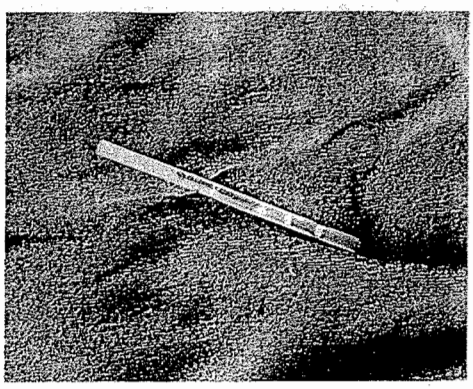


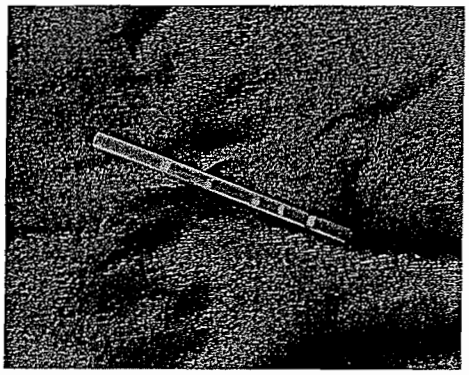
Single Tube Design- Glass/Stainless Steel

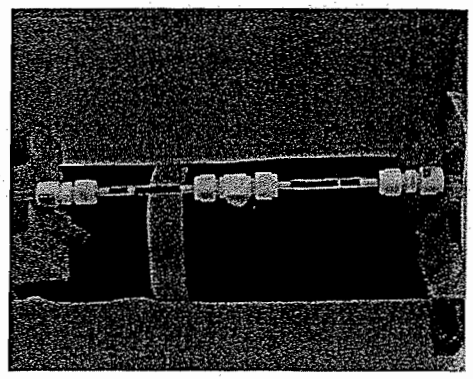


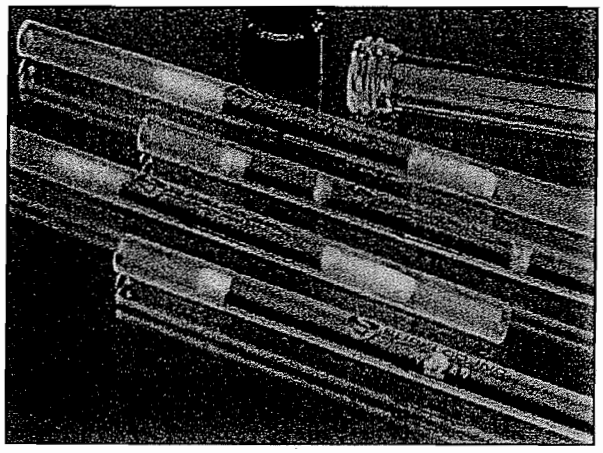
Multi-bed Adsorbent Trap











Adsorbent Tube Sampling

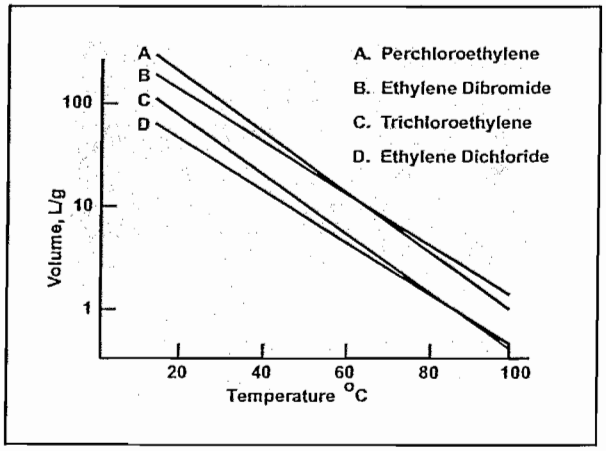
- Strengths
  - Sample compact and easy to use
  - Sample returned to laboratory for analysis
  - Good sample storage time

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



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

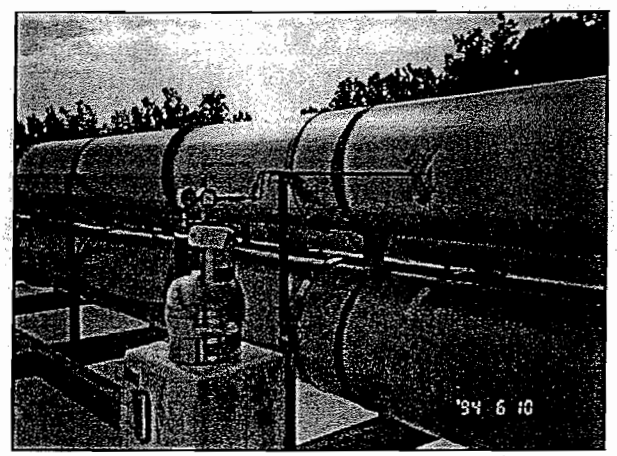
- Only place where canister sampling is allowed
- Typically grab sample, qualitative analysis, GC/MS for identification
- Canisters can be used during pre-survey

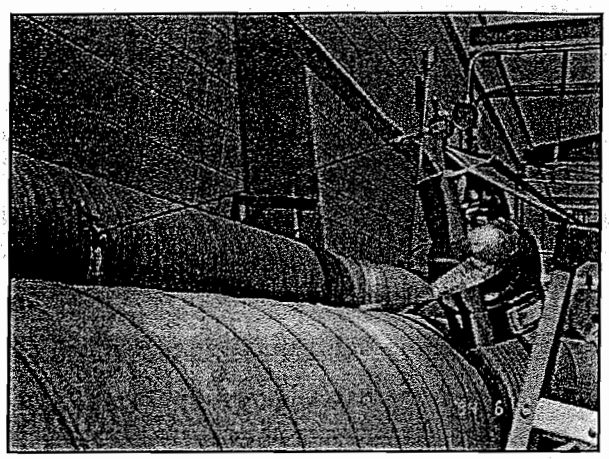
FRM 18 Pre-survey Requirements

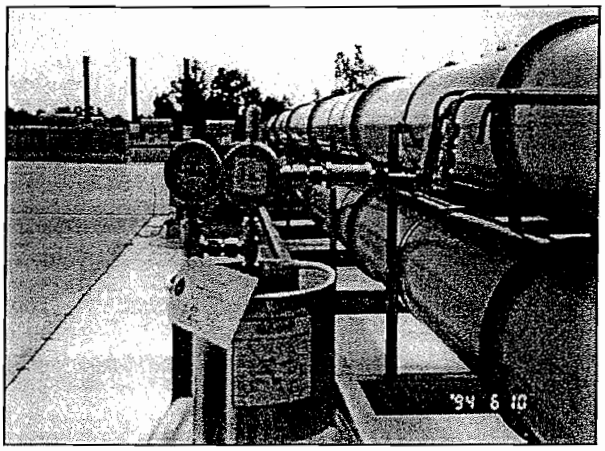
- Obtain stack temperature and temperature range
- Obtain approximate particulate concentration
- Obtain static pressure and water vapor content

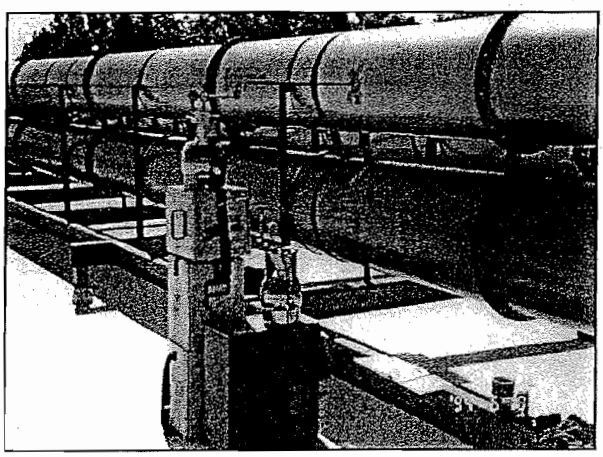
FRM 18 Pre-survey
Sample Train Selection

- 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









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

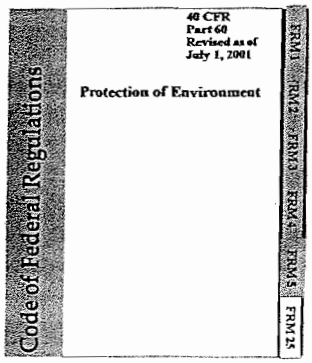
FRM 18 Summary

- 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



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

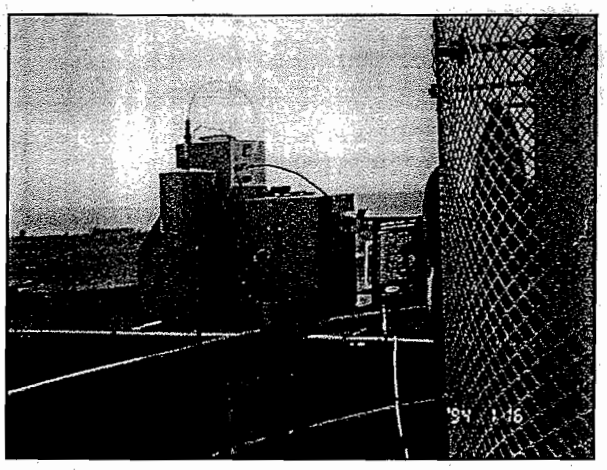
- Concerns
  - Not applicable for measuring emissions from sources whose principle solvents are chlorinated hydrocarbons
  - Generally, for any situation where a more simpler procedure is more accurate
  - High organic droplets in gas stream can cause high bias or data variability

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



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

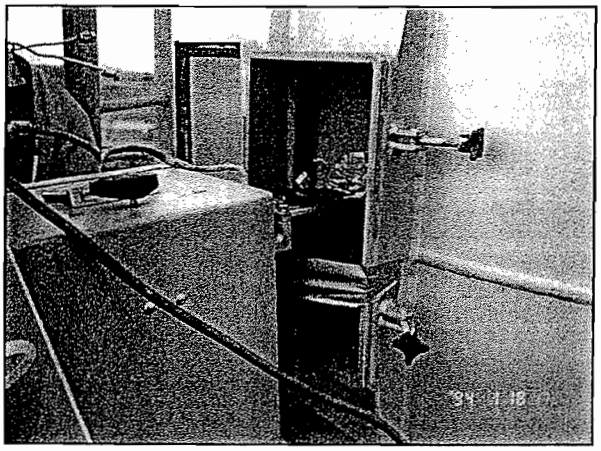
- Withdraw emission sample from stack through chilled condensate trap (dry ice) into evacuated cylinder
- Analyze contents of trap and cylinder separately
- Oxidize organic content of trap to CO_2
- Reduce to methane, measure with FID

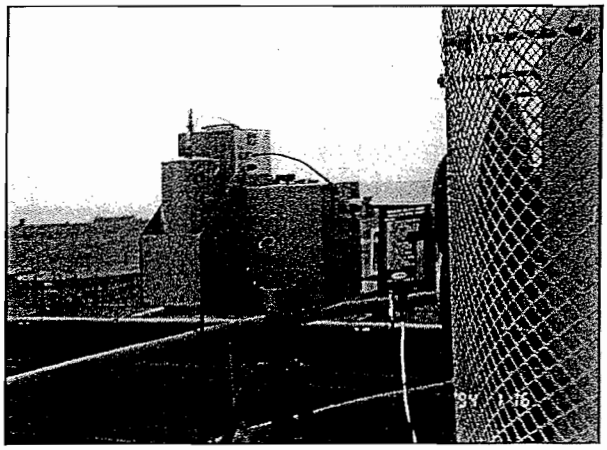
Method 25 Summary

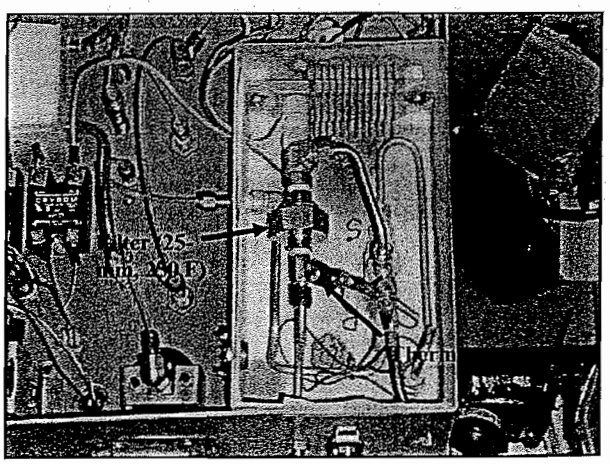
- Inject portion of cylinder sample into GC to separate non-methane organics, oxidize NMO to CO_2, reduce to methane, and measure with FID
- Combine results (condensable and non-condensable) and report as total gaseous nonmethane organics (TGNMO)

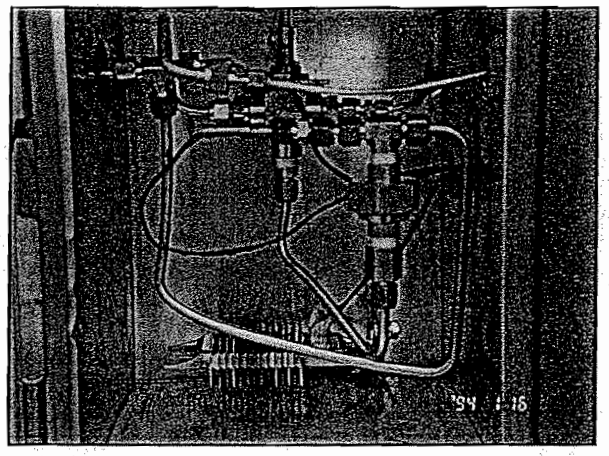
Method 25 Apparatus

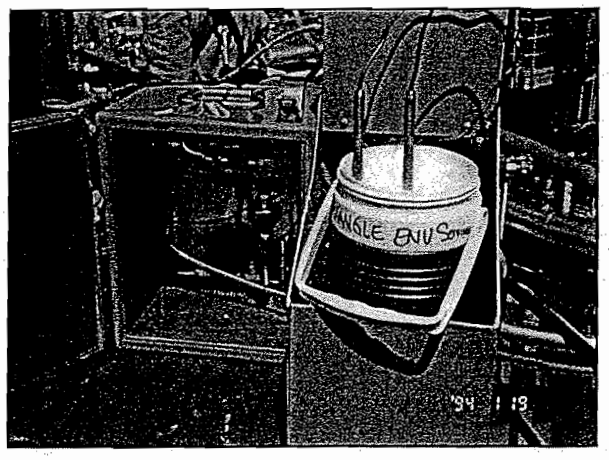
- Sampling System
  - Probe (260 °C)
  - Filter (250 °C +/- 5 °C)
  - Condensate trap (-78 °C) for condensables
  - Flow control system
  - Sample tank for non-condensables







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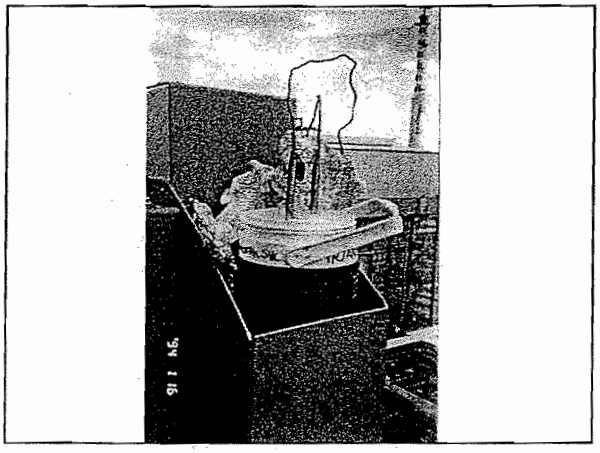

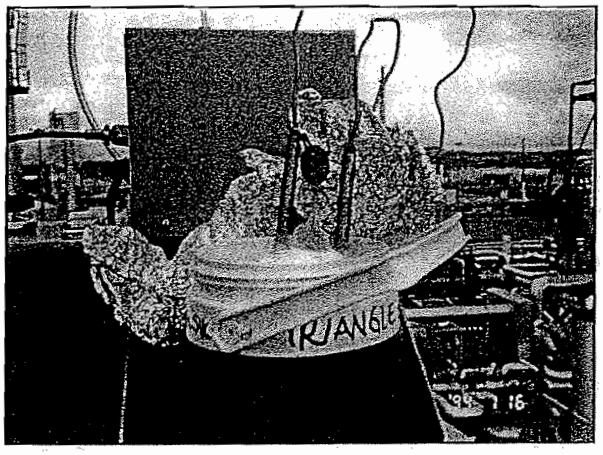
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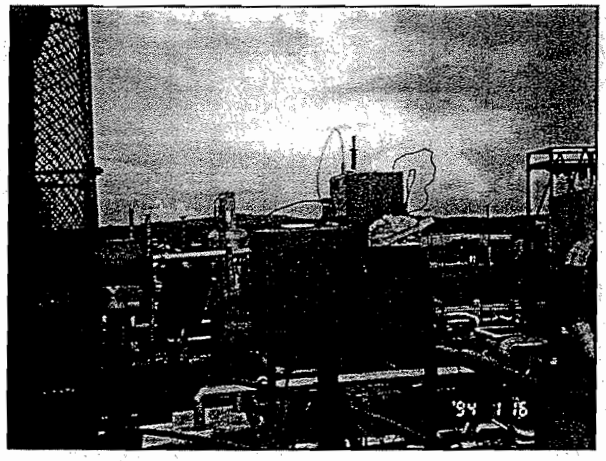
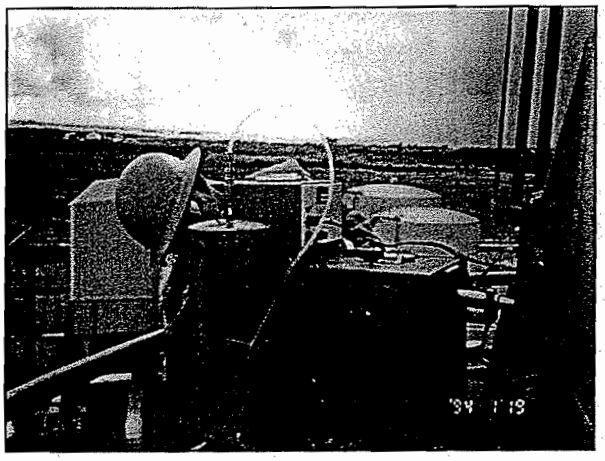
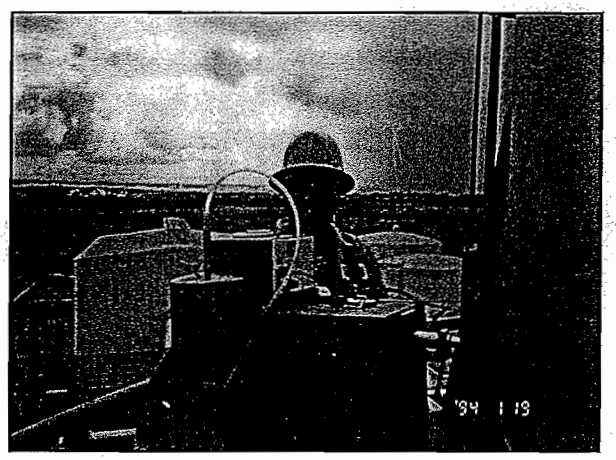
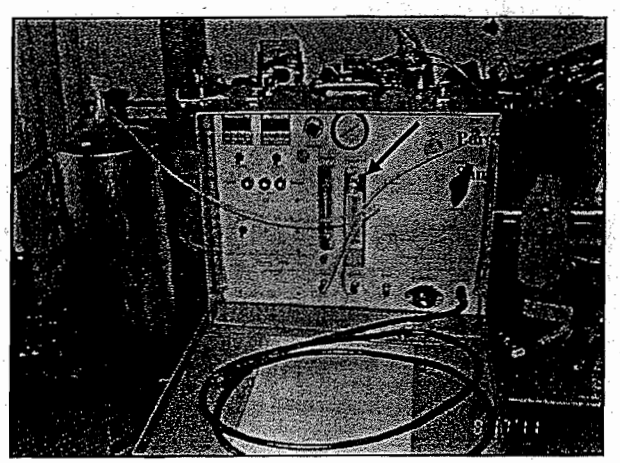
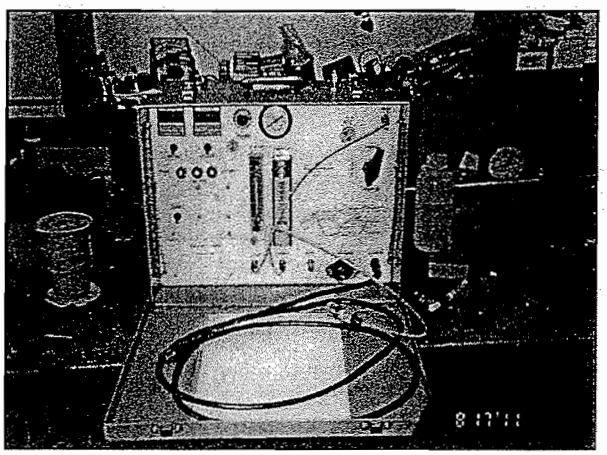
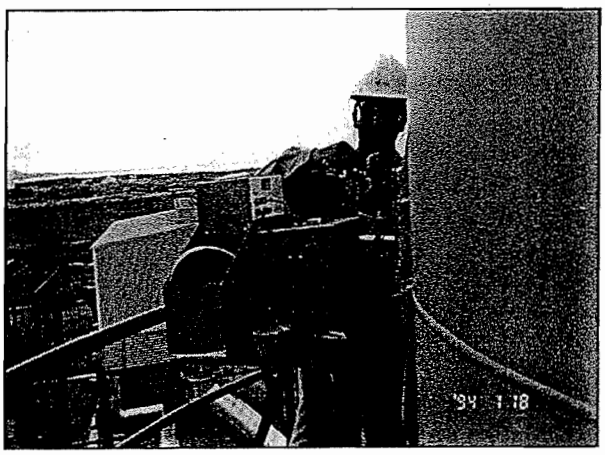


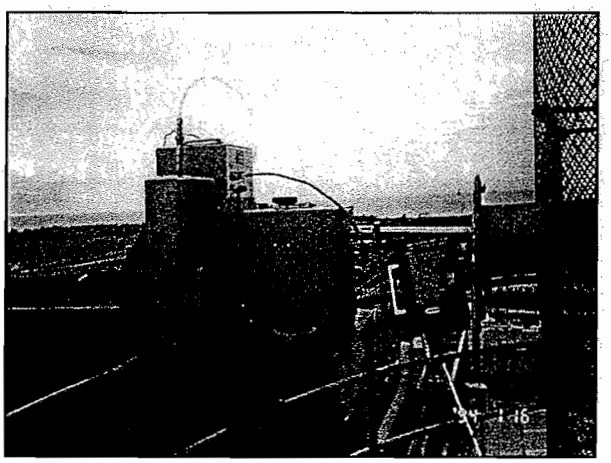


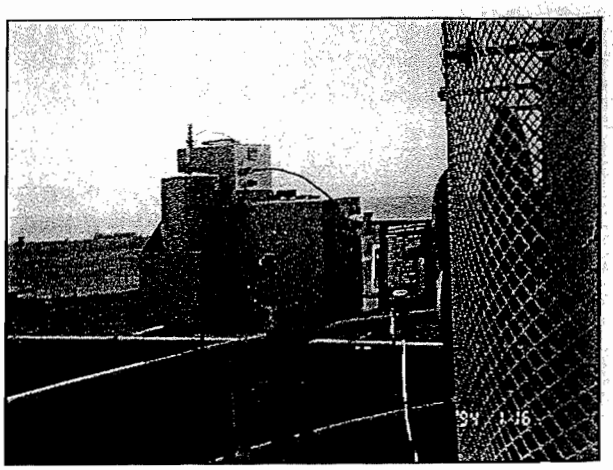












Calibration of Sampling System

- 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

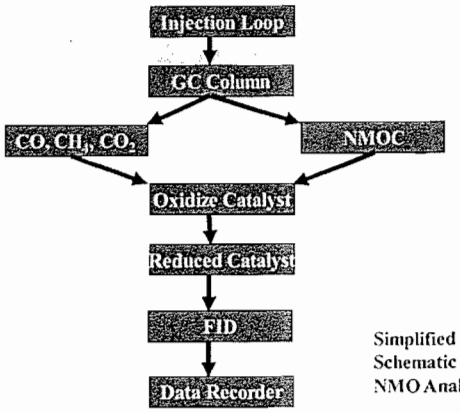
- Attach trap to sampling train
- Position probe tip perpendicular to stack gas flow (Take plug off end)
- Purge sampling train, then adjust flow rate

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

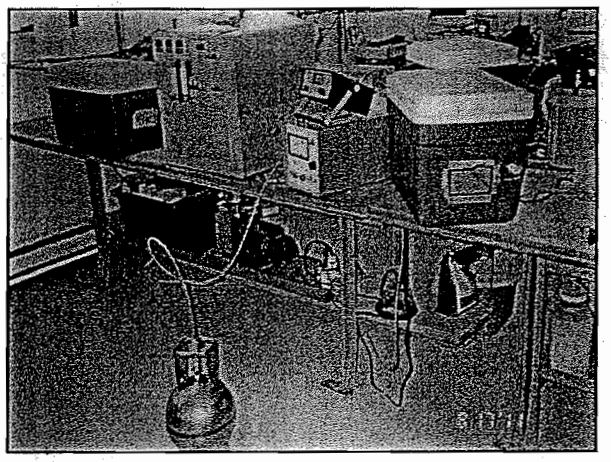
- Non Condensables
  - The non-condensables sample in the original field sample tank (#1) is injected into the analyzer
  - Methane, CO, CO_2, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO_2, reduced to methane and detected with an FID

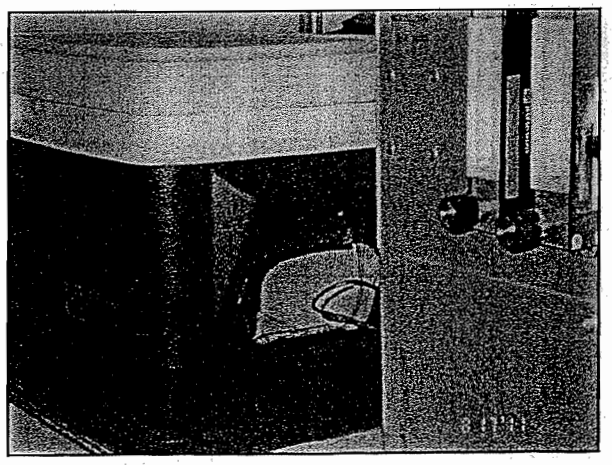
Method 25 Apparatus

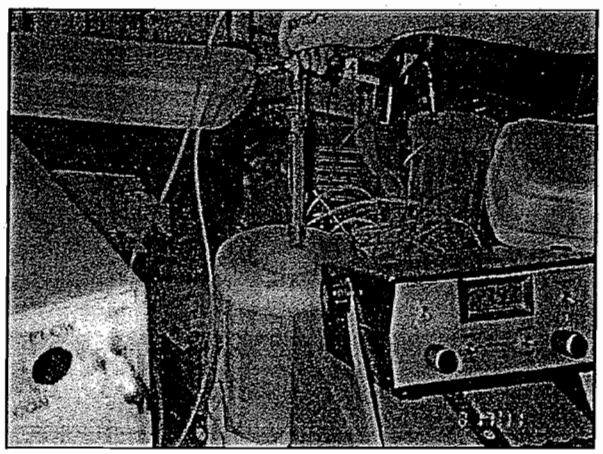
- Analytical System
  - Oxidation system for recovery and conditioning of condensate trap contents
    - Heat source
    - Oxidation catalyst (chromia@ 650 C)
    - Non-dispersive infrared analyzer (NDIR)
    - Intermediate evacuated canister (#2)

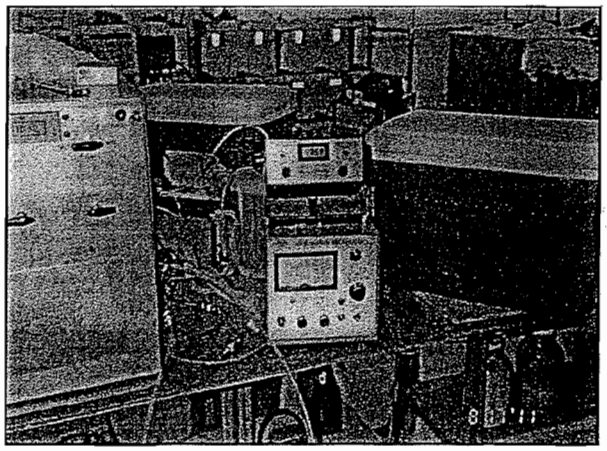
Method 25 Apparatus

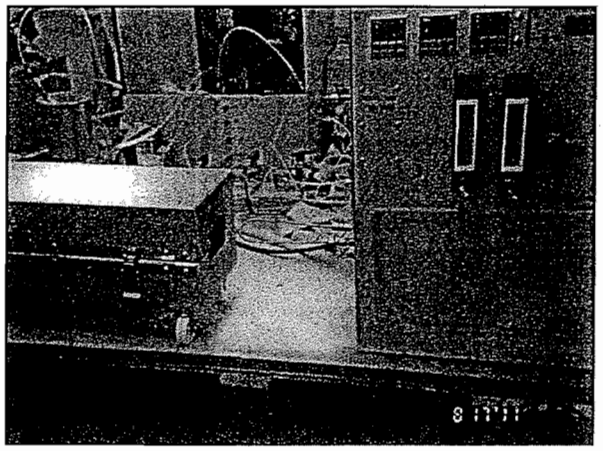
- NMO Analyzer
  - GC with back-flush capability
  - Oxidizing/reducing catalyst
    (Ni @ 400 C)
  - FID

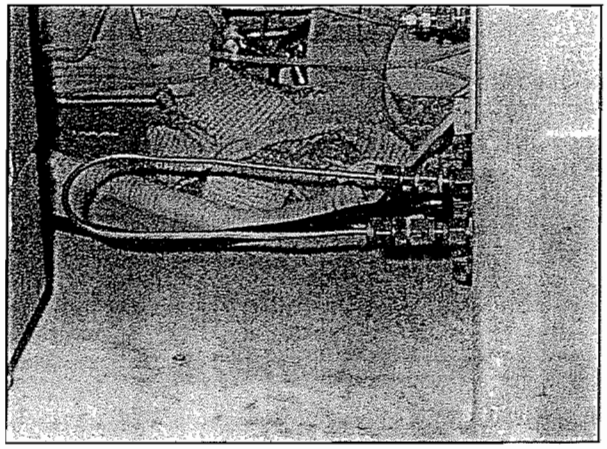


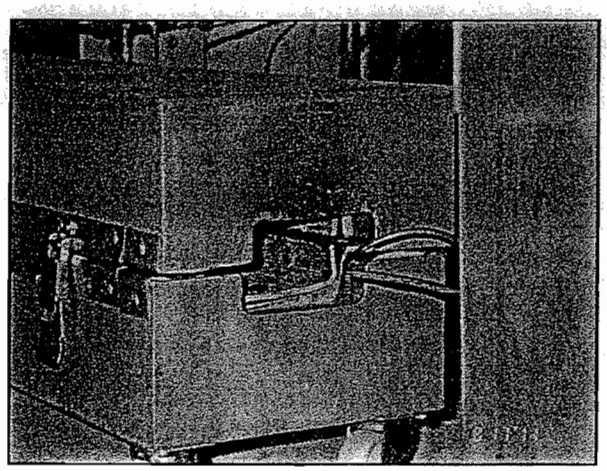


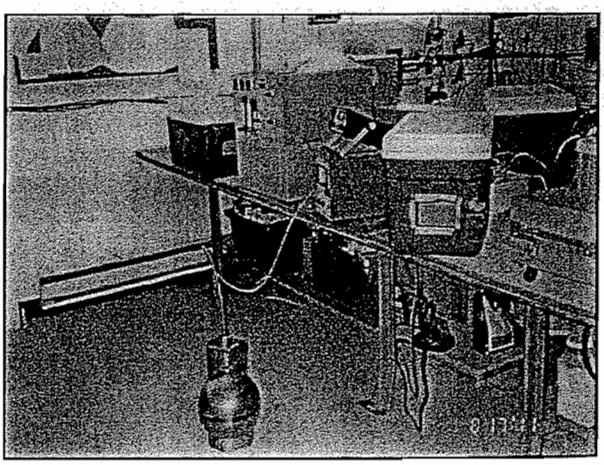


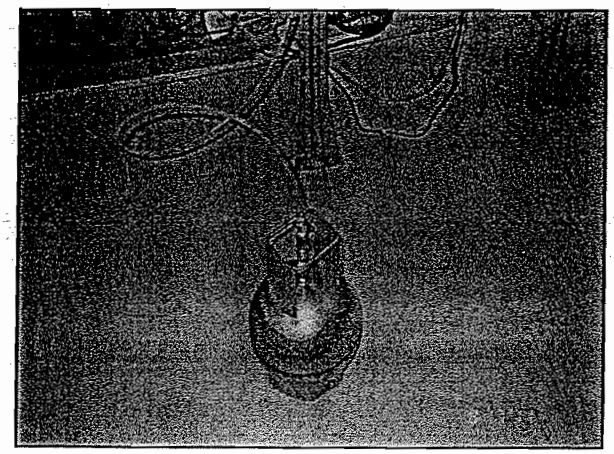


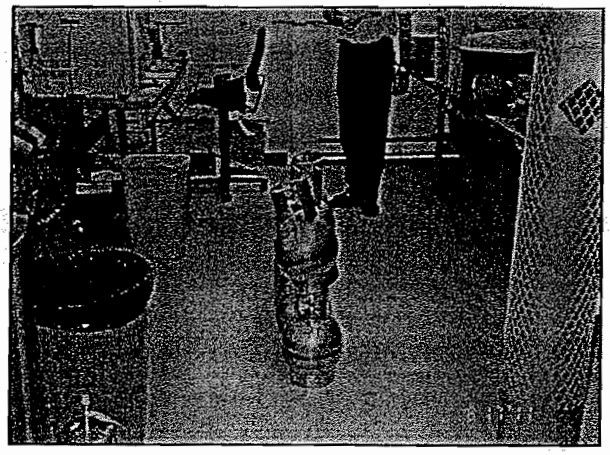


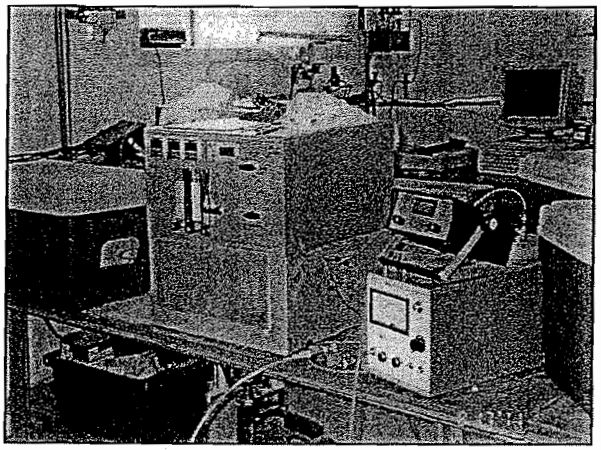












Initial Performance Check of Condensate Recovery and Conditioning Apparatus

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

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

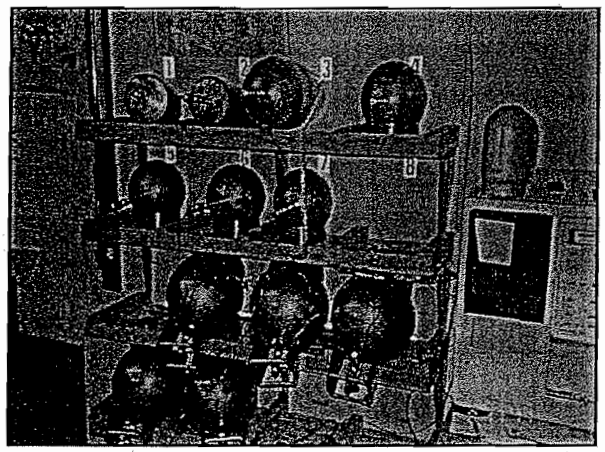
- Remove condensate trap from dry ice and allow to warm to room temperature
- Heat trap by placing it in a furnace at 200°C

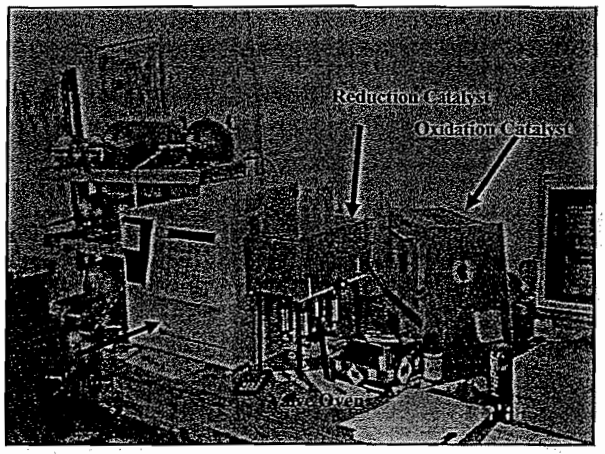
Condensable Organic Fraction Recovery

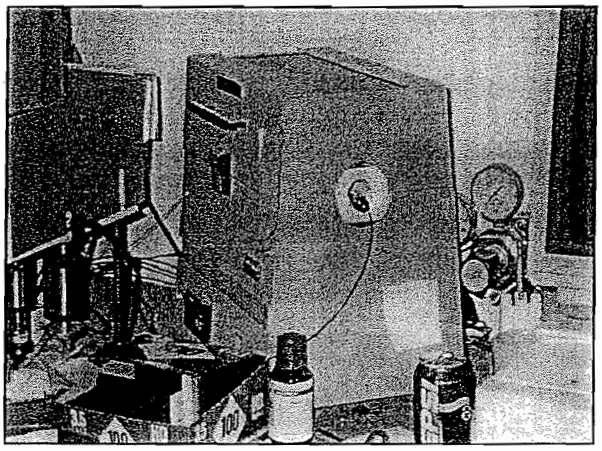
- Recovery of condensable organics
  - After NDIR analyzer indicates a CO_2 concentration of < 10,000 ppm, begin heating the tubing that connects the condensate trap to the oxidation catalyst with a heat gun

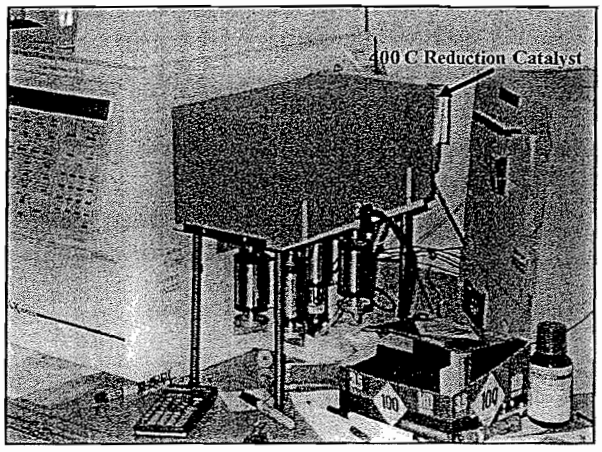
Condensable Organic Fraction Recovery

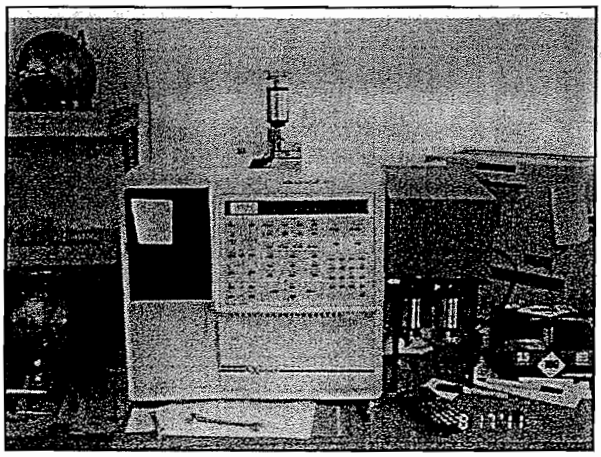
- Continue trap heating and purging until the CO_2 concentration is below 10 ppm
- Pressurize the ICV (i.e., #2) to approximately 1060 mm Hg

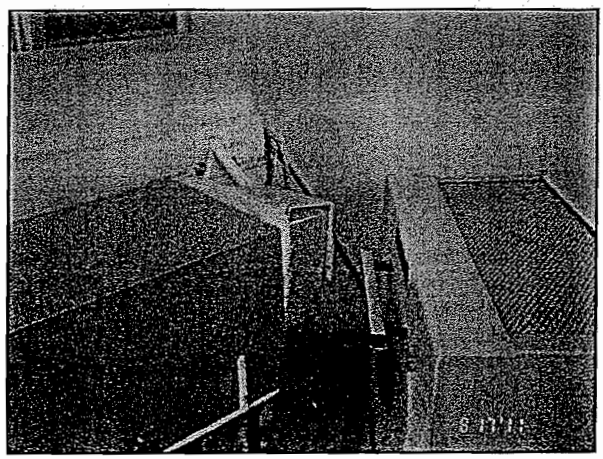


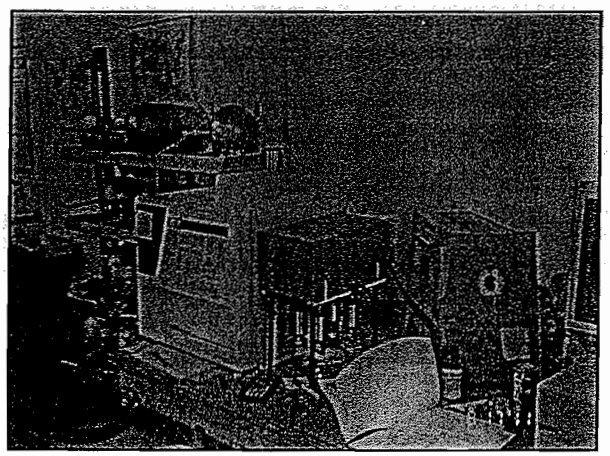

Reduction Catalyst
Oxidation Catalyst




400 C Reduction Catalyst





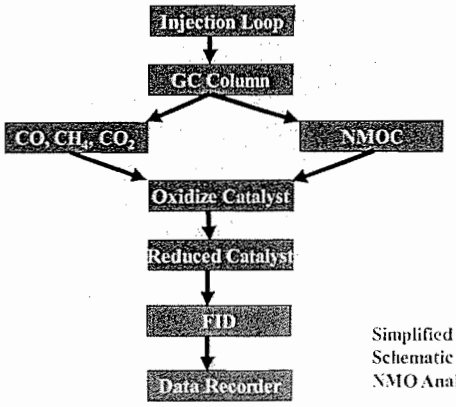


Method 25 Apparatus

- 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

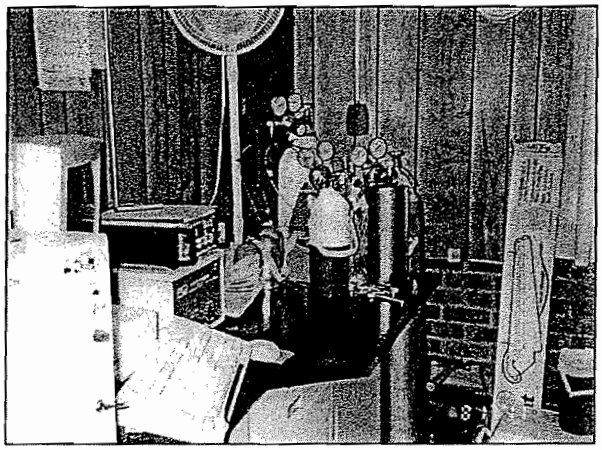
- After detection of any NMOC, return column oven temperature to 85°C
- Record the CO_2 peak area and NMO peak area
- Repeat analysis two additional times

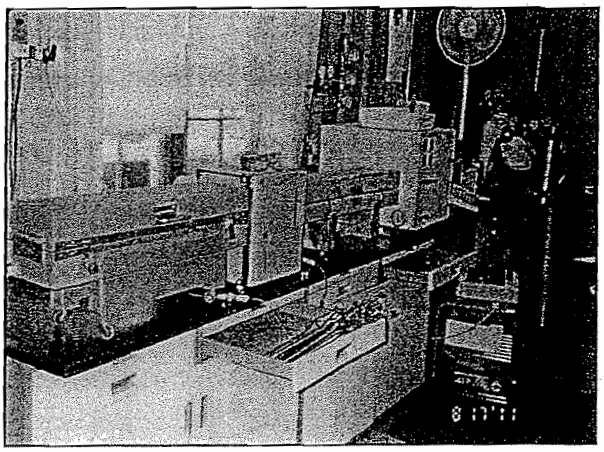
Method 25 Analysis

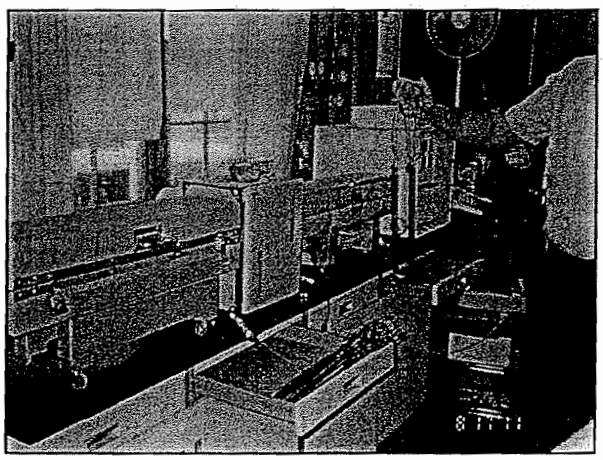
- Sample Tank (#1): Same as ICV (#2)
  - Inject triplicate samples from the sample tank and record the values obtained for nonmethane organics only
  - Perform three analyses and average the NMO values

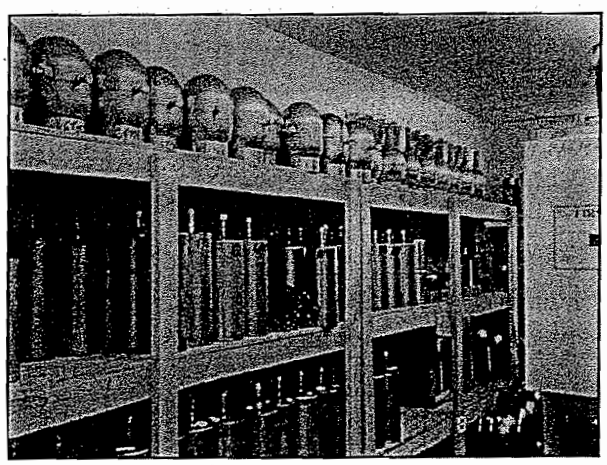
Method 25 Calculations

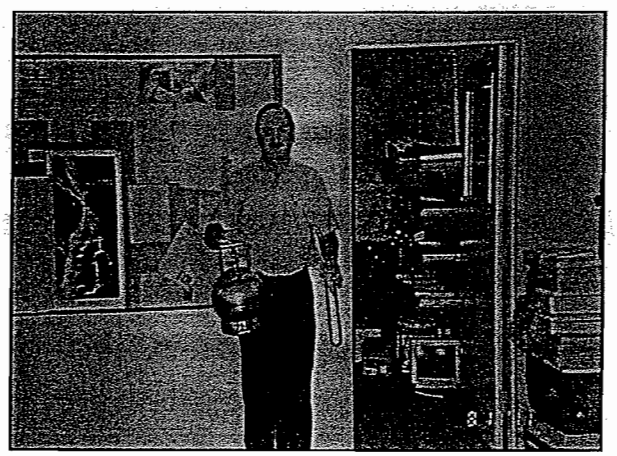
- Sample volume
- Noncondensable organics
- Condensable organics
- Total gaseous nonmethane organics
- Percent recovery
- Relative standard deviation
- EPA provides audit sample











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 <10 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

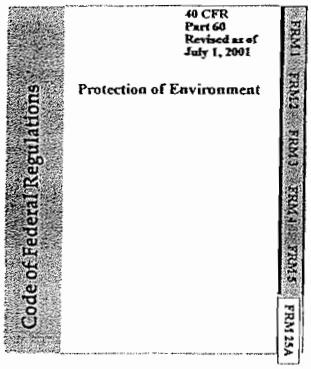
Observations

- 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

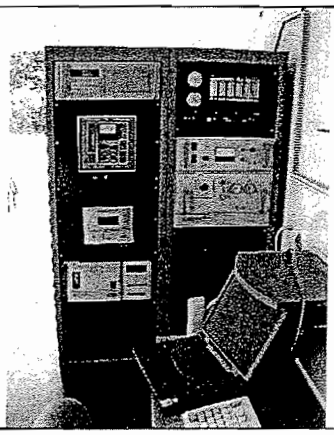
- If you are sampling a source with high moisture (> 20%) and high CO2 (>20%), then there is a real possibility that your trap will freeze at the very top of the trap.
  - Use hair dryer to unfreeze trap
  - Remove foil and let the sun melt the plug at the top of the trap
  - Add a dry water impinger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

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



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)

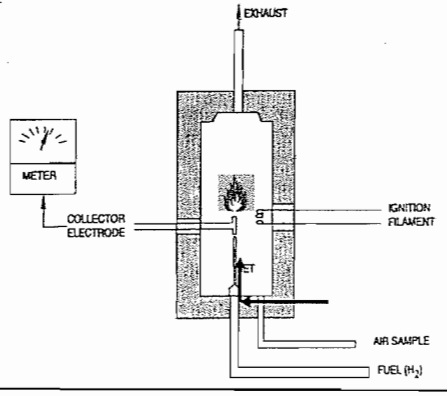
Principle

- 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

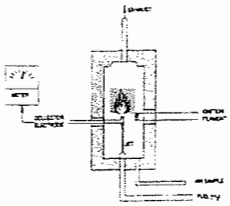
FID Theory

- 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

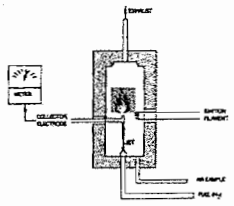


Flame Ionization Detection



- 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:

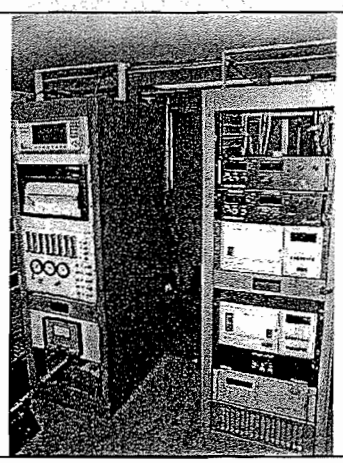
K = 1 for methane
K = 2 for ethane
K = 3 for propane
K = 4 for butane
K = Appropriate response factor for other organic calibration gases

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

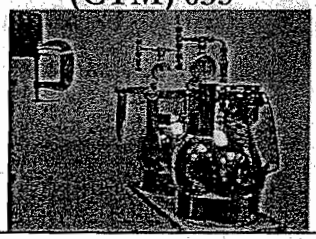
Principle

- 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

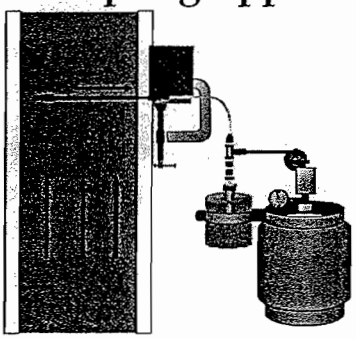
Applicability

- 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)

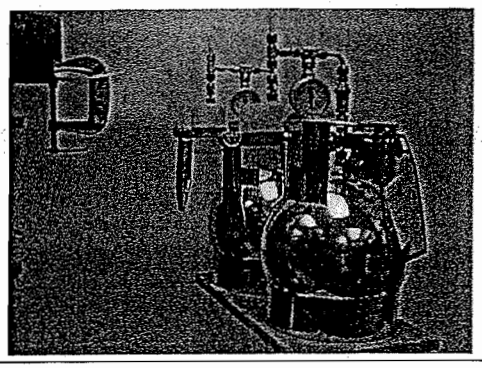
EPA's CTM-035 Sampling

- Simple self contained sampler
  - No power, no heaters, no adjustments
  - Analysis is completed off-site
- Duplicate sampling
  - Probes are placed flush with port entrance

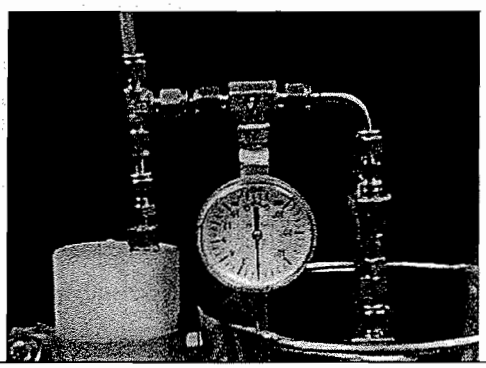
Sampling Apparatus



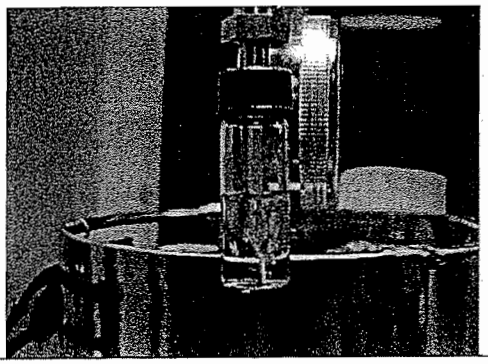
Duplicate Samplers



Trap Assembly



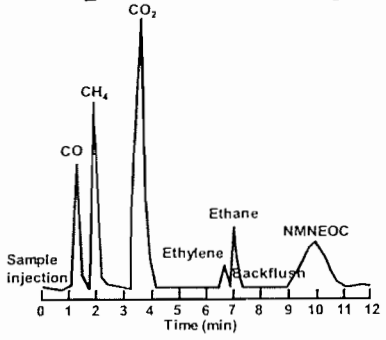
Condensate Trap

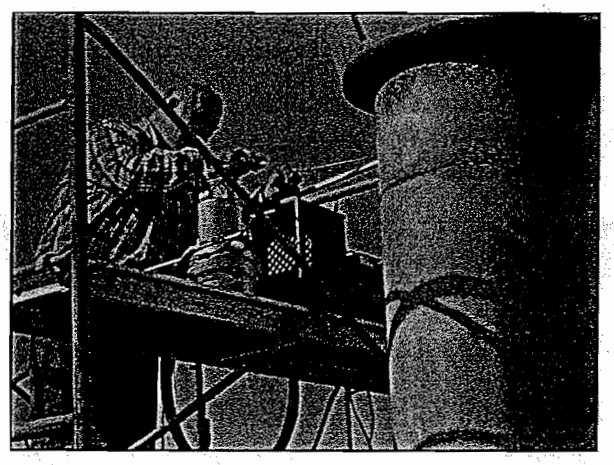


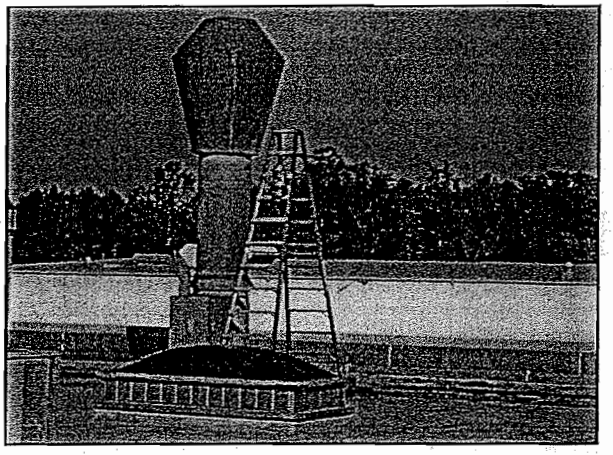
Analysis

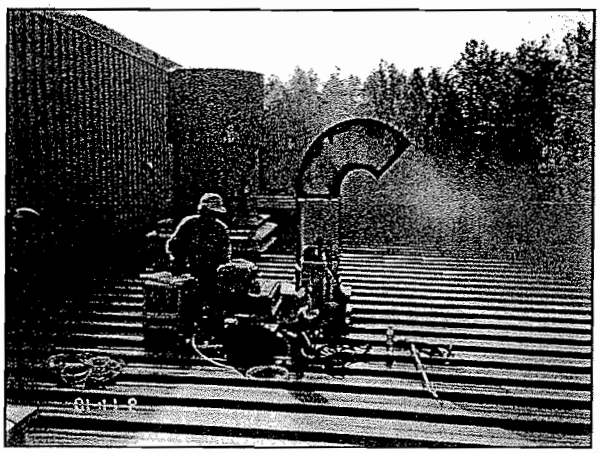
- Condensate by infrared total organic carbon analyzer
  - Lower detection limit 1 ppmC
- Canister by Method 25.1 modified for low concentration
  - GC/oxidation/reduction/FID
  - Lower detection limit 1 ppmC

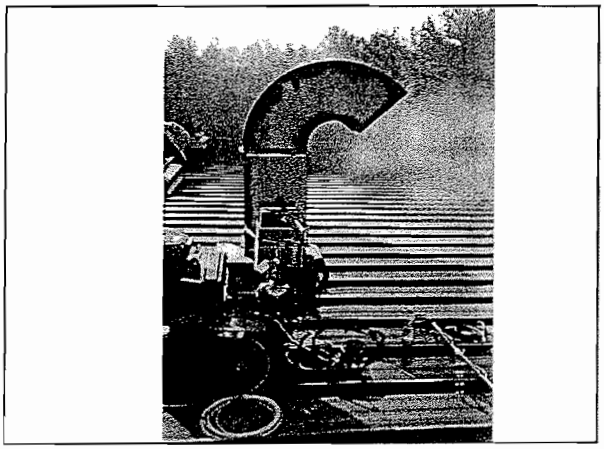
Example Chromatogram

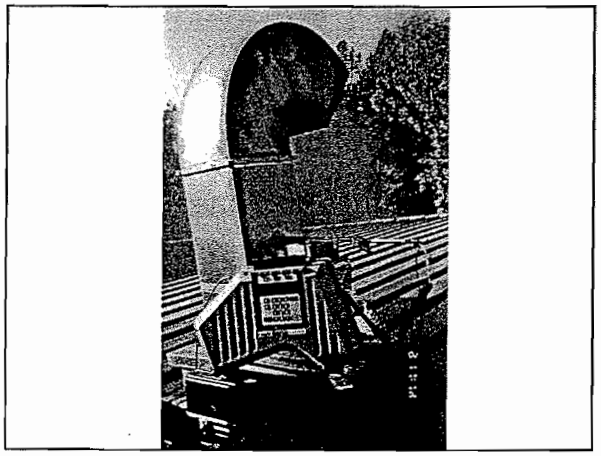


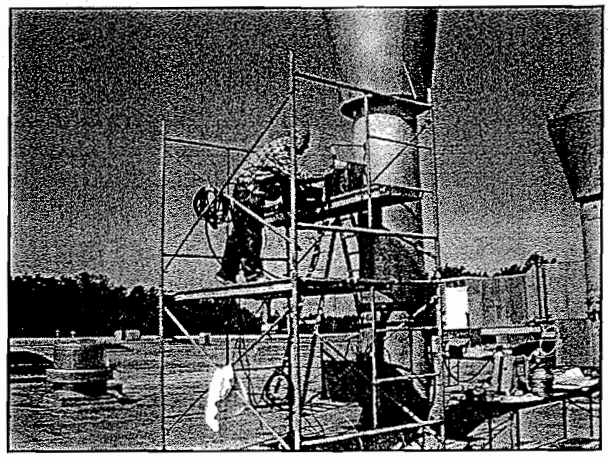


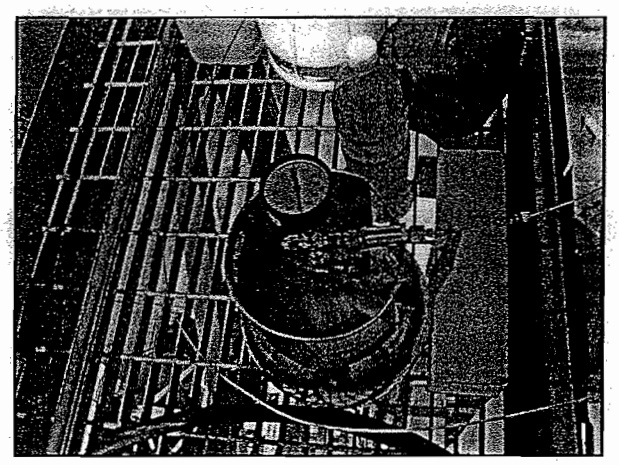


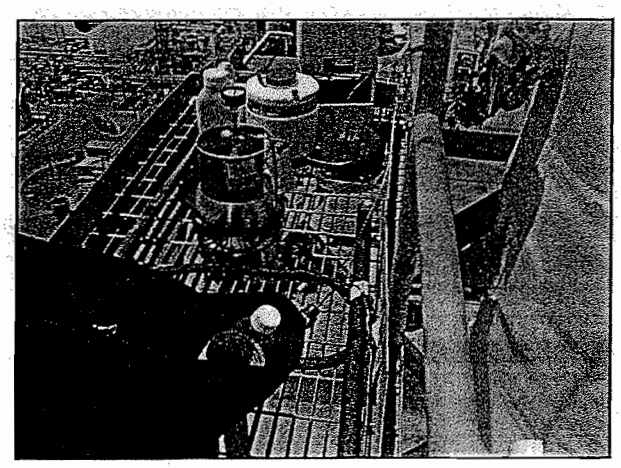












Method Development

- 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

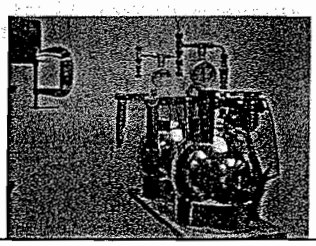
NCASI Impinger and Canister Method

- 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

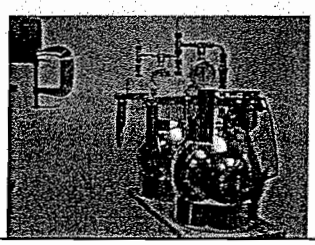
FRM 18 Reporting

- 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

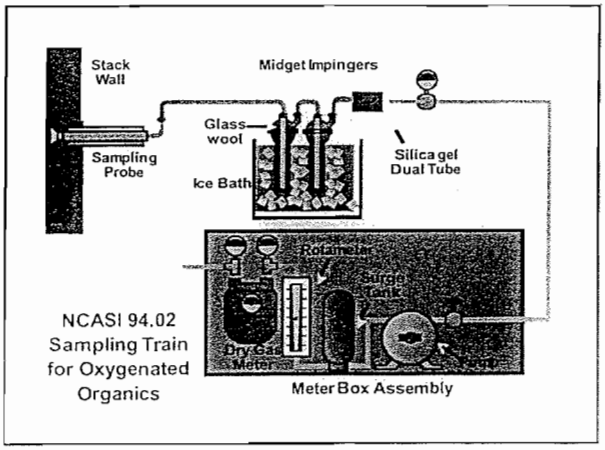
- Total Organic Compounds
- Acetaldehyde
- Acetic Acid
- Ethanol
- Formaldehyde
- Formic Acid
- 2-Furaldehyde
- Methanol

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)

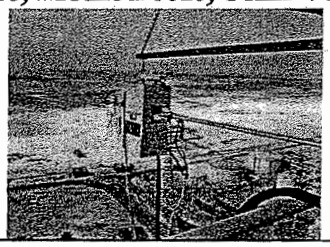


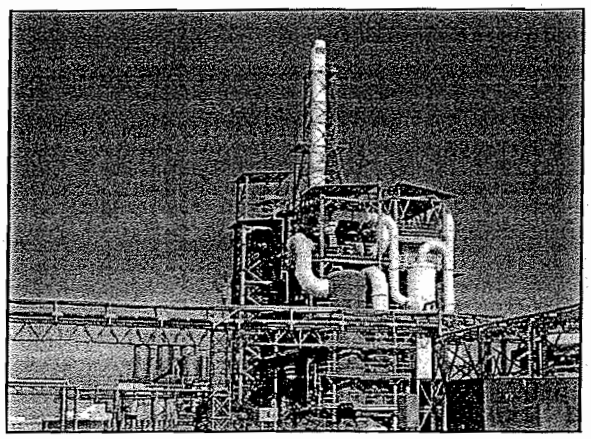
Measurement of Oxygenated Organics in Using MSF Protocol

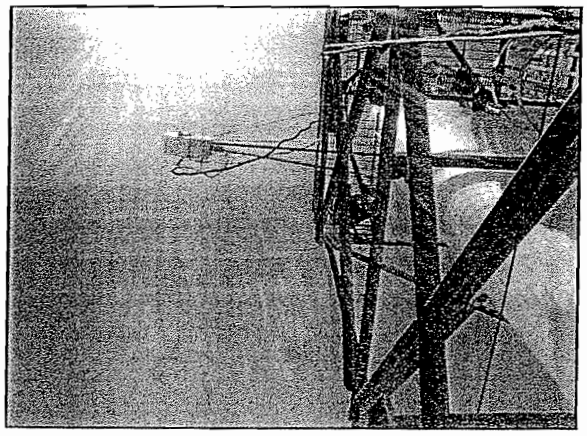
- NCASI Chilled Impinger/Silica Gel Tube Test Method Analytical Finish for Oxygenated Organics:
  - Impinger water analyzed by GC/FID
  - Silica gel desorbed with 3% solution of n-propanol, then direct injection to GC/FID
  - Formaldehyde analyzed by the acetylacetone derivatization/spectrophotometric analysis method

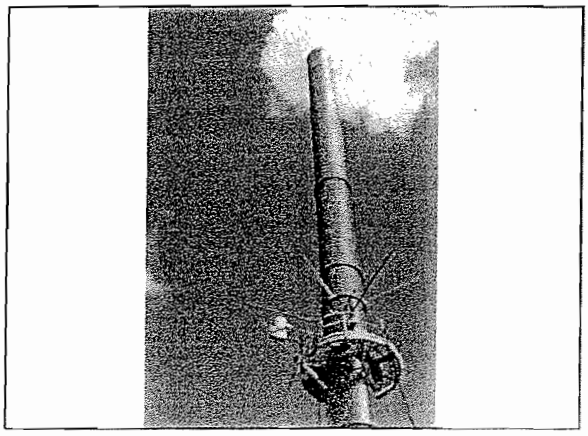
U.S. EPA APTI
Compliance Test and Source Test Observation
Agency Observer Method Specific Checklist for FRMs

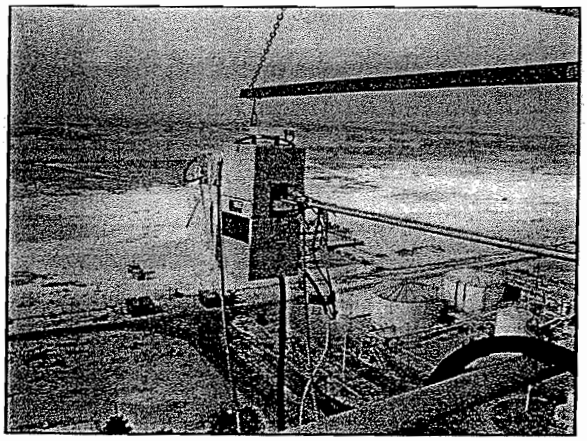
U.S. EPA APTI
Compliance Test and Source Test Observation
SW-846, Method 0010, Semi-Volatiles











Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHCs) from incinerator systems
- Procedure-Based Method

Destruction Removal Efficiency (DRE)

$DRE = (W_{in}-W_{out}) / W_{in} \times 100$

DRE> 99.99%

Definition of Semi-Volatiles

- Semi-volatile compounds are those with boiling points greater than 200°C

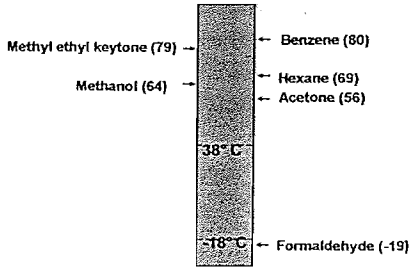
Definition of Semi-Volatiles

- Four major groups
  - Polycyclic Aromatic Hydrocarbons (PAHs)
  - Dioxin and Furans (D/Fs)
  - Biphenyls (PCBs)
  - Herbicides/Pesticides

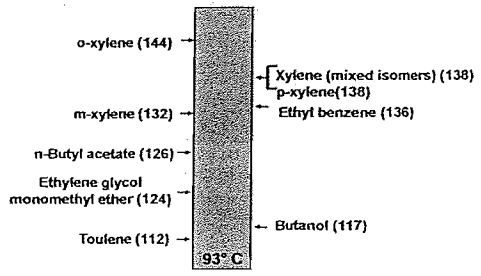
General Classification of VOCs

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

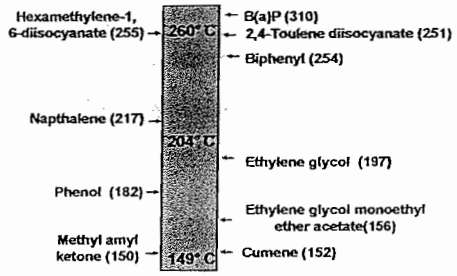
Boiling Points of Volatile Organic Compounds



Boiling Points of Volatile Organic Compounds



Boiling Points of Semi-volatile Organic Compounds



Semi-Volatile Compound Boiling Points(°C)

- Bis(chloromethyl)ether - 104°C
- Chlorobenzene - 132°C
- Benzyl Chloride - 176°C
- Hexachlorobutadiene - 215°C
- 2,4,6-Trichlorophenol - 245°C
- 3,3'-Dichlorobenzidine - 402°C

34 Title III Semi-Volatiles SW-846, Method 0010 Analytes

Acetaldehyde
Acetonitrile
Biphenyl
Bromoform
1,3 - Butadiene
Carbonyl Sulfide
Chlorobenzene
Cresols
Cumene
1,4 - Dichlorobenzene
Ethylbenzene
Ethylene Glycol
Ethylene Oxide
Methanol
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Naphthalene
Phenol
Propionaldehyde
Styrene
Toluene
Xylenes (o -, m-, p -)

34 Title III Semi-Volatiles SW-846, Method 0010 Analytes

Benzotrichloride
Benzyl chloride
Chloroacetophenone
Trans-1,3-Dichloropropene
Dichloroethyl Ether
Ethylene Dibromide
Hexachloroethane
Pyridine
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
1,2,4-Trichloroethane
2,4,5-Trichlorophenol

Interferences

- Oxides of nitrogen (NO_x) in the determination of certain water-soluble compounds (dioxane, phenol, and urethane)

Interferences

- Formation of water-soluble organic salts on the resin bed
- Stability of the compounds in methylene chloride (extraction solution)
- Solvent extraction efficiency (control spike performance check before testing)

Method 0010 Design Requirements

- Gas flow measurement system (EPA Methods 2-4)
- Modified Method 5 sampling train (Isokinetic sampling)

Method 0010 Design Requirements

- Addition of condenser and XAD-2 resin trap and optional drop-out jar
- Minimum sample volume of 105.9 ft^3
- Minimum sample time of 3.5 hrs.

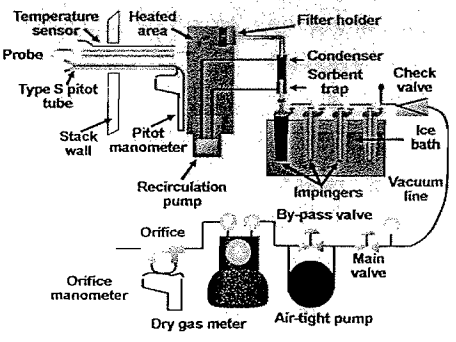
Method 0010 Sampling Train

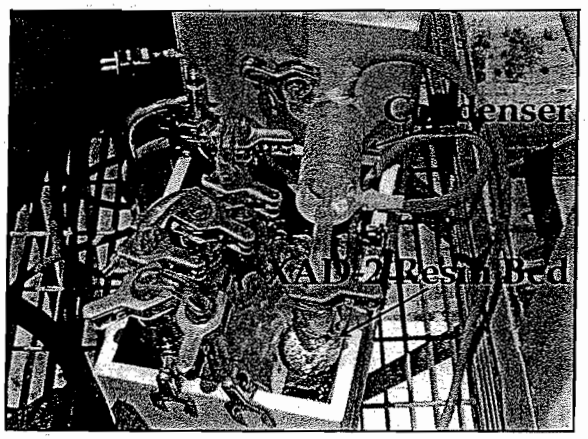
- Probe with nozzle
- Pitot tube/temperature sensor array
- Heated filter assembly (cyclone may be added if PM >100 mg)
- Condenser/XAD-2 resin trap assembly

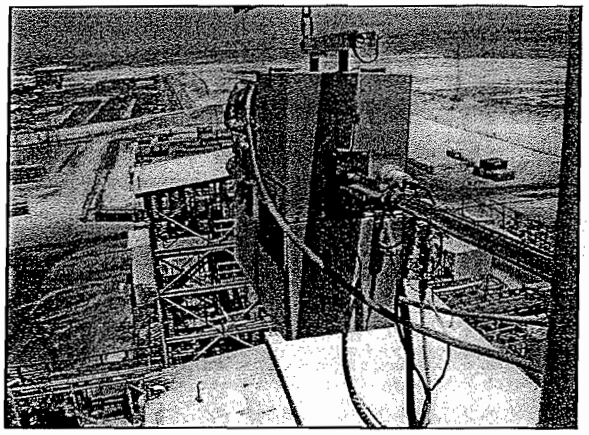
Method 0010 Sampling Train

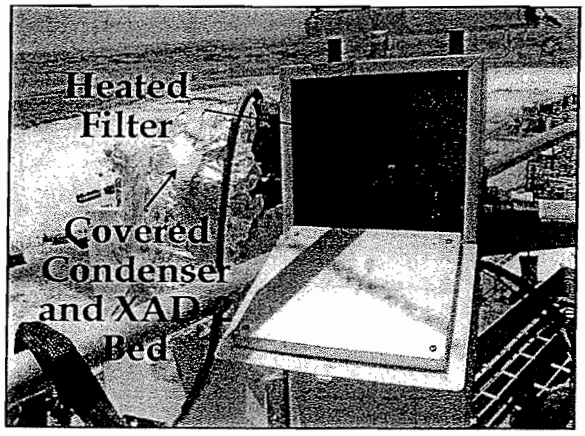
- Condensing impingers
- Silica gel
- Pump/dry gas meter/ orifice assembly

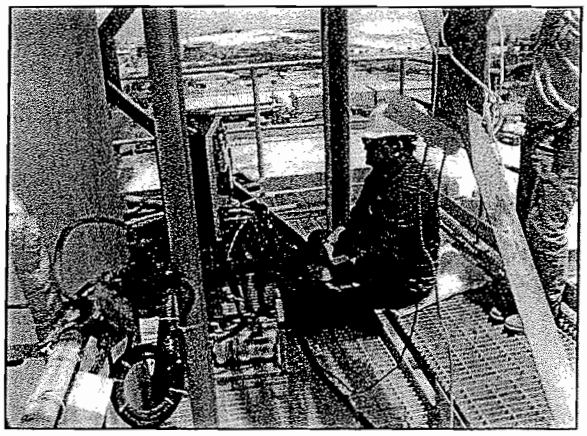
Method 0010 Sampling Train

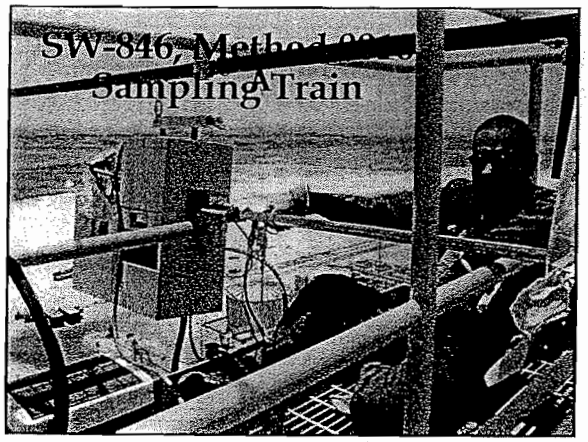












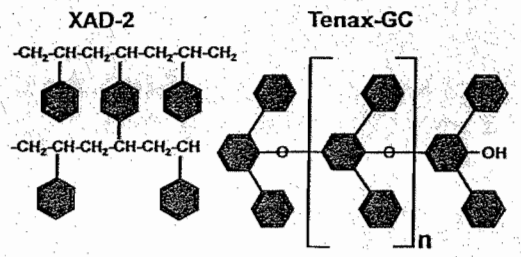
Method 0010 Configuration

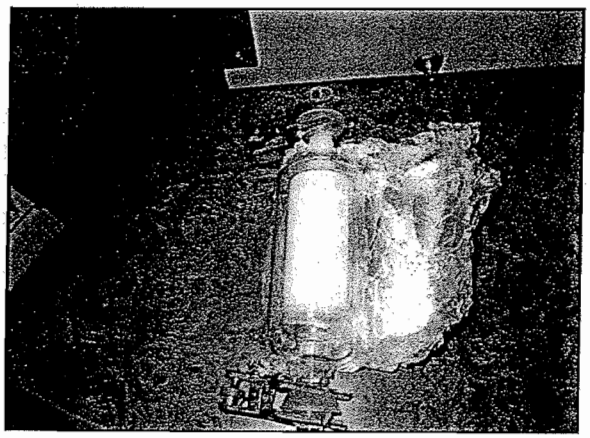
- Same configuration used for PCBs and dioxin/furans
- Collect all in one train for better detection limits
  - 10 µg for PAHs
  - 1 ng for D/F's

XAD-2 Resin Trap

- XAD-2 is a cross-linked styrene-divinylbenzene
  - Organic Polymeric Adsorbent

Chemical Structure of Typical Adsorbent Resins





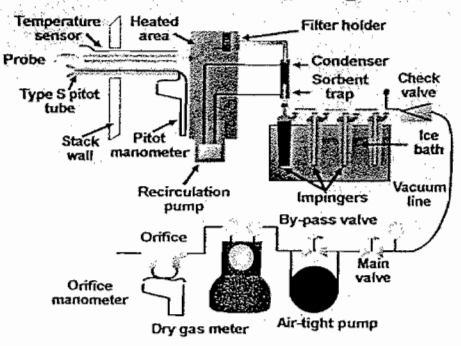
XAD-2 Resin Trap

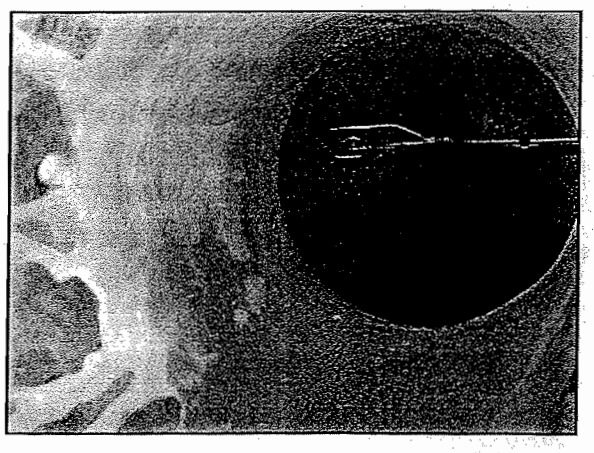
- Amberlite XAD-2 physical characteristics
  - Mesh Size: 20-60
  - Bulk Density: 1.08 g/mL
  - Surface Area: 300 m^2/g
    - large surface area
  - Temp. Max: 190°C
    - Therefore, it can't be thermal desorbed due to breakdown of XAD-2

Weaknesses of XAD-2 Resin

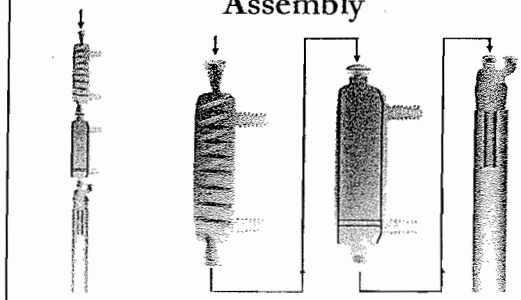
- Thermal stability questionable, therefore must solvent extract
- Compounds below C7 breakthrough extensively during sampling (below toluene @ 110°C)
- Produces sulfur compounds as artifacts (SO_2)

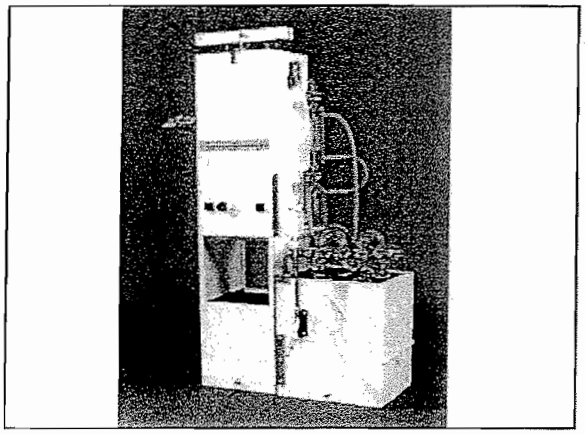
Method 0010 Sampling Train

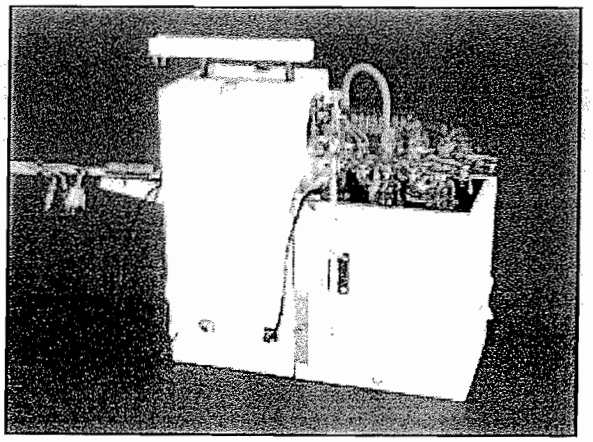


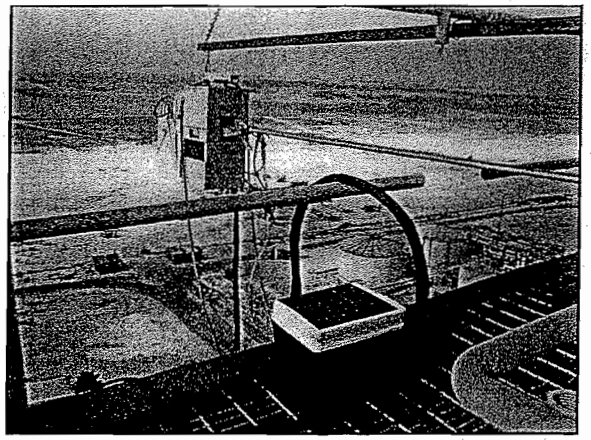


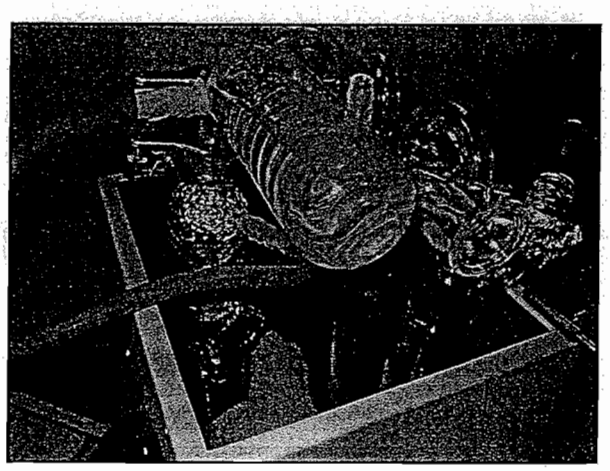
Vertical Condenser/XAD-2 Trap Assembly

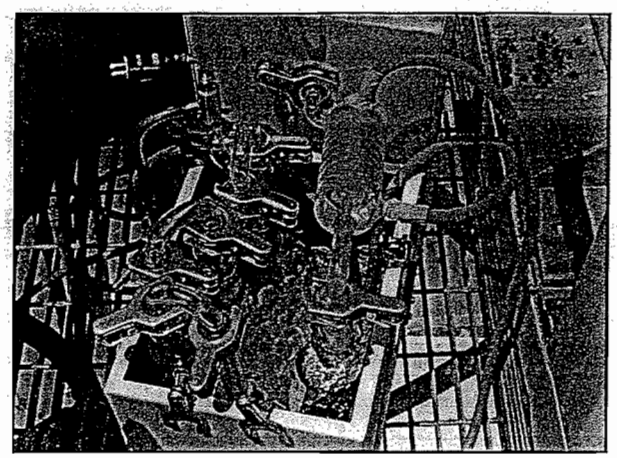


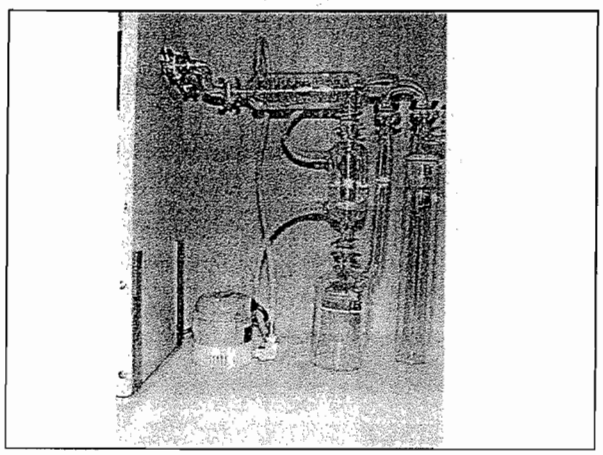


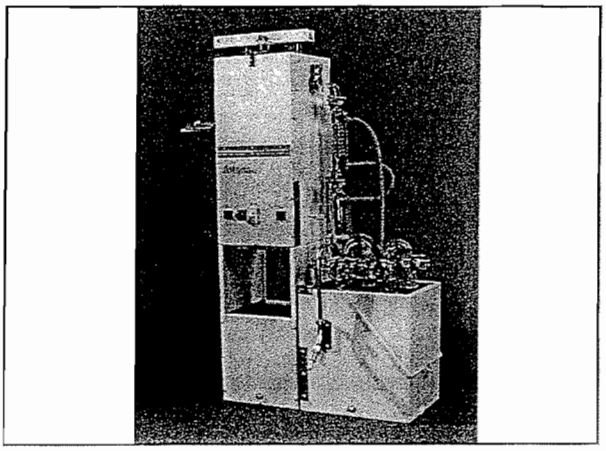




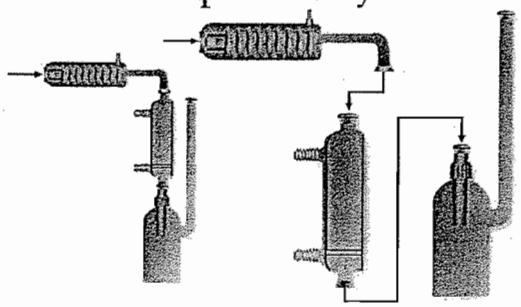




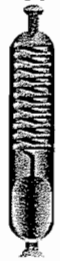


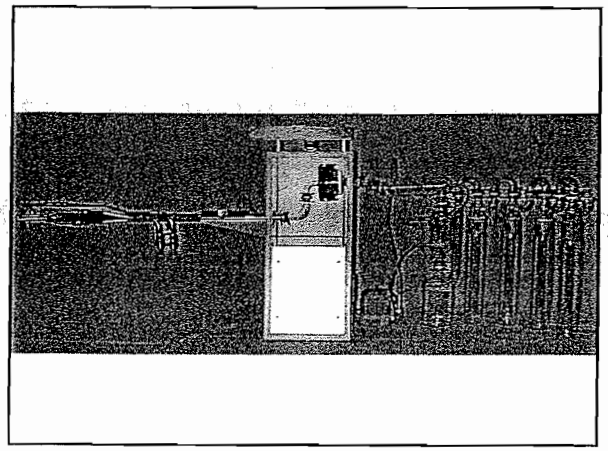


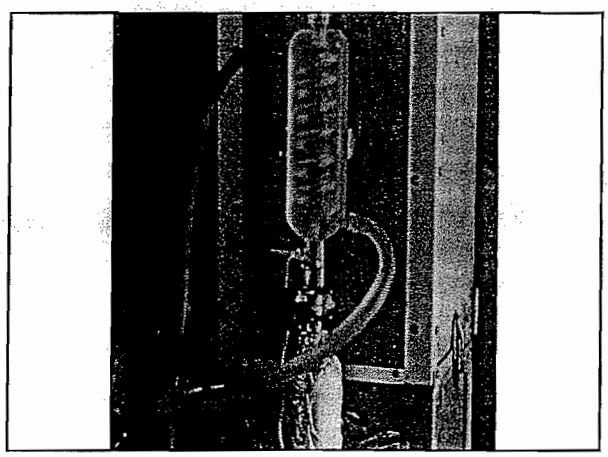
Horizontal Condenser/ XAD-2 Trap Assembly

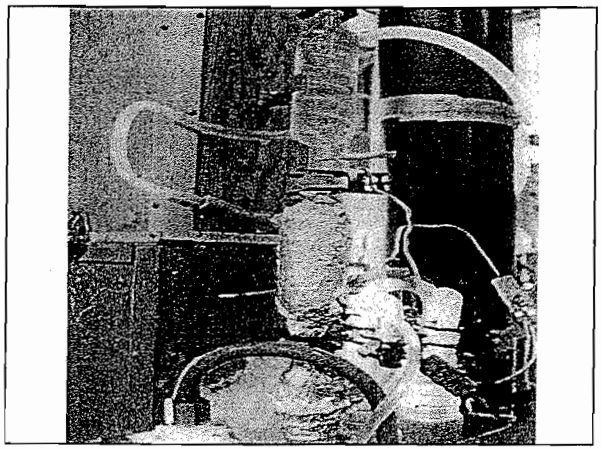


Vertical Single Unit Condenser/ XAD-2 Trap Assembly









Glassware Cleaning Requirements

- 3X with tap water
- 3X with DI water
- 3X with Acetone
- 50/50 v/v rinse with methanol/ methylene chloride

Glassware Cleaning Requirements

- Bake
- Cover

Certification of Cleanliness XAD-2

- Soxhlet extraction, three 22-hour periods with methyl alcohol, methylene chloride and fresh methylene chloride respectively

Certification of Cleanliness XAD-2

- Resin blank should not have higher than 4 mg/kg of total chromatographic organics (TOCs)
- Resin should be used within 4 weeks

Method 0010 Operational Requirements

- Multi-point integrated sampling
- Isokinetic sampling rate (~0.53 dsctm)
- Collect at least 3 cubic meters (105.9 cubic feet) sample gas (minimum volume)
- Minimum sample time of 3.5 hours

Method 0010 Configuration

- Sample volumes required depends on minimum sample detection limit and expected compound stack gas concentration

Method 0010 Operational Requirements

See Observer Checklist

- Probe/filter at 120°C (248°F)
- Sorbent resin trap inlet < 20°C (68°F)
- Leak-free system

Method 0010 Record - Keeping Requirements

- Calibration of
  - Temperature sensors
  - Stack, probe, filter, XAD-2 resin, silica gel exit, gas meter inlet/outlet
  - Metering pump
  - Pitot tubes

Method 0010 Record -Keeping Requirements

- Periodic Sampling Information
  - Gas flow measurements
  - Sampling train parameters
- Sample Recovery and Laboratory Data

Preliminary Field Determination

- Select sampling site according to FRM 1
- Select nozzle size and establish isokinetic sample train operation

Preliminary Field Determination

- Select probe liner and proper length
- Determine total length of sampling for minimum sample volume of 3 dscm (105.9 dscf)

Preparation of Sample Train

- Obtain certified clean sorbent trap from sample custodian, log trap number into field data sheet
  - Adsorbent trap should be wrapped with aluminum foil, end caps in place and assigned trap number
  - No field surrogate spiking required on clean sorbent trap

Preparation of Sample Train

- Charge impingers with appropriate solutions (100 mL first two, third empty and 200-300 g silica gel in fourth)

Preparation of Sample Train

- Place labeled/pre-weighted filter in filter holder
- Filter must be free of PAHs with no organic binder

Preparation of Sample Train

- Install selected nozzle and mark probe

  (Remember, nozzle can't be changed during sample run)

Preparation of Sample Train

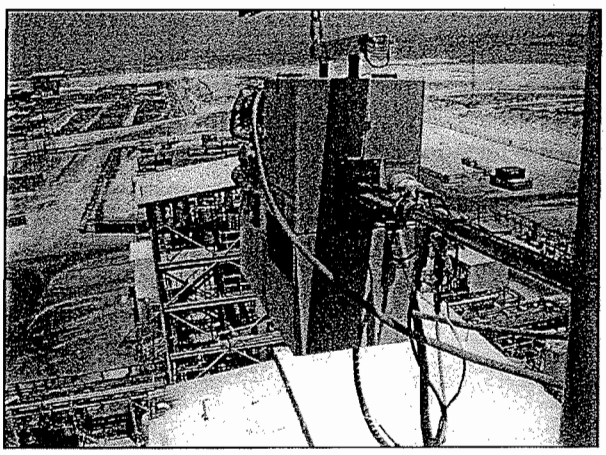
- Assemble sample train (no silicone grease upstream of organic module)
- Cyclone may be used if > 100mg of total particulate catch
- Place crushed ice around impingers

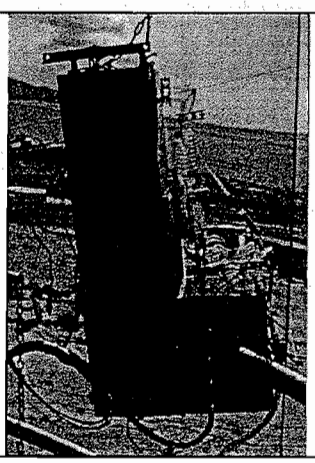
Preparation of Sample Train

- Turn on filter/probe heating systems
- Turn on sorbent and condenser coil coolant recirculating pumps (must maintain resin bed at < 20°C)
- Leak check system at -15 in Hg vacuum; rate not to exceed 4% of average sampling rate (< 0.02 cfm)

Preparation of Sample Train

- Clean stack access port
- Insert probe to first sampling point and record initial train information on Field Test Data Sheet
- Block off openings around probe to prevent dilution of sample gas





Sample Train Operation

- Begin sampling when all temperatures are at required settings:
  - Probe/Filter: 120 ± 14°C
  - Sorbent Bed: < 20°C
  - Exit Silica Gel Impinger: < 20°C
- Sample at each point, maintaining isokinetic sampling rate to within 10% of true isokinetic

Sample Train Operation

- Record sample train operating parameters
  - Sampling time
  - Sample train vacuum
  - Differential pressures: pitot tube, orifice
  - Dry gas meter (DGM) volume
  - Temperatures: DGM, filter, stack, XAD-2 sorbent, exit last impinger

Sample Train Operation

- If the pressure drop across filter or adsorbent is too high, then one can change components
  - Must leak check system prior to change and after change of train component
  - If exceeds leak rate limit, run is voided

Sample Train Recovery

- Turn off coarse adjust valve, remove probe from stack, turn off pump
- Leak check to specifications
- Calculate percent isokinetics to determine whether the run is valid

Sample Train Recovery

- Front half (Container #2)
  - Nozzle, probe cyclone, filter housing: methanol/methylene chloride (1:1) rinses
  - Condenser: weigh, rinse with methanol/methylene chloride(1:1)
- Filter (Container #1)
  - Recover in pre-clean aluminum foil

Sample Train Recovery

- XAD-2 sorbent trap (Container #3)
  - Weigh for moisture/cap ends
  - Wrap in original aluminum foil
  - Ship to lab under blue ice (< 4°C)

Sample Train Recovery

- Impingers
  - Measure volumes in 1st (Container #4)
  - 2nd and 3rd (Container #5)
  - Weigh 4th silica gel impinger and note color change (Container #6)

Criteria for On-site Test Invalidation

- Minimum sample volume not met (may not have enough analyte for MDL)
- XAD-2 temperature exceeds 68°F (loss of sample from resin due to no adsorption)

Criteria for On-site Test Invalidation

- Minimum sampling volume of 105 scf not reached
- Acetone used as recovery solvent

Criteria for On-site Test Invalidation

- Use of wrong recovery solvents (may not collect analyte)
- Pre-test leak check >0.02 cfm (4% of average sampling rate)
- Calculated percent isokinetic outside 90-110%

Analysis

- Weight filter, then add to XAD-2 sorbent bed for Soxhlet extraction
- Add laboratory surrogate compounds to XAD-2 sorbent bed

Analysis

- Examples of laboratory surrogates
  - Naphthalene-d12
  - Chrysene
  - Phenol
  - Nitrobenzene

  Note: no field surrogates are required

Analysis

- Laboratory surrogates added to condensate water trap
- Soxhlet extraction with methylene chloride for 16 hours (XAD-2 must be extracted within 14 days)
- Sample concentrated to 10 mL, analyzed by GC/MS

Analysis

- Sample analyzed within 40 days
- GC/MS analysis by Method 8270
  - GC/MS initial tuning
  - 5-point initial calibration
  - Continuing calibration checks
  - Surrogate spiking
  - Quantitation by internal standards
- GC/MS operated in full "scan" mode

Requirements of Method Blanks

- Proof blank of glassware
- Field blank for XAD-2 adsorbent trap
- Trip blank for XAD-2 adsorbent trap
- Laboratory reagent blank

Requirements of Method Blanks

- Rinse solvent blank
- Laboratory blank

Calculation

- C(POHC) = Sum of C(µg/mL) X sample volume (10 mL)
- Volume of stack gas sampled, corrected to standard temperature (68°F) and pressure (29.92 in. Hg)
- POHC(µg/m^3)= (total µg)/(std. volume of gas sampled)

Method 0010 Key Points

- XAD-2 must be certified clean (< 4 mg/kg of total semi-volatiles) and good for 4 weeks
- Adsorbent temperature during sampling can not exceed 68°F
- Analysis if GC/MS in full scan mode (40-450 amus); SW-846, Method 8270

Method 0010 Key Points

- Pre- and component change leak check required and must meet < 0.02 cfm or invalidate sample run
  (NOTE: No adjusted volume allowed)

Method 0010 Key Points

- Filter/XAD-2 adsorbent trap extracted together and within 14 days of sampling
- Laboratory surrogates and internal standards used with GC/MS analysis (no field surrogates required)
- Shipment of samples to laboratory under blue ice (< 4°C)

Method 0010 Key Points

- Use no stopcock grease in front of resin bed
- If pressure drop >20 in. Hg during sampling, replace XAD-2/filter; Must leak check before replacement
- Clean all glassware by specified rinse procedure
- Control spike performance evaluation sample strongly suggested

Method 0010 Key Points

- Filter certified free of PAHs and with no organic binder
- Concurrent Method 5 sampling allowed; Rinse probe with acetone only
- May replace filter/XAD-2 adsorbent trap is during sampling vacuum become too high (i.e., > 20 inches of mercury vacuum)

Method 0010 Key Points

- Minimum sample volume of 105.9 scf and minimum sample time of 3.5 hours
- Cyclone may be added to sample train if particulate matter >100 mg

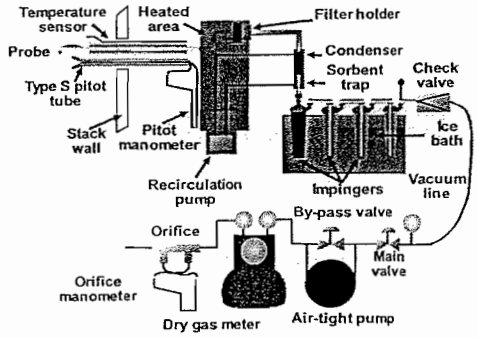
Method 0010 Key Points

- Methylene chloride/methanol (1:1) extraction solvent
- Field sample train blank
  - No gases pass through train, but recovery the same

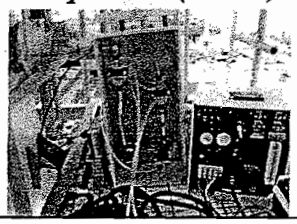
What Happens If Your Analyte Hasn't Been Validated Using Method 0010?

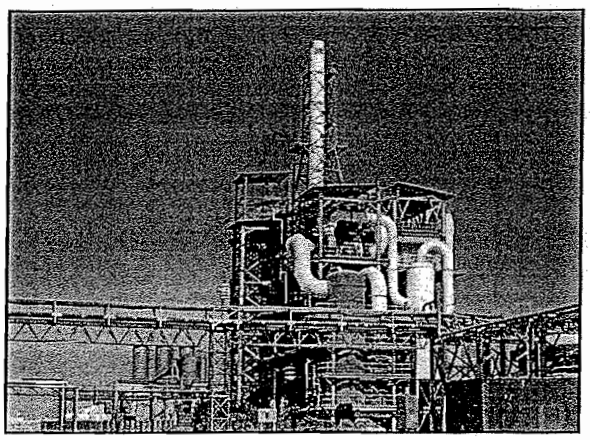
- Validate in the laboratory by spiking XAD-2 resins with target analyte, then pulling clean ambient air through the plug at method sampling rate and time. Recover and analyze according to methodology. Recovery should be between 70-130 % to validate analyte

Method 0010 Sampling Train



U.S. EPA APTI
Compliance Test and Source Test Observation
SW-846, Method 0030, Volatile Organic Compounds (VOCs)





Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of 99.9% for volatiles and Principal Organic Hazardous Compounds (POHCs), from incinerator systems

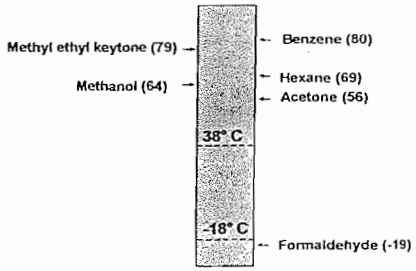
Definition of Volatile Organic Compounds (VOCs)

- Volatile organic compounds (VOCs) are those compounds with boiling points < 100°C, but normally above 30°C
- VOCs with boiling points < 30°C may break through adsorbent

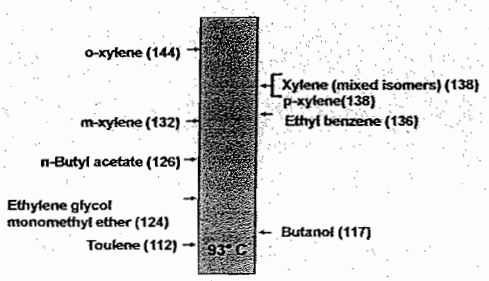
General Classification of VOCs

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

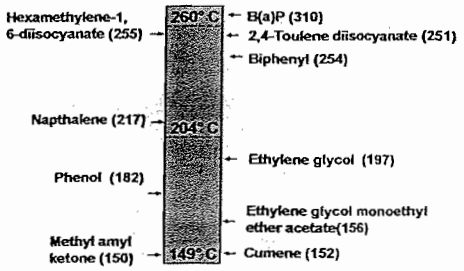
Boiling Points of Volatile Organic Compounds



Boiling Points of Volatile Organic Compounds



Boiling Points of Semi-volatile Organic Compounds



Volatile Organic Compounds Boiling Points

- Acrylonitrile 77.0°C
- Benzene 80.0°C
- Carbon Tetrachloride 77.0°C
- Chloroform 60.5°C

Volatile Organic Compounds Boiling Points

- Methyl Bromide 4.0°C
- Tetrachloroehtylene 121.0°C
- Trichloroethylene 86.9°C
- Vinyl Chloride -13.4°C

(may want to use Method 0031)

Title III Method 0030 Analytes

Acrylonitrile
Benzene
Carbon Disulfide
Carbon Tetrachloride
Chloroform
Chloroprene
Ethyl Chloride
Ethylene Dichloride
Methyl Chloride
Methyl Chloroform
Methylene Chloride
Propylene Dichloride
Propylene Oxide
Tetrachloroethylene
Trichloroethylene
Vinyl Acetate
Vinyl Chloride

Potential Problems and Interferences

- Interference from background concentration of contamination of sorbent trap prior to or after sample collection from
  - Benzene, toluene, ethylbenzene
- Low-level contamination of train components

Potential Problems and Interferences

- Breakthrough volume
  - No more than 30% of analyte in back traps
- Oxidation of trapped VOCs on adsorbent
- Concentration range

Method 0030 Design Requirements

- Modified Method 6 sampling train
  - Single point sampling
- Removal of midget impingers and addition of condensers and adsorbent tubes
- Detection limits of 0.1 $\mu g/m^3$

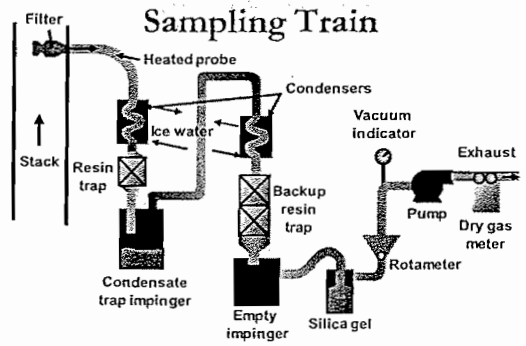
Method 0030 Sampling Train

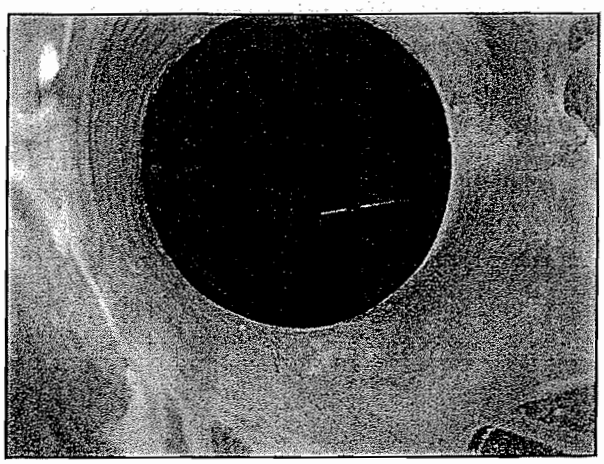
- Straight-end glass lined probe with isolation valve and heat-trace line
  - All heated to >120°C
- Condenser with first adsorbent trap of Tenax®
  - No stopcock grease
- Condensate trap impinger

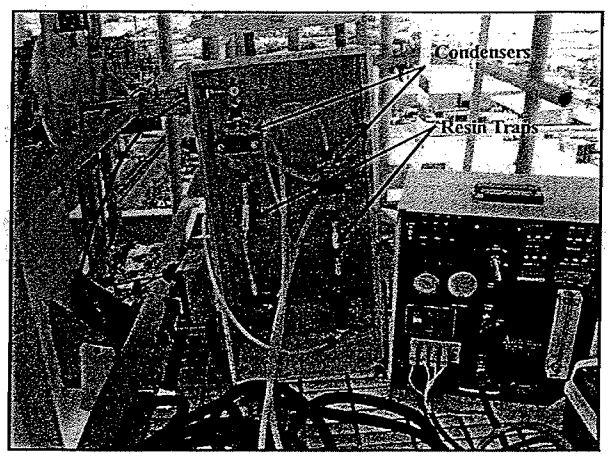
Method 0030 Sampling Train

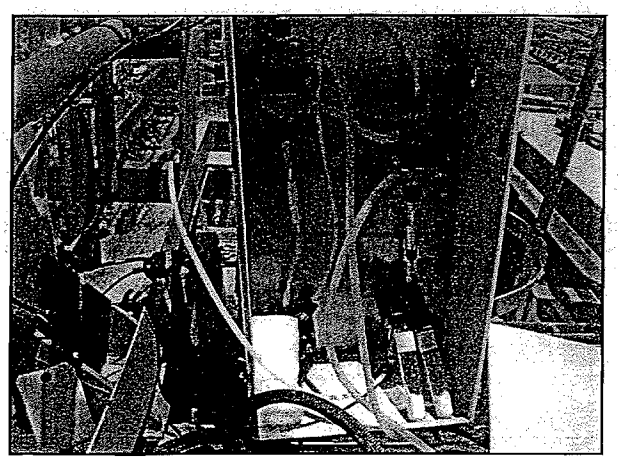
- Second condenser with second adsorbent trap of Tenax®/charcoal
- Metering system (vacuum gauges/pump)
- Method 0030 has been modified in some cases to put first adsorbent trap after condensate trap impinger

SW-846, Method 0030 Sampling Train









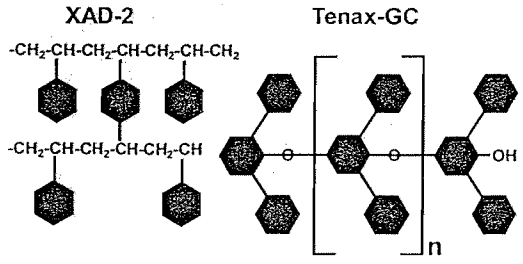
Common Adsorbents Utilized in Air Pollution Studies

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

Common Adsorbents Utilized in Air Pollution Studies

- Carbon molecular sieve
- XAD Series
- Carbosieve S-III
- Carbotrap
- Carbotrap C

Chemical Structure of Typical Adsorbent Resins



Advantages of Sorbent Technology

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

Sorbent Selection-Capture Process

- Carbosieve S-III for VOCs -15° C to 80° C
- Carbotrap for VOCs 0° C to 100° C
- Carbotrap C for VOCs 80° C to 250° C

Sorbent Selection-Capture Process

- Tenax-TA for VOCs from 30° C to 200° C
- XAD-2 for VOCs from 120° C to 350° C

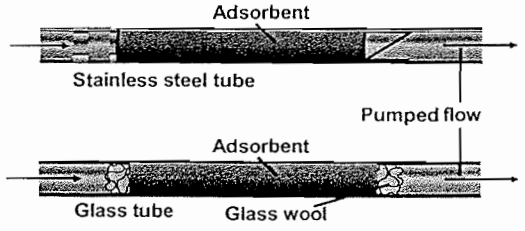
Sorbent Selection-Two Recovery Processes

- Thermal Desorption
  - Entire sample analyzed
  - More readily automated
  - Possibility only one analysis

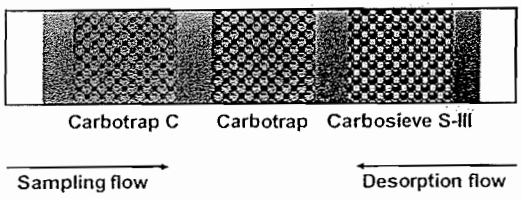
Sorbent Selection-Two Recovery Processes

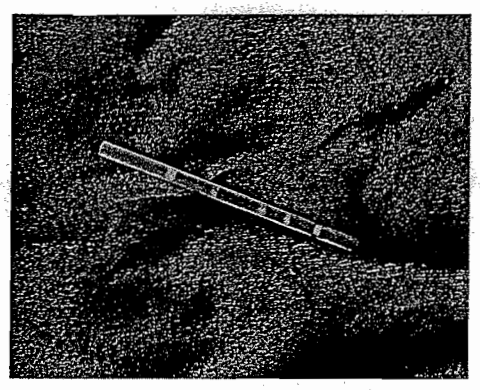
- Solvent Extraction
  - Able to adjust concentration
  - Replicate analysis
  - No thermal desorbtion breakthrough products
  - However, dilute sample

Single Tube Design-Glass/Stainless Steel



Multi-bed Adsorbent Trap





SW-846, Method 0030 Tenax® Resin Trap

- Tenax® is 2,6-diphenyl-p-phenylene oxide polymer

Tenax® Resin Trap

- Tenax® physical characteristics
  - Mesh size: 35-60
  - Bulk Density: 0.58 g/mL
  - Surface Area: 23.5 m^2/g
  - Temp. Max: 400°C
  - Therefore can thermal desorb

Weaknesses of Tenax®

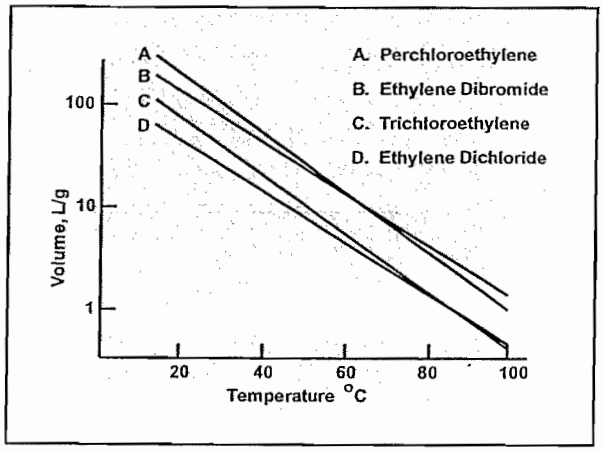
- Poor desorption of highly polar (alcohol) compounds
- Possible oxidation of compounds by O_2
- Limited range of VOCs applicability

Weaknesses of Tenax®

- Resin background concentration of VOCs
- Low breakthrough volume for some VOCs

Breakthrough Volume

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



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

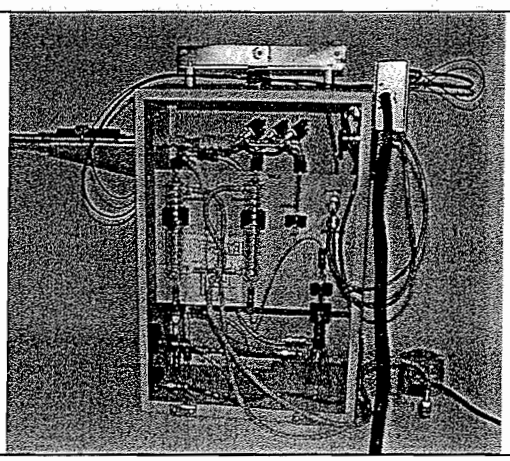
- Safe sample volume is the published breakthrough volume (liters/gram of adsorbent) divided by 1.5 times the weight of the adsorbent used in the system

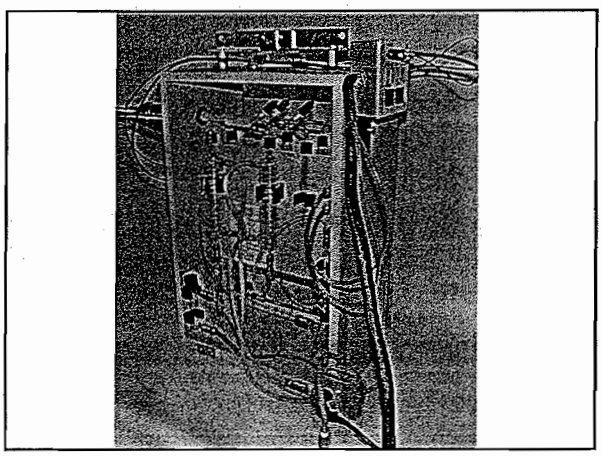
Published Safe Sample Volumes

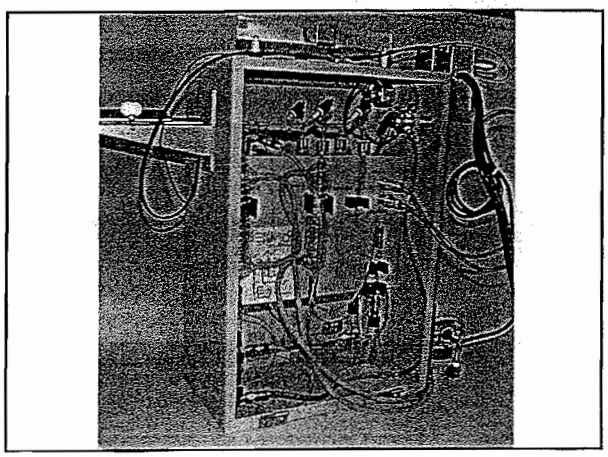
- Vinyl Chloride <1.0 L/g
- p-Dichlorobenzene 290.0 L/g
- Chlorobenzene 74.0 L/g
- Benzene 14.0 L/g
- Carbon Tetrachloride 11.0 L/g

Tenax® Certification of Cleanliness

- Thermal desorption of packed Tenax® and Tenax® /charcoal traps
- Resin blank should be no higher than 1 ng for total target volatile organic compounds
- Resin traps should be used within 4 weeks and refrigerated until use







Method 0030
Operational Requirements

- No gas flow measurement system required
- Single point sampling (non-isokinetic sampling)
- Constant sampling rate (1 L/min) for 20 minutes per set of traps (6 pairs of traps/ run) at single point, 2 hr total sampling time

Method 0030
Operational Requirements

- Probe at 120°C (248°F)
- Sorbent resin traps inlet < 20°C (68°F)
- Line from probe to first condensate trap <5 ft. and can be Teflon®

Method 0030
Performance Audit

- Performance audit performed with sample train used in the test protocol
- Obtain performance audit gas cylinder with selected POHCs

Method 0030
Performance Audit

- May be done at the laboratory or in the field
- Analysis done by same person who will analyze regular samples
- Audit results should agree within 50-150 percent of expected values for each specific target compounds

Preparation of Sampling Train

- Obtain certified clean sorbent traps(Tenax®, Tenax®/charcoal) from sample custodian, log trap numbers into field data sheet
- Attach traps to sampling train (Tenax® only as first trap followed by Tenax®/charcoal)

Preparation of Sampling Train

- Ensure proper orientation of traps
  - Tenax® first trap, then Tenax®/charcoal second trap
- Turn on cooling water pump

Preparation of Sampling Train

- Turn on probe heating system
- Leak check system by closing valve at inlet of 1st adsorbent trap and pulling a vacuum of 10 in. Hg
- Leak rate should not be more than 2.5 mm Hg after 1 minute

Sample Train Operation

- Clean stack access port
- Position probe at least 1 meter from inside wall of stack
- Block off openings around probe to prevent dilution of sample gas
- Purge probe using alternative pump

Sample Train Operation

- Begin sampling when all temperatures are at required settings
- Sample at 1 L/min at the same point for 20 minutes with sampling adsorbent tubes (paired)

Sample Train Operation

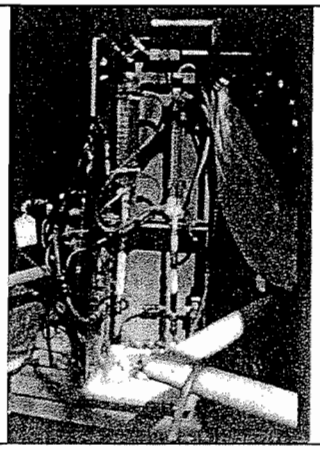
- Sample time
  - 2 hour total sample time for 6 pairs of tubes
  - 40 minutes total sample time at 0.5 L/min for 3 pairs of tubes

Sample Train Operation

- Record sample train operating parameters
  - Time (5 minute intervals)
  - Rotameter setting (L/min)
  - Temperatures
    - Condenser, DGM, probe
  - DGM readings
  - Vacuum gauge readings

Sample Train Operation

- After 20 L of sample, stop the sampling, leak check the train
- Remove the first set of adsorbent tubes, cap and store under blue ice

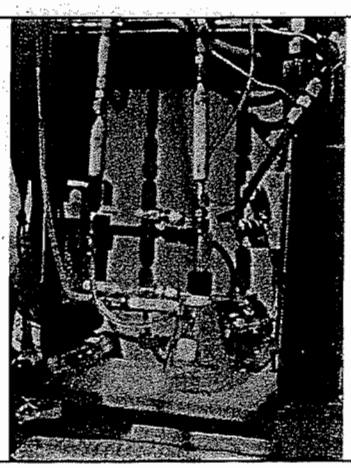


Sample Train Operation

- Replace with two certified clean adsorbent tubes; leak check and sample
- Repeat after an additional 20 L of sample with two new certified clean adsorbent tubes
- Obtain 6 pairs of exposed absorbent tubes for a total of 2 hrs of sampling time

Sample Train Operation

- Field blanks are exposed during exchanging of adsorbent tubes (1 pair/six pair of sample cartridges)
- Trip blanks include one pair of cartridges per shipment to field
- Stop sampling after obtaining six pair of exposed adsorbent traps



Sample Train Recovery

- Cap all recovered adsorbent traps and wrap in aluminum foil
- Store all sample adsorbent traps (six pair), field blanks (one pair/six pair) and trip blank (one pair/ shipment) at 4°C until analysis

Sample Train Recovery

- Collect condensate from condensate trap impinger, rinse and fill to top of recovery bottle (zero head space)

Criteria for On-site Test Invalidation

- Low probe temperature (condensation in probe causes loss of analyte)
- Temperature inlet to resin exceeds 68°F (loss of sample from resin due to no adsorption)
- Final leak check >0.1 in. Hg/min. (dilution of sample)

Analysis

- GC/MS analysis by Method 5040 (purge and trap technology)
- Desorption of tubes (individually or all onto analytical trap as one) onto an analytical trap through a water purge
- Tube must be placed in desorber in proper direction

Analysis

- Adsorbent traps desorption/ analysis within 14 days of sampling event
- Condensate trap recovery also analyzed

Analysis

- If concentration of analyte is greater than maximum calibration point, then
  - Split sample before analysis
  - Resample
  - Use dilution technique
  - Use canister/dilution technique

Analysis

- Method 5040
  - GC/MS initial tuning
  - 5-point calibration curve using adsorbent cartridges
  - Continuing calibration checks
  - Quantitation by internal standards
  - Daily analysis of spiked traps with 2 ng of benzene and toluene

Calculation

C(POHC)= Sum of C (µg)

- Volume of stack gas sampled, corrected to standard temperature (68°F) and pressure (29.92 in. Hg)

POHC (µg/m^3) = Total µg/
(Std. volume of gas sampled)

Calculation

ppb = (24.04)(µg/L)(1000)/(MW)

DRE = W_{in}-W_{out}/W_{in}

Method 0030 Key Points

- No stopcock grease used in sampling train
- Method developed for only a few VOCs with boiling points 30-100°C
- No addition of field or laboratory surrogates

Method 0030 Key Points

- Sampling rate of 1 L/min with pair of tubes (six pairs/run), single point sampling (non-isokinetic)

Method 0030 Key Points

- Method suggest spiking of traps with target compound list and verifying methodology for detection limits (100 ng/m^3) and identification
- Prior to field use, traps are certified clean <2 ng for total VOC-TCL

Method 0030 Key Points

- Analysis by purge-and-trap, GC/MS
- Sample line from probe to first condenser must be < 5 ft
- Shipment of samples under blue ice (<4°C)
- No stopcock grease in sample train

Method 0030 Key Points

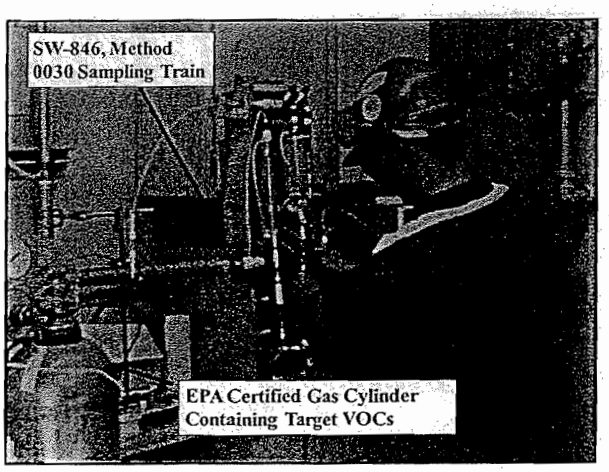
- Less complex method than SW-846, Method 0010
- Very sensitive method due to thermal desorption during the analytical procedure
- However, does not measure volumetric flow rates

Method 0030 Key Points

- Required limited sampling time per pair of adsorbent tubes to minimize "breakthrough" from occurring
- Adsorbent tubes orientation very important

Method 0030 Key Points

- Must perform Performance Evaluation (PE) sample containing target compound list
  - Acceptance of 50-150% recovery



Method 0030 Key Points

- Certification of adsorbent tubes good for 30 days
  - After sampling must be analyzed within 14 days
- Condensate trap also analyzed

Method 0030 Key Points

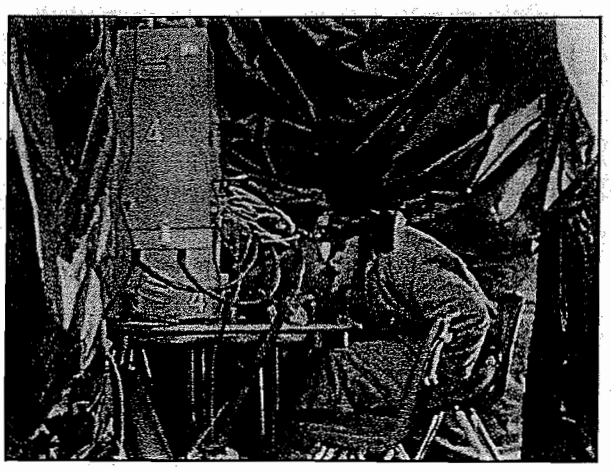
- Can analyze traps separately or together
- Analyze back trap at least once to check for breakthrough
- Adsorbent trap must be kept < 68°F during sampling
- Purge probe before sampling

Method 0030 Key Points

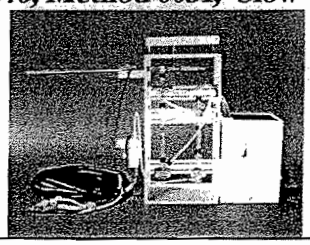
- Detection limit of 100 ng/m^3 for most target analytes
- For analytes with boiling points < 30°C
  - May want to use Method 0031 or lower sampling rate to between 250-500 cc/min

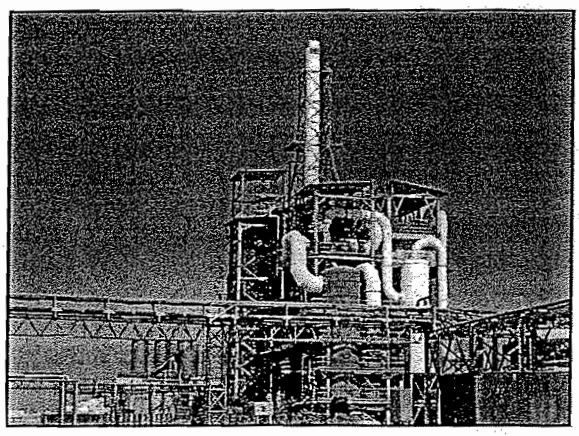
Method 0030 Key Points

- Method blanks required
  - Field blank
  - Trip blank
  - Laboratory blank
- Daily analysis of spiked traps (2 µg of toluene and benzene)
- Daily analysis must not vary ±25% of certified value



U.S. EPA APTI
Compliance Test and Source Test Observation
SW-846, Method 0031, Slow-VOST





Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of 99.9% for volatiles and Principal Organic Hazardous Compounds (POHCs), from incinerator systems

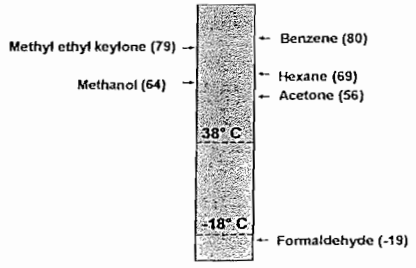
Application of Sampling Trains

- Volatile organic compounds (VOCs) are those compounds with boiling points < 100°C, but normally above 30°C. Therefore use VOST
- VOCs with boiling points < 30°C may break through adsorbent, therefore use Slow-VOST

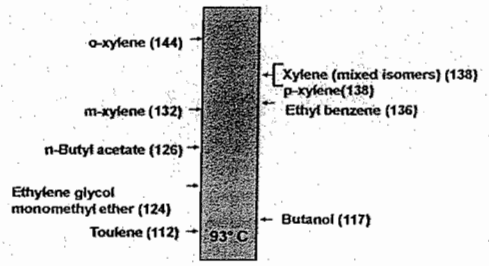
General Classification of VOCs

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

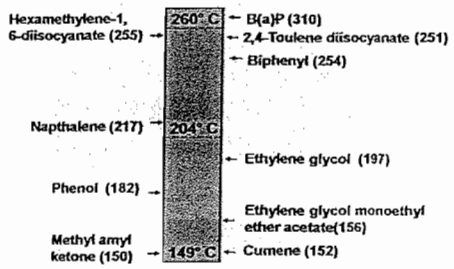
Boiling Points of Volatile Organic Compounds



Boiling Points of Volatile Organic Compounds



Boiling Points of Semi-volatile Organic Compounds



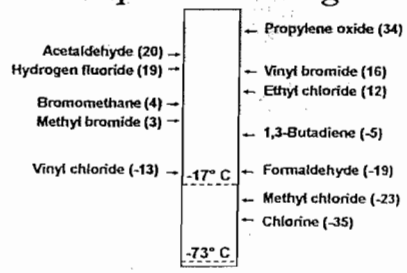
Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of volatile Principal Organic Hazardous Compounds (POHCs) from incinerator systems and a variety of other stationary sources

Definition Of Volatile Organic Compounds (VOCs)

- Volatile organic compounds (VOCs) are those compounds with boiling points between -15° C and 121° C

SW-846, Method 0031 Slow-VOST Applicability For Organic Compounds Boiling Points



Method 0031 Validated Target Compound List

Acrylonitrile
Benzene
Bromodichloromethane
Carbon Disulfide
Carbon Tetrachloride
Chlorodibromomethane
Chloroform
Chloroprene
Dibromomethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
Trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropene
Methylene Chloride
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
Bromomethane
Chloroethane
Vinyl Bromide
Vinyl Chloride

Method 0031 Non-Validated Compounds

Allyl Chloride
Acetone
Methyl Ethyl Ketone
Chloromethane
Epichlorohydrin
Chloromethyl Methyl Ether
Bis(chloromethyl) Ether
Acetonitrile
Acetaldehyde
Acrolein
Methanol
Ethanol
Isopropyl Alcohol

Interferences

- Interference from background concentration of contamination of sorbent trap prior to or after sample collection (condition traps/blanks)
- Low-level contamination of train components (seal train)

Interferences

- Breakthrough volume possibility for very volatile VOCs, therefore 3 adsorbent tube arrangement
- High stack concentration (preliminary distributive volume sampling)

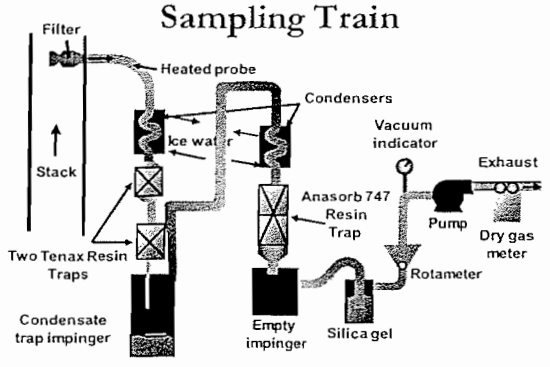
Method 0031 Design Requirements

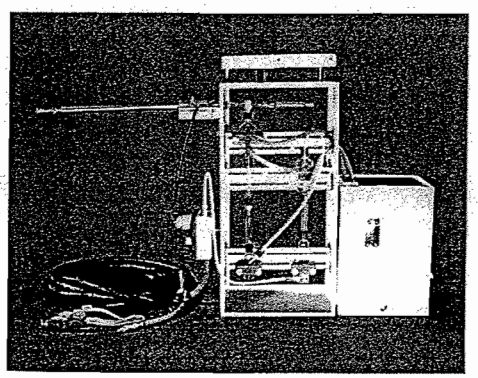
- Modified Method 0030 sampling train
- Addition of one Tenax adsorbent tube and replacement of tenax/charcoal tube from Method 0030 with Anasorb-747

Method 0031 Sampling Train (Typically Same As Method 0030)

- Straight-end glass lined probe with isolation valve and heat-trace line
- Condenser in front of tubes
- Metering system

SW-846, Method 0031 Sampling Train





Three (3) Resin Traps In SW-846, Method 0031

- Two (2) Tenax (2,6-diphenylene oxide polymer) Adsorbent Tubes In Series
- Final Third Anasorb-747 (Carbon Molecular Sieve) Adsorbent Trap

Weaknesses Of Tenax/Anasorb

- Poor desorption of highly polar (alcohol) compounds
- Possible oxidation of compounds by O_2
- Limited range of VOCs applicability (Used mostly for very volatile VOCs)

Weaknesses Of Tenax/Anasorb

- Resin background concentration of VOCs
- Low breakthrough volume for some VOCs
  - However, use of three traps minimizes breakthrough

Method 0031 Adsorbent Tubes

- Same configuration of Method 0030 Adsorbent Tubes

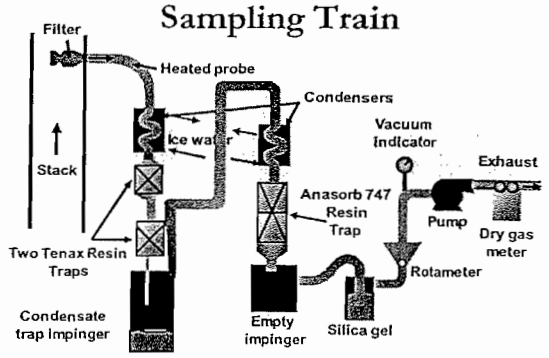
Certification Of Cleanliness

- Thermal desorption of packed Tenax traps at 220° C for 8-12 hrs at a nitrogen flow rate of 80-100 mL/min
- Thermal desorption of packed Anasorb-747 at 300° C for 18-24 hrs at a nitrogen flow rate of 80-100 mL/min

Certification Of Cleanliness

- Resin blank should be no higher than 1 ng for total target volatile organic compounds
- Resin traps should be used within 4 weeks and refrigerated until use

SW-846, Method 0031 Sampling Train



Method 0031 Operational Requirements

- No gas flow measurement system required
- Single point sampling (non-isokinetic sampling)

Method 0031 Operational Requirements

- Constant sampling rate [1 L/min or slower(SLO-SMVOC)] for 20 minutes per set of traps (6 pairs of traps/run)
- Probe at 130° C (266° F)
- Sorbent resin traps inlet < 20° C (68° F)

Method 0031 Performance Audit

- Performance audit performed with sample train used in the test protocol
- Obtain performance audit gas cylinder with selected POHCs

Method 0031 Performance Audit

- May be done at the laboratory or in the field
- Analysis done by same person who will analyze regular samples

Method 0031 Performance Audit

- Audit results should agree within 50-150 of expected values for each specific target compounds

Preparation And Operation Of Sampling Train

- Same as SW-846, Method 0030 with leak checking, exchanging of tubes, and sample recovery

Analysis

- GC/MS analysis by Method 5040 (Purge and trap technology)
- Desorption of tubes (individually or all onto analytical trap as one) onto an analytical trap through a water purge

Analysis

- Adsorbent traps desorption/analysis within 14 days of sampling event
- Condensate trap also analyzed

Calculation

- C(POHC)= Sum of C (µg)
- Volume of stack gas sampled, corrected to standard temperature (68° F) and pressure (29.92 in. Hg)
- POHC (µg/m^3)= (Total µg/(Std.volume of gas sampled)

Method 0031 QA/QC Requirements

- Same as Method 0030

Method 0031 Key Points

- No stopcock grease used in sampling train
- Method developed for very volatile organic compounds with boiling points -15° to 121° C. Method validation requite if analys boiling point < 0 C
- Probe purge which was not in Method 0030

Method 0031 Key Points

- No addition of field surrogates
- Sampling rate of 1 L/min or slower with 3-adsorbent tubes (six 3-tubes/run)
- Method 0031 not applicable to particulate or aerosol sampling since not isokinetic sampling

Method 0031 Key Points

- Method suggest spiking of traps with target compound list and verifying methodology for detection limits and identification
- Analysis by purge-and-trap, GC/MS
- Method not good with polar water-soluble analytes and reactive VOCs

Method 0031 Key Points

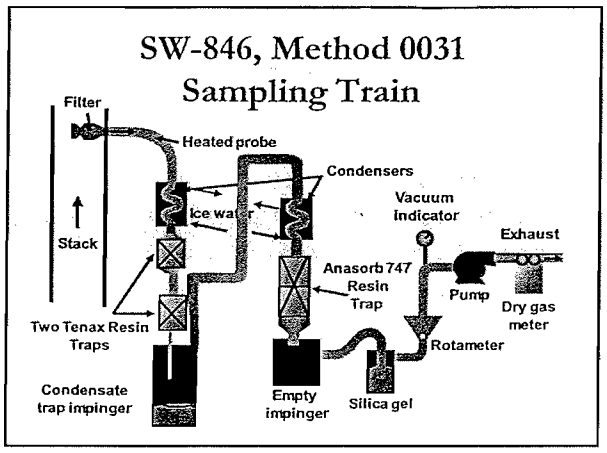
- Sample line from probe to first condenser must be < 5 ft
- Shipment of samples under blue ice (<4° C)
- Upper limit of 1.5 ppm
- Sample train can be operated at 0.5 L/min for a total of 3 40-minute periods, but no slower than 0.25 L/min

Method 0031 Key Points

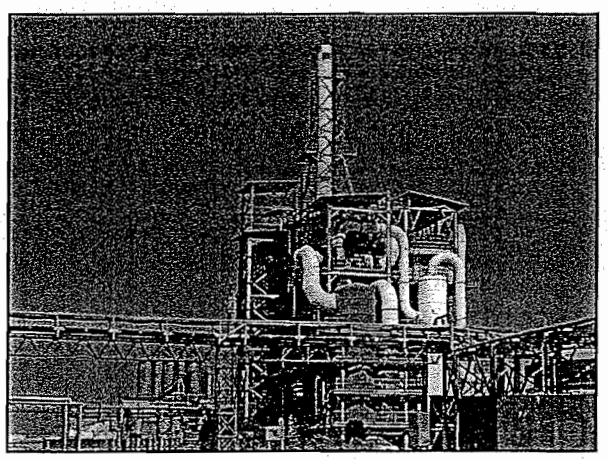
- Less complex method than for Method 0010
- Very sensitive method due to thermal desorption
- Does not measure volumetric flow rates

Method 0031 Key Points

- Short sampling time per 3-adsorbent tubes
- Adsorbent tubes orientation very important


SW-846, Method 0031
Sampling Train
Filter
Heated probe
Condensers
Vacuum
Indicator
Exhaust
Stack
Anasorb 747
Resin
Trap
Pump
Dry gas
meter
Two Tenax Resin
Traps
Rotameter
Condensate
trap impinger
Empty
impinger
Silica gel

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 23/SW-846 Method 0023A,
Dioxin/Furans



Applicability

- This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources utilizing FRM 23 and SW-846, Method 0023A

Applicability

- Simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), semi-volatile organic compounds (SVOCs), and polybrominated diphenyl ethers (PBDE) can also be performed along with PCDDs and PCDFs

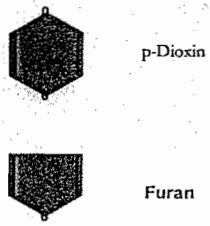
Applicability

- SW-846, Method 0023A is used to determine destruction removal efficiency (DRE) of PCDDs and PCDFs at 99.9999% (six 9's) from incinerators
- General detection limits are 0.010 pg/m^3
- FRM 23 is used to quantify PCDD's and PCDF's from stationary sources

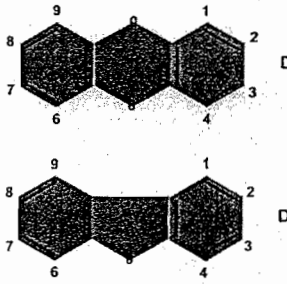
What Are Dioxins?

- Dioxins are a family of 210 different molecules with one or two basic structures
  - The dioxin structure with two oxygen atoms
  - The furan structure with one oxygen atom

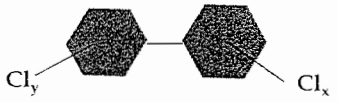
Structure



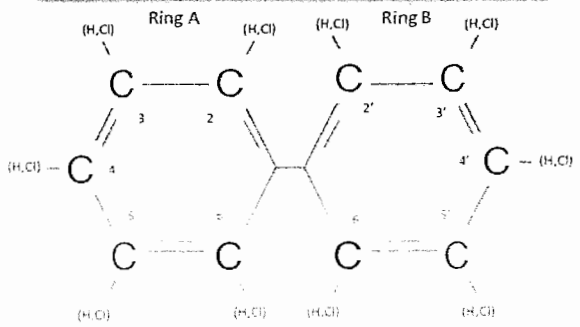
Structures of Dioxins and Furans



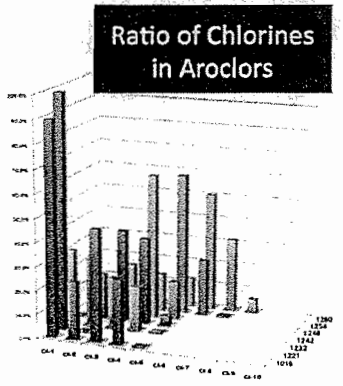
Polychlorinated Biphenyl Structure



Structure of PCB (Polychlorinated Biphenyl)

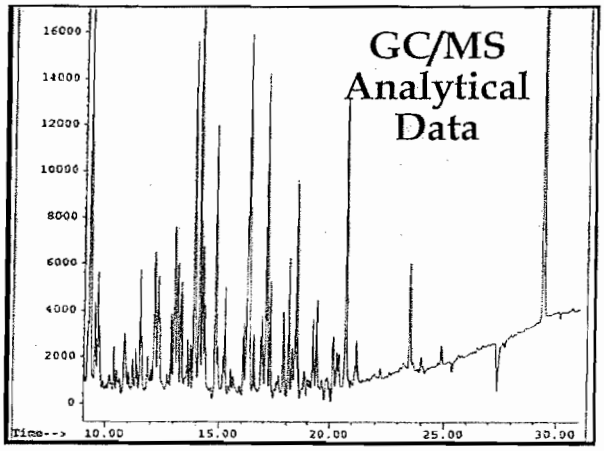


Ratio of Chlorines in Aroclors



Chlorine Distribution in Aroclors

	1016	1221	1232	1242	1248	1254	1260
Cl-1	90.0%	99.4%	31.5%	0.6%			
Cl-2	24.3%	0.6%	28.2%	19.5%	0.7%		
Cl-3	47.1%		21.5%	39.1%	22.0%		
Cl-4	27.3%		18.7%	36.7%	61.3%	16.0%	0.3%
Cl-5	0.4%		0.4%	4.2%	16.3%	59.9%	12.2%
Cl-6						23.8%	50.3%
Cl-7						0.4%	31.4%
Cl-8							5.9%
Cl-9							
Cl-10							



Differences Between Molecules

- The differences between the molecules lie in the number and attachment positions of chlorine atoms

Examples
2,3,7,8 - TCDF
2,3,7,8 - TCDD
1,2,3,7,8 - PeCDD

Chlorinated Dioxins and Furans

- 7-2,3,7,8-substituted chlorinated dioxins
- 75 total chlorinated dibenzo-p-dioxins
- 10-2,3,7,8-substituted chlorinated furans
- 135 total chlorinated dibenzofurans

Levels of Chlorination

- 4 level chlorination: Tetra
- 5 level chlorination: Penta
- 6 level chlorination: Hexa
- 7 level chlorination: Hepta
- 8 level chlorination: Octa

TEF Values

Analyte	TEF Value
2,3,7,8 - TCDD	1.0
2,3,4,7,8 - PeCDD	0.5
2,3,4,6,7,8 - HxCDD	0.1
1,2,3,4,6,7,8 - HpCDD	0.01
1,2,3,4,6,7,8,9 - OCDD	0.001

Congeners

- Molecules with different chemical formulas and the same basic structure are referred to as *congeners*
- Generally, the most common one is octachlorodibenzo-p-dioxin (OCDD), with chlorine in all eight available positions

Aroclor PCBs

- Aroclor PCBs were manufactured by simply chlorinating biphenyl to specific weight percentage of chlorine

Aroclor PCBs

- Aroclor mixtures are characterized by a four digit number - ie., Aroclor 1242
  - 12 represents the parent compound, biphenyl
  - 42 represents weight percentage of chlorine in the mixture

Aroclors

- Each Aroclor mixture consists of biphenyl molecules chlorinated to levels from 1 through 10
- Each level of chlorination produces a chromatographic pattern unique to that PCB
- Many Aroclors have similar peaks, but differ in their ratio

Aroclors

- Quantification of multi-component mixtures requires area summation of all components and comparison to the summed area from the corresponding Aroclor standard
- To remove interfering peaks, sample clean-up with Florisil is required

Interferences

- If not using high resolution GC/MS, then interferences from polychlorinated biphenyls and polychlorinated diphenyl ethers could effect low resolution techniques

Interferences

- Very high amounts of other organic compounds in the matrix will interfere with the analysis
- Contamination in solvents, reagents, glassware, and other sampling processing hardware (all glassware must be cleaned thoroughly before use)

FRM 23 and SW-846 Method 0023A Design Requirements

- Gas flow measurement system (EPA Methods 2-4)
- Modified Method 5 sampling train, retaining heated filter
  - Sample time of 6.25 hours
- Addition of condenser and XAD-2 resin trap (~65 grams)

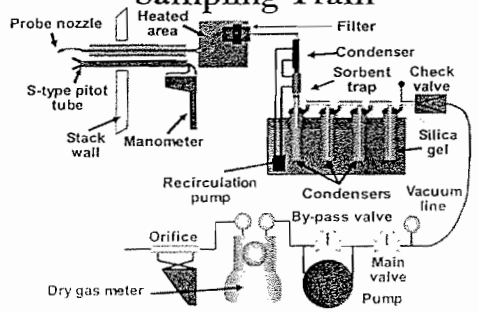
FRM 23 and SW-846 Method 0023A Sampling Train

- Probe with nozzle
- Pitot tube/temperature sensor array
- Heated filter assembly (Teflon®)
- Condenser/XAD-2 resin trap assembly

FRM 23 and SW-846 Method 0023A Sampling Train

- Condensing impingers
- Silica gel
- Pump/dry gas meter/orifice assembly

FRM 23/Method 0023A Sampling Train



XAD-2 Resin Trap

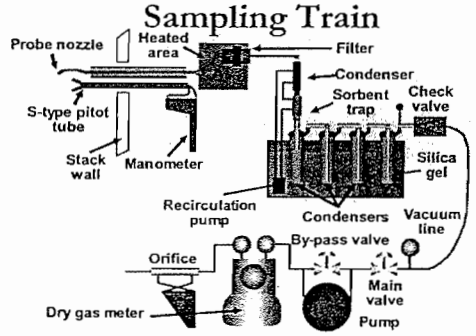
- XAD-2 is a cross-linked styrene-divinylbenzene - Organic Polymeric Adsorbent
- Amberlite XAD-2 physical characteristics

Mesh Size: 20-60
Bulk Density: 1.08 g/mL
Surface Area: 300 m2/g
Temp. Max: 190°C

Weaknesses of XAD-2 Resin

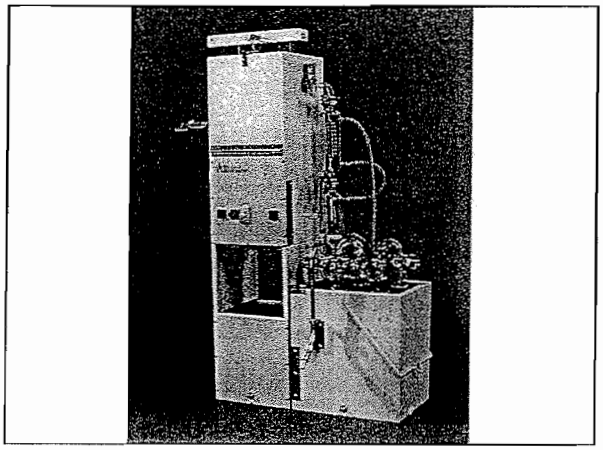
- Thermal stability questionable, therefore must solvent extract
- Compounds below C7 breakthrough extensive during sampling
- Produces sulfur compounds as artifacts

FRM 23/Method 0023A Sampling Train

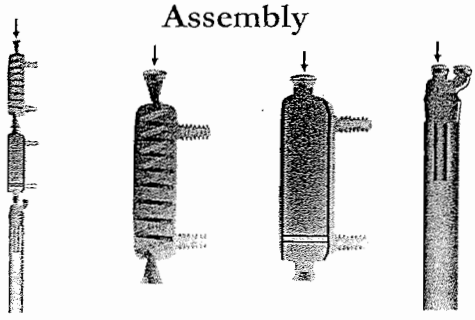


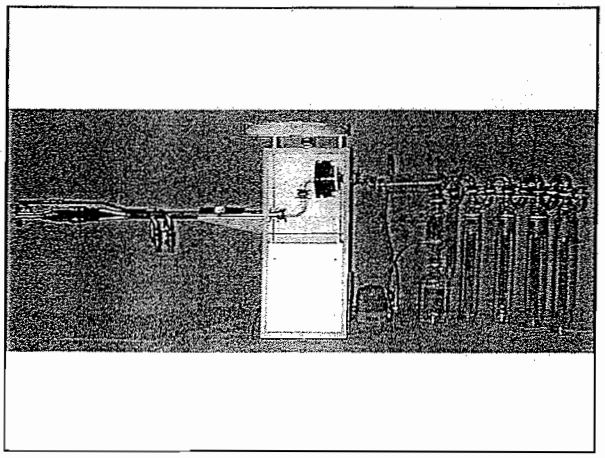
Percent Phase Distribution of Dioxins in Sampling Train

Phase	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Vapor	55	26	4	2	1
Particle	45	74	96	98	99

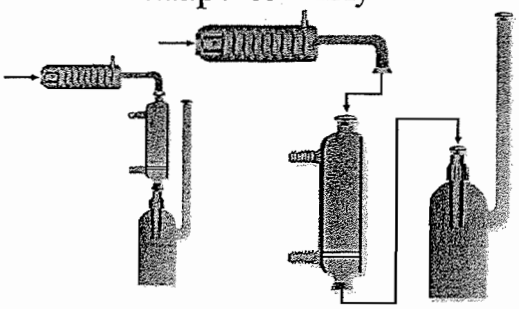


Vertical Condenser/XAD-2 Trap Assembly





Horizontal Condenser/ XAD-2 Trap Assembly



Filter Certification of Cleanliness

- Glass fiber filter without organic binder
- Soxhlet extracted with toluene for 16 hours
- No analytes observed above the detection limits of 0.010 pg/m^3

XAD-2 Certification of Cleanliness

- Rinse twice with reagent water
- Place resin in thimble with methlyene chloride, Soxhlet extract with water for 8 hours, repeat with methanol for 22 hours
- Repeat with methylene chloride, then with toluene, then nitrogen drying

XAD-2 Certification of Cleanliness

- Resin blank should have no analytes above method detection limits for targeted species
- Spike resin bed with isotopically labeled PCDD/PCDF standards prior to field sampling (surrogate spikes)

XAD-2 Certification of Cleanliness

- Wrap cartridge in hexane-rinsed aluminum foil

FRM 23/Method 0023A Typical Field Surrogates (i.e., Surrogate Standards)

- Added to clean cartridge prior to field deployment
  - $^{37}C_4$-2,3,7,8-TCDD
  - $^{13}C_{12}$-2,3,4,7,8-PeCDF
  - $^{13}C_{12}$-1,2,3,4,7,8-HxCDD
  - $^{13}C_{12}$-1,2,3,6,7,8-HxCDF
  - $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF

FRM 23/Method 0023A Glassware Preparation

- Soak all glassware in hot soapy water
- Rinse with tap water
- Rinse with DI water

FRM 23/Method 0023A Glassware Preparation

- Bake at 400°C for 2 hours
- Rinse (3 times) with methylene chloride
- Rinse (3 times) with toluene
- Cap glassware with cleaned aluminum foil

FRM 23/Method 0023A Glassware Preparation

- Mark glassware with color-coded stickers
- Rinse glassware immediately before use with acetone and methylene chloride

FRM 23/Method 0023A Operational Requirements

(See Field Observation Checklist)

- Multi-point integrated sampling
- Isokinetic sampling rate (average sampling rate should be within 0.5 to 0.75 cfm)
- Collect calculated sample volume based upon analyte detection limits

FRM 23/Method 0023A Operational Requirements

- Probe/filter at 120°C (248°F)
- Sorbent resin trap inlet < 20°C (68°F)
- Leak-free system

Calculation of Sample Duration

- Minimum sample time = Analytical Detection Limit/[(Sample Rate) X (Desired Gas Concentration Detection Limit)]

Example Calculation

- Assumptions
  - Average sampling rate 0.5 cfm
  - Analytical detection limit 0.5 ng
  - Desired gas concentration 0.1 ng/m^3

Example Calculation

- Minimum sample time = 0.5 ng/[(0.85 m^3/hr) X (0.1 ng/m^3)] = 5.88 hours minimum sample time
- Minimum sample time should be greater than or equal to the calculated total sample time (minimum 2 minutes per sampling point)

FRM 23/Method 0023A Record Keeping Requirements

- Calibration of
  - Temperature sensors
  - Metering pump
  - Pitot tubes

FRM 23/Method 0023A Record Keeping Requirements

- Periodic sampling information
  - Gas flow measurements
  - Sampling train parameters
- Sample recovery and laboratory data

Preliminary Field Determination

(See Field Inspection Checklist)

- Select sampling site according to FRM 1
- Select nozzle size and establish isokinetic sample train operation
- Select probe liner and proper length

Preliminary Field Determination

- Determine total length of sampling based upon method detection limits
- Establish sampling time per point based upon calculation

Preparation of Sample Train

- Obtain certified clean isotopically spiked (i.e., field surrogates) sorbent trap from sample custodian, log trap number into field data sheet
- Obtain clean quartz fiber filter from sample custodian

Preparation of Sample Train

- Charge impingers with appropriate solutions (first impinger empty, second and third impingers filled with 100 mL water, fourth impinger contains 200-300 g silica gel)
- If analyzing for SVOCs, then use HPLC-grade water in impingers

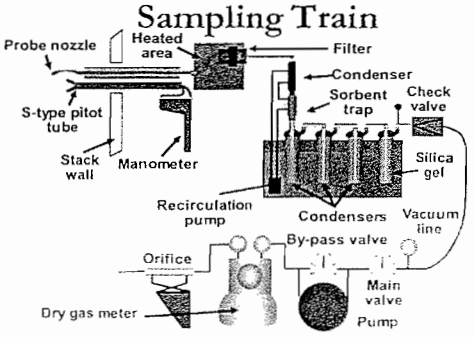
Preparation of Sample Train

- Place labeled/pre-weighted filter in filter holder
- Install selected nozzle and mark probe

Preparation of Sample Train

- Assemble sample train (no silicone grease upstream of organic module)
- Place crushed ice around impingers

FRM 23/Method 0023A Sampling Train



Preparation of Sample Train

- Turn on filter/probe heating systems
- Turn on sorbent and condenser coil coolant recirculating pumps (must maintain resin bed at < 20°C)

Preparation of Sample Train

- Leak check system at 15 in. Hg vacuum; rate not to exceed 4% of average sampling rate (< 0.02 cfm)

Preparation of Sample Train

- Clean stack access port
- Insert probe to first sampling point and record initial train information on field test data sheet
- Block off openings around probe to prevent dilution of sample gas

Sample Train Operation

- Begin sampling when all temperatures are at required settings:
  - Probe/Filter: 120 ± 14°C
  - Sorbent Bed: < 20°C
  - Exit Silica Gel Impinger: < 20°C

Sample Train Operation

- Sample at each traverse point, maintaining isokinetic sampling rate to within 10% of true isokinetic

Sample Train Operation

- Record sample train operating parameters-sampling time
  - Sample train vacuum
  - Differential pressures: pitot tube, orifice
  - Dry gas meter (DGM) volume
  - Temperatures: DGM, filter, stack, sorbent, exit last impinger
  - Maintain isokinetics ($\Delta H = K\Delta p$)

Sample Train Operation

- If the pressure drop across filter or adsorbent is > 15 in. Hg, then one must change components
  - Must leak check system prior to change and after change of train component
  - If exceeds leak rate limit, run is voided

Sample Train Recovery

- Turn off coarse adjust valve, remove probe from stack, turn off pump
- Leak check to specifications
- Calculate percent Isokinetics to determine whether the run is valid

Sample Train Recovery by FRM 23/Method 0023A

- Filter (Container #1: FRM 23/Method 0023A)
  - Recover in pre-clean aluminum foil or container
- Front Half Rinse (Container #2/Method 0023A) and Back Half Rinse (FRM 23)
  - Nozzle, probe liner, filter housing: 3X acetone, then methylene chloride (FRM 23/Method 0023A)
  - 2X with toluene (SW-846, Method 0023A)

Sample Train Recovery by FRM 23/Method 0023A

- XAD-2 sorbent trap (Container # 3/Method 0023A). No container for FRM 23 sorbent trap
  - Weigh for moisture/cap ends (FRM 23)
  - Wrap in original aluminum foil
  - Ship to lab under blue ice (< 4°C)
- Back half rinse (Container #4/Method 0023A)
  - Back half filter holder, connecting lines, condenser with 3X acteone, 2X methylene chloride, 2X toluene

Sample Train Recovery by FRM 23/Method 0023A

- Impingers - measure/weigh entrained water and note any color in first three impingers (if analyzing for SVOCs, retain)
- Silica Gel - note color, weigh

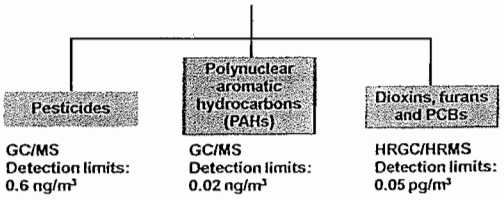
Criteria for On-site Invalidation

- Minimum sample volume not met (may not have enough analyte for MDL)
- XAD-2 temperature exceeds 68°F (loss of sample from resin due to no adsorption)

Criteria for On-site Invalidation

- Use of wrong recovery solvents (may not collect analyte)
- Pre-test leak check >0.02 cfm (4% of average of sampling rate)
- Calculated percent isokinetics outside 90-110%

Analysis



HRGC/HRMS Analysis

- HRGC/HRMS initial tuning
- 5-point initial calibration curve
- Continuing calibration checks

HRGC/HRMS Analysis

- Soxhlet extraction spiked
- Quantitation by internal standards
- PE sample analyzed

Ions Monitored by HRGC/HRMS

- 2,3,7,8-TCDD
  - 258.9300
  - 319.8965
  - 321.8936
  - 331.9368

Ions Monitored by HRGC/HRMS

- 1,2,3,4,7,8-HxCDD
  - 326.8521
  - 389.8156
  - 391.8127

Ions Monitored by HRGC/HRMS

- OCDD
  - 394.7742
  - 457.7377
  - 459.7347

Analysis For FRM 23

- Analysis by FRM 23 combines filter and XAD-2 resin as one analysis
- Analysis by SW-846, Method 0023A performed in two fractions
  - Fraction #1: Filter (with surrogate spiking) and front half rinses (Containers 1 and 2)
  - Fraction #2: Sorbent trap and back half rinses (Containers 3 and 4)

Method 0023A Laboratory Surrogates

- **Added to filter prior to extraction**
  - $^{37}C_4$-2,3,7,8-TCDD
  - $^{13}C_{12}$-2,3,4,7,8-PeCDF
  - $^{13}C_{12}$-1,2,3,4,7,8-HxCDD
  - $^{13}C_{12}$-1,2,3,6,7,8-HxCDF
  - $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF

Analysis

- This allows filter surrogate recoveries/XAD-2 surrogate standard recoveries determined

Analysis

- Surrogate standards are added to the filter/front half fraction immediately prior to extraction whereas the field surrogate standards have already been added to XAD-2 resin prior to field deployment

Analysis by FRM 23

- Container #1 (filter)
  - Extract extraction thimble/ 1 g of silica gel and glass wool with for 3 hrs toluene
  - Add filter and XAD-2 resin in the extraction thimble containing the 1 g silica gel

FRM 23 Analysis

- Container #2 (Acetone and Methylene Chloride Rinses)
  Concentrate to 1-2 mL and added to filter/XAD-2 resin in the extraction thimble
- Add 100 µL of internal standard solution
- Container #3 (Toluene Rinse)
  Concentrate and analyze separately

Both Method Analysis

- Soxhlet extraction in toluene/16 hours
- Concentrate to 100 µL, redissolve in 5 mL of hexane
- Cleanup with alumina/carbon columns
- Add recovery standards
- Analyze by HRGC/HRMS

Both Method Analysis

- Samples must be extracted within 30 days and analyzed within 45 days
- Extracted samples spiked with Recovery Standards (40 µL)

Both Method Analysis

- Extracted samples divided into two portions
  - Portion #1: archived for future analysis
  - Portion #2: solvent exchanged to hexane, then subject to 3 column chromatographic cleanup by Method 8290

Both Method Analysis

- GC/MS analysis by Method 8290
  - HRGC/HRMS initial tuning
  - 5-point initial calibration
  - Continuing calibration checks
  - Recovery standard solutions
  - Quantitation by internal standards

Calculation

$C_i(\mu g/m^3)$ = (Total mass of analyte collected, µg) / (Std. volume of gas sampled, m^3)

Both Method Acceptance Criteria

- All PCDD/PCDF surrogate recoveries should be within 70% to 130%
- If all isomer recoveries are greater than 130% or less than 70%, repeat sample run

Both Method Acceptance Criteria

- Must perform field, method, reagent, and proof blanks
- Must pre-clean filter and sorbent cartridge

Both Method Key Points

- XAD-2 and filter must be certified clean and good for 4 weeks
- Adsorbent temperature during sampling can not exceed 68°F
- Pre- and component change leak check required and must meet < 0.02 cfm or invalidate sample run

Both Method Key Points

- Filter spiked with surrogates prior to extraction (Method 0023A)
- XAD-2 adsorbent trap spiked with surrogates prior to field deployment

Both Method Key Points

- Surrogate, internal and recovery standards used with HRGC/HRMS analysis
- Shipment of samples to laboratory under blue ice (< 4°C)
- No grease used in front of sorbent trap

Both Method Key Points

- Extensive cleaning of glassware prior to use
- Must calculate sample volume needed to meet method detection limits
- Can't use stainless steel nozzles

Both Method Key Points

- Extraction and analysis performed in two fractions so filter and XAD-2 surrogate recoveries can be determined separately (Method 0023A only)
- Sampling is isokinetic
- Sample must be extracted in 30 days and analyzed within 45 days

PCB Congeners

PCB Isom Group	Cong. #	Chlorine Sub.
Monochlorobiphenyl	1	2
Trichlorobiphenyl	29	2,4,5
Pentachlorobiphenyl	87	2,2',3,4,5'
Octachlorobiphenyl	200	2,2',3,3',4,5', 6,6'

LONG-TERM DIOXIN & FURAN SAMPLING SYSTEMS

- AMESA (German Instrument)
  - Adsorption Method for Sampling of D/F
- DMS (Austria Instrument)
  - Dioxin Monitoring System

APPLICATIONS DIOXIN/FURAN EMISSIONS

- MUNICIPAL INCINERATORS
- HAZARDOUS WASTE INCINERATORS
- HOSPITAL WASTE INCINERATORS
- SEWAGE SLUDGE INCINERATORS
- OTHER COMBUSTION SOURCES

SAMPLING PRINCIPLES AMESA & DMS

- Auto-isokinetic Sampling
- Titanium Probe & Nozzle
  - Heated application
  - Air or water cooled application
- Sampling Periods
  - 4 hrs to 4 weeks
  - Usually 2 weeks per XAD module

AMESA SAMPLING EQUIPMENT & PROTOCOL

- Titanium Probe Positioned at Average Velocity Sampling Point
- Electronic System Leak-Check Valve
- Collects D/F in XAD-2 Module
- Collects & Measures Stack Moisture
- Monitors & Records Temperatures

DMS SAMPLING EQUIPMENT & PROTOCOL

- Two Titanium Probes Positioned at Average Velocity Sampling Points
- Electronic System Leak-Check Valve
- Collects D/F on Filter & PUF Cartridges
- Does Not Measure Stack Moisture
- Monitors & Records Temperatures

DMS SAMPLING EQUIPMENT & PROTOCOL

- Dual Titanium Probes Positioned at Average Velocity Sampling Points.
- Probes Switch Every 30 Minutes
- Uses the "Null Nozzle" Concept
- Stack Sample is Diluted & Cooled
- Electronic System Leak-Check Valve
- Collects D/F on Polyurethane Foam (PUF)
- Does Not Collect Stack Moisture

DMS SAMPLING PROTOCOL

- Null Nozzle Sampling Approach
  - Design assumes by adjusting the nozzle sample flow to produce a "null condition" for the manometer pressures, isokinetic sampling can be achieved.
  - Reliability of null sampling nozzles is a function of design and use.
  - Isokinetic sampling conditions are not always guaranteed.

DMS SAMPLING PROTOCOL

- Dilution Sampling Method
  - Stack gas is sampled isokinetically
  - Mixed with dried, cleaned, D/F-free compressed air
  - Purpose of dilution air is to cool and dilute the stack gas to a dew point where little or no condensate is realized
  - Dry gas mixture passes through a filter and two PUFs for D/F collection

DMS SAMPLING PROTOCOL

- Polyurethane Foam (PUFs)
  - Two PUFs in series collect D/F
  - PUFs are cleaned and vacuum dried prior to use
  - Glass fiber filter and two PUFs are installed in field module
  - 100 ul of a recovery standard surrogate is applied to glass fiber filter surface
  - Module is assembled by laboratory

AMESA & DMS SAMPLING EQUIPMENT

- Measures Stack Gas Velocity, Temperature, & Pressure
- Optional System Can Measure O2 & CO2
- Sampling Range – 0.0001 to 10 ng/m^3
- Condensate Can Be Collected & Analyzed For AMESA

AMESA & DMS SAMPLING PROTOCOL

- Isokinetic Sampling Procedures
- Duplicates M23 Sampling Rates
- Collects Approx. 0.85 m^3/hour (0.85 m^3 X 24 hrs = 20 m^3/day)
- Volume For a Two Week Period – >280 m^3

AMESA & DMS SAMPLE MULTIPLE ANALYSES

- From a 280 m^3 XAD Sample Extract:
  - Dioxins/Furans
  - Polynuclear Aromatic Hydrocarbons (PAHs)
  - Polychlorinated Biphenyls (PCBs)
  - CAA Semivolatile HAPs
  - Other Organic Target Compounds

AMESA SUMMARY

- Conducts Isokinetic Sampling
- Sampling Probe/Nozzle
  - Titanium materials
  - Single average-point sampling
  - Usually not heated (can be modified)
  - Probe sample fraction usually not recovered (20% factor added to XAD catch)
- No Fiber Glass Filter (can be added)
- Collects Stack Gas Moisture

DMS SUMMARY

- Conducts Isokinetic Sampling
- Null Sampling Probe/Nozzle (2)
  - Titanium materials
  - Two average-point sampling locations
  - Usually not heated (can be modified)
  - Probe sample fraction usually not recovered (20% factor added to XAD catch)

DMS SUMMARY

- Stack Gas Dilution
- Fiber Glass Filter & PUFs
- No Stack Gas Moisture

AMESA & DMS SUMMARY

- Can Measure D/F 52 Weeks/Year
- Estimated Cost (less analysis)
  - Purchase price - ~$100,000 US
  - Lease Price (12 months) - $4000/month
- AMESA – 55 Units in Operation
- DMS – 5 Units in Operation

AMESA & DMS CONCLUSIONS

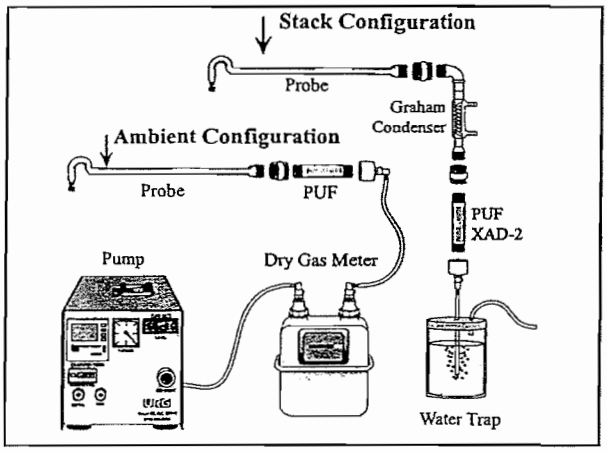
- Allows for Long-Term D/F Measurements – up to 4 weeks
- Annual D/F Method 23 Estimates for Plants Have Increased 15 to 25% When Measured by AMESA & DMS
  - Increases attributed to: 1) daily plant operation variations and 2) that very few of the D/F are "non detects" as seen in Method 23 analyses.

AMESA & DMS AS ALTER. TEST METHODS

- Must Meet M 301 Acceptance Criteria as Compared With EPA Method 23
- Procedures Could be Approved
  - As alternative compliance test method
    - At specific industry category
    - Facility by Facility approval (each emission point must be evaluated)

AmbStack Dioxin Sampling

- Two part sample train/1 person
  - Unheated probe and pre-cleaned PUF/XAD-2 module
  - Metering console contain flow control, pump and volume meter
- Analysis by bioassay based on the Chemically Activated Luciferase Expression (CALUX) Assay

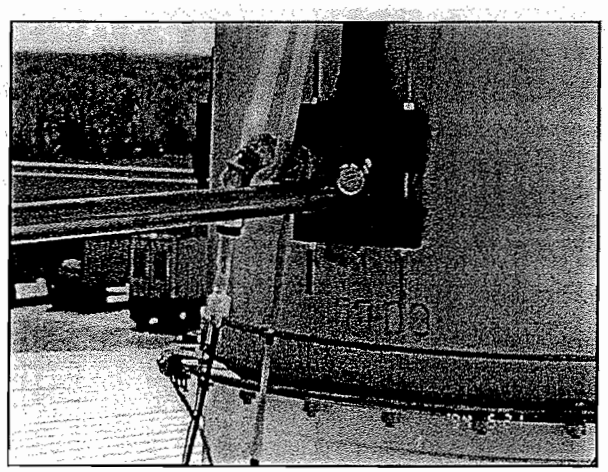


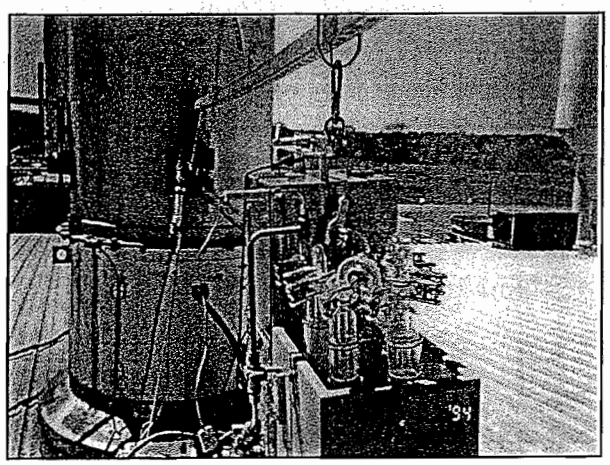
AmbStack Dioxin Sampling

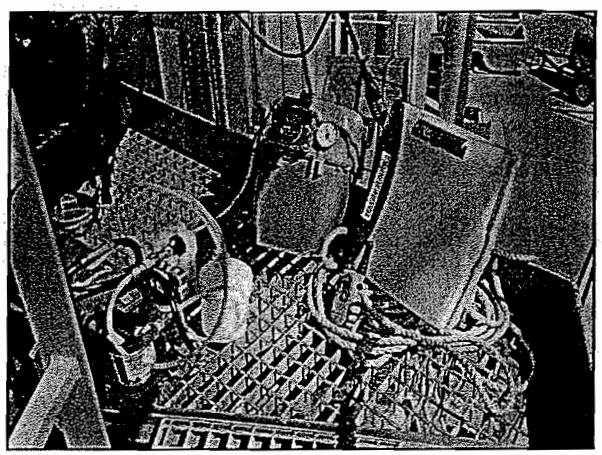
- System operated non-isokinetically and at a constant rate (~ 2L/min) at a single point (average velocity) in the stack. Sampling typically 3 hours
- Assay uses genetically engineered cells with the Luciferase gene under control of a dioxin-responsive promoter

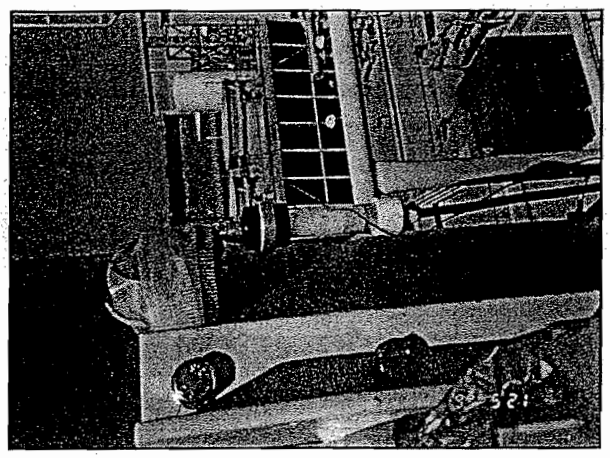
AmbStack Dioxin Sampling

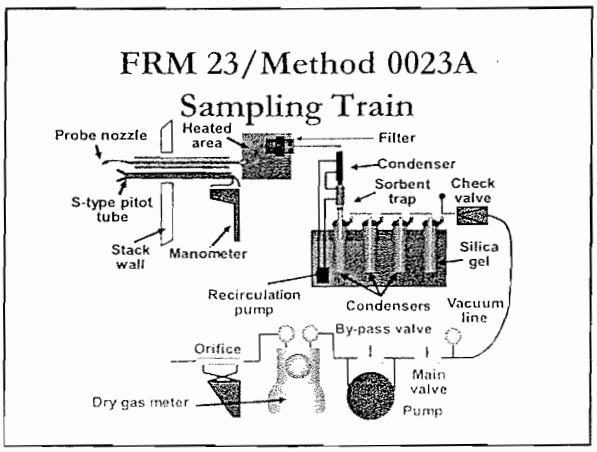
- If dioxin/furans are present, the dioxin-responsive promoter emits light and recorded
- Dioxin TEQ is proportional to the amount of light emitted in response to a sample







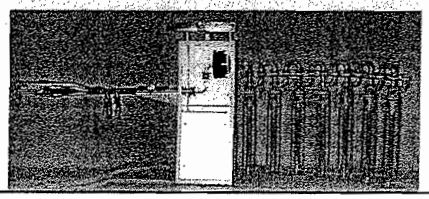


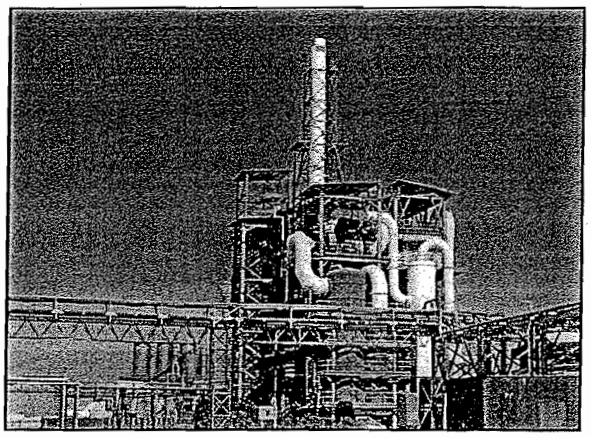

FRM 23/Method 0023A
Sampling Train
Probe nozzle
Heated area
Filter
Condenser
Sorbent trap
Check valve
S-type pitot tube
Stack wall
Manometer
Silica gel
Recirculation pump
Condensers
Vacuum line
By-pass valve
Orifice
Main valve
Dry gas meter
Pump

U.S. EPA APTI

Compliance Test and Source Test Observation

FRM 29/SW-846, Method 0060, Multi-Metals Sampling, FRM 12 for Inorganic Lead and FRM 306 for Chromium





Applicability

- This method is used to determine the concentration of metals in stack emissions from hazardous waste incinerators and similar combustion processes
- May also determine particulate matter concentration concurrently utilizing FRM 5

Metals Detected

- The following 17 metals can be detected by FRM 29/Method 0060:
  - Antimony (Sb)
  - Arsenic (As)
  - Barium (Ba)
  - Beryllium (Be)
  - Cadmium (Cd)
  - Total Chromium (Cr)
  - Cobalt (Co)
  - Copper (Cu)
  - Lead (Pb)
  - Manganese (Mn)

Metals Detected

- Mercury (Hg)
- Nickel (Ni)
- Phosphorus (P)
- Selenium (Se)
- Silver (Ag)
- Thallium (Th)
- Zinc (Zn)

Interferences

- Stainless steel and other metals associated with the sampling train and recovery components will interfer with the quantitation of metals
- Can't use metal components

Interferences

- Spectral interferences can be minimized through the proper selection of analytical methodology
- "Dated" reagents may provide high metal background concentration, thus, high bias

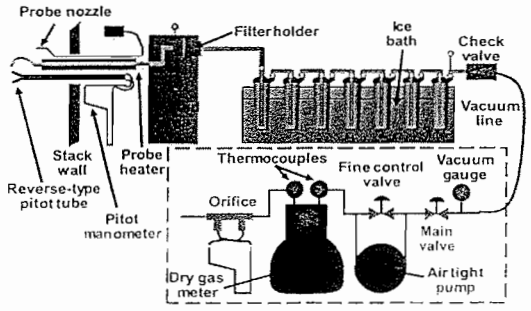
FRM 29/Method 0060 Design Requirements

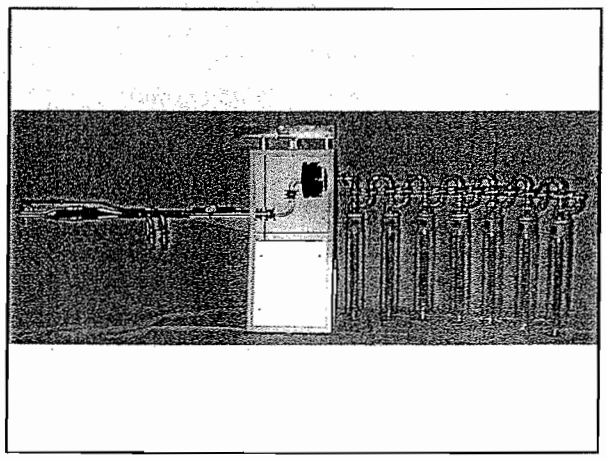
- Gas flow measurement system (FRM 2-4)
- Modified Method 5 sampling train
- Addition of three more impingers

FRM 29/Method 0060 Sampling Train

- Probe with quartz nozzle and liner
- Pitot tube/temperature sensor array
- Heated filter assembly
- Seven impingers
- Pump/dry gas meter/orifice assembly

FRM 29/Method 0060 Sampling Train





FRM 29/Method 0060 Operational Requirements

- See Field Observation Checklist
- Multi-point integrated sampling
- Isokinetic sampling rate
- 2-hr sample with minimum sample volume of 45 cf

FRM 29/Method 0060 Operational Requirements

- Probe/filter at 120°C (248°F)
- PM metals (and FRM5 PM) collected in front half, gaseous metals collected in back half

FRM 29/Method 0060 Operational Requirements

- Recovery of front half and back half separate
- Samples are acid digested to dissolve inorganics and remove organic constituents
- If stack gas moisture < 100 mL, then can eliminate first impinger

FRM 29/Method 0060 Impinger Arrangement

- 1st Impinger- empty (Optional)
- 2nd & 3rd Impinger- 5% HNO_3/10% H_2O_2 (vapor multi-metals)
- 4th Impinger- empty

FRM 29/Method 0060 Impinger Arrangement

- 5th & 6th Impinger- 4% $KMnO_3$/10% H_2SO_4 (For mercury vapor)
- 7th Impinger- Silica gel

FRM 29/Method 0060 Glassware Preparation

- Hot tap water rinse
- Wash with hot soapy water
- Rinse 3 times with tap water, then 3 times with cleaned, DI water
- Soak in 10% HNO_3 for 4 hours

FRM 29/Method 0060 Glassware Preparation

- Rinse 3 times with cleaned, DI water
- Rinse with acetone and air dry
- All openings covered with paraffin until used

FRM 29/Method 0060 Sample Train Requirements

- Glass or Teflon® nozzle
- Nonmetallic probe line
- Nonmetallic brushes

FRM 29/Method 0060 Sample Train Requirements

- Daily preparation of $KMnO_4$ solution
- Polypropylene tweezers
- Storage bottles of glass with Teflon lined caps

FRM 29/Method 0060 Operation

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

FRM 29/Method 0060 Operation

- Prevent $KMNO_4$ from contacting other glassware and prevent H_2O_2 from mixing with $KMnO_4$
- Leak check in accordance with FRM 5
- Sample collection in general accordance with FRM 5

FRM 29/Method 0060 Operation

- No metal components in the sample train and during sample recovery

FRM 29/Method 0060 Sample Train Recovery Containers

1- Petri Dish (Filter)

2- Acetone rinse from probe nozzle/liner, and front half of filter holder (exactly 100 mL)

3- HNO_3 rinse of probe nozzle/liner, and front half of filter holder (exactly 100 mL)

Sample Train Recovery Containers

4- Combined impingers 1, 2 and 3 (measured) and HNO_3 acid rinse of impingers and back half of filter holder (exactly 100 mL)

Sample Train Recovery Containers

5A- Impinger 4 (measured) and HNO_3 rinse of impinger 4 (100 mL)

5B- $KMnO_4$ impingers contents (measured) and $KMnO_4$ (100 mL) + water (100 mL)

Sample Train Recovery Containers

5C- 8 M HCl (25 mL) rinse of the two impingers and transferred to container containing water (200 mL)

Sample Train Recovery Containers

6- Silica gel contents (note color, weigh)

7- Acetone blank (100 mL)

8A- HNO_3 reagent blank (300 mL)

8B- Water reagent blank (100 mL)

Sample Train Recovery Containers

9- 5 % HNO_3/10% H_2O_2 reagent blank (200 mL)

10- $KMnO_4$ reagent blank (100 mL)

11- 8 M HCl reagent blank (200 mL of water + 25 mL of 8 M HCl)

12- Filter blank

Analysis

- Weigh filter if need FRM 5 PM
- Acid digestion of filter and sample train recovery reagents
- Analysis by ICAP for all metals (except mercury)
- Aliquots taken of recovery reagents for mercury analyzed by CVAAS

Calculation

- M(i) = (C)(F)(V)
  where:
  - C = concentration of metal from calibration curve, ug/mL
  - F = dilution factor
  - V = total volume of digested sample

Calculation

- Total metal concentration in sample train:
  M(f) = [M(ifh)-M(fhb)] + [M(ibh)-M(bhb)]
- where:
  - M(f) = total mass of each metal in complete sample train
  - M(ifh) = total mass of each metal in front half (fh) of sample train

Calculation

M(f) = [M(ifh)-M(fhb)] + [M(ibh)-M(bhb)]

- M(fhb) = total metal found in front half blank
- M(ibh) = total metal found in back half of sampling train
- M(bhb) = total metal found in back half blank

Calculation

- Stack gas concentration is calculated:
  - C($\mu g/m^3$) = M(μg)/(Std. volume of gas sampled, m^3)

FRM 29/Method 0060 Key Points

- All active sample train components must be made of glass or Teflon® (no metal components)
- All active sample train components must be cleaned through a detailed clean-up scheme

FRM 29/Method 0060 Key Points

- FRM 5 PM can also be determined concurrent with Method 0060
  - Front half of train: particulate metals
  - Back half of train: gaseous metals
- If not sampling for mercury, do not need impingers 4, 5 & 6 in the sample train

FRM 29/Method 0060 Key Points

- Storage containers must be made of glass with Teflon®-lined caps
- Front half of train captures particulate metals while back half captures gaseous metals
- Imperative to use exactly 100 mL of rinsing solutions for blank correction in final concentration calculation

FRM 29/Method 0060 Key Points

- If sampling for total metals only (not FRM 5 PM), then filter does not have to be desiccated or weighed
- Do not need 1st impinger if water is determined to be < 100 mL
- Impinger reagents made daily
- Must use exact volume of rinses for background correction

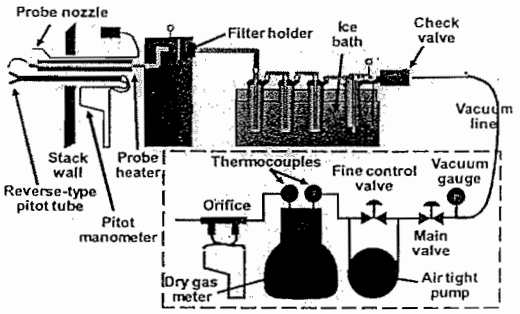
FRM 29/Method 0060 Key Points

- Special cleaning of glassware
- Exact blank volumes/composition must be acquired for blank correction

U.S. EPA APTI Compliance Test and Source Test Observation Course #468

FRM 12, Inorganic Lead

FRM 12 Sampling Train



40CFR63, Subpart X: National Emission Standards for Secondary Lead Smelters

- 06/09/94: Proposed rule
- 06/23/95: Final rule for new and existing secondary lead smelters
- 06/13/97: Direct final rule (Amendments to final rule)
- 08/18/99: Proposed amendments Title V
- 12/14/99: Final rule

Test Methods Identification

- FRM 1: Port location
- FRM 2: Volumetric flow rate
- FRM 3 or 3A: Correct conc. meas.
- FRM 4: Moisture content
- FRM 12: Determination of inorganic lead

FRM 12 Applicability

- This method is used to determine the concentration of particulate matter (PM) lead and gaseous lead emissions from stationary sources
- Sources comprise mostly of 23 smelters (15 major and 8 area sources) located in 13 states

Summary of Method

- FRM 5 sample train with glass nozzle and probe liner
- Filter temperature maintained @ 248°F
- Particulate lead caught on filter while gaseous lead caught in impingers
- Analysis by acid digestion followed by flame atomic absorption (FAA)

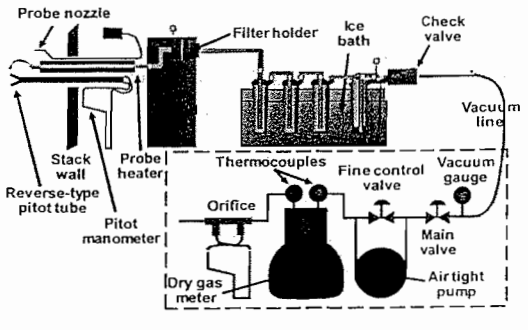
FRM 12 Design Requirements

- Gas flow measurement system (FRM 1-4)
- FRM 5 sampling train
- Operated isokinetically

FRM 12 Sampling Train

- Probe with quartz nozzle and liner
- Pitot tube/temperature sensor array
- Heated filter assembly
- Standard FRM 5 impingers with impingers 1 and 2 containing 100 mL of 0.1 HNO_3
- Pump/dry gas meter/orifice assembly

FRM 12 Sampling Train



Sample Recovery

- FRM 12 Recovery
  - Container #1: Recover filter for lead PM same as FRM 5
  - Container #2: Front-half 0.1 N HNO_3 rinse up to front-half filter compartment
  - Container #3: Note color of silica gel to determine whether it has been completely spent. Transfer the silica gel to its original container, weigh on site or transport back to laboratory for weighting

Sample Recovery

- FRM 12 Recovery
  - Container #4: Measure and collect the impinger nitric acid solutions from first three impingers; Rinse twice with 30 mL 0.1 N HNO_3 each impinger and collect in container #4
  - Container #5: Reagent blank of 200 mL of 0.1 N HNO_3

Sample Analysis

- Container #1: Filter cut into strips and digested with 10 mL of 50% of HNO_3, heat on hot plate, add 10 mL of 3 % H_2O_2 and 50 mL of DI water, heat for 20 minutes. Filter and dilute to 100 mL. Also must determine filter blank (FB) with 2 unexposed filters from same lot following same procedure

Sample Analysis

- Containers #2 and #4: Transfer to Erlenmeyer flask, heat on hot plate to dryness, add 30 mL of 3 % H_2O_2 and 50 mL of hot DI water, heat for 20 minutes. Filter and dilute to 250 mL

Sample Analysis

- Container #3: Weigh silica gel to nearest 0.5 grams (B_{ws})
- Container #5: Dry the 200 mL on a steam bath to dryness, add 15 mL of 50 % H_2O_2 and 50 mL of hot DI water, dilute to a total volume of 100 mL

Sample Analysis

- Flame Atomic Absorption (FAA)
  - Calibration of FAA using standard solutions
  - Check matrix effects by using the method of additions
    - Spiked sample vs. unspiked sample
  - Stability of calibration curve
    - Run a blank and standard after every 5th sample

FRM 12 Operational Requirements

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

FRM 12 Operational Requirements

- Probe/filter at 120°C (248°F)
- Lead PM collected on front-half of sampling train, while gaseous lead collected in impingers

FRM 12 Impinger Arrangement

- 1st and 2nd Impinger- 100 mL 0.1 N HNO_3
- 3rd Impinger- Dry
- 4th Impinger- 200-300 g silica gel

FRM 12 Operation

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

FRM 12 Operation

- Pre-/post leak check in accordance with FRM 5
- Sample collection in general accordance with FRM 5
- Sample recovery in general agreement with FRM 5 except rinsing with 0.1 N HNO_3

FRM 12 Key Points

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

FRM 12 Key Points

- FRM 5 PM can be determined concurrent with FRM 12
  - Front half of train: particulate matter (PM) with acetone rinse
  - Impinger solution: 0.1 N HNO_3
  - Use of glass fiber filter with low background lead concentration
  - Treat and analyzes the entire sample train contents, including the impingers, for lead

FRM 12 Key Points

- FRM 17 may be used provided that:
  - Use of glass-lined probe and at least 2 impingers each containing 100 mL of 0.1 N HNO_3 after the in-stack filter
  - Recovery of probe and impinger contents for lead. Recovery of sample from the nozzle with acetone if a PM determination is to be made

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

Federal Reference Method 306: Sampling and Analysis for Chromium Emissions from Decorative and Hard Chromium Electroplating/Anodizing Operations

Principle

- Gaseous and particulate chromium pollutants are withdrawn isokinetically from the source and collected in a unheated FRM 5 sample train without filter
- Gaseous and particulate chromium pollutants are collected in the impingers containing 0.1 N NaOH or 0.1 N $NaHCO_3$

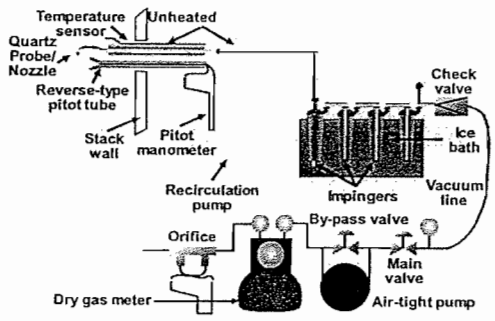
FRM 306 Summary

- Chromium extracted isokinetically from the source
- FRM 5 sampling train except:
  - Unheated quartz probe/nozzle; No SS
  - No heated filter box
  - Replacement of water in impingers with 0.1 N NaOH or 0.1 N $NaHCO_3$
  - Don't have to brush probe for recovery

FRM 316 Summary

- 2-hour sample run
- Options for analysis
  - Total chromium: Collect all impinger
  - Cr^{+6}: Evaluate pH of first impinger; Should be > 8.5 pH
- Audit sample required

FRM 306 Sampling Train



Discussion

- Sampling Train: Tradition FRM 5 Without Heating; No Filter or Filter Component; All Quartz Components
- Sampling: Isokinetic, FRMs 1-4, Sample Time > 2 Hrs
- Analytical Finish: Inductively Coupled Plasma Emission Spectrometry (ICP); Cr^{+6} by Ion Chromatography (IC)

Discussion

- Cr^{+6} Emissions?
  - If Cr^{+6} emissions, then at end of sampling run, 1st impinger must have pH of >8.5 or must discard sample run (No requirement for total chromium)
  - Must store samples at 4 °C until analysis (Total chromium can store samples at room temperature)
  - Samples must be analyzed within 14 days (60 days for total chromium)
  - Analysis by ion chromatography equipped with post-column reactor (IC/PCR)

Discussion

- Total Chromium (TC) Emissions?
  - High Concentrations: Inductively coupled plasma emission spectrometer (ICP) @ 267.72 nm
  - Low concentrations: Digestion with HNO_3, then graphite furnace atomic absorption spectroscopy (GFAAS) @ 357.9 nm

Discussion

- Interferences: Stack and ICP Interferences
  - High SO_2 Concentrations reduces 0.1 N NaOH concentration in impingers
  - Spectral: Overlapping of spectral lines (Fe, Mn, U)
  - Physical: Dissolved solids in sample
  - ICAP background interferences
- Concentration: No Blank Correction

Discussion

- GFAA Interferences
  - Spectral: CN^-
  - Chemical: Ca and PO_4^-
- IC/PCR
  - Compounds which cause Cr^{+6} to Cr^{+3} etc.
  - Coeluting compounds

Sampling

- Must traverse the stack to each sampling point determined by FRM 1 (may need probe extension)
- Sample a minimum of 2 minutes per point and required minimum sample time of > 2 hrs
- Must follow all FRM 5 QC requirement (i.e., leak checks, nozzle selection, isokinetic sampling maintained etc.)

Sampling

- Assemble sampling train, but keep all openings covered with Teflon or aluminum foil (0.1 N NaOH in impingers)
- Clean portholes prior to test run
- If stack is under negative pressure, one may start pump prior to putting filter into stack at 1st sampling point
- Block off opening around the probe to prevent in-leakage

Sampling

- Add ice to condenser impinger to maintain exit temperature < 68 F
- Sample isokinetically and make adjustments if variable change by 10 %
- At end of run, wipe off particulate matter on outside of probe nozzle and perform final leak check

Recovery

- Recover impinger solutions and measure for moisture determination and place in labeled container along with completed COC
  - Option #1: Total Cr Sample Option
  - Option #2: Cr^{+6} Sample Option

Recovery

- Option #1: Total Cr Sample Option
  - Measure volume of liquid in first, second, and third impingers
  - Rinse nozzle, probe liner, connecting glassware and all three impingers with ~ 200-300 mL of 0.1 N NaOH
  - Do not have to refrigerate
  - Must be analyzed within 60 days
  - Retain the silica gel for follow-up weighting for moisture determination

Recovery

- Option #2: Cr^{+6} Sample Option
  - Measure volume of liquid in first, second, and third impingers
  - Measure pH with indicator strip of 1st impinger. Must be > 8.5 for 0.1 N NaOH or > 8.0 for $NaHCO_3$. If not, discard and redo test

Recovery

- Option #2: Cr^{+6} Sample Option
  - Rinse nozzle, probe liner, connecting glassware and all three impingers with ~ 200-300 mL of 0.1 N NaOH
  - Refrigerate @ 4 °C until analysis
  - Must be analyzed within 14 days
  - Retain the silica gel for follow-up weighting for moisture determination

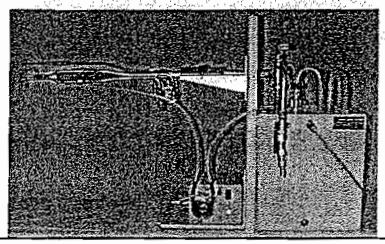
Recovery

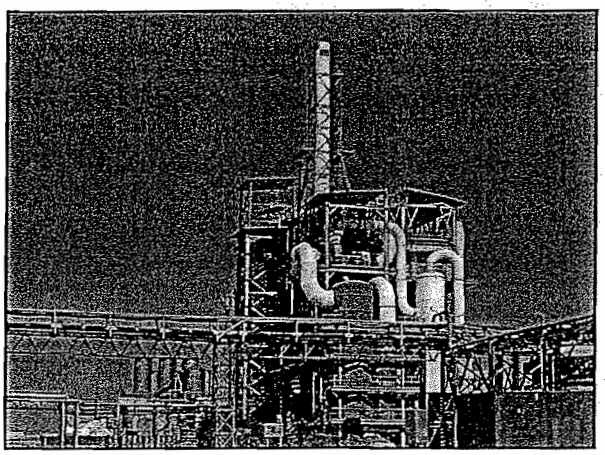
- Prepare a field reagent blank for analysis (i.e., 0.1 N NaOH) into a second bottle
- Seal all bottles and store properly until analysis
- Complete chain-of-custody (COC)

In-stack Detection Limits

- 1.4 µg Cr/dscm for ICAP
- 0.15 µg Cr/dscm for GFAAS
- 0.015 µg Cr^{+6}/dscm for IC/PCR with preconcentration

U.S. EPA APTI
Compliance Test and Source Test Observation
SW-846, Method 0061 for Cr^{+6}





Applicability

- This method provides procedures for the determination of hexavalent chromium (Cr^{+6}) and total chromium from hazardous, municipal, and sewage sludge incinerators
- Detection limit for Cr^{+6} is 16 ng/m³ for 3 dscm(0.1ppb)

Limitations/Interferences

- Compounds may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) and Cr^{+3} converted to Cr^{+6}
- Sample cross-contamination during analysis from high level to low level sample concentration
- Method has only been evaluated at sources with stack temperature <300° F

Limitations/Interferences

- Method has "reagent blank" correction, so must accurately rinse components to specific volumes during sample recovery

Method 0061 Design Requirements

- Gas flow measurement system (FRMs 2-4)

Method 0061
Design Requirements

- Modified Method 5 sampling train (all Teflon® components except for silica gel impinger)
  - Isokinetic sampling
  - Unheated probe
  - Ion chromatography (IC) analysis for Cr^{+6}

Method 0061
Design Requirements

- Addition of Teflon® aspirator behind probe nozzle, recirculation line and pump
- Post-sampling N_2 purge and sample filtration
  - 10 L/min for 30 minutes

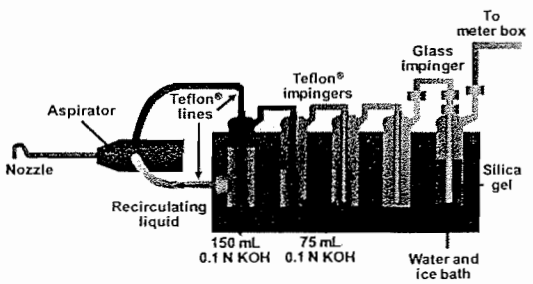
Method 0061
Design Requirements

- 14 day holding time for recovered reagents

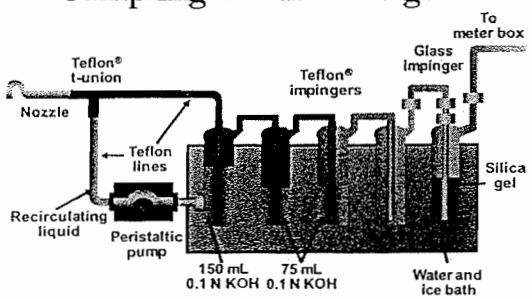
Method 0061
Sampling Train

- Unheated probe with nozzle (glass or Teflon®)
- Teflon® aspirator, Teflon® sample and recirculation lines
- Four Teflon® impingers + one glass silica gel impinger
- Pump/dry gas meter/orifice assembly

Method 0061
Sampling Train - Design 1

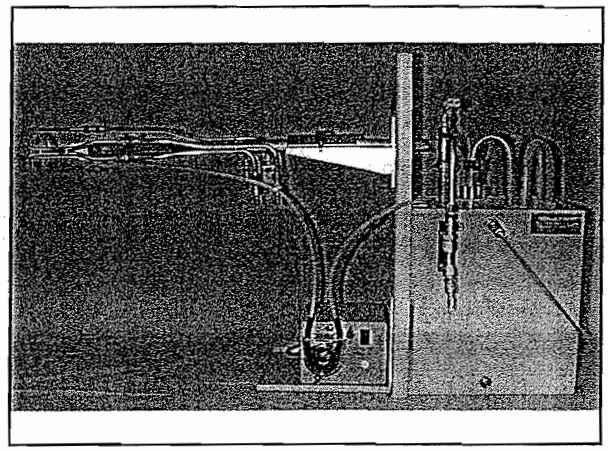


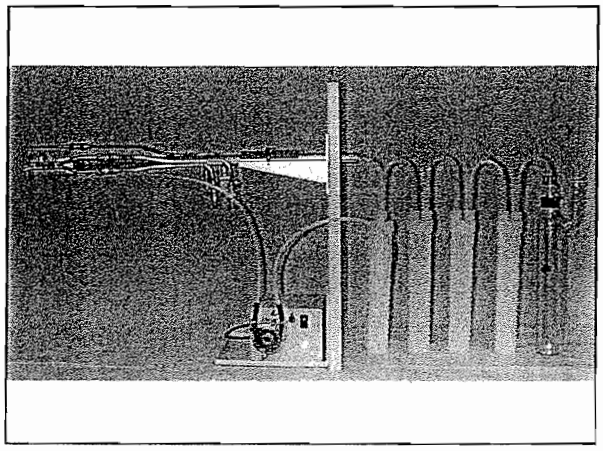
Method 0061
Sampling Train - Design 2

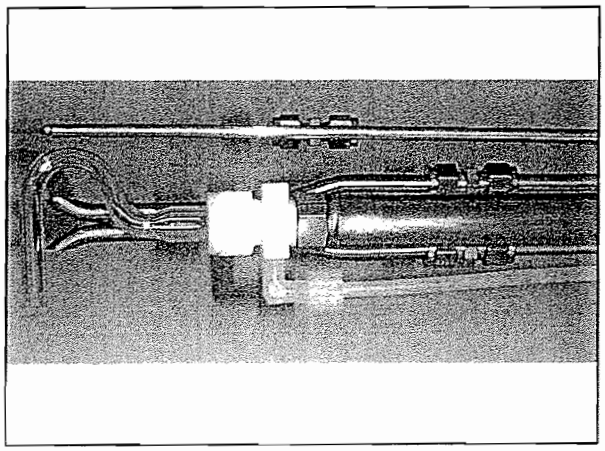


Method 0061 Sampling Reaction

- 0.1 N KOH reacts with Cr^{+6} to form a stable $Cr(OH)_2$ in the impinger solution







Remember!

- If stack gas is > 200°F, it may be necessary to wrap the "recirculating line" in the ice bath to prevent overheating of reagent
- If stack is > 300°F, then use "inner tube" technique so recirculating lines are not exposed to high temperatures

Remember!

- If source has high SO_2, then increase concentration of KOH in first impinger from 0.1 N to 0.5 N to keep pH > 8.5

Method 0061 Operational Requirements

- Multi-point integrated sampling
- Isokinetic sampling with recirculating train
- 3 dscm gas sample volume minimum

Method 0061 Operational Requirements

- Final pH of first impinger solution must be > 8.5 or discard run
- Post-sampling purge and filtration (N_2 purge)

Must Maintain pH of First Impinger > 8.5

- Increase concentration from 0.1 N to 0.5 N
- Use more volume in first impinger
- Check pH during RUN
  - On-line or instrument measurement
  - pH paper during test

Method 0061 Impinger Arrangement

- 1st Impinger- Teflon® recirculating containing 0.1 N KOH (150 mL)
- 2nd & 3rd Impinger- Teflon® containing 0.1 N KOH (75 mL)
- 4th Impinger- Teflon® (empty)
- 5th Impinger- Glass containing 200-400 g silica gel

Method 0061 Glassware Preparation

- Hot tap water rinse
- Wash with hot soapy water
- Rinse 3 times with tap water, then 3 times with cleaned, DI water
- Soak in 10% HNO_3 for 4 hours

Method 0061 Glassware Preparation

- Rinse 3 times with cleaned, DI water
- Rinse with acetone and air dry
- All openings covered with paraffin until used

Method 0061 Sampling Train Requirements

- Glass or Teflon® nozzle
- Nonmetallic, unheated probe liner
- Nonmetallic brushed
- Storage bottles of glass with Teflon®-lined caps

Method 0061 Operation

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

Method 0061 Operation

- Leak check in accordance with FRM 5; ice impingers
- Sample collection in general accordance with FRM 5 (sampling rate design for 0.75 cfm)
- No metal components in the sample train and during sample recovery

Method 0061 Operation

- If stack gas temperature > 200°F, then wrap Teflon recirculating line in ice bath to keep recirculating reagent cool
- If stack gas temperature > 300°F, use "inner tube" technique

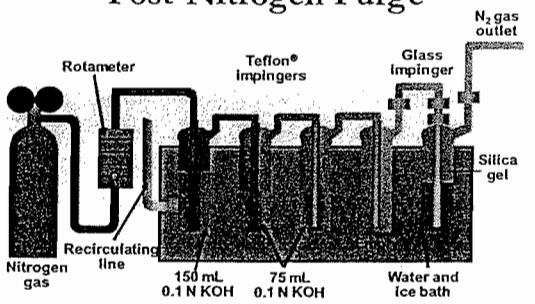
Method 0061 Operation

- Monitor pH of 1st impinger during run; at end of run, check pH of 1st impinger; must be > 8.5 or discard run
- Leak check (mandatory)
- Post-nitrogen purge at 10 L/min for 30 minutes

Post-Nitrogen Purge

- Removes SO_2 from impingers
- Safeguards against Cr^{+6} conversation to Cr^{+3}, preventing negative bias in data

Sample Train Post-Nitrogen Purge



Sample Train Recovery

- If pH of first impinger < 8.5, discard the solution, discard the run, and prepare a clean sampling train

Sample Train Recovery

- To insure > 8.5 pH
  - Use stronger KOH (0.5 M)
  - Use extra KOH (~200 mL)
  - Use shorter sampling time
  - Monitor pH during sampling (must leak check)

Sample Train Recovery Containers

1- Combine impingers 1-3 (measured) + water rinse 4X

Rinse nozzle, aspirator, recirculation line, and impingers

2- 0.1 N HNO_3 rinse 3X (optional if monitoring total chromium)

Sample Train Recovery Containers

3- Silica gel contents (note color, weigh)

4- 0.1 N KOH reagent blank (mL = mL charged in sample train)

Sample Train Recovery Containers

5- Water reagent blank (mL = mL used to rinse train during recovery)

6- 0.1 N HNO_3 reagent blank (mL = mL used to rinse train during recovery)

Analysis

Cr^{+6} analysis by SW-846, method 7199, ion chromatography

- Immediately filter entire impinger samples through 0.45 micron acetate filter to remove insoluble material
- Rinse container and filtration unit
- Measure final volume
- Holding time from sample recovery to analysis is 14 days

Analysis

- Samples should be filtered immediately after sampling to remove insoluble matter

Analysis

- If total chromium is to be determined:
  - Recover filter from filtration step and acquire residue
  - Digest 5 mL of 70% HNO_3
  - Analyze by ICAP
- Performance audit sample analyzed with samples

Calculation

- Total µg Cr^{+6} in sample train:
  - $Mf = [(Ms-Mb)(Vf)(D)]$

where:

- Mf = Mass of Cr^{+6} in sample, µg
- Ms = Mass of Cr^{+6} in sample, µg/mL
- Mb = Mass of Cr^{+6} in blank, µg/mL
- Vf = Volume of filtrate, sample, mL
- D = Dilution factor

Calculation

- Stack gas concentration is calculated

$C(\mu g/m^3) = M\ (\mu g)/(\text{Std. volume of gas sampled, } m^3)$

Method 0061 Key Points

- All active sample train components must be made of glass or Teflon® (no metal components)
- All active sample train components must be cleaned through a detailed clean-up scheme

Method 0061 Key Points

- Total chromium can be determined along with Cr^{+6} with 10% nitric acid rinse followed by water rinse of components
- Must maintain pH of KOH in first impinger > 8.5 during and at sample recovery
- Post-nitrogen purge to reduce conversion of Cr^{+6} to Cr^{+3}

Method 0061 Key Points

- To minimize reduction of Cr^{+6} to Cr^{+3} during sampling, a recirculating impinger design has been incorporated
- Methodology has been tested only at sources < 300°F

Method 0061 Key Points

- Performance Evaluation (PE) sample should be obtained
- Do not heat probe

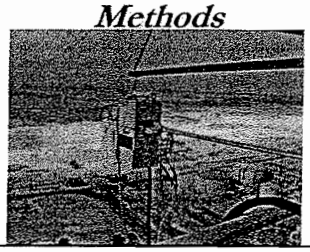
Method 0061 Key Points

- Accuracy recovery and rinses must be acquired because of "reagent blank" correction

U.S. EPA APTI
Compliance Test and Source Test Observation
Agency Observer Method Specific Checklist for SW-846

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

Introduction to Sulfur-Based Methods



Sulfur

- Sulfurs occurs in nature as elemental sulfur (yellow crystalline rhombic solid), as sulfides [galean (PbS), iron pyrites (FeS_2), and argentite (Ag_2S)], and as organic substances

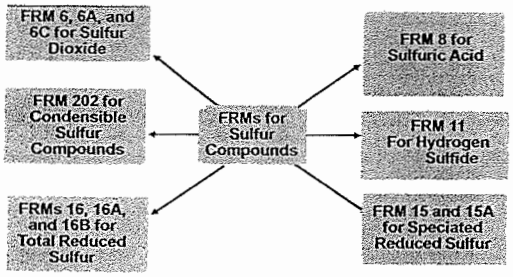
Chemistry of Sulfur

- With excess air present, monoatomic S reacts with O_2 to form different oxidized compounds
  - SO_2, SO_3, H_2SO_4
- Typical industries affected by SO_2 controls: fossil-fuel-fired steam generators, industrial boilers burning fuel oil, sulfuric acid plants, and refineries

Chemistry of Sulfur

- Depletion of oxygen in the process causes the monoatomic S to combine with hydrogen (H) to form reduced sulfur compounds
  - Hydrogen sulfide (H_2S)
  - Methyl sulfide (CH_3SH)
  - Dimethyl sulfide ($(CH_3)_2S$)
  - Dimethyl disulfide ($(CH_3)_2S_2$)

Federal Register Methods Covering Sulfur Compounds



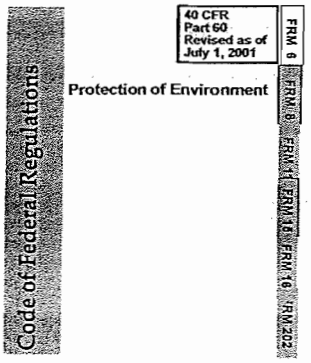
FRMs Sulfur Sampling System

FRM	Analytes Detected	Sampling System
15	Hydrogen Sulfide, Carbonyl Sulfide, Carbon Disulfide	Heated Probe and Filter, SO_2 Scrubber Impingers, Pump, Dilution System, GC/FPG
15A	Total Reduced Sulfur (TRS)	Heated Probe and Filter, Oxidizing Oven, Peroxide Impingers and Meter Box Assembly

FRMs Sulfur Sampling System

FRM	Analytes Detected	Sampling System
16	Hydrogen Sulfide, Methyl Mercaptan, Dimethyl Sulfide, Dimethyl Disulfide	Heated Probe and Filter, SO_2 Scrubber Impingers, Pump, Dilution System (Optional), GC/FPG
16A	Total Reduced Sulfur (TRS)	Heated Probe and Filter, SO_2 Scrubber Impingers, Oxidizing Oven, Peroxide Impingers and Meter Box Assembly
16B	TRS as Hydrogen Sulfide, Methyl Mercaptan, Dimethyl Sulfide, Dimethyl Disulfide	Heated Probe and Filter, SO_2 Scrubber Impingers, Oxidizing Oven, Pump, Dilution System , GC/FPG

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 6 for Determination of Sulfur Dioxide



FRM 6 Applicability

- This method is applicable for the determination of sulfur dioxide emissions from stationary sources

Chemistry of Sulfur

- With excess air present, monoatomic S reacts with O_2 to form different oxidized compounds
  - SO_2, SO_3, H_2SO_4
- Typical industries affected by SO_2 controls: fossil-fuel-fired steam generators, industrial boilers burning fuel oil, sulfuric acid plants, and refineries

Sulfur Dioxide Emissions

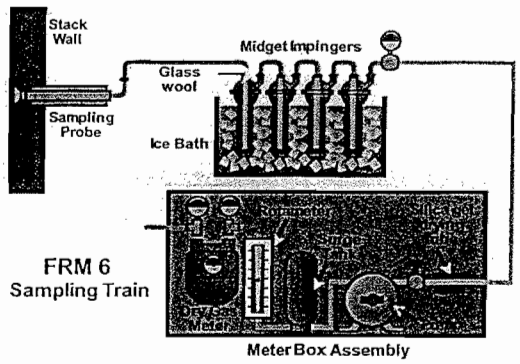
- Increased use of sulfur-containing fuels for energy has increased the emissions of oxides of sulfur from power plants
  - $S + O_2 = SO + O$
  - $SO + O_2 = SO_2 + O$

Sulfur Dioxide Emissions

- Other oxides of sulfur are also emitted, but in lesser quantities
  - $O + SO_2 = SO_3$
  - $SO_3 + H_2O = H_2SO_4$

Federal Reference Method 6 Sampling Apparatus

- Midget impinger sampling train
- Transfer line
- Meter box assembly



FRM 6 Sampling Apparatus

- Probe: 6 mm I.D. borosilicate glass or stainless steel with a heating system and glass wool plug
- Bubbler and impingers: One midget bubbler with medium-coarse glass frit and borosilicate
  or quartz glass wool packed in top

FRM 6 Sampling Apparatus

- Bubbler and impingers: 4 impingers total, connected in series with leak-free glass connectors
- Transfer line: Containing temperature connection for measuring temperature of outlet of last impinger along with tubing/electrical for connecting to meter box assembly

FRM 6 Sampling Apparatus

- Meter box assembly: Containing silica gel drying tube, leak-free diaphragm pump, surge tank, rate/rotameter, and volume/dry gas meter along with temperature gauges for measuring inlet/outlet temperature of dry gas meter

FRM 6 Impinger Contents

- Bubbler: 15 mL of 80% isopropanol to remove SO_3/H_2SO_4
- Top of bubbler: Borosilicate or quartz glass wool plug
- Impingers: 15 mL of 3% hydrogen peroxide into the first two impingers
  - Last impinger remains dry

FRM 6 Pre-test Preparation

- Calibrate the meter system
- Determine the number and location of sampling points

FRM 6 Pre-test Preparation

- Prepare sampling train
  - Add 15 mL of 80% IPA to bubbler
  - Add 15 mL of 3% H_2O_2 to next two impingers
  - Leave final impinger dry
  - Place ice and water around bubbler/impingers
  - Adjust probe heater to desired temperature

FRM 6 Sampling

- Leak check the sampling system (Optional)
- Record initial DGM reading and barometric pressure
- Position tip of probe at selected sampling point
  (> 1 meter from side of wall)

FRM 6 Sampling

- Adjust flow rate to 1 L/min ±10% during the entire sampling run
- Traverse, if applicable, taking reading every 5 minutes and recording on FTDS

FRM 6 Sampling

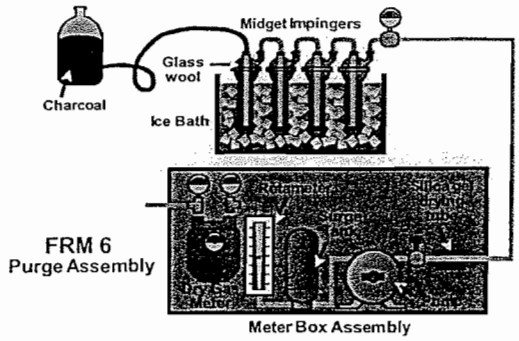
- Add more ice during run to maintain last impinger outlet < 68°F
- Reaction in impingers:
  $SO_2 + H_2O_2 = H_2SO_4$

FRM 6 Sampling

- At conclusion of run, turn off the pump, remove probe from stack, and record final DGM reading
- Leak check the sampling train (mandatory)

FRM 6 Sample Recovery

- Drain the ice bath and purge the train for 15 minutes at 1 L/min
  - Purge ambient air through charcoal filter
  - May also use ambient air without purification
  - Extra midget impingers containing 15 mL of 3% H_2O_2
- Disconnect impingers after purging



FRM 6 Sample Recovery

- Collect the 80% IPA impinger contents and save to explain possible anomalies
- Pour the content of the midget impingers into a leak-free polyethylene bottle for shipment
- Rinse the three midget impingers and U-tubes with water and pour into the polyethylene bottle

FRM 6 Sample Recovery

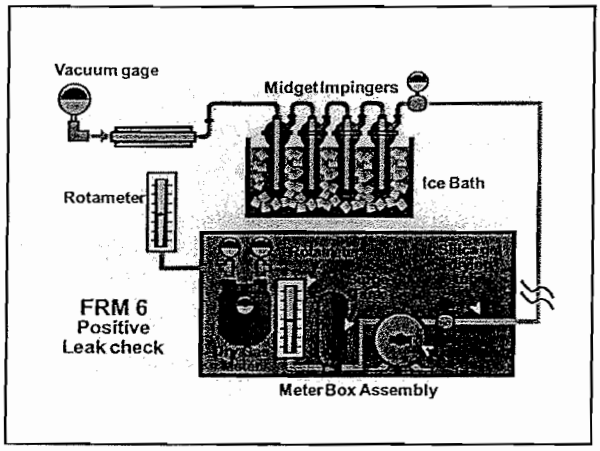
- Seal, identify the sample container, and mark liquid level
- Complete "chain-of-custody" for sample run
- Complete field test data sheet (FTDS)
- Collect 30 mL of H_2O_2 as absorbing solution for reagent blank

FRM 6 Meter Box Leak Check Procedures

- Positive Leak Check
  - Attach a piece of rubber tubing and incline manometer to outlet of DGM
  - Shut off the needle valve in meter box

FRM 6 Meter Box Leak Check Procedures

- Blow into tubing until 3 to 4 inches of water are displayed on the incline manometer
- Pinch off tubing and observe manometer for 1 minute
- A loss of pressure indicates a leak

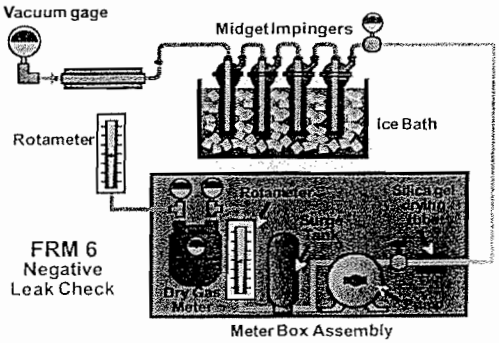


FRM 6 Meter Box Leak Check Procedure

- Negative Leak Check
  - Attach vacuum gauge to inlet of meter box by way of quick disconnect
  - Open needle valve

FRM 6 Meter Box Leak Check Procedure

- Turn on pump and pull a vacuum of 10 in. Hg
- Pinch outlet of flow meter
- Turn off the pump
  - Any deflections in vacuum reading indicates a leak



FRM 6 Sampling Train Leak Check Procedure

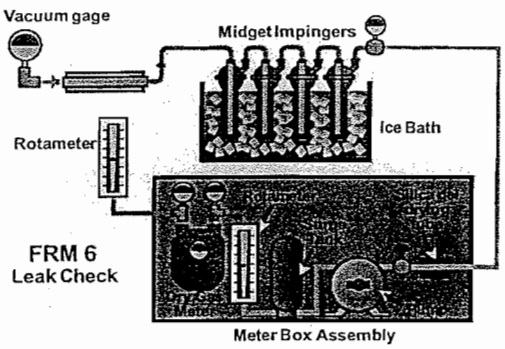
- Completely assemble the sampling train (impinger system, transfer line, and meter box assembly)
- After assembly, perform the following
  - Adjust probe heater to operating temperature

FRM 6 Sampling Train Leak Check Procedure

- Attach rotameter (0-40 mL/min) to outlet of DGM
- Attach vacuum gauge to probe inlet
- Turn on pump and pull vacuum of 10 in. Hg as indicated by vacuum gauge
- Note the flow rate indicated by rotameter on the outlet of DGM
  - Let stabilize for 1 minute

FRM 6 Sampling Train Leak Check Procedure

- A leak-rate of < 2% of the average sampling rate is acceptable (20 mL/min for a 1 Lpm sampling rate)
- Carefully release the vacuum gauge connection, then turn off pump



FRM 6 Initial Calibration of Dry Gas Meter Procedure

- Leak check the meter box assembly containing the DGM
- Connect a 1 L/rev wet test meter (or another calibrated DGM) to the inlet of the meter box
- Make three independent calibration runs using at least five revolutions of the DGM per run

FRM 6 Calibration of DGM Procedure

- Calculate the calibration factor, Y, for each run, and the average results (must be < 2% from the average)

FRM 6 Post-test Calibration of DGM Procedure

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

FRM 6 Other Components Needing Calibration

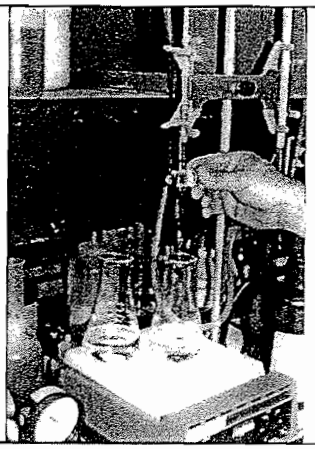
- Thermometers: Calibrated against mercury-in-glass thermometers
- Rotameter: Need not be calibrated, but should be cleaned and maintained according to manufacturer's instruction
- Barometer: Calibrated against a mercury barometer

FRM 6 Audit Vial

- Obtained from EPA
  - U.S. Environmental Protection Agency
    Emission Measurement Center
    Research Triangle Park, NC 27711

FRM 6 Audit Vial

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



FRM 6 Key Points

- During titration, have two flasks next to the titration assembly to compare to your sample
- One flask is the yellow starting point, while the second flask is the pink endpoint

FRM 6 Key Points

- If you feel that SO_2 will be high (2,000-5,000 ppm) then increase strength of H_2O_2 to 10% to minimize depleting it's strength

FRM 6 Key Points

- Analyzing for SO_3/H_2SO_4 can be accomplished by analyzing the 80% IPA impinger
- If metals are high in the stack gas, then use in-stack high efficiency filter rather than probe plug

FRM 6 Key Points

- To remove ammonia interference, use high efficiency in-stack filter (Whatman 934 AH) and operate probe at 525°F

FRM 6A Critical Orifice Sampling Train

- Uses FRM 6 sampling train except the DGM is removed and a critical orifice is placed at the entrance of the meter box assembly
- Calibration of critical orifice performed on site with soap bubble meter attached to inlet of probe

FRM 6A Critical Orifice Sampling Train

- Calculate standard volumes sensed by soap bubble meter vs. critical orifice

FRM 6A Sulfur Dioxide, Moisture, and Carbon Dioxide

- Use FRM 6 train except addition of Drierite in last impinger and addition of CO_2 adsorber behind last impinger
- Weigh all four impingers before and after sampling event to calculate stack gas moisture

FRM 6A Sulfur Dioxide, Moisture, and Carbon Dioxide

- Weigh CO_2 adsorber before and after sampling event to obtain percent CO_2 in stack gas

FRM 6B FRM 6A for 24 hrs

- Use FRM 6A train except when sampling is performed 2 to 4 minutes on a 2-hr repeating cycle or other specified cycle
- Do not include the IPA bubbler (an empty impinger may be used in its place)

FRM 6B FRM 6A for 24 hrs

- Include a filter (either in-stack, out-of-stack, or both)
- Use different circuit for probe heater

FRM 6B FRM 6A for 24 hrs

- Include a timer switch to control on/off of pump
- Sampling may be conducted continuously if a low flow-rate sample pump is used (20 to 40 mL/min.)
  - Total gas volume collected should be between 20 and 60 L

FRM 6B FRM 6A for 24 hrs

- If continuous operation, then molecular sieve material may be substituted for Ascarite II as the CO_2 adsorbing material

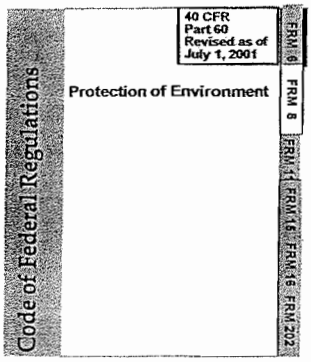
FRM 6C Sulfur Dioxide Instrumental Analyzer Procedure

- Use of instrumental methods for monitoring SO_2

FRM 6C Sulfur Dioxide Instrumental Analyzer Procedure

- Calibration gases used to determine
  - Analyzer 3-point calibration error
  - Sampling system bias check
  - Zero/upscale calibration drift

U.S. EPA APTI Compliance Test and Source Test Observation FRM 8 for Determination of Sulfuric Acid Mist



Chemistry of Sulfur

- With excess air present, monoatomic S reacts with O_2 to form different oxidized compounds
  - SO_2, SO_3, H_2SO_4
- Typical industries affected by SO_2 controls: fossil-fuel-fired steam generators, industrial boilers burning fuel oil, sulfuric acid plants, and refineries

Sulfur Dioxide Emissions

- Increased use of sulfur-containing fuels for energy has increased the emissions of oxides of sulfur from power plants
  - $S + O_2 = SO + O$
  - $SO + O_2 = SO_2 + O$

Sulfur Dioxide Emissions

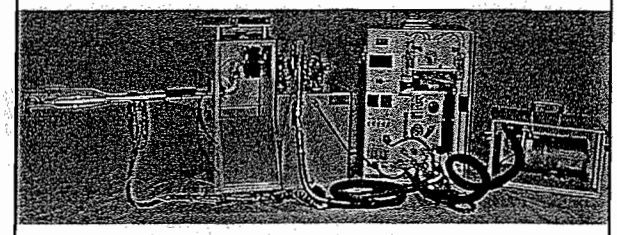
- Other oxides of sulfur are also emitted, but in lesser quantities
  - $O + SO_2 = SO_3$
  - $SO_3 + H_2O = H_2SO_4$

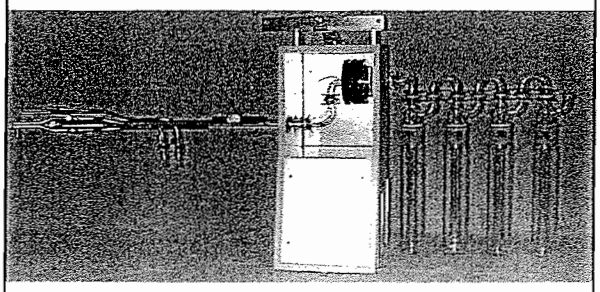
FRM 8 Applicability

- This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide emissions from stationary sources

FRM 8 Sampling Train

- Nozzle/heated probe
- Heated filter box assembly (optional)
- Impinger assembly with unheated filter
- Meter box assembly





FRM 8 Principle

- Particulate matter and SO_3/H_2SO_4 is drawn isokinetically
- If applicable, particulate matter is collected concurrently on a glass fiber filter maintained at a regulated temperature (usually 120°C ± 14°C)

FRM 8 Principle

- SO_3/H_2SO_4 is trapped in the isopropanol impinger while SO_2 is collected in the hydrogen peroxide impingers

FRM 8 Principle

- During sampling, the SO_3/H_2SO_4 is separated from the SO_2 by solubility of absorbing solutions in the impinger train
- Both fractions are measured separately by the barium-thorin titration method

FRM 8 Principle

- Because SO_3/H_2SO_4 can be absorbed on particulate matter, FRM 8 requires isokinetic sampling

FRM 8 Objective

- The objective of performing FRM 8 is to determine the pollutant mass rate (pmr) or emission rate (E) of SO_3/H_2SO_4 from the regulated source
  - pmr = $(c_s)(Q_s)$
  - E = pmr/Q_h

FRM 8 Interferences

- Fluorides
- Free ammonia
- Dimethyl aniline

FRM 8 Applicability

- SO_3/H_2SO_4 and SO_2 determination
- Particulate matter emissions (Concurrent FRM 5)
- Stack gas moisture determination (Concurrent FRM 4)

FRM 8 Sample Nozzle

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

FRM 8 Sample Nozzle

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

FRM 8 Sample Nozzle

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

FRM 8 Pitot Tube

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

FRM 8 Pitot Tube

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

FRM 8 Pitot Tube

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

FRM 8 Sampling Probe

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

FRM 8 Sampling Probe

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

FRM 8 Sampling Probe

- Probe designed to protect liner
- Material of construction determined by temperature/compounds being monitored
  - Borosilicate Glass liners up to 480°C
  - Quartz liners up to 90°C

FRM 8 Sampling Probe

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

FRM 8 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 equirements
- Need for water drain tap

FRM 8 Impinger System

- Connecting Joints
  - Ball joints without Teflon® compression rings
    - Must use non-volatile silicone grease
    - Original design works well

FRM 8 Impinger System

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

FRM 8 Impinger System

- First Impinger: 100 mL of 80% Isopropanol
- Unheated Filter: Between first and second impinger
- Second and Third Impinger: 100 mL each of 3% hydrogen peroxide
- Fourth Impinger: 200 g of silica gel

FRM 8 Umbilical Cord

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

FRM 8 Meter Console Desirable Features

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

FRM 8 Meter Console Desirable Features

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

FRM 8 Meter Console Required Calibrations

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

FRM 8 Isokinetic Rate Equation

- The relationship between "v_s" and "v_n" is the core understanding of FRM 8 isokinetic sampling
- Reading the "p" from the pitot tube and setting the proper "ΔH" on the meter box allows one to sample isokinetically

FRM 8 Isokinetic Rate Equation (Simplified)

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

FRM 8 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
- Heavy grain loading, causing plugging of filter so can't achieve proper ΔH

FRM 8 Causes for not Meeting 100% Isokinetics

- Large temperature variations not corrected in isokinetic rate equation
- 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 temp
- Impinger stem too restricted
- Filter disc plugging
- Nozzle too small/large for velocity of stack gas

FRM 8 Pre-test Preparation

- Calibrate the meter system
- Determine the number and location of sampling points
- Prepare sampling train
  - Add 100 mL of 80% IPA to first impinger
  - Add unheated filter between first and second impinger

FRM 8 Pre-test Preparation

- Add 100 mL of 3% H_2O_2 to next two impingers
- Add 200 g silica gel in last impinger

FRM 8 Pre-test Preparation

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

FRM 8 Sampling

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

FRM 8 Sampling

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

FRM 8 Sampling

- Add more ice during run to maintain last impinger outlet < 68°F
- Reaction in impingers:
  - $SO_3/H_2SO_4 + C_3H_6O = H_2SO_4$
  - $SO_2 + H_2O_2 = H_2SO_4$

FRM 8 Sampling

- At conclusion of run, turn off the pump, remove probe from stack, and record final DGM reading
- Leak check the sampling train (mandatory)

FRM 8 Leak Check

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

FRM 8 Sample Recovery

- Drain the ice bath, and purge the train for 15 minutes at average flow rate
- Use of charcoal filter
  - Extra midget impinger containing 15 mL of 3% H_2O_2
  - Use ambient air without purification
- Disconnect impingers after purging

FRM 8 Sample Recovery

- Note: If moisture is to be determined, all impingers must be weighted or solutions measured
- Also weigh the silica gel impinger
- Note: If FRM 5 particulate matter is to be determined, collect heated filter. Then condition following FRM 5 procedures for determining mass emissions

FRM 8 Sample Recovery

- Collect the 80% IPA impinger contents, glassware rinses, and unheated filter in Container #1, dilute to 250 mL with 80% IPA
- Collect the 3% hydrogen peroxide impingers and glassware rinses into container #2
- Dilute to 1000 mL volume with DI water

FRM 8 Sample Recovery

- Seal, identify the sample container, and mark liquid level
- Complete "chain-of-custody" for sample run
- Complete field test data sheet (FTDS)
- Collect 30 mL of H_2O_2 as absorbing reagent blank

FRM 8 Analytical Procedure

- Analysis involves standardized barium perchlorate as a titrant with thorin indicator as an end-point

FRM 8 Analytical Procedure

- 100 mL of Container #1 (IPA field solution) is extracted, 2-4 drops of thorin indicator added, and the sample is titrated with the barium perchlorate from a yellow to a pink end-point

FRM 8 Analytical Procedure

- Repeat until duplicates agree within ±1% or ±0.2 mL, whichever is larger, and then average the titration volumes
- Run a blank with each series of samples

FRM 8 Analytical Procedure

- From Container #2, extract a 10 mL aliquot, add 40 mL of 100% IPA, 2-4 drops of thorin indicator, and titrate from a yellow to pink endpoint with 0.0100 N barium perchlorate

FRM 8 Analytical Procedure

- Run a blank with each series of samples
- Run analysis of audit sample along with series of samples

FRM 8 Post-test Calibration Requirements

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

FRM 8 Post-test Calibration Requirements

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

FRM 8 Other Components Needing Calibration

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

FRM 8 Audit Vial

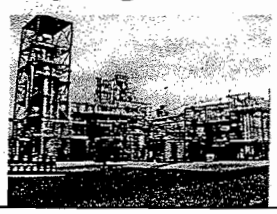
- Obtained from EPA
  - U.S. Environmental Protection Agency
    Emission Measurement Center
    Research Triangle Park, NC 27711

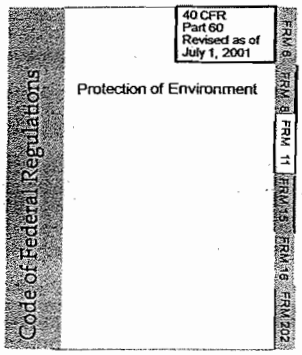
FRM 8 Audit Vial

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

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

FRM 11 for Determination of Hydrogen Sulfide





FRM 11 Applicability and Sources

- This method is applicable for the determination of hydrogen sulfide (H_2S) from petroleum refineries
- H_2S is produced naturally through decomposition of carbonaceous materials by bacteria. H_2S also occurs naturally as a constituent of natural gas, petroleum, sulfur deposits and numerous volcanic gases. By far, the largest source of H_2S is through natural occurrence.

H_2S Sources

- Industrially, hydrogen sulfide is a byproduct of many processes, especially petroleum facilities. EPA limits the amount of H_2S emissions from refineries through the NSPS. The regulation addressed H_2S in an effort to control sulfur dioxide emissions from refinery processes. Sulfur enters the process as a constituent of the crude oil.

Chemistry of Sulfur

- With excess air present, monoatomic S reacts with O_2 to form different oxidized compounds
  - SO_2, SO_3, H_2SO_4
- Typical industries affected by SO_2 controls: fossil-fuel-fired steam generators, industrial boilers burning fuel oil, sulfuric acid plants, and refineries

Chemistry of Sulfur

- Depletion of oxygen in the process causes the monoatomic S to combine with hydrogen (H) to form reduced sulfur compounds
  - Hydrogen sulfide (H_2S)
  - Methyl sulfide (CH_3SH)
  - Dimethyl sulfide $(CH_3)_2S$
  - Dimethyl disulfide $(CH_3)_2S_2$

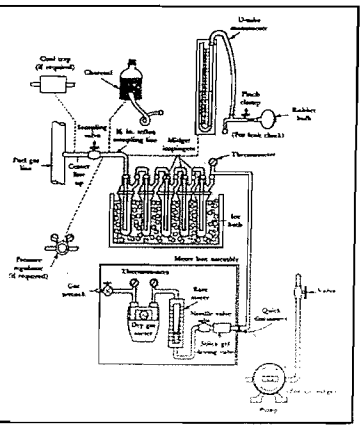
Federal Reference Method 11 Sampling Apparatus

- Unheated probe/sample line with regulator
- Midget impinger sampling train similar to FRM 6 sampling train with one (1) additional midget impinger
- Typical FRM 6 Transfer line
- Typical FRM 6 meter box assembly without pump

Federal Reference Method 11 Sampling Apparatus

- Supplemental Equipment:
  - Pressure regulator for controlling fuel gas flow to impinger system
  - Charcoal impinger to be used after sampling to purge H_2S from the H_2O_2 impinger
  - U-tube water manometer and rubber bulb to be used before sampling to leak-check sampling train under positive pressure
  - Sampling pump and valve connection to be used only during air purge after sampling

Supplemental Equipment Needs for FRM 11 Sampling System

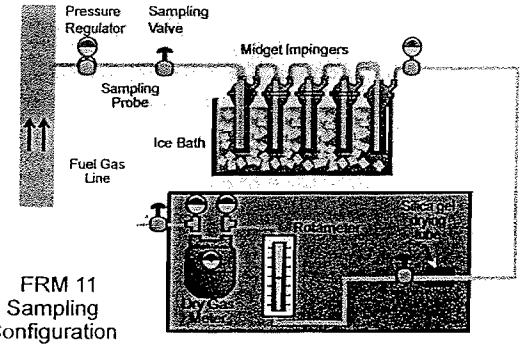


FRM 6 Sampling Apparatus

- Probe/Sample Line: Sample line made of stainless steel or Teflon® tubing connected to a pressure-reduction regulator. This line does not have to be heated since the sample is extracted under pressure.
- Impinger Train: Five (5) midget 30-mL capacity impingers similar to FRM 6.

FRM 11 Sampling Apparatus

- Transfer line: Containing temperature connection for measuring temperature of outlet of last impinger along with tubing/electrical for connecting to meter box assembly
- Meter box assembly: Containing silica gel drying tube, rate/rotameter, and volume/dry gas meter along with temperature gauges for measuring inlet/outlet temperature of dry gas meter, similar to FRM 6 except no pump (except for air purge) and no surge tank.



FRM 11 Sampling Configuration

FRM 11 Impinger Contents

- 1st Midget Impinger: 15 mL of 5% H_2O_2. The hydrogen peroxide serves to remove and oxidize the SO_2 in the fuel gas stream to $SO_4^=$.
- 2nd Midget Impinger: The 2nd impinger remains dry to prevent carry-over from the H_2O_2 impinger to the following three (3) impingers.
- 3rd, 4th, and 5th Midget Impingers: Each contain 15 mL of cadium sulfate ($CdSO_4$) to capture and react with the H_2S in the fuel gas stream.

FRM 11 Chemistry in Impingers

- 1st Midget Impinger: 15 mL of 5% H_2O_2

$$SO_2 + H_2O_2 = H_2SO_4$$

- 2nd Midget Impinger: Dry impinger, no reaction
- 3rd, 4th, and 5th Midget Impingers: 15 mL of $CdSO_4$ in each impinger

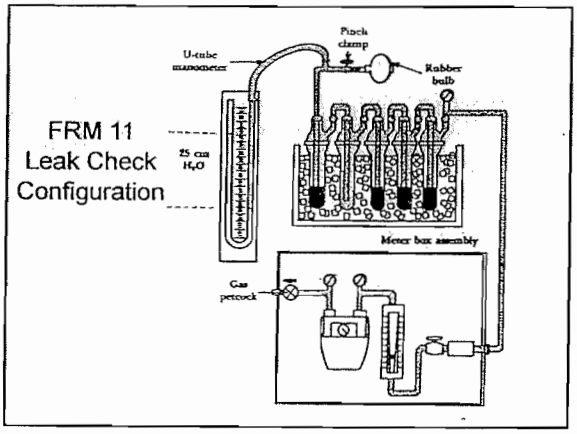
$$H_2S + CdSO_4 = CdS + H_2SO_4$$

FRM 11 Pre-test Preparation

- Prepare sampling train
  - Add 15 mL of 5% H_2O_2 to first impinger
  - Leave second impinger dry
  - Add 15 mL of $CdSO_4$ in each of the next three (3) impinger s
  - Place ice and water around the impingers

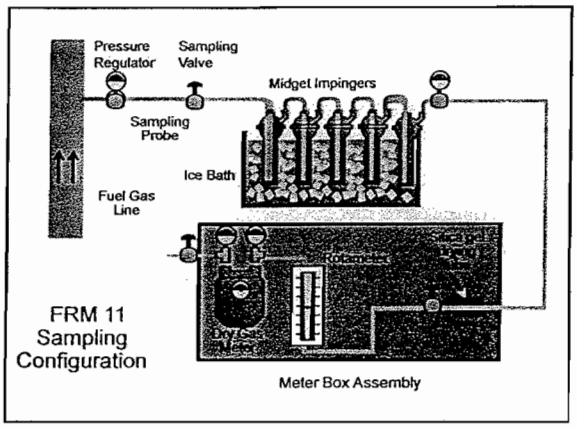
FRM 11 Leak Check

- Leak check the sampling system under positive pressure
  - Connect the rubber bulb/manometer assembly to the first impinger using glass adapter. Use appropriate clamp to ensure a tight connection.
  - Close the gas petcock on the dry gas meter outlet
  - Using the squeeze bulb, pressurize the complete sampling train to 10 in.H_2O as indicated by the water U-tube manometer
  - Once the water U-tube manometer indicates 10 in. of H_2O, close off the tube and the column should stay with < 0.5 in. of H_2O drop in one (1) minute.



FRM 11 Sampling

- After the impinger train is prepared and leak checked, the sample inlet line is purged for ~ 1 minute
- After 1 minute purge, close the sampling valve and connect sample inlet line to the sample train
- Open the sampling valve and adjust the flow to ~ 1 Lpm. Fill out the Field Test Data Sheet (FTDS) with sample location, time, dry gas meter initial and final readings, rotameter readings and dry gas meter temperatures



FRM 11 Sampling

- Add more ice during run to maintain last impinger outlet < 68°F
- Sample for 10-20 minutes, recording sampling information on the FTDS every 5 minutes
- A yellow precipitate, CdS, will develop in the 3rd and 4th impingers by the following reaction:

$$H_2S + CdSO_4 = CdS + H_2SO_4$$

- If a yellow precipitate develops in the 5th impinger , stop sampling
- At the end of sampling, close the sampling valve and complete FTDS

FRM 11 Field Test Data Sheet (FTDS)

Date of Test/Location _____

Barometric Pressure/Atmospheric Temperature_____

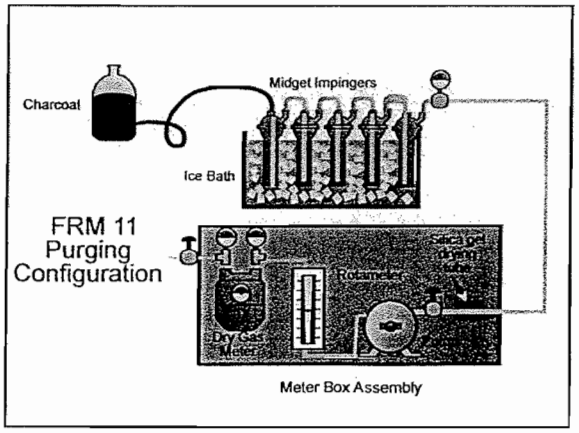
Leak Check Performed_____

Name of Tester _____

Clock Time, Min.	Dry Gas Meter Reading, ft³	Gas Volume Through Meter, ft³	Rotameter Setting, L/min	Dry Gas Meter Temperature, °F
0				
5				
10				
15				
20				

FRM 11 Purging of Sampling Train

- At conclusion of run, close the sampling valve and remove the sampling train from the sampling area to the recovery area
- Connect the charcoal impinger and tubing to the inlet of the sampling train. Connect a pump to the outlet of the impinger train and before the rotameter.
- Purge the FRM 11 sampling train with clean air for 15 minutes to remove any H_2S that might be retained in the 1st impinger containing H_2O_2



FRM 11 Sample Recovery

- Make a solution of 50 mL of 0.01 N iodine and 10 mL of 3 M HCl into an Erlenmeyer flask. Mix well. Stopper and set aside.
- Discard the contents of the 1st impinger.
- Pour the content of the 3rd, 4th, and 5th midget impingers into a 500 mL iodine numbered flask.
- Rinse the three midget impingers and U-tubes with the iodine solution and pour into the sample iodine flask

FRM 11 Sample Recovery

- Chemically, the following two reactions are now occurring:

$$CdS + 2\,HCl = H_2S + CdCl_2$$

$$H_2S + I_2 = 2\,HI + S$$

- Follow the iodide rinses with distilled water and collect in the sample iodide flask

FRM 11 Sample Analysis by Titration

- Allow the sample iodine flask to stand about 30 minutes in the dark for absorption of the H2S into the iodine
- Titrate the solution in the numbered sample iodine flask with standardized 0.0100 N sodium thiosulfate until the solution is light yellow

FRM 11 Sample Analysis by Titration

- At this point, add 4 mL of starch indicator and continue titrating until the blue color just disappears
- The color change will be from a dark blue to clean
- Record mL of standardized 0.0100 N sodium thiosulfate required to reach a clear endpoint.

FRM 11 Sample Analysis by Titration

- The titration of the sample iodine flask has completed the following reaction:

$$2\,Na_2S_2O_3 + I_2 \xrightarrow{\text{Starch}} Na_2S_4O_6 + 2\,NaI$$

FRM 11 Calculations

- Dry Gas Meter Sample Volume, Corrected to Standard Conditions:

$$V_{m(std)} = V_m Y\,(T_{std}/T_m)(P_{bar}/P_{std})$$

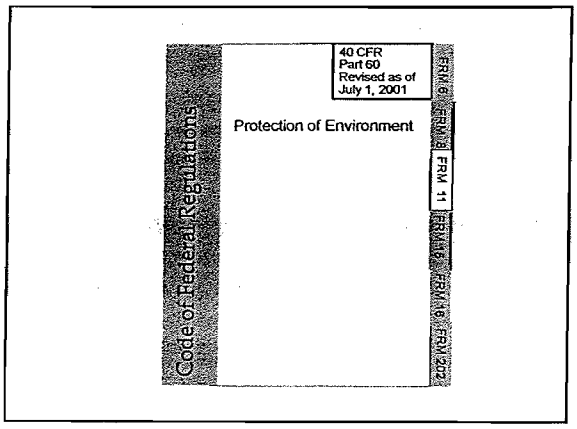
FRM 11 Calculations

- Emission Rate of H_2S at Standard Conditions:

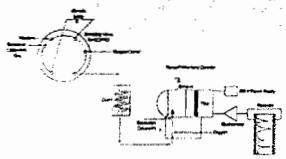
$$c_{H_2S} = \frac{K\,[(V_{Tf}N_t - V_{Ti}N_T)_{sample} - (V_{Tf}N_t - V_{Ti}N_T)_{blank}}{V_{m(std)}}$$

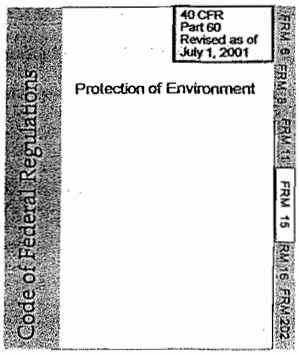
- Calculate the Concentration of H2S in ppm:

$$H_2S\ (ppm) = (K)(c_{H_2S})$$


Code of Federal Regulations
40 CFR
Part 60
Revised as of
July 1, 2001
Protection of Environment
FRM 6
FRM 18
FRM 11
FRM 16
FRM 16
FRM 22

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 15 for Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide from Stationary Sources





FRM 15 Determination of Total Reduced Sulfur (TRS)

- This method is applicable to the determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide from tail gas control units of sulfur recovery plants and other stationary sources
- Method uses the up-front sampling system of FRM 16A except the tube furnace is removed and a dilution system is added to the sampling system. The analytical finish is a gas chromatography (GC) with a flame photometric detector (FPD)

FRM 15 Determination of Speciated Reduced Sulfur Compounds

- FRM 15 specifically designed to detect speciated reduce sulfur compounds such as:
  - Hydrogen Sulfide (H_2S)
  - Carbonyl Sulfide (COS)
  - Carbon Disulfide (CS_2)

FRM 15 Interferences

- Moisture Condensation
  - Keep probe, filter and connections heated
  - Keep SO_2 scrubber in an ice water bath
- Carbon Monoxide (CO) and Carbon Dioxide (CO_2)
  - May still be a problem with 9:1 dilution air
  - Show chromatograms with and without CO/CO_2
- Elemental Sulfur
  - Observe buildup on filter and monitor

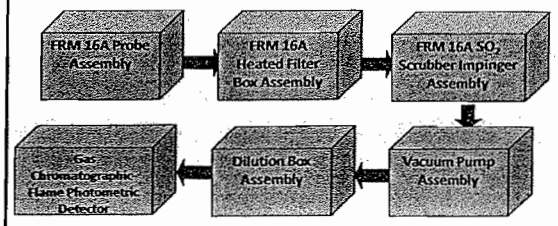
FRM 15 Interferences

- Sulfur Dioxide (SO_2)
  - Monitor efficiency of SO_2 impinger scrubber
- Alkali Mist
  - Alkali mist may change the pH of the SO_2 impinger scrubber system. Change after each sample run.

Federal Reference Method 15 Sampling Apparatus

- Probe/Filter Assembly
- Sample Conditioning System
  - Three (3) SO_2 scrubber impinger assembly
- Vacuum Pump
- Gas Dilution System
- Gas Chromatographic (GC) with Flame Photometric Detector (FPD)

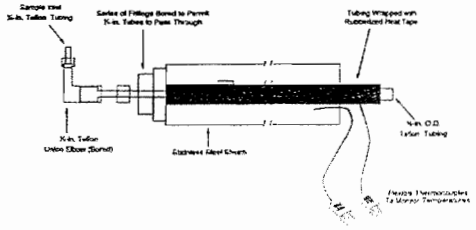
FRM 16B Sampling System



FRM 15 Sampling Apparatus

- Probe (Same as FRM 16A): 0.6 cm diameter Teflon® tubing wrapped with heat resistant tape with an outer stainless steel sheath to maintain temperature 250 °F. The FRM 15 nozzle is the end of the Teflon® tube and points downstream of the gas flow to minimize particulate matter from entering the sampling train

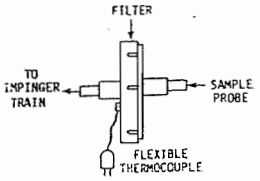
FRM 15 Probe Assembly



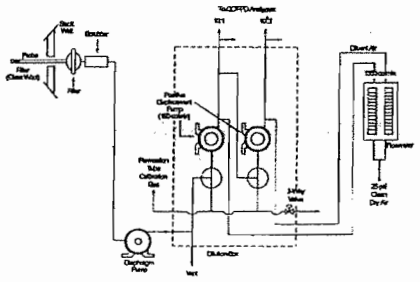
FRM 15 Sampling Apparatus

- Sample Conditioning System
  - Particulate Filter (Same as FRM 16A): 50-mm Teflon® heat maintained at 250 °F
  - SO_2 Scrubber System (Same as FRM 16A): The SO_2 scrubber system containing three (3) Teflon® 300 mL impingers containing citric acid buffer solution to remove interference from SO_2 from the gas stream
  - Dilution System (New): Sample dilution system contact with gas stream must be made of Teflon® with a dilution ratio of 9:1

FRM 15 Filter Assembly



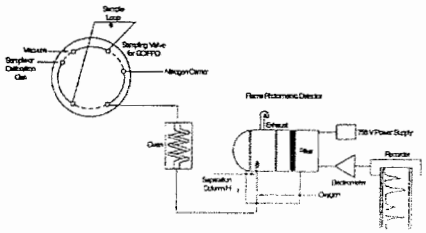
FRM 15 Dilution System

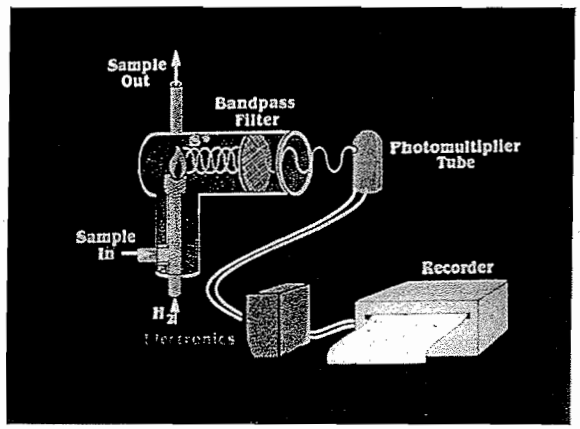


FRM 16A Sampling Apparatus

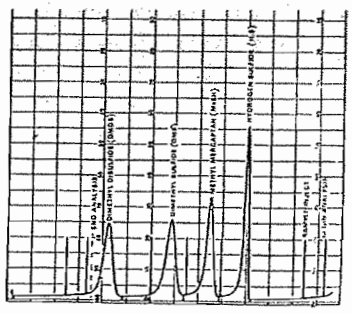
- Pump: Capable of extracting a sample from the source and directing the sample to the gas chromatography (GC) with a flame photometric detector (FPD)
- GC/FPD: The GC must contain a column able to speciate the targeted reduce sulfur compounds

FRM 15 with GC/FPD)

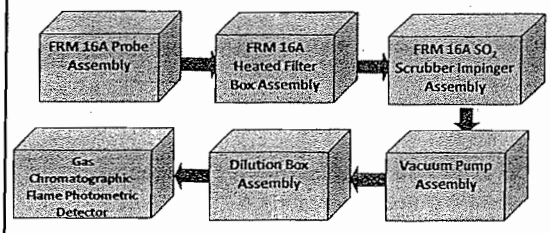


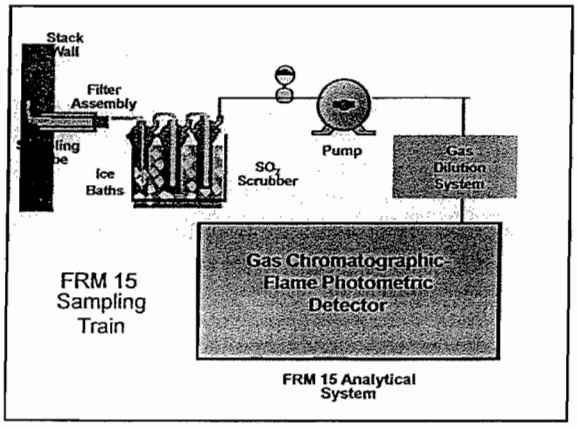


FRM 15 GC/FPD Speciation



FRM 15 Sampling System





FRM 15 Pre-Test Procedures

- Assemble sampling system: Allow probe/filter and all GC/FPD system components to warm to operating temperatures
- Leak check:
  - Upstream of sample pump, attach manometer of vacuum gauge to probe inlet. Start pump and pull 2 in. Hg vacuum. Stop pump and should retain 2 in. Hg vacuum over 1 minute. Downstream of pump, apply slight pressure and use "snoop" to detect any leaks

FRM 15 Pre-Test Procedures

- Calibration:
  - Analytical System- Generate of series of three or more known concentrations (0-10 ppm) for each of the three reduce sulfur compounds (i.e., Hydrogen sulfide, carbonyl sulfide, and carbon disulfide). Three injections of each of the target compounds must yield a ± 13 % from the mean of the three injections. Standards can be generated either from a permeation tube system or NIST traceable gas cylinder coupled to a gas dilution system . Generate a calibration curve.

FRM 15 Pre-Test Procedures

- Calibration (Cont'd):
  - Dilution System- Generate of series of three or more known concentrations (0-10 ppm) for each of the three reduce sulfur compounds (i.e., Hydrogen sulfide, carbonyl sulfide, and carbon disulfide). Inject three injections of each of the target compounds into the gas dilution system which then leads to the GC/FPD. Determine if the three injections of the three different calibration gases yield a ± 13 % from the mean of the three injections. Standards can be generated either from a permeation tube system or NIST traceable gas cylinder coupled to a gas dilution system

FRM 15 Sampling

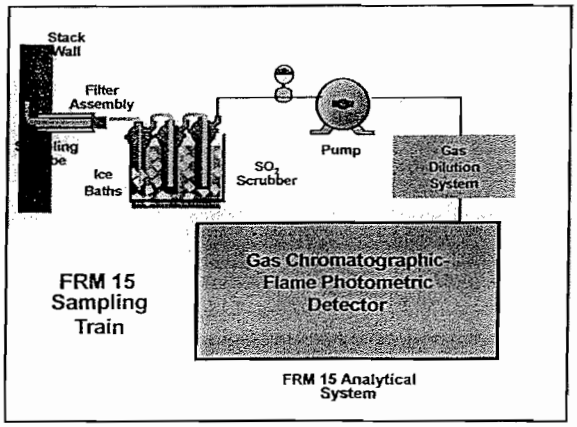
- Position sampling probe at sampling point within the source
- Sample source emissions through the probe and filter assembly, through the SO_2 scrubber system, through the dilution system (9:1 dilution ratio) to the GC/FPD
- A sample run is composed of 16 individual analysis (injections to the GC/FPD) over a period of not less than 3 hours and not more than 6 hours
- Observe clogging of filter or SO_2 scrubber system

FRM 15 Post-Test Procedure

- Sample Line Loss: After the sample run, remove the probe from the source, but maintain its temperature. Inject a known concentration of H_2S at the level of the applicable standard (± 20 %) to the inlet of the probe to determine sample line losses. Sample line losses of > 20 % is unacceptable. With sample losses between 0-20 %, the final emissions must be corrected to the percent sample losses.

FRM 15 Post-Test Procedure

- Post-Sampling Calibration: Using only H_2S, recalibrate the GC/FPD using three concentration levels. Compare the post-sample calibration to the pre-sample calibration. If the drift between the two curves exceeds > 5%, the previous runs are not valid.



U.S. EPA APTI

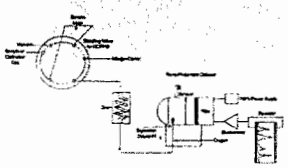
Compliance Test and Source Test Observation

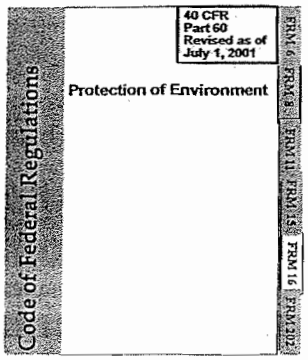
FRM 15A for Determination of Total Reduced Sulfur (TRS) From Sulfuric Recovery Plants in Petroleum Refineries

FRM 15A

- FRM 15A is similar in sampling apparatus and methodology found in FRM 16A except there is no SO_2 scrubber in the sampling system. All other components, QA/QC activities, operation of the sampling train and analysis are the same.

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 16 Semicontinuous Determination of Sulfur Emissions from Stationary Sources





FRM 16 Semicontinuous Determination of Sulfur Emissions from Stationary Sources

- This method is applicable to the determination of sulfur emissions (i.e., hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) from stationary sources, recovery furnaces, lime kilns, and smelt dissolving tanks at Kraft pulp mills.

FRM 16 Determination of Speciated Reduced Sulfur Compounds

- FRM 16 specifically designed to detect speciated reduce sulfur compounds such as:
  - Hydrogen Sulfide (H_2S)
  - Methyl Mercaptan (CH_3SH)
  - Dimethyl Sulfide $(CH_3)_2S$
  - Dimethyl Disulfide $(CH_3)_2S_2$

FRM 16 Interferences

- Moisture Condensation
  - Keep probe, filter and connections heated (248 °F)
  - Keep SO_2 scrubber in an ice water bath
- Carbon Monoxide (CO) and Carbon Dioxide (CO_2)
  - May still be a problem with 9:1 dilution air
  - Show chromatograms with and without CO/CO_2. Should agree ±5%

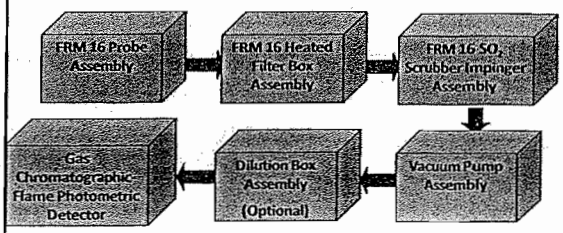
FRM 16 Interferences

- Sulfur Dioxide (SO_2)
  - Monitor efficiency of SO_2 impinger scrubber
- Alkali Mist
  - Alkali mist may change the pH of the SO_2 impinger scrubber system. Change after each sample run.

Federal Reference Method 16 Sampling Apparatus

- Probe/Filter Assembly
- Sample Conditioning System
  - Three (3) SO_2 scrubber impinger assembly
- Vacuum Pump
- Gas Dilution System (Optional: Need only for high sample concentrations)
- Gas Chromatographic (GC) with Flame Photometric Detector (FPD)

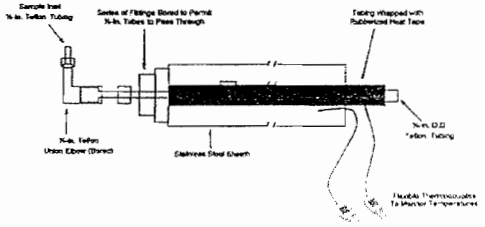
FRM 16 Sampling System



FRM 16 Sampling Apparatus

- Probe (Same as FRM 16A): 0.6 cm diameter Teflon® tubing wrapped with heat resistant tape with an outer stainless steel sheath to maintain temperature 250 °F. The FRM 16 nozzle is the end of the Teflon® tube and points downstream of the gas flow to minimize particulate matter from entering the sampling train (Same as FRM 16A)

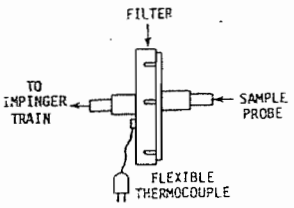
FRM 16 Probe Assembly (Same as FRM 16A)



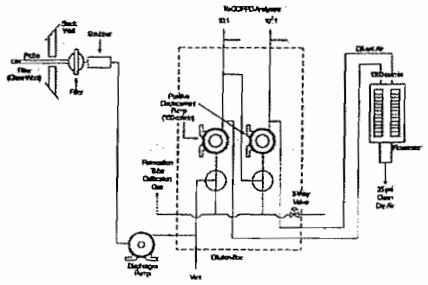
FRM 16 Sampling Apparatus

- Sample Conditioning System
  - Particulate Filter (Same as FRM 16A): 50-mm Teflon® heat maintained at 250 °F
  - SO_2 Scrubber System (Same as FRM 16A): The SO_2 scrubber system containing three (3) Teflon® 300 mL impingers containing citric acid buffer solution to remove interference from SO_2 from the gas stream
  - Dilution System (Optional: Same as FRM 15): Sample dilution system contact with gas stream must be made of Teflon® with a dilution ratio of 9:1

FRM 16 Filter Assembly



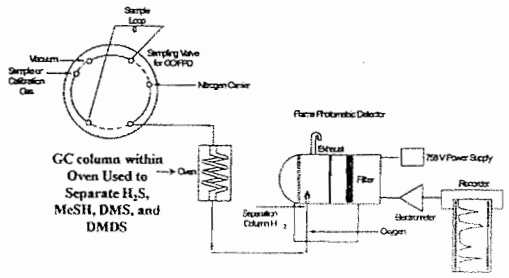
FRM 16 Dilution System (Optional: Same as FRM 15)

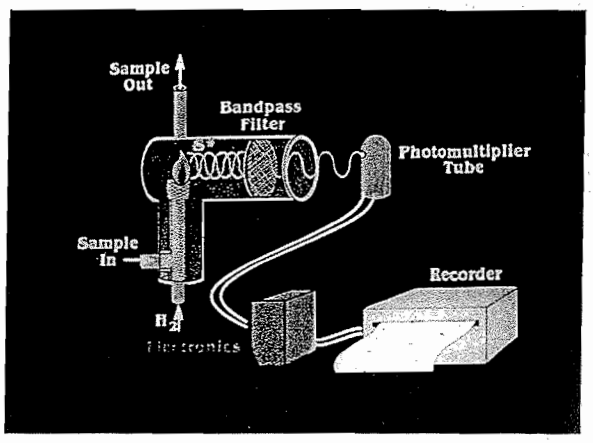


FRM 16 Sampling Apparatus

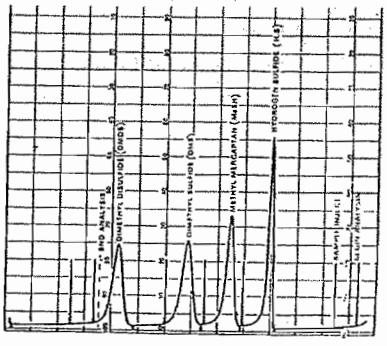
- Pump: Capable of extracting a sample from the source and directing the sample to the gas chromatography (GC) with a flame photometric detector (FPD)
- GC/FPD (Same as FRM 15) : The GC must contain a column able to speciate the targeted reduce sulfur compounds

FRM 16 with GC/FPD (Same as FRM 15)

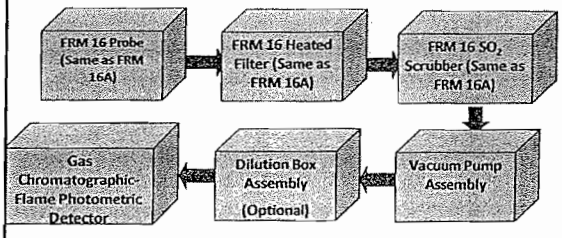


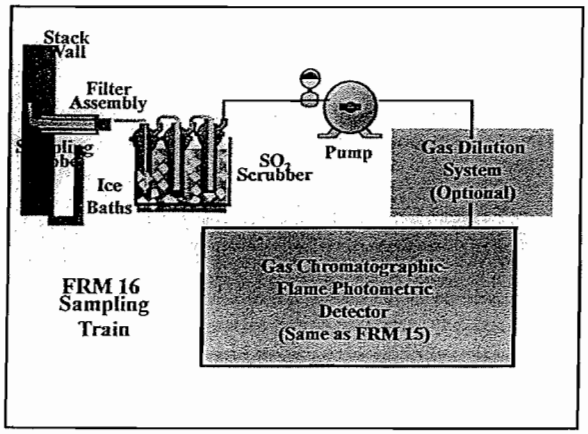


Example of FRM 16 GC/FPD Speciation



FRM 15 Sampling System





FRM 16 Pre-Test Procedures

- Assemble sampling system: Allow probe/filter and all GC/FPD system components to warm to operating temperatures
- Gas Chromatogram Columns: Must demonstrate that the GC column can resolve H_2S, MeSH, DMS and DMDS. Must submit chromatogram prior to testing showing resolution

FRM 16 Pre-Test Procedures

- Assemble sampling system: Allow probe/filter and all GC/FPD system components to warm to operating temperatures
- Leak check:
  - Upstream of sample pump, attach manometer of vacuum gauge to probe inlet. Start pump and pull 2 in. Hg vacuum. Stop pump and should retain 2 in. Hg vacuum over 1 minute. Downstream of pump, apply slight pressure and use "snoop" to detect any leaks

FRM 16 Pre-Test Procedures

- Calibration:
  - Analytical System- Generate of series of three or more known concentrations (0.5-10 ppm) for each of the four reduce sulfur compounds (i.e., H_2S, MeSH, DMS, and DMDS). Three injections of each of the target compounds must yield a $\pm$ 5 % from the mean of the three injections. Standards can be generated either from a permeation tube system or NIST traceable gas cylinder coupled to a gas dilution system . Generate a calibration curve.

FRM 16 Pre-Test Procedures

- Calibration (Cont'd):
  - Dilution System (If Applicable)- Generate of series of three or more known concentrations (0-10 ppm) for each of the three reduce sulfur compounds (i.e., Hydrogen sulfide, carbonyl sulfide, and carbon disulfide). Inject three injections of each of the target compounds into the gas dilution system which then leads to the GC/FPD. Determine if the three injections of the four different calibration gases yield a $\pm$ 5 % from the mean of the three injections. Standards can be generated either from a permeation tube system or NIST traceable gas cylinder coupled to a gas dilution system

FRM 16 Sampling

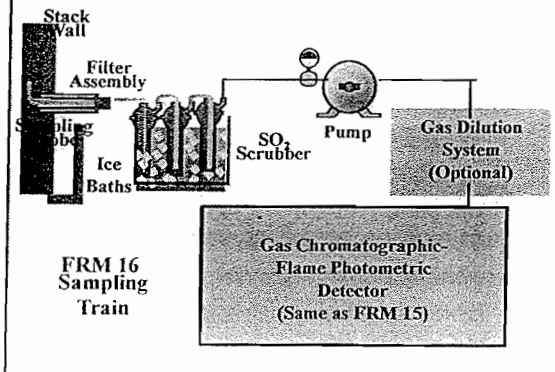
- Position sampling probe at sampling point within the source
- Sample source emissions through the probe and filter assembly, through the SO_2 scrubber system, through the dilution system (if applicable) to the GC/FPD
- A sample run is composed of 16 individual analysis (injections to the GC/FPD) over a period of not less than 3 hours and not more than 6 hours
- Observe clogging of filter or SO_2 scrubber system

FRM 16 Post-Test Procedure

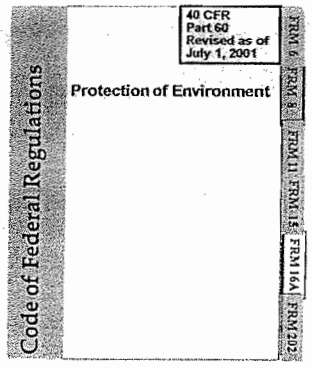
- Sample Line Loss: After the sample run, remove the probe from the source, but maintain its temperature. Inject a known concentration of H_2S at the level of the applicable standard (± 20 %) to the inlet of the probe to determine sample line losses. Sample line losses of > 20 % is unacceptable. With sample losses between 0-20 %, the final emissions must be corrected to the percent sample losses.

FRM 15 Post-Test Procedure

- Post-Sampling Calibration: Using only H_2S, recalibrate the GC/FPD using three concentration levels. Compare the post-sample calibration to the pre-sample calibration. If the drift between the two curves exceeds > 5%, the previous runs are not valid.



U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 16A for Determination of Total Reduced Sulfur (TRS) Compounds



FRM 16A Applicability

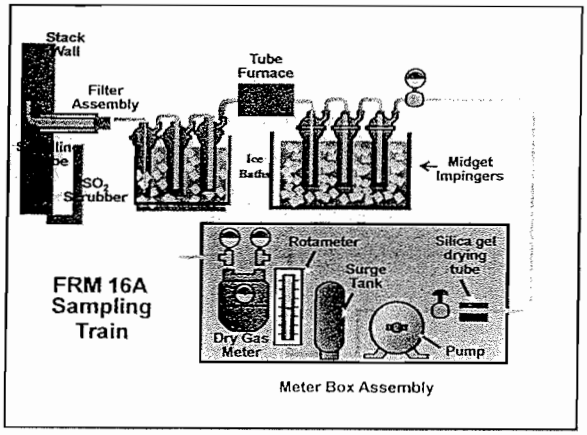
- This method is applicable for the determination of total reduced sulfur (TRS) from recovery boilers, lime kilns, and smelter dissolve tanks at Kraft pulp mills, and from other sources as specified in the applicable subpart of the regulations

FRM 16A Principle

- An integrated gas sample is extracted from the stack. SO_2 id removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by FRM 6 barium-thorin titration procedure

Federal Reference Method 16A Sampling Apparatus

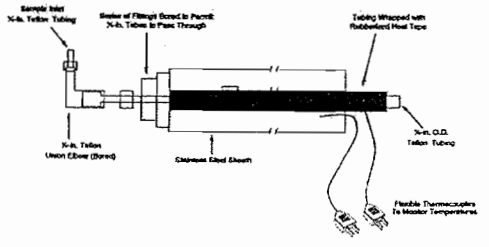
- Probe/Filter Assembly
- Sample Conditioning System
  - Three (3) SO_2 scrubber impinger assembly
  - Combustion Tube Furnace
- Impinger System
- Meter Box Assembly



FRM 16A Sampling Apparatus

- Probe: 0.6 cm diameter Teflon® tubing wrapped with heat resistant tape with an outer stainless steel sheath to maintain temperature 250 °F. The FRM 16A nozzle is the end of the Teflon® tube and points downstream of the gas flow to minimize particulate matter from entering the sampling train

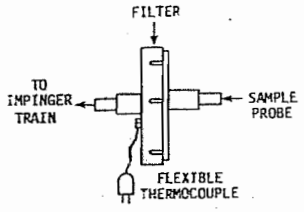
FRM 16A Probe Assembly



FRM 16A Sampling Apparatus

- Sample Conditioning System
  - Particulate filter, 50-mm Teflon® heat maintained at 250 °F
  - SO_2 scrubber system containing three (3) Teflon® impingers containing citric acid buffer solution to remove interference from SO_2 from the gas stream
  - Combustion furnace containing quartz glass tube heated to 800 ± 100 °C to oxidize the remaining TRS compounds to SO_2

FRM 16A Filter Assembly



FRM 16A Sampling Apparatus

- Peroxide Impingers: Three (3) midget impingers total, connected in series with U-tubes. The first two (2) impingers contains hydrogen peroxide while the third impinger is empty
- Transfer line: Containing temperature connection for measuring temperature of outlet of last impinger along with tubing/electrical for connecting to meter box assembly

FRM 16A Sampling Apparatus

- Meter box assembly: Containing silica gel drying tube, leak-free diaphragm pump, surge tank, rate/rotameter, and volume/dry gas meter along with temperature gauges for measuring inlet/outlet temperature of dry gas meter

FRM 16A Impinger Contents

- Sample Conditioning System: First two (2) Teflon® impingers containing 100 mL of citric acid buffer solution, while the third impinger remains dry
- Sample Collection: 20 mL of 3% hydrogen peroxide into the first two midget impingers, while the last impinger remains dry

FRM 6 Pre-test Preparation

- Prepare sampling train
  - Add 100 mL of citric acid buffer solution to the first two impingers in the sample conditioning train. Leave the last impinger dry.
  - Add 20 mL of 3% H_2O_2 to the first two impingers in the SO_2 impinger collection train. Leave final impinger dry
  - Place ice and water around impingers
  - Adjust probe and filter temperatures to desired settings

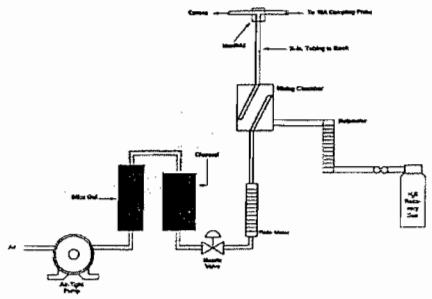
FRM 16A Pre-test Preparation

- Calibrate Meter System (Same as FRM 6)
- System Performance Checks (New to methodology not found in FRM 6)
- Sampling (Similar to FRM 6 except sampling rate of 2 L/min for 1 to 3 hours)
- Sample recovery (Same as FRM 6)
- Sample Analysis (Same as FRM 6 with barium-thorin titration)

FRM 16A Pre-test Preparation

- System Performance Checks
  - A system performance check (± 20%) is done to:
    - Validate the sampling train components and procedures; and
    - To validate a test run (after the run)

FRM 16A System Performance Check Apparatus



FRM 16A Pre-test Preparation

- System performance check done in the field prior to testing consisting of two (2) 30-minute samples taken through the probe/conditioning/impinger/meter box assembly from a certified NIST traceable compress gas cylinder containing know concentration of SO_2
- System performance check from known concentration of SO_2 must meet 80-120 % recovery

FRM 16A Sampling

- Leak check the sampling system (Optional)
- Record initial DGM reading and barometric pressure
- Position tip of probe at selected sampling point (> 1 meter from side of wall) with probe nozzle pointing downstream of gas
- Bring probe and filter to operating temperatures
- Place ice around impingers

FRM 16A Sampling

- Begin sampling with flow rate to 2 L/min ±10% during the entire sampling run
- Traverse, if applicable, taking reading every 5 minutes and recording on FTDS
- Sample run is from 1 to 3 hours

FRM 16A Sampling

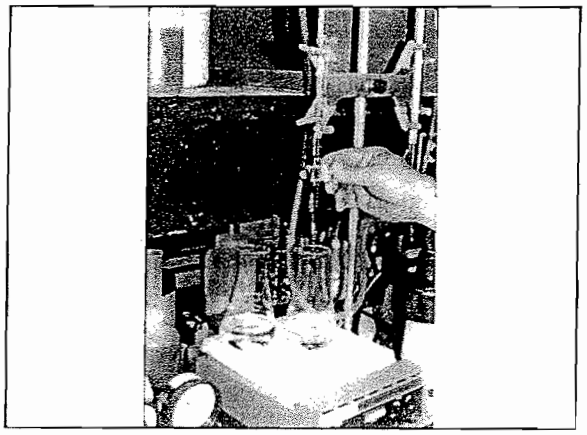
- Add more ice during run to maintain last impinger outlet < 68°F
- At conclusion of run, turn off the pump, remove probe from stack, and record final DGM reading
- Leak check the sampling train (mandatory)

FRM 16A Sample Recovery

- Drain the ice bath
- Disconnect sampling impingers
- Pour the content of the 3 midget impingers into a leak-free polyethylene bottle for shipment
- Rinse the three midget impingers and U-tubes with water and pour into the polyethylene bottle

FRM 16A Sample Recovery

- Seal, identify the sample container, and mark liquid level
- Complete "chain-of-custody" for sample run
- Complete field test data sheet (FTDS)
- Collect 30 mL of H_2O_2 as absorbing solution for reagent blank
- Titrate samples by barium-thorin titration (Same as FRM 6)



FRM 16A Calibration of DGM Procedure

- Calculate the calibration factor, Y, for each run, and the average results (must be < 2% from the average). Same as FRM 6

FRM 16A Post-test Calibration of DGM Procedure

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

FRM 16A Other Components Needing Calibration

- Thermometers: Calibrated against mercury-in-glass thermometers
- Rotameter: Need not be calibrated, but should be cleaned and maintained according to manufacturer's instruction
- Barometer: Calibrated against a mercury barometer

FRM 16A Key Points

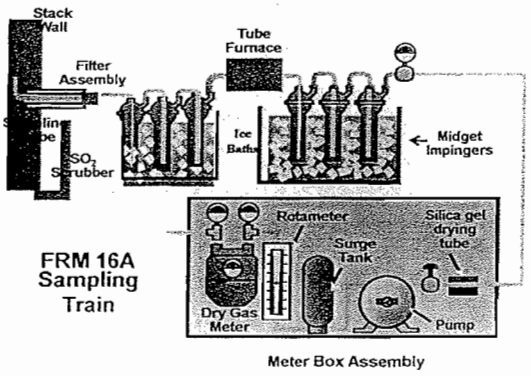
- During titration, have two flasks next to the titration assembly to compare to your sample
- One flask is the yellow starting point, while the second flask is the pink endpoint

FRM 16A Key Points

- If you feel that SO_2 (generated from the tube furnace of TRS conversion to SO_2) will be high (2,000-5,000 ppm) then increase strength of H_2O_2 to 10% to minimize depleting it's strength

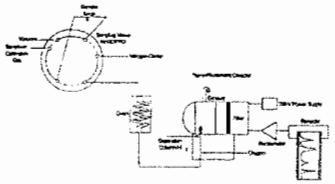
FRM 16A Key Points

- Must perform system performance check with NIST traceable SO_2 compress gas cylinder prior to testing through the complete sampling train (i.e., probe, filter, SO_2 scrubber, thermal furnace, impinger assembly, and meter box assembly. Must meet criteria of 80-120 % recovery of known concentration of SO_2



FRM 16A Sampling Train

U.S. EPA APTI Compliance Test and Source Test Observation FRM 16B for Determination of Total Reduced Sulfur (TRS) Compounds



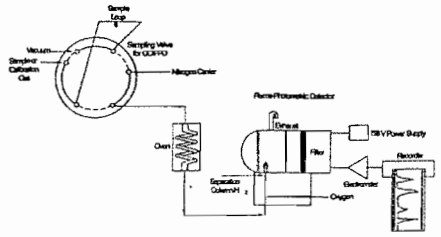
FRM 16B Determination of Total Reduced Sulfur (TRS)

- This method is applicable to the determination of TRS from recovery furnaces, lime kilns, and smelt dissolving tanks at Kraft pulp mills
- Method uses the up-front sampling system of FRM 16A except the H_2O_2 impingers are replaced with gas chromatography with a flame photometric detector (FPD)

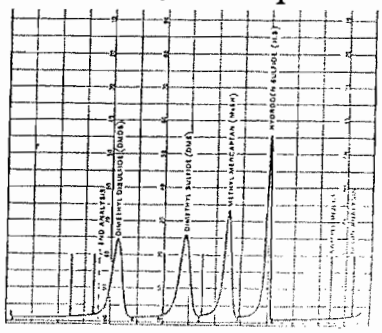
FRM 16B Determination of Total Reduced Sulfur (TRS)

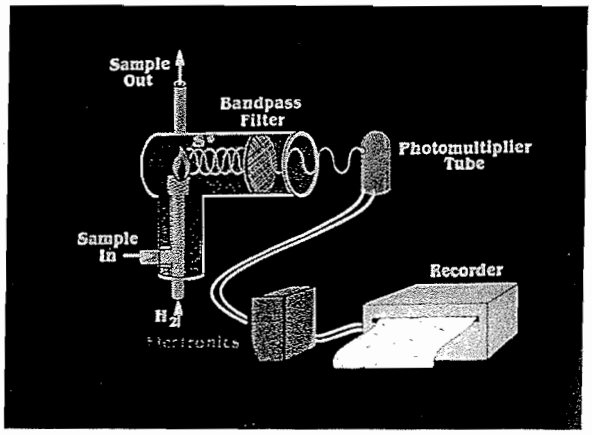
- FRM 16B specifically designed to detect speciated TRS compounds including:
  - Hydrogen Sulfide (H_2S)
  - Methyl Mercaptan (CH_3SH)
  - Dimethyl Sulfide $(CH_3)_2S$
  - Dimethyl Disulfide $(CH_3)_2S_2$

FRM 16B with Gas Chromatography/Flame Photometric Detector (FPD) (Same as FRM 15)

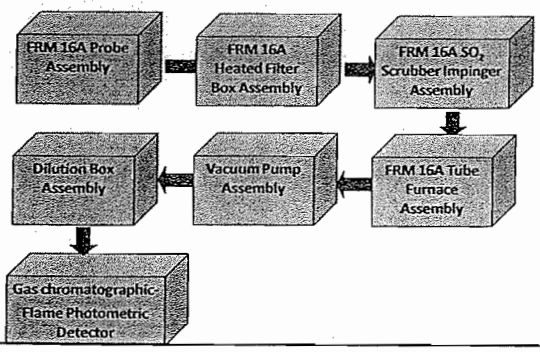


FRM 16B GC/FPD Speciation





FRM 16B Sampling System



U.S. EPA APTI
Compliance Test and Source Test Observation
FRMs Sulfur-Based Observer Checklists

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

FRMs 26/26A and SW-846, Methods 0050/0051 Determination of HCl and Cl_2

Applicability

- SW-846, Method 0050 and FRM 26A are both isokinetic methods which provide procedures for the determination of HCl/Cl_2 from hazardous waste incinerators and municipal waste combustors, especially suited for those sources with wet scrubbers emitting acid particulate matter (e.g., HCl dissolved in water droplets)

Applicability

- Method detection limit (MDL) is 20 ppm
- SW-846, Method 0050 and FRM 26A is for water-droplet stack gas environments requiring isokinetic sampling. Additionally, FRM 5 can be performed concurrent with FRM 26A and SW-846, Method 0050

Interferences

- Volatile material which produces chloride ions upon dissolution during sampling
- Diatomic chlorine (Cl_2) for sampling HCl (Cl_2 disproportionate to HCl and HClO in water)

FRM 26A/Method 0050 Design Requirements

- Gas flow measurement system (FRMs 2-4)
- Modified Method 5 sampling train
  - All glass/Teflon filter assembly
  - Can't use stainless steel
- Addition of two more impingers to the traditional FRM 5 sampling train

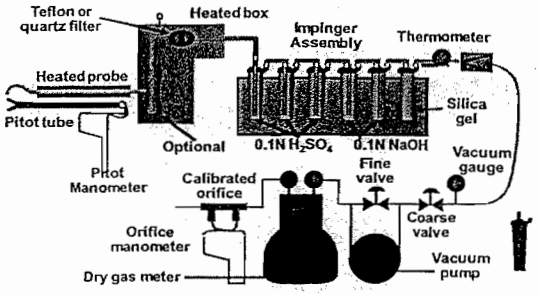
FRM 26A/Method 0050 Sampling Train

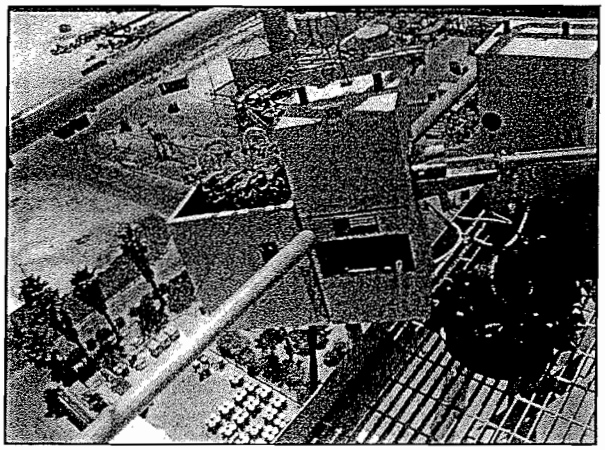
- Glass lined probe and nozzle
  - Can't use stainless steel unions in probe assembly
  - If stack gas >210°C, must use one piece nozzle/probe made of quartz
- Pitot tube/temperature sensor array
- Optional glass cyclone

FRM 26A/Method 0050 Sampling Train

- Heated filter assembly
  - Filter and filter gaskets must be Teflon
- Condensing impingers (glass)
- Pump/dry gas meter/orifice assembly

FRM 26A/Method 0050 Sampling Train





FRM 26A/Method 0050 Operational Requirements

- Multi-point integrated sampling
- Isokinetic sampling rate
- 2-hr sample at an anticipated rate of 0.75 cfm
- Probe/cyclone/filter at 120°C (248°F)

FRM 26A/Method 0050 Operational Requirements

- Post-sampling Ascarite purge (30 minutes) to remove trapped HCl/Cl_2 from filter to impingers
- Leak-free system
- Performance Evaluation (PE) sample required

FRM 26A/Method 0050 Chemistry

- Impingers 1,2 &3 remove HCl from sample gas stream by the following equation
  - $HCl + 0.1\ N\ H_2SO_4 \rightarrow H_3O + Cl^-$

FRM 26A/Method 0050 Chemistry

- Impingers 4 & 5 remove Cl_2 from the stack gas stream by the following equation
  - Cl_2 + 0.1N NaOH → H^+ + Cl^- + HClO
    - Must keep basic to prevent Cl_2 losses

FRM 26A/Method 0050 Impinger Arrangement

- 1st Impinger(Optional)- 50 mL of 0.1 N H_2SO_4
- 2nd and 3rd Impingers- 100 mL of 0.1 N H_2SO_4

FRM 26A/Method 0050 Impinger Arrangement

- 4th and 5th Impingers- 100 mL of 0.1 N NaOH
- 6th Impinger- 200-300 g of Silica Gel

FRM 26A/Method 0050 Operation

- Preliminary field determination (sample location, nozzle size, probe length) same as FRM 5
- Sample train preparation (charging of filter and impingers) same as FRM 5

FRM 26A/Method 0050 Operation

- Pre-leak check (optional) in accordance with FRM 5
- Sample collection in general accordance with FRM 5 (2-hr sample run)

FRM 26A/Method 0050 Operation

- The last impinger of the 0.1 N NaOH must be maintained strongly basic during sampling. Monitor pH of solution frequently during the run to prevent loss of Cl_2

FRM 26A/Method 0050 Operation

- To resolve:
  - Use stronger base (0.5 N)
  - Add volume to impinger (~200 mL)
  - Recharge impinger during sampling
  - Halfway through run, check pH of last impinger to validate basic nature of absorbing solution

FRM 26A/Method 0050 Operation

- Leak check before/after component changes during sample run
- Post-sampling Ascarite purge of system (30 minutes)
- Post-leak check in accordance with FRM 5
  - Leak rate must be <0.02 cfm

Sample Train Recovery Containers

1- Petri dish (filter)

2- Acetone rinse from probe nozzle/liner and front half of filter holder

Sample Train Recovery Containers

3- Combined impingers 1, 2 and 3 (measured) and water rinses

4- Combined impingers 4 and 5 (measured) and water rinses
(add 2 mL of $Na_2S_2O_3$)
The addition of $Na_2S_2O_3$ keeps the hypochlorous acid from dissociating

Sample Train Recovery Containers

5- Silica gel contents
(note color, weigh)

Analysis

- Weigh filter if need FRM 5 PM
- Analysis of recovery reagents for Cl^- by SW-846, Method 9057, ion chromatography

FRM 26A/Method 0050 Key Points

- Sampling system uses FRM 5 sampling train, so can also quantitate PM
- Sampling is isokinetic, 2-hr sample time
- Methodology quantitates HCl from Cl_2 emissions

FRM 26A/Method 0050 Key Points

- Complete Performance Evaluation (PE) sample prior to test
- Method Detection Limit (MDL) is 20 ppm

FRM 26A/Method 0050 Key Points

- Post-sampling Ascrite purge to move HCl from the cyclone/filter to impingers for 30 minutes at average ΔH

FRM 26A/Method 0050 Key Points

- Must maintain last impinger of NaOH at 0.1 N by
  - Using stronger base
  - Using more volume in impinger
  - Changing impinger during run
  - Checking frequently during run

FRM 26A/Method 0050 Key Points

- Can't change nozzle during sampling to maintain isokinetics
- Can't use stainless steel in probe assembly
- If stack gas >210°C, then must use one piece nozzle/probe assembly
- Filter analyzed for particles, but not for Cl_2/HCl

FRM 26/SW-846 Method 0051

Sampling and Analysis for HCl and Cl_2 Emissions

(Constant Rate Approach)

Applicability

- This method provides procedures for the determination of gaseous HCl and Cl_2 from hazardous waste incinerators and municipal waste incinerators

Interferences

- This method is designed to collect gaseous HCl and Cl_2 in relatively dry, particulate-free gas streams
- Must use FRM 26A/SW-846, Method 0050 (Isokinetic) with sources controlled by wet scrubbers that emit acid particulate matter and have water droplets

FRM 26?Method 0051 Design Requirements

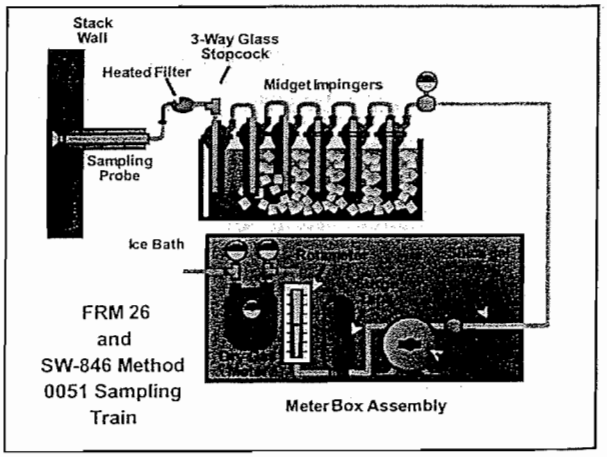
- Modified Method 6 sampling train
- Addition of 3-way stopcock and two more impingers to Method 6 sampling train
- 3-way stopcock used to purge probe

FRM 26/Method 0051 Sampling Train

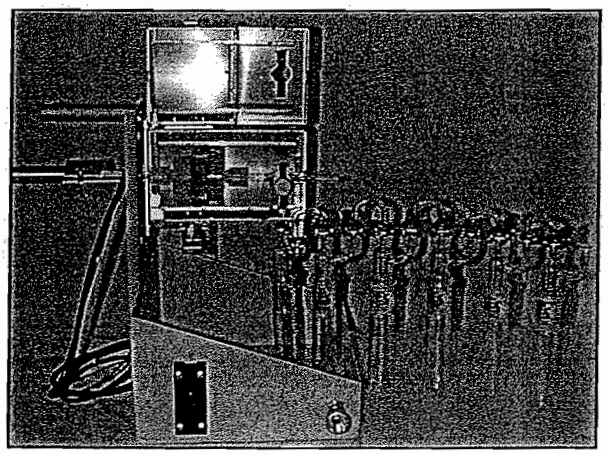
- Glass lined probe and Teflon elbow inlet
  - nozzle points downstream
- Heated Teflon mat Pallflex filter and three-way stopcock valve
  - can't use glass wool as particle control due to bias effects

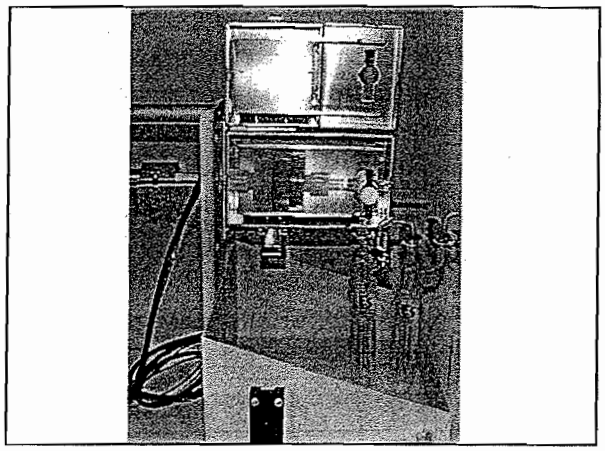
FRM 26/Method 0051 Sampling Train

- Midget impinger system (5 midget + 1 Mae West/drying tube)
- Pump/rotameter/dry gas meter



FRM 26 and SW-846 Method 0051 Sampling Train





Operational Requirements

- Single point (> 1 meter from stack wall) integrated sampling
- Purging of probe for 5 minutes prior to sampling

Operational Requirements

- Probe/filter at 120°C (248°F)
- Sampling at 2 L/min for 60 minutes
  - 120 liters total sample volume

Operational Requirements

- Leak-free system
- Performance evaluation (PE) sample

Two Tier Leak Check

- Stopcock, probe and filter
- Impingers and meter box assembly

FRM 26/Method 0051 Chemistry

- Impinger #1 empty
- Impingers #2 & #3 remove HCl from sample gas stream by the following equation:

$HCl + 0.1\ N\ H_2SO_4 \rightarrow H_3O + Cl^-$

FRM 26/Method 0051 Chemistry

- Impingers #4 & #5 remove Cl_2 from the stack gas stream by the following reaction:

$Cl_2 + 0.1\ N\ NaOH \rightarrow H^+ + Cl^- + HClO$

FRM 26/Method 0051 Impinger Arrangement

- 1st impinger (Optional)
  - empty
- 2nd and 3rd impingers
  - 15 mL of 0.1 N H_2SO_4

FRM 26/Method 0051 Impinger Arrangement

- 4th and 5th Impingers
  - 15 mL of 0.1 N NaOH
- 6th Impinger/drying tube
  - 30 g silica gel

FRM 26/Method 0051 Operation

Field Observation Checklist

- Preliminary field determination (sample location, recovery area) same as FRM 6
- Sample train preparation (charging of filter and impingers) same as FRM 6

FRM 26/Method 0051 Operation

Two Tier Leak Check

- Pre-leak check (-10 in. Hg) stopcock, probe, and filter prior to inserting probe into stack
- Pre-leak check (-10 in. Hg) impinger and meter box assembly before testing

FRM 26/Method 0051 Operation

- Purge probe/filter assembly at 2 L/min for 5 minutes
- Position probe/Teflon®-elbow pointing downstream
- Sample collection in general accordance with FRM 6
- Sample at 2 L/min for 60 minutes
  - 120 liters total sample volume

FRM 26/Method 0051 Operation

- The last impinger of the 0.1 N NaOH must be maintained strongly basic during sampling
- Monitor pH of solution frequently

FRM 26/Method 0051 Operation

- To resolve
  - Use stronger base (0.5 N)
  - Add volume to impinger (30 mL)
  - Recharge impinger during sampling
  - Half-way through run, check pH of last impinger to validate basic nature

FRM 26/Method 0051 Operation

- Leak check before/after component changes during sample run
- Post-leak check in accordance with FRM 6

Sample Train Recovery Containers

1- Combined impingers #1, #2 and #3 (measured) and water rinses

2- Combined impingers #4 and #5 (measured) and water rinses

(add 2 mL of $Na_2S_2O_3$ to prevent hyperchlorous acid from dissociating)

Sample Train Recovery Containers

3- Silica gel contents (note color; not weighted)

Analysis

- Analysis of recovery reagents for Cl- by SW-846, Method 9057, Ion Chromatography (IC)

FRM 26/Method 0051 Key Points

- System uses a modified FRM 6 sampling train
- Sampling is performed at 2 L/min for 60 minutes

FRM 26/Method 0051 Key Points

- Methodology quantitates HCl from Cl_2 emissions
- Must maintain last impinger of NaOH strongly basic
  - Use stronger base (0.5 N NaOH)
  - Add more volume to impingers
  - Change out during sample run

FRM 26/Method 0051 Key Points

Two tier pre-test leak check (-10 in. Hg):

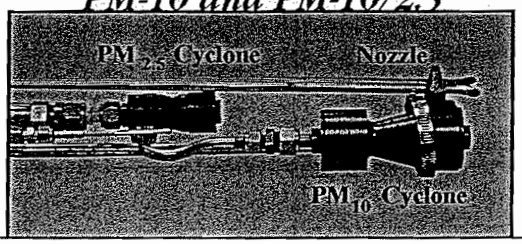
1. Stopcock, probe, and filter
2. Impinger and meter box assembly

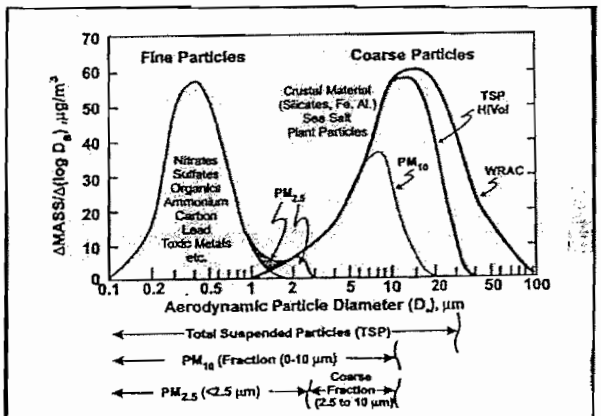
- Can also determine moisture of stack gas

FRM 26/Method 0051 Key Points

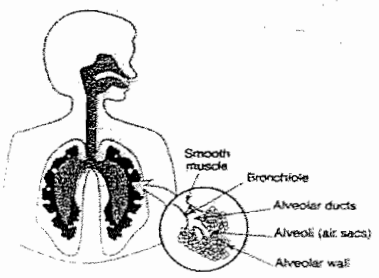
- Glass lined probe/Teflon® elbow and Teflon® filter assembly only
- Methodology limited to relatively dry, particulate-free gas streams
- Weigh filter, but can't analyze for HCl/Cl_2

U.S. EPA APTI
Compliance Test and Source Test Observation
FRMs 201/201A and CTM 040 For PM-10 and PM-10/2.5





Particles ≤ 1 µm collect in most remote portions of lungs – the air sacs (or alveoli)



FRM 201/201A and CTM 040

PROBLEM

Since we are sampling particulate matter, we must stay isokinetically. If you are using cyclones, must use the flow rate design for the cyclone to maintain proper particulate cut size!

FRM 201 Exhaust Gas Recirculation (EGR)

- 40CFR51, Appendix M
- Qc = Qs + Qr to maintain constant cut size
- Sample isokinetically at each sample point

FRM 201 Exhaust Gas Recirculation (EGR)

- Must use cyclone, in-stack; probe pre-heated
- FRM 5 glassware can be used, so condensibles can be added by FRM 202
- EGR method uses new technology

FRM 201
Exhaust Gas Recirculation (EGR)

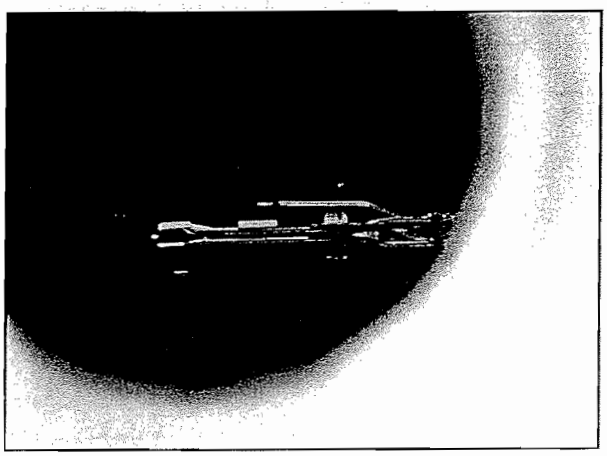
- EGR method is recommended if:
  - A total particulate number is also needed because sampling is isokinetically.
  - Stack gas velocities fluctuate

FRM 201
Exhaust Gas Recirculation (EGR)

- EGR modification of FRM 5
  - Nozzle has a recycle attachment
  - The recycle gas is heated to stack temperature
  - Adds in-stack cyclone to capture PM-10
  - Delete out-of-stack filter

FRM 201
Exhaust Gas Recirculation (EGR)

- Cyclone does have to be calibrated
- Must leak-check: positive and negative
- Can use condenser rather than FRM 5
- Each point isokinetically and same dwell time



FRM 201A
Constant Sampling Rate (CSR)

- Uses available equipment
- Sample at constant sampling rate required by the PM-10 cyclone or impactor
- Relaxes FRM 5 +/- 10% isokinetic rate to 20-40 % based upon stack gas velocity (Must keep sampling rate within delta p min and delta p max)

FRM 201A
Constant Sampling Rate (CSR)

- Select nozzle based upon delta p min/max
- Interested in small particles, so isokinetic no as importrant as FRM 5
- Dwell time at each point is proportional to stack gas velocity

FRM 201A
Constant Sampling Rate (CSR)

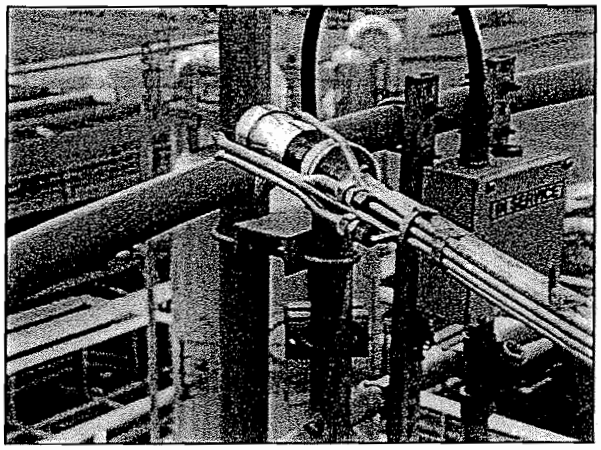
- Total catch may not be accurate as FRM 5
- Can use impactor or cyclone
- If using impactor, must be calibrated

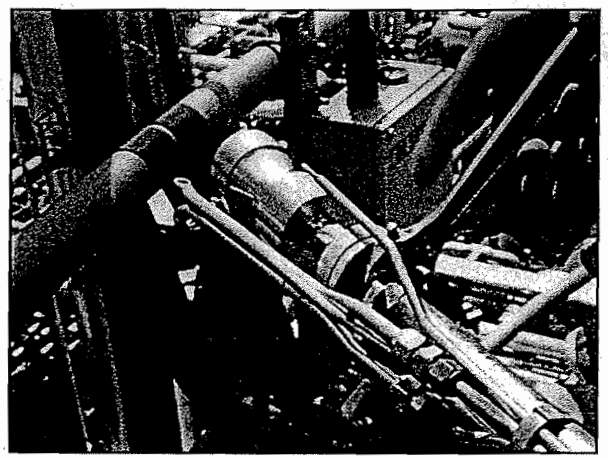
FRM 201A
Constant Sampling Rate (CSR)

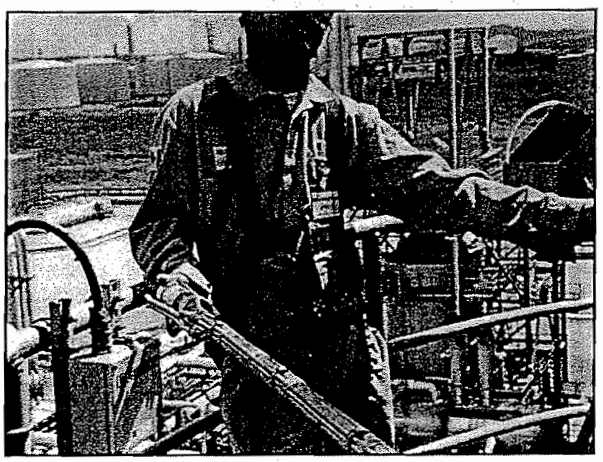
- FRM 201A can also be used with FRM 202
- CSR is recommended if:
  - Particle sizing is desired
  - Low concentration of PM-10

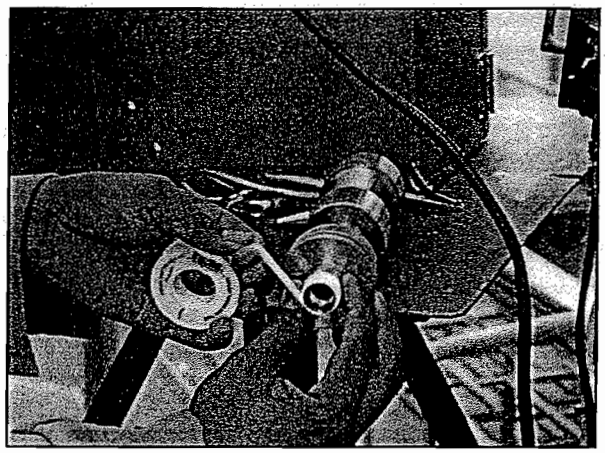
FRM 201/201A Review

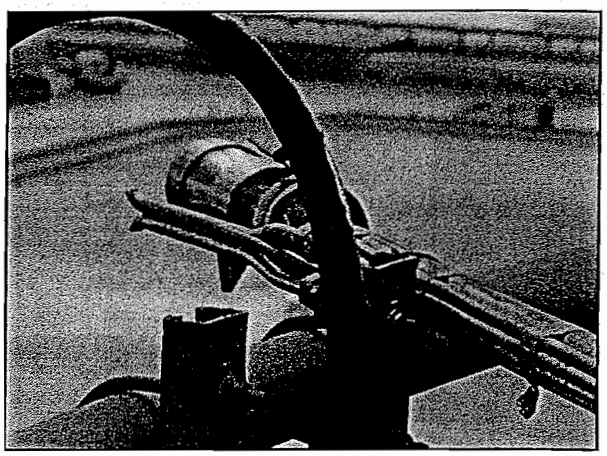
- Both methods measure PM-10 in-stack
- EGR new technology, CSR uses standard test equipment (i.e., FRM 5)

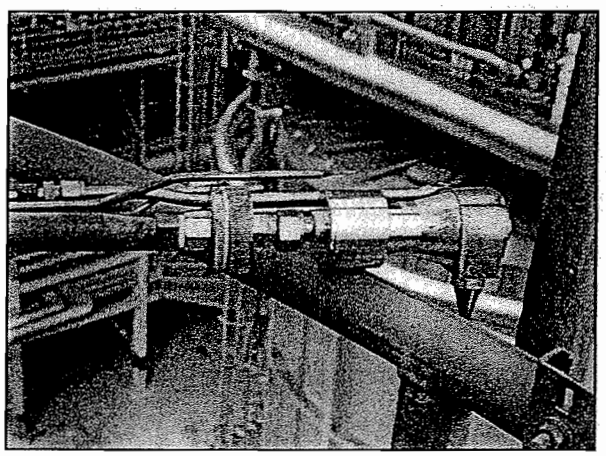












FRM 201/201A Review

- EGR uses a PM-10 cyclone. CSR can use either a cyclone or impactor
- EGR samples isokinetically, therefore total mass is accurate. CSR doesn't sample isokinetically, therefore mass not as accurate

FRM 201/201A Review

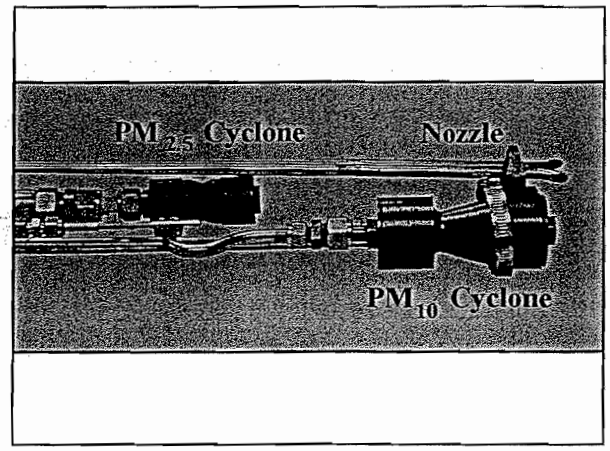
- If stack velocities fluctuate, the CSR may require more than one sample train
- PM-10 cyclones do not have to be calibrated if they meet design specification. Impactors (201A) must be calibrated

FRM 201/201A Review

- CSR calibration of metering system and leak check procedures same as FRM 5
- CSR requires constant sampling rate and dwell time is proportional to stack gas velocity
- EGR is isokinetically and sampling time same as FRM 5

CTM-040 Determination of PM-10/PM-2.5

- Predetermined constant sampling rate for combined PM-10 and PM-2.5
- In-stack cyclones used to capture PM-10 and PM-2.5
- Method used with FRM 202



CTM-040 PM-10 and PM-2.5

- Method applies to in-stack measurement of particulate matter equal to or less than PM-10 and PM-2.5
- Use of optimum sampling rate (within limits of flows for PM-10 and PM-2.5 cyclones) near isokinetic conditions
- Methodology uses two in-stack cyclones (PM-10 followed by PM-2.5) followed by ultimate filter

CTM-040 PM-10 and PM-2.5

- Sampling train identical to FRM 201A except a PM-2.5 cyclone is inserted between the PM-10 cyclone and the ultimate filter
- The particulate mass is determined gravimetrically for each size fraction (i.e., PM-10 cyclone, PM-2.5 cyclone, and < 2.5 filter) after removal of uncombined water

CTM-040: Method for Determination of PM10/PM2.5

- Variations from isokinetic stack conditions maintained with well-defined flow rate
- Filter after PM-2.5 cyclone to trap final particulate matter
- Sampling train is similar to FRM 17
- Sampling rate selected for combined cyclone heads

CTM-040: Method for Determination of PM10/PM2.5

- Flow rate determination for cyclones determined from manufacturer's graph

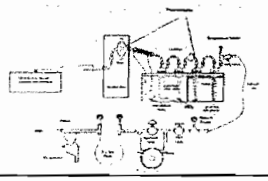
CTM-040: Method for Determination of PM10/PM2.5

- Sampling same as FRM 5 (i.e., sample points and time)
- PM-10/PM-2.5 software package available

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

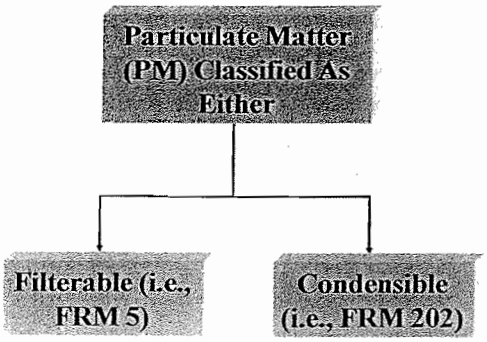
FRM 202 Condensible Particulate Matter (CPM)

Dry Impinger Train Round 2



EPA's Defines Emitted Particulate Matter (PM) in 40CFR51.100

"Particulate matter emissions mean all finely divided solid or liquid materials, other than uncombined water, emitted to the ambient air as measured by an applicable reference method, or an equivalent or alternative method, specified in the regulations, or by a test method specified in an approved State Implementation Plan (SIP)."



Basic Measurement Methods for Particulate Matter (PM)

- External Heated Filter: Total particulate matter as measured by FRM 5 at defined temperature
- In-stack Filtration: Total particulate matter as measured by FRM 17 at stack temperature and pressure
- In-stack Cyclone: PM-10 particulate matter using FRM 201/201A
- In-stack Cyclone: PM-10/PM-2.5 particulate matter using Conditional Test Method 040 (CTM-040)

Basic Measurement Methods for Condensibles

- FRM 6: Determination of Sulfur Dioxide Emissions from Stationary Sources
- FRM 8: Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources
- FRM 202: Determination of Condensible particulate Emissions from Stationary Sources

Basic Measurement Methods for Condensibles

- FRM 315: Determination of Particulate and Methylene Chloride Extractable Matter (MCEM) From Selected Sources At Primary Aluminum Production Facilities
- Conditional Test Method 039 (CTM-039): Determination of PM10 and PM2.5 Emissions by Dilution Sampling

Regulatory Background CPM

- FRM 8 (1971): New source measurement method for SO_3/H_2SO_4 emissions
- PM-10 NAAQS (1987): EPA acknowledges the effect of PM-10 on human health
- FRM 201/201A (1990): New source measurement methods for PM-10 for quantifying emissions

Regulatory Background CPM

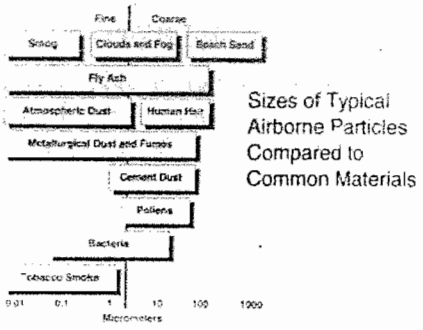
- FRM 202 (1991): EPA acknowledges that some emissions in the vapor phase at stack conditions are converted to the condensed phase (as a liquid or solid) immediately upon discharge into the ambient air and those compounds are not captured on a particulate filter during stack testing

Regulatory Background CPM

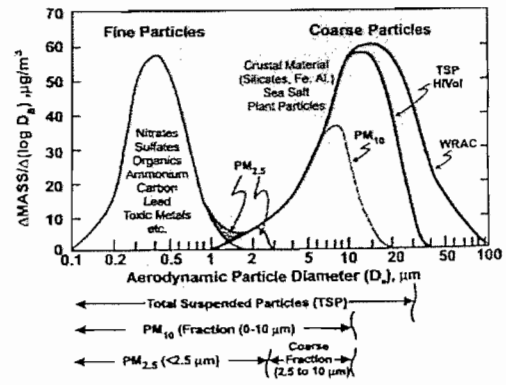
- PM-2.5 NAAQS (1997): EPA acknowledges that effect of fine particulate matter (i.e., PM-2.5) on human health
- Conditional Test Method 040 (2004): EPA proposes test method for combined PM-10 and PM-2.5
- Conditional Test Method 039 (2004): EPA proposes test for PM-10 and PM-2.5 by dilution sampling

Condensible Particulate Matter

- Condensible particulate matter (CPM) consists of species that are emitted from a source in the vapor phase at stack gas temperature but condenses into a liquid or solid aerosol at ambient temperature



Sizes of Typical Airborne Particles Compared to Common Materials



Historical Measurement Methods for CPM

- Condensible Particulate Matter by FRM 202: Particulate matter captured in the back half of the FRM 5 sampling train, including water and organic soluble extraction components
- Total Particulate: The sum of the filterable particulate (i.e., front half of the FRM 5 sampling train) and the condensible particulate matter (i.e., the back half of the FRM 5 sampling train, including water and organic soluble extractions)

ESTIMATION OF THE IMPORTANCE
OF CONDENSED PARTICULATE MATTER
TO AMBIENT PARTICULATE LEVELS

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Task Manager
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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

April 1983

TABLE 2. EPA METHOD 5 TEST RESULTS--RATIO OF FRONT HALF (FILTERABLE) TO BACK HALF PARTICULATES BY SOURCE TYPE

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Anode baking furnace	65.8	34.2	7
Asphalt plants	67.9	32.1	17
Boiler/coal (industrial)	90.1	9.9	10
(utility)	55.6	44.4	15
Boiler/oil	42.7	57.3	27
Boiler/wood	85.0	15.0	14
Brick and tile kilns	72.2	27.9	9
Chemical production			
Potassium still	65.2	34.7	1
Chrome oxide kiln	94.3	5.7	1
Boric acid	44.1	55.9	2
Electric arc furnaces			
BOF	62.9	37.1	3
Open hearth	77.3	22.7	3
Coke ovens	71.7	28.3	4
Sandblast	65.2	31.8	2
Heat treating	69.9	30.1	2
Elemental phosphorous	46.0	54.0	1
Fiberboard dryer	57.5	42.5	2
Glass plant	73.0	27.0	14
Grain dryers	74.5	25.5	3
Incinerators			
Municipal	59.7	40.3	4
Industrial	35.1	64.9	1
Sewage sludge	61.4	38.6	2
Iron and steel			
Iron foundries	76.1	23.9	6
Iron and steel sinter plants	71.1	28.9	14
Kraft pulp			
Recovery boilers	81.7	18.3	32
Lime kiln	66.5	33.5	7
Smelt dissolve tank	73.1	26.9	6
Lime kiln	69.5	30.8	5

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Mineral products			
Gypsum	87.3	12.7	1
Clay dryer	0.5	99.5	1
Feldspar dryer	11.6	88.4	1
Clay kiln	87.4	12.6	2
Mineral wool	60.7	39.3	3
Petroleum refineries			
Heaters	45.6	54.4	1
FCC	76.1	23.9	2
Catalycic regenerator	46.6	53.4	3
Portland cement			
Kiln (gas-fired)	90.1	9.9	1
(coal-fired)	73.8	26.2	1
(wet-process)	65.5	34.5	8
(dry-process)	37.9	62.1	1
(process not specified)	46.4	53.6	1
	81.1	18.9	1
	82.9	17.1	1
Finish mill (wet-process)	48.0	52.0	1
	73.6	26.4	3
Primary nonferrous smelters			
Zinc sweat kiln	24.7	75.3	1
Zinc fume kiln	86.6	13.4	1
Zinc ore briquet dryer	82.7	17.3	1
Lead sinter line	95.6	4.4	2
Lead blast furnace	37.7	62.3	1
Copper converter	69.5	30.5	1
Copper converter, electric arc furnace, and fluid bed roaster	39.8	60.2	1
Copper reverberatory furnace	44.1	55.9	1
Copper roasters	49.3	1.0	1
Molybdenum roasters	97.5	2.5	1
Roofing			
Saturated felt	55.4	44.6	2
Asphalt blowing	56.8	43.2	4

Recent History

- Pre - PM- 10 & PM – 2.5 NAAQS
  - Recognized condensable PM impact
    - Crustal PM was cause of most non-attainment areas for TSP
    - Condensable PM was a small consideration
  - Condensable PM method proposed 1990
    - Was a "Consensus Method" addressing several State specific compliance test methods
    - Incorporates several analytical options

Why A Condensible Test Method?

- New NAAQS for particulate matter (PM-2.5)
- New emission inventories required
- More comprehensive emission factors required

Why A Condensible Test Method?

- More comprehensive test methods now required to address non-attainment questions
- Expanded use of dispersion models
- Expanded use of receptor models

Components of Direct $PM_{2.5}$

- Filterable $PM_{2.5}$
  - Solid or liquid material at stack temperature and higher (measured at ~250° to 320° F)
  - Stable in atmosphere and collected on ambient sampler
- Condensable $PM_{2.5}$
  - Vapor or gas at stack temperature
  - Condenses to liquid or solid at stack exit
  - Stable in atmosphere and collected on ambient sampler

Precursors to Condensibles

Ammonia	Nitrates
HCl	Organics
HF	Chlorides
Sulfates	

List of Precursors Reactions to Condensibles

Condensible Organics	$H_xC_y(g) = H_xC_y(a)$
SO_3	$SO_3(g) + H_2O(g) = H_2SO_4(a)$
SO_3 w/NH_3	$SO_3(g) + H_2O(g) + 2NH_3 = (NH_4)_2SO_4(s)$

List of Potential Precursors Reactions to Condensibles

HCl	$HCl(g) + H_2O(g) = HCl(l)$
HF	$HF(g) + H_2O(g) = HF(l)$
Trace Metals	$M(g) = M(l)$ or $M(s)$
Nitrates	$NO_3(g) + H_2O(g) = HNO_3(l)$

FRM 202 for Measurement of CPM

- Needed to measure CPM instead of solid PM
- Allows the determination of both filterable and condensible PM simultaneously

Condensible Test Method

- Allow for speciation of collected particulate
  - Elements Al through Pb
  - Major Ions (Sulfates, Nitrates, Ammonium, Sodium, Potassium etc.)
  - Total Mass, Carbon (Elemental and Organic)
  - Others (Semi-volatiles, Ds/Fs, PCBs, Volatiles etc.)

Reasons to Consider Condensable $PM_{2.5}$ Emissions

- Condensable fraction of direct $PM_{2.5}$ can be significant
  - 10 to 50 percent of $PM_{2.5}$ emissions depending on control measures, temperature, other source-specific conditions

Reasons to Consider Condensable $PM_{2.5}$ Emissions

- Combustion, metallurgical & wood product sources emit large quantities of vapors that condense to form $PM_{2.5}$
  - Acids (e.g., sulfuric acid from coal combustion)
  - Neutralized acids (e.g., $[NH_4]_2[SO_4]$, NH_4Cl)
  - Organic materials (e.g., alkanes, PAHs, PCBs, PCDDs, acids)
  - Metals (e.g., As, Se, Sb, Pb Compounds)

Reasons to Consider Condensable $PM_{2.5}$ Emissions

- A small fraction of point sources are responsible for the majority of condensable PM emissions

Inventories and $PM_{2.5}$ Emissions

- Filterable PM
  - Historically only PM included in databases
  - Some States include filterable PM_{10} or $PM_{2.5}$
- Condensable PM
  - Current knowledge is spotty
  - Some SIP databases fail to include PM_{cond} (even when required)
  - When PM_{cond} included - calculated from emissions factors (e.g., AP-42) that are often based on incorrect test methods

Inventories and $PM_{2.5}$ Emissions

- Inventories reflect database errors
  - Federal inventory includes some adjustments
  - Underestimate some sources' contributions, overestimate others

Issues to Consider for CPM

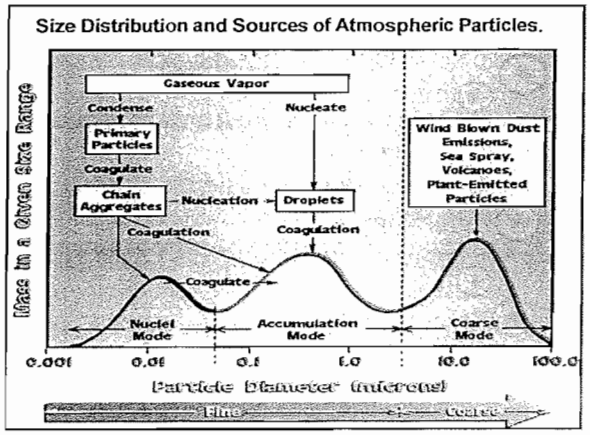
- Most current regulations do not address PM_{cond} Effect on SIP Regulations
  - Focus on filterable PM
  - Force control technology towards filterable PM
- Some regulations do include PM_{cond}, but with incorrect test methods

Issues to Consider for CPM

- Final rule creates a transition period
  - Regulations addressing PM_{cond} encouraged but not required
  - Develop more precise and accurate PM_{cond} emissions for inventories and rules

CPM in Relation to Air Quality Issues

- Potential impacts on PSD review applicability for PM-10 and PM-2.5 (Threshold levels: Rural vs. urban)
- Potential impacts on dispersion modeling analysis
  - Current NAAQS and PSD increments (Class I areas)
  - Monitoring *de minimis* levels
- Visibility impairment (VISCREEN vs. MESOPUFF-II models)
- Human health issues



Biases from Condensibles

Positive

- Some condensibles that are not intended to be regulated condense below stack temperature and are collected on heated filter

Biases from Condensibles

Negative

- Some condensibles that are to be regulated do not condense at filter temperature and pass through the filter and are not counted

Steps to Handle Condensibles

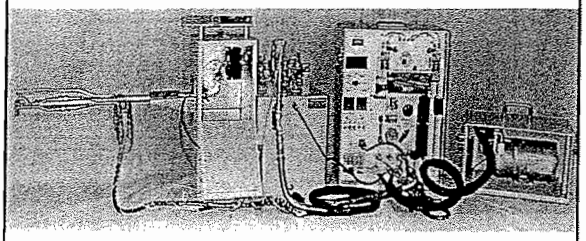
- Determine if condensibles are to be regulated by applicable emission regulations
- Design proper sampling and analytical procedures to match intention of the regulation

Cautions on Condensible Sampling Techniques

- EPA Reference Method 5 sample box temperature may not be an accurate indication of sample gas temperature
- Condensed particulate matter may change its chemical composition after condensation

Cautions on Condensible Sampling Techniques

- Although temperature is major parameter for collection of condensibles, several other factors can greatly affect condensibles (i.e., moisture content, dilution air, presence of other compounds)



EPA FRM 202

- Used with filterable PM method
- Requires post sample conditioning in field
- Uses existing methodology and equipment
- Is used by several State agencies

FRM 202 CPM Sampling Program

- Impinger portion of a FRM 17 type sampling train
- Nitrogen purge to remove dissolved SO_2

FRM 202
CPM Sampling Program

- Extraction of impingers with methylene chloride
- Total of both fractions (water and methylene chloride) represent CPM

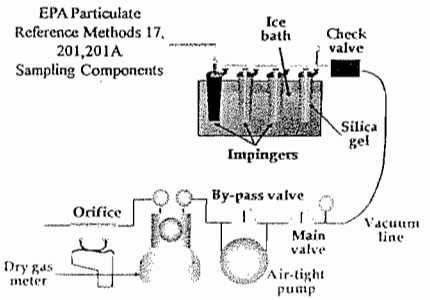
EPA FRM 202

- Requires post sample separation in field
- Requires post sample adjustments in lab
- Limited speciation

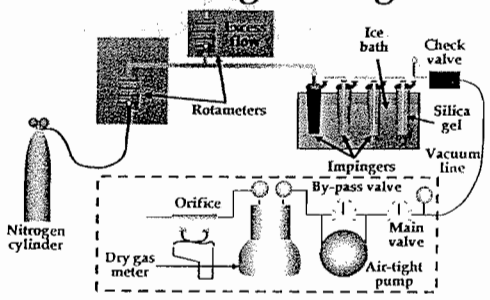
FRM 202

- FRM 202 is subject to false positive bias because of conversion of nonparticulate species into CPM in the method's sampling train

FRM 202 Sampling Train



FRM 202
Post Nitrogen Purge



FRM 202 Biases

- Normally noncondensible gases may react with other gases or condensibles to form condensible PM
- Oxidation of dissolved SO_2 in the impinger water to form H_2SO_4
- Stabilization of H_2SO_4 with NH_4OH when pH of the impinger solution is > 4.5

FRM 202 Biases

- Use of water impingers to concentrate consensibles has bias given the potential to affect chemical reaction rate. Chemical reaction rates generally increase with concentration

% Condensible Particulate Matter (FRM 202)

Source Category	% of Total Catch in Back Half
Fossil fuel fired gen.	50
Incinerator	20-30
Asphalt Plant	40-85
Smelters	35-85

Results of FRM 202 For Condensibles

- Coal-burning Boilers: Condensibles were ~76 % of the total PM-10 stack emissions
- Oil/Natural Gas/Kerosene Combustion Turbines: Condensibles were ~ 68 % of the total PM-10 stack emissions
- Oil/Natural Gas Boilers: Condensibles were ~ 49 % of the total PM-10 stack emissions

FRM 202 Testing Conclusion

- Condensible particulate matter (CPM) is composed mostly of inorganic matter, independent of source type (boiler or turbine) or fuel burned (coal, oil or natural gas)
- Inorganic matter is composed of mostly sulfate associated compounds

FRM 202 Testing Conclusion

- Close relationship between ambient sulfate concentrations and fine PM (i.e., PM-2.5)
- Based on review of FRM 202 stack tests, the condensible PM emissions can make a significant contribution PM constitutes a portion of the total PM-10 emissions from FFFSGs

Special Considerations When Using Method 202

- May not be applicable at sources that emit high levels of ammonia
- If SO_2 is present, the sample must be purged with N_2, but recent studies indicate that not all the SO_2 is purged from the impingers

Other Test Method 28 (OTM-28)

[April 15, 2009]

Dry Impinger Method For Determining Condensible Particulate Emissions from Stationary Sources

OTM-28

1. **Scope and Applicability**
2. **Summary of Method**
3. **Definitions**
4. **Interferences [Reserve]**
5. **Safety**
6. **Equipment and Supplies**
7. **Reagents and Standards**
8. **Sample Collection, Preservation, Storage and Transport**
9. **Quality Control**

OTM-28 (Cont'd)

10. **Calibration and Standardization**
11. **Analytical Proce3dure**
12. **Calculations and Data analysis**
13. **Method Performance [Reserved]**
14. **Pollution Prevention [Reserved]**
15. **Waste Management**
16. **Alternative Procedures [Preserved]**
17. References

Definitions

- Primary PM- Primary PM (also known as direct PM) means particles that enter the atmosphere as a direct emission from a stack or an open source. Primary PM comprises two components: filterable PM and condensable PM

Definitions

- Filterable PM- Filterable PM means particles that are emitted directly by a source as a solid or liquid at stack or release conditions and captured on the filter of a stack test train.
- Primary PM-10- Primary PM-10 (also known as direct PM-10, total PM-10, PM-10 or filterable PM-10, and condensable PM, individually) means PM with an aerodynamic diameter of 10 micrometers.

Definitions

- Primary PM-2.5- Primary PM-2.5 (also known as direct PM-2.5, total PM-2.5, PM-2.5 or filterable PM-2.5, and condensable PM, individually) means PM with an aerodynamic diameter of 2.5 micrometers from an air emission source or gaseous emissions or liquid droplets from an air source. Direct PM-2.5 emissions include elemental carbon, directly emitted organic carbon, directly emitted sulfate, directly emitted nitrate, and other inorganic particles

Definitions

- Condensable PM (CPM)- Condensable PM means material that is vapor phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. All CPM is assumed to be in the PM-2.5 size fraction.

OTM-28 Train Components

- Upfront EPA Particulate Reference Methods 5, 17, or 201A Sampling Components
- A FRM 23 Type Condenser
- Empty Drop-out Impinger or Flask Immersed in Water Bath ~ 85 °F
- Empty Modified Greenburg-Smith Impinger With an Open Tube Tip Immersed in Water Bath ~ 85 °F

OTM-28 Train Components

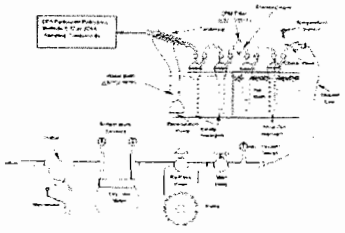
- A CPM 47-mm Teflon® Membrane Filter That Does Not Have Organic Binder and Maintained at 85 °F
- A Thermocouple Capable of Measuring the Gas Stream Behind the CPM Filter Holder
- Long-stem Greenburg Smith Impinger Containing 100-mL of Water Immersed in an Ice Bath

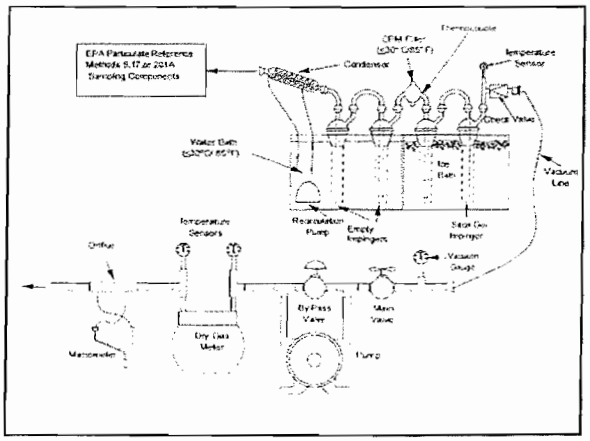
OTM-28 Train Components

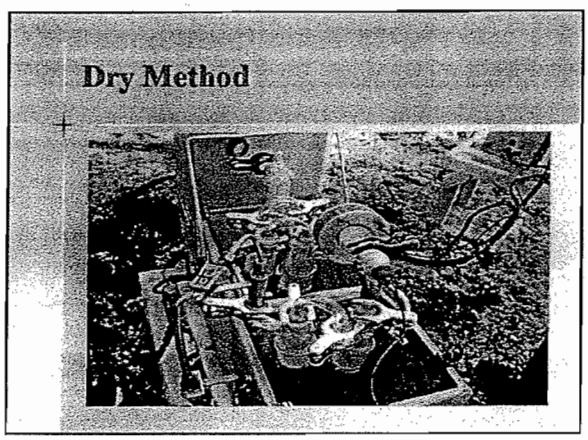
- Traditional Greenburg Smith Impinger Containing 200-300 g of Silica Gel
- Traditional FRM 5 Transfer Line and Meter Box Assembly (i.e., Vacuum Gauge, Main Valve, By-Pass Valve, Pump, Dry Gas Meters with Temperature Sensors, and Orifice Meter/Inclined Manometer

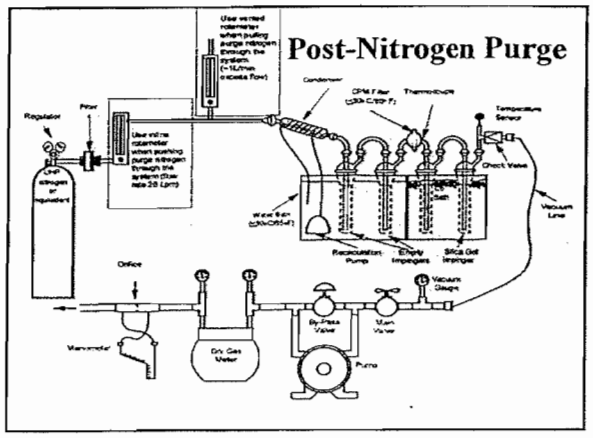
OTM-28 Train Components

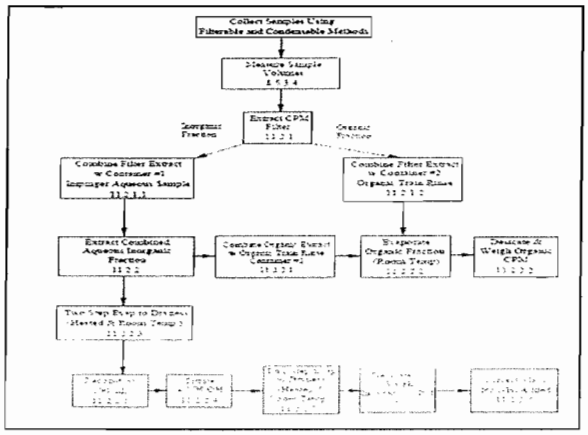
- Sample Train is Operated Similar to FRMs 5, 17, or 201A

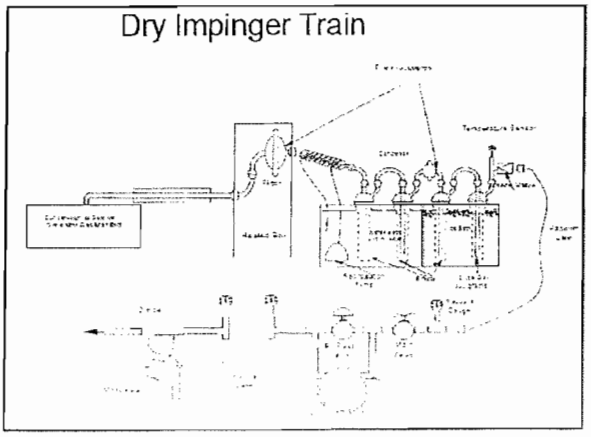










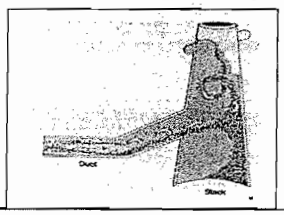


http://www.epa.gov/ttn/emc/methods/method202.html

EPA Updated Method 202

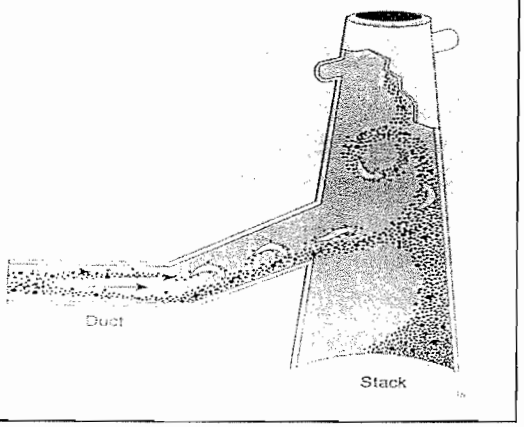
- Recommending use of Method 201A (existing filterable PM_{10} test method) with supplemental hardware for filterable $PM_{2.5}$ added to updated 202 (OTM-28)
- Revise Method 202 in Appendix M
  - Add filterable $PM_{2.5}$ measurement
  - Add condenser followed by dry impingers
  - First two impingers in water
  - Second two impingers in ice water
  - Promulgate 2008/2009

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 2F Cyclonic and Non-Parallel Flows

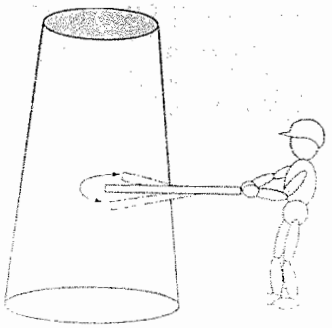


Definition of Cyclonic Flow

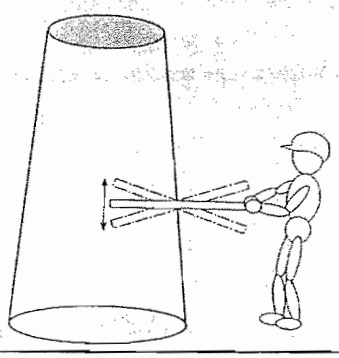
Cyclonic , swirling, or non-parallel flow is defined to exist in the stack when the average flow at designated sample points in the stack average greater than 20 degrees off parallel with stack walls



Yaw Angle

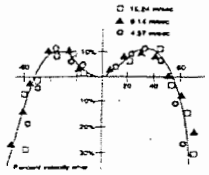


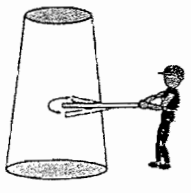
Pitch Angle



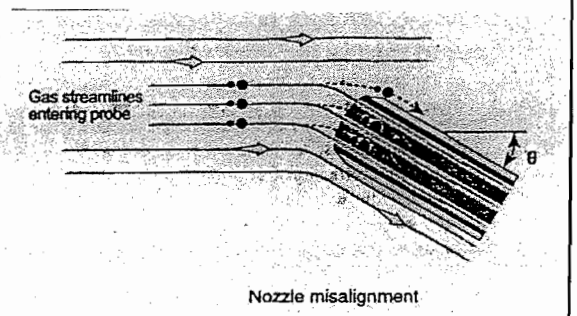
Yaw Angle

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





Nozzle Misalignment Due to Cyclonic Flow



Known Facts When Sampling in Non-Parallel Flow

- Measured particulate concentration will be bias low (less than true value); non-parallel flow does not affect measured gaseous concentration
- Measured stack gas volumetric flow rate will be biased high (greater than true value)

Historical Approaches to Sampling Under Cyclonic Flow

- Blind Man's Approach
- Alignment Approach
- Compensation Approach
- Source Modification Approach

Blind's Man's Approach

- Testing is performed in the normal manner and the angular flow variations and biases are ignored
- Results produce particulate concentration low (bias low)
- Volumetric flow rate is biased high
- Mass emission rate bias cannot be determined

Alignment Approach

- Nozzle is pointed into direction of flow in an effort to compensate for angular misalignment; angle is recorded at each point
- Sample time at each point is compensated for mathematically by cosine of misalignment angle

Alignment Approach

- Mathematical compensation is made on flow readings using velocity pressure and alignment angle

Alignment Approach

- Sampling time at point adjusted according to misalignment angle

t' = t(cos angle)

t' = 2(cos 10 degrees) = 1.97 min.

t' = 2(cos 45 degrees) = 1.41 min.

Alignment Approach

- Results
  - Testing is very difficult and time consuming
  - Particulate concentration contains less bias except
    - Nozzle is not corrected for the angular misalignment
    - Particles do not follow flow pattern

Alignment Approach

- Results
  - Flow rate will be more accurate
  - Mass emission rate may contain less bias

Compensation Approach

- Testing is performed in normal manner with exception that a larger nozzle is used to correct for misalignment error and higher than true flow rate

Compensation Approach

- Two errors must be compensated for
  - Misalignment of particulate approaching nozzle
    - Reduced effective nozzle opening

Compensation Approach

- $n' = n_s/(\cos \text{angle})$
  - 10 degree misalignment and 0.29 in. = 0.294
  - 45 degree misalignment and 0.29 in. = 0.410

Compensation Approach

- Results
  - Particulate concentration is less biased
  - Volumetric flow rate is biased high
  - Mass emission rate is biased high

Compensation Approach Procedure

- Determine ideal nozzle diameter in normal manner with velocity traverse
- Record all misalignment angles during velocity traverse
- Divide ideal nozzle size by cosine of average angle of misalignment

Compensation Approach Procedure

- Select nozzle that is closest to this diameter for use
- Multiply actual nozzle diameter by cosine of average angle of misalignment ($n' = n_s(\cos \text{angle})$)

Historical Approaches

- Source Modifications
  - Place a flow straightening device in stack to interrupt cyclonic flow
  - Test in normal manner on parallel flow
  - Particulate concentration should be accurate
  - Flow rate should be more accurate

Recommended Particlate Emissions Sampling in Cyclonic Flow (January 2003)

- #1: Find Another Sampling Location
- #2: Install Flow Straightening Vanes Upstream Sampling Location

Recommended Particlate Emissions Sampling in Cyclonic Flow (January 2003)

- #3: Apply a Modified Sampling Procedure
  - Alignment Method
  - Time-weighted Alignment Method

Recommended Particlate Emissions Sampling in Cyclonic Flow
(January 2003)

- #4: Use Method 2F (Recommended)

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)

Federal Register Entry

- *"On May 5, 1999 the EPA Administrator signed a direct final rulemaking authorizing Federal Register publication of three test methods for velocity and volumetric flow rate determination in stacks or ducts. "*

WHY?

- Under 40CFR75 and Title IV of the Clean Air Act Amendments of 1990, electric utility units are required to install and operate continuous emission monitoring systems (CEMS)

WHY?

- The Acid Rain Program requires reporting of emissions in mass emission rate units
(i.e., lbs SO_2/Hour)

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)

Why Not Use FRM 2?

- In presence of non-axial flow, current Federal Reference Method 2 may over-estimate volumetric flow at a source
- Federal Reference Method 2 equipment does not allow measurements for yaw or pitch angle determination

How Does FRM 2F Work?

- Method 2F derives axial velocity of non-axial flow by measuring
  - Yaw component of flow through yaw angle determination procedure
  - Pitch component of flow through use of pitch calibration curves
  - Impact velocity through use of velocity pressure calibration curves

Where Do You Use FRM 2F?

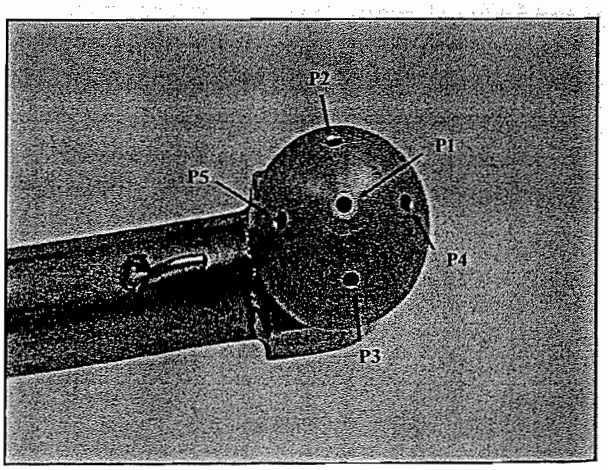
- Sites where yaw and/or pitch components of flow are present
  - Where you have directional velocity (non-axial flow) of flow
  - With directional velocity, you have yaw and pitch components which, when using FRM 2 pitot tube, gives a combined over estimation (+ bias) to the source v_s and Q_s

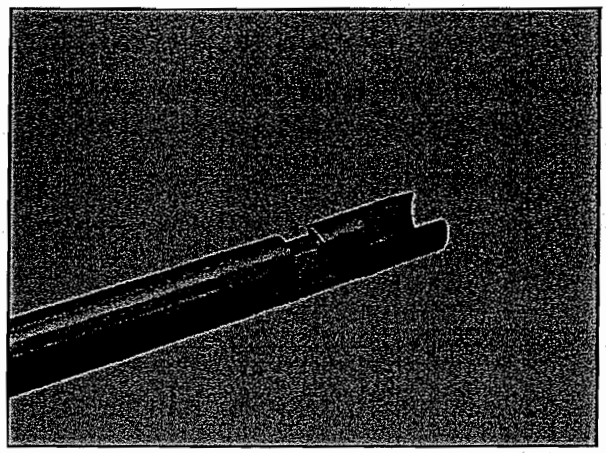
Method 2F Equipment

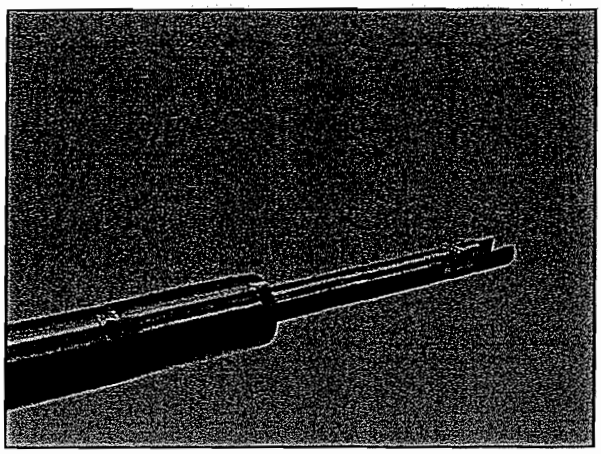
- 3D Probes
  - Spherical
    - Easy Leak Check
    - More Sensitive than Type S
    - Less Costly Than Velocity CEMS
  - Prism (DAT)

3-D Probe Measurements

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







3-D Measurements

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

3-D Equipment

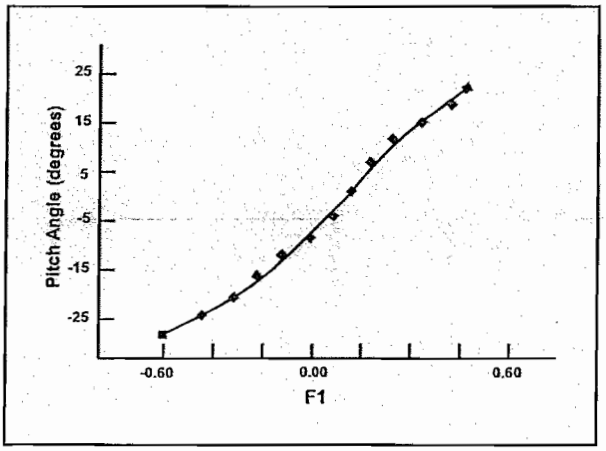
- Probe (Spherical or Prism)
- Console containing magnehlics
  - P1-P2 (Velocity)
  - P2-P3 (Yaw Angle to null)
  - P4-P5 (Pitch Angle)
- 3-D probe specific manufacturer's F1 and F2 calibration curves

Velocity and Pitch Calibration is Performed by Manufacturer at Qualified Wind Tunnel

- Use pressure measurements to derive two calibration curves
  - F1 (P4-P5/P1-P2) vs. pitch angle curve
    - Used to determine the pitch angle of flow

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)



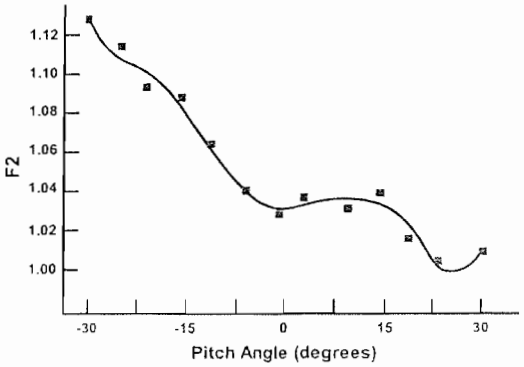
Velocity and Pitch Calibration is Performed by Manufacturer at Qualified Wind Tunnel

- F2 (velocity coefficient) vs. pitch angle
  - Used to determine velocity calibration coefficient at each pitch angle

Velocity Coefficient Curve (F2 Calibration Curve)

$$F2 = C_{p(std)}\sqrt{\frac{\Delta p_{(std)}}{P1 - P2}}$$

- Manufacturer Plots F2 vs. Pitch Angle at Qualified Wind Tunnel at Two Flow Rates (60 and 90 ft/sec)



Resultant Axial Velocity Based Upon Manufacturer's F1 And F2 Curves

$$V_{a(i)} = K_p F2_{(i)}\sqrt{\frac{(P1 - P2)(T_{s(i)})}{P_s M_s}}(CosY)(CosP)$$

Inspector's Role in 3-D Probe Application

- Verify probe geometry (FRM 2F/Scribe Line)
- Obtain manufacturer's F1 and F2 calibration curves from test team and verify data
  - F1: Pitch Angle Curve
  - F2: Velocity Coefficient Curve

Inspector's Role in 3-D Probe Application

- Inspect probe for dents/nicks and recalibrate if needed
- Check probe's horizontal straightness
- Verify that team has zero and calibrated pressure devices

Inspector's Role in 3-D Probe Application

- Verify leak check of 3-D probe system
- Observe and verify marking of traverse point positions on 3-D probe system

Inspector's Role in 3-D Probe Application

- Observe insertion of probe into port and verify sealing of port
- Verify probe sitting at 1st traverse point, as defined by FRM 1
- Wait response time

Inspector's Role in 3-D Probe Application

- Observe measurement of velocity
  - Yaw angle to null; Record yaw angle
  - Observe impact pressure (P1-P2)
  - Observe pitch angle pressure (P4-P5)
  - Insure procedure is repeated at each determined traverse point and record on field test data sheet (FTDS)

Inspector's Role in 3-D Probe Application

- Observe calculation of site barometric pressure (corrected for altitude), molecular weight of stack gas (FRM 3), moisture of stack gas (FRM 4) and static pressure measurement
- Verify that plugging of 3-D probe doesn't occur; use positive pressure to clear probe periodically

Inspector's Role in 3-D Probe Application

- Verify stack testing team is using proper manufacturer's generated pitch angle curve (F1) and velocity coefficient curve (F2) for that specific 3-D probe system

Inspector's Role in 3-D Probe Application

- Observe calculation of resultant axial velocity
  - Obtain P4-P5 and P1-P2 measurements for each traverse point
  - Calculate F1 (P4-P5/P1-P2) for each traverse point
  - Locate F1 value on F1 pitch angle curve, move up to intercept, then across to record pitch angle for each traverse point

Inspector's Role in 3-D Probe Application

- Observe calculation of resultant axial velocity (Con't)
  - Locate the recorded pitch angle on the F2 velocity coefficient curve, move up to intercept, then across to record F2 for each traverse point

Calculate Resultant Axial Velocity For Each Traverse Points

$$V_{a(i)} = K_p F2_{(i)} \sqrt{\frac{(P1-P2)(T_{s(i)})}{P_s M_s}} (CosY)(CosP)$$

Calculate Resultant Axial For Each Traverse Point (FRM 1)

- R_i = arc cosine [(cosine Y_i)(cosine P_i)

(If resultant average of R_i for all traverse points > 20 degrees, then you have cyclonic flow across the stack and at this sampling location

AND

If the calculated standard deviation of the R_i values > 10 degrees, then can not sample at this location.)

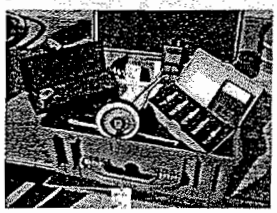
In Summary Method 2F

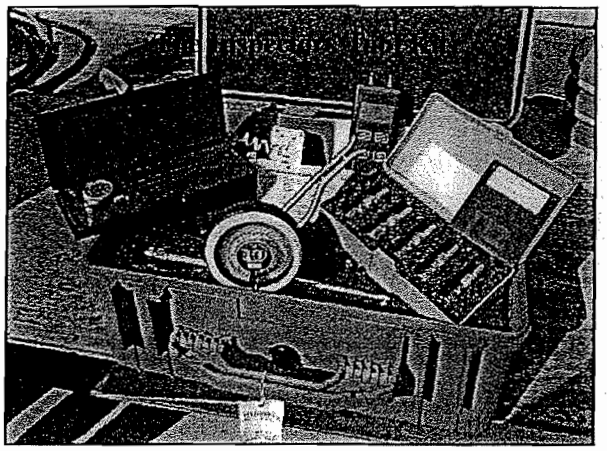
- Derives axial velocity by measuring
  - Yaw component of flow through yaw angle determination procedure
  - Pitch component of flow through use of pitch calibration curves
  - Impact velocity through use of velocity pressure calibration curves

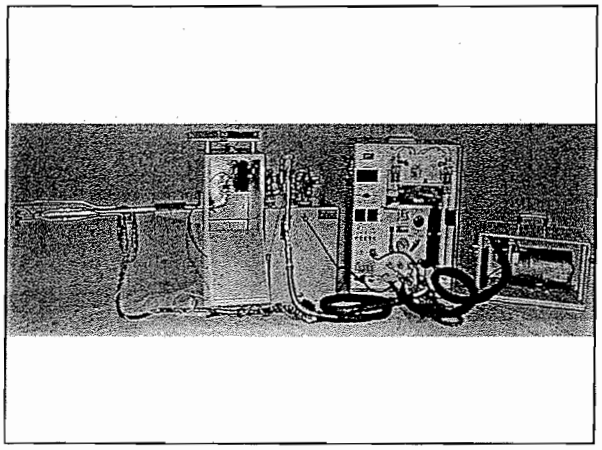
In Summary Method 2F

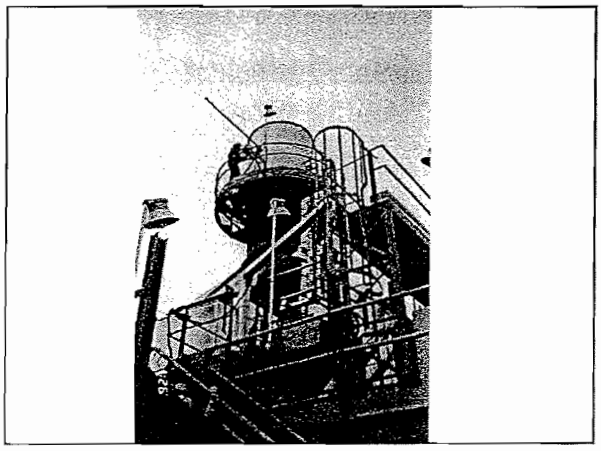
- Measurements provide accurate determination of axial velocity at non-parallel flow situations

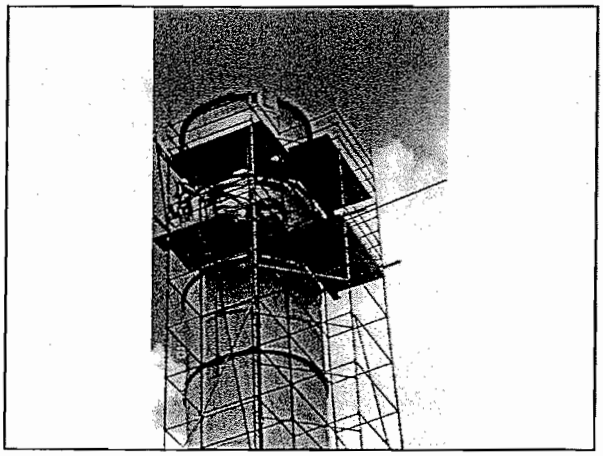
U.S. EPA APTI
Compliance Test and Source Test Observation
Agency Inspector's Tool Kit

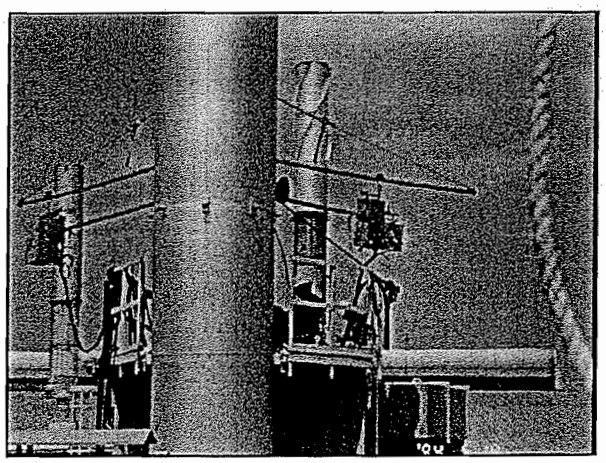


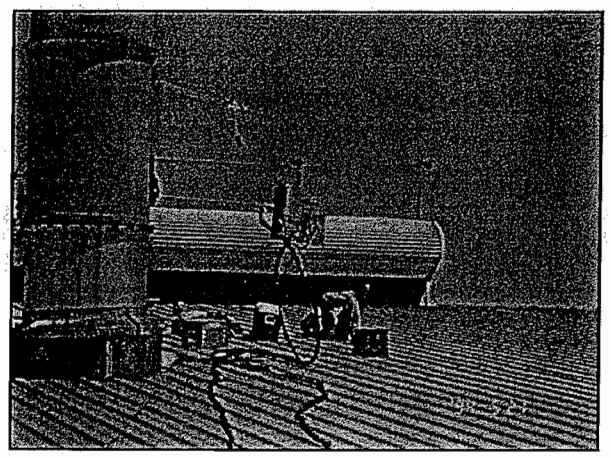










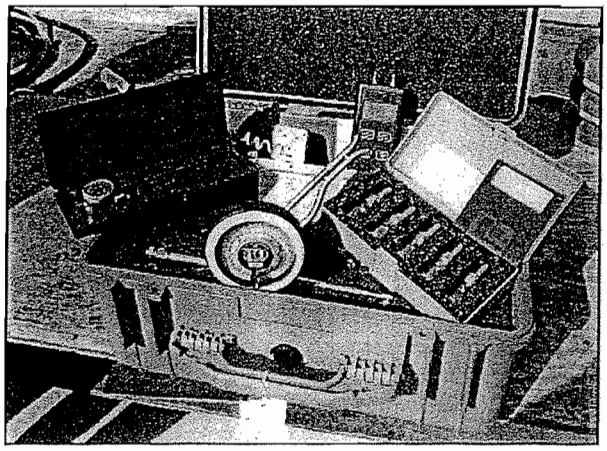


Required FRM 5 Calibrations

- Nozzle
- Nozzle and pitot tube orientation
- Thermocouples (stack, probe, filter, impinger, dry gas meter)
- Pitot tube
- Dry gas meter γ and $\Delta H@$
- Probe and filter box heater settings

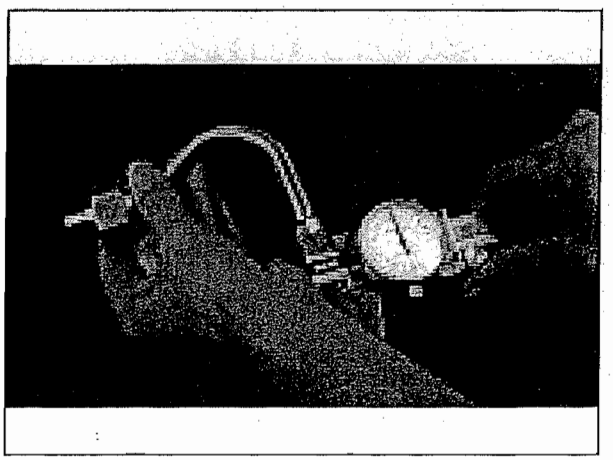
FRM 5 Meter Console Required Calibrations

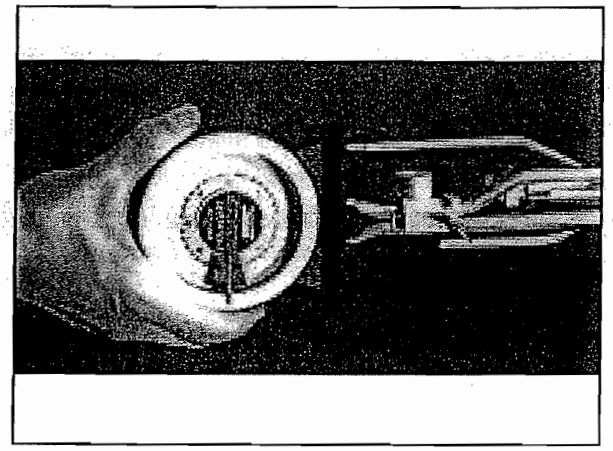
- Leak check both positive and negative (< 0.04 cfm)
- Dry gas meter gamma value of 0.98-1.02
- Therometers calibrated to $\pm$ 2°F
- Orifice meter "$\Delta H_@$" documented and verified



Inspector's Tool Kit

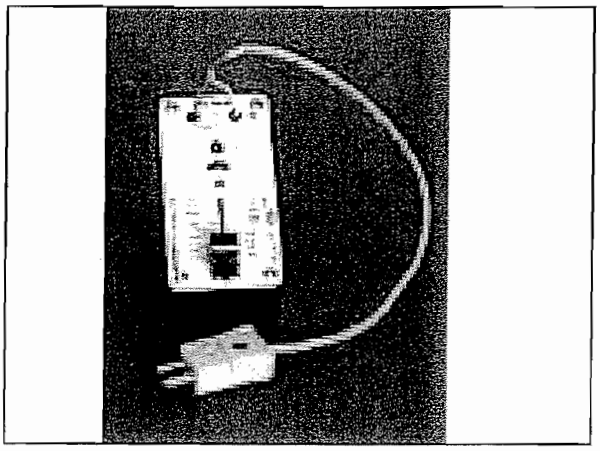
- Dial Caliper- Used for measuring nozzle diameter and orientation of pitot tube/nozzle/thermocouple
- Level Indicator- Used for verifying proper construction dimensions and spacing for Type S pitot tube and used in yaw/pitch angle for cyclonic flow determination

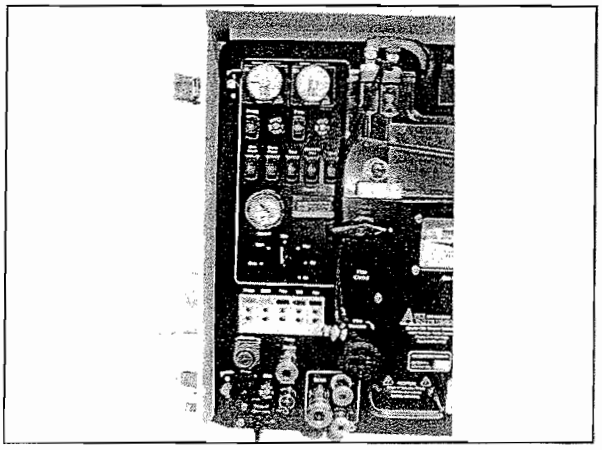


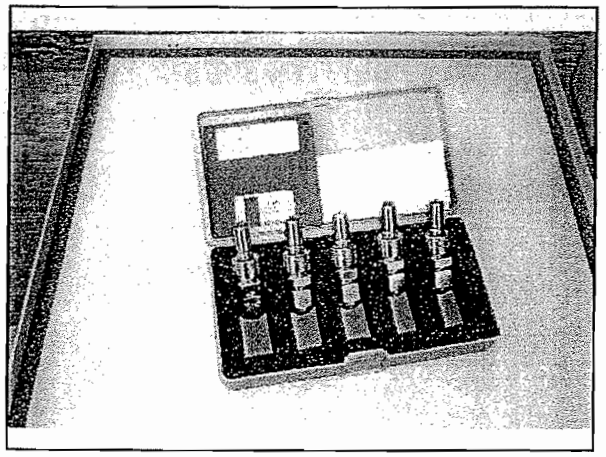


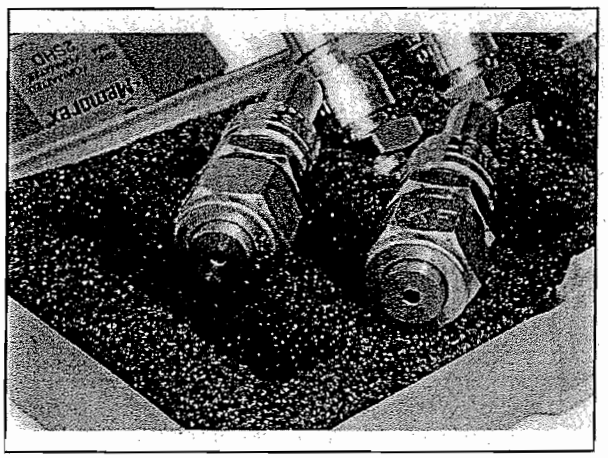
Tool Kit

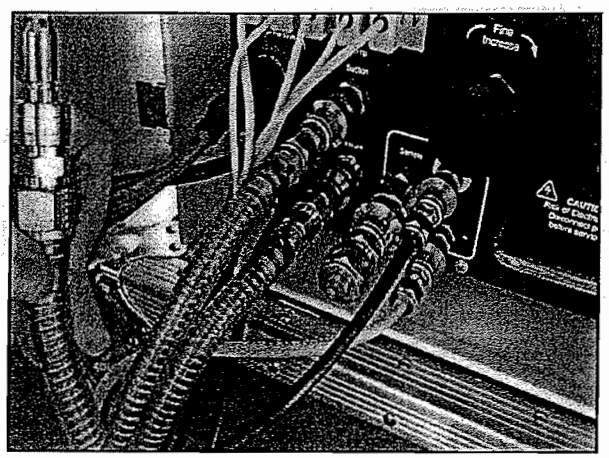
- Thermocouple Simulator Source- Used to verify accuracy of temperature displays and controllers
- Calibration Orifice Set- Used for calibration and auditing of $\Delta H_{@}$ and γ of dry gas meter





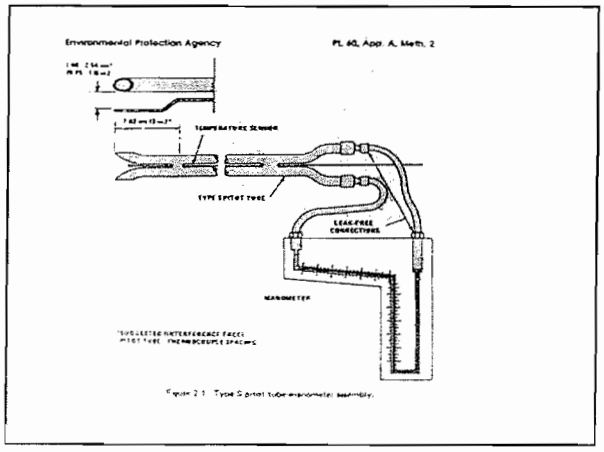






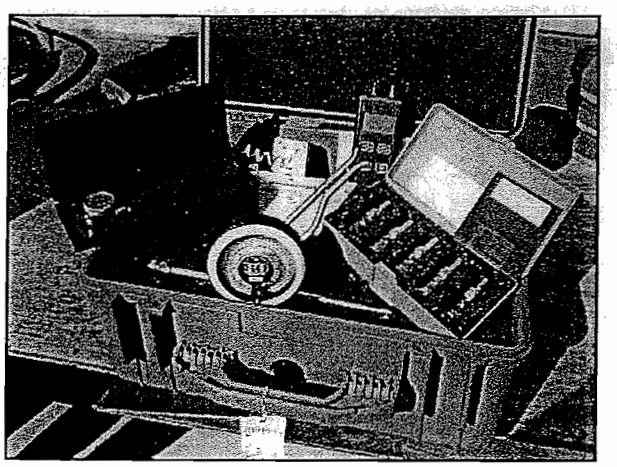
Tool Kit

- IsoCal Software- Used for integrated isokinetic source sampling calculations
- Pocket Barometer- Used to determine atmospheric pressure within 0.02 inches of mercury
- Modular Pitot Tube- Used to measure stack gas velocity, static pressure and cyclonic flow

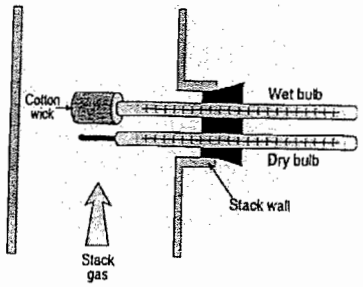


Tool Kit

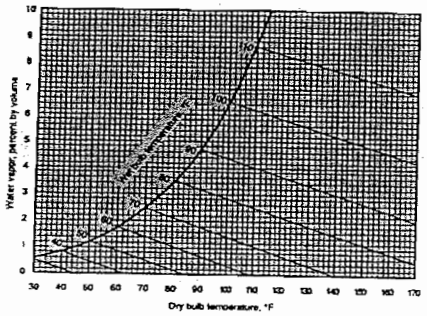
- Hand-held Manometer- Used in conjunction with modular pitot tube
- Hand-held Digital Thermometer- Used to measure stack temperature and filter box temperature
- Bull's Eye Level- Used for indicating level of pitot tube during evaluation of level indicator



Wet Bulb/Dry Bulb



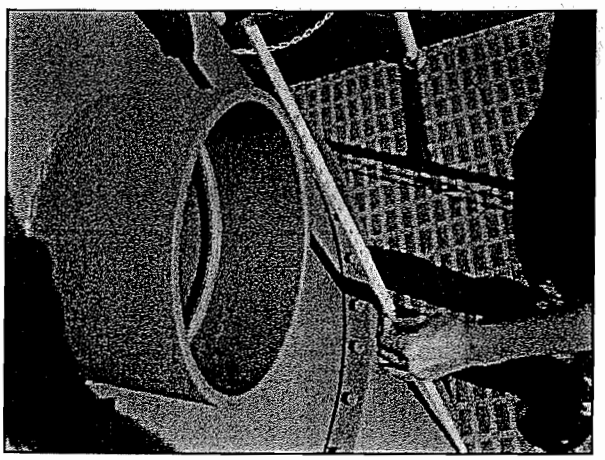
Psychrometric Chart



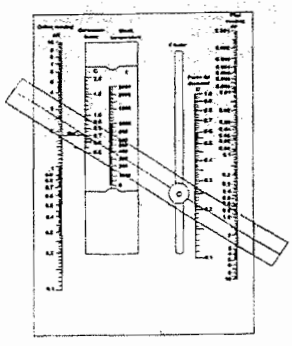
Psychrometric chart expressing volume of water vapor by percent

Tool Kit

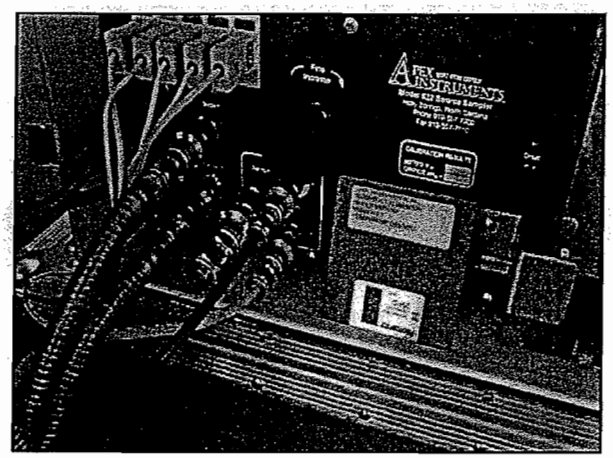
- Tape Measure- Used to document stack geometry and sampling port location. Also used to locate sampling points on stack gas probe.
- Agency Checklist- Used to assist Agency inspectors in evaluating stack test methods
- Field Nomographs- Used to estimate stack gas moisture, excess air, velocity and volumetric flow rate, and concentration



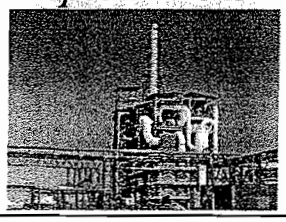
FRM 5 Nomograph

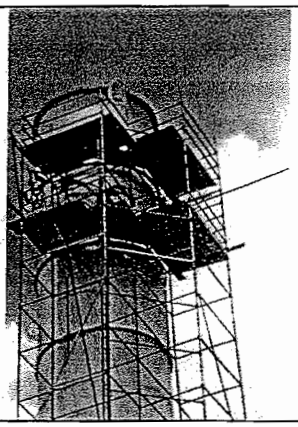


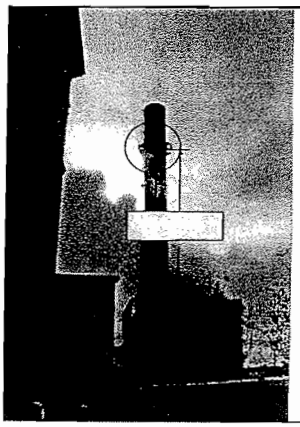
Nomograph

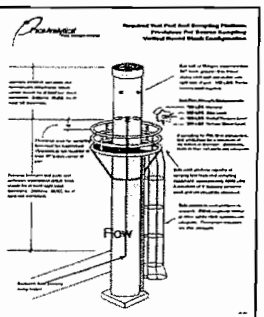

APEX INSTRUMENTS

U.S. EPA APTI
Compliance Test and Source Test Observation
Sampling and Port Locations and Specifications





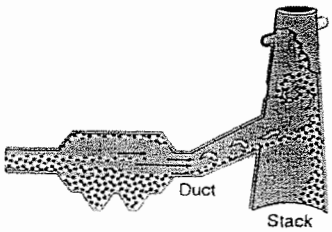




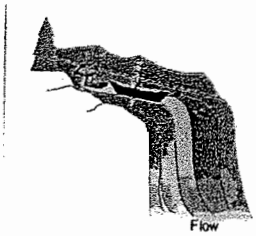
Common Stack – Leakage?

District Energy

FRM 1 Sampling Site Locations

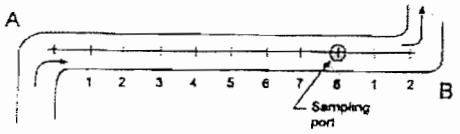


FRM 1 Siting Criteria

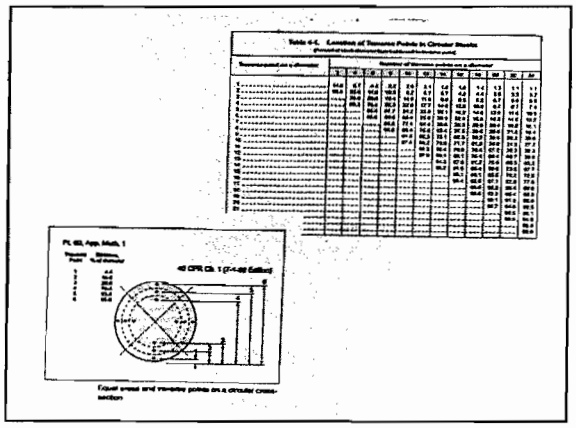


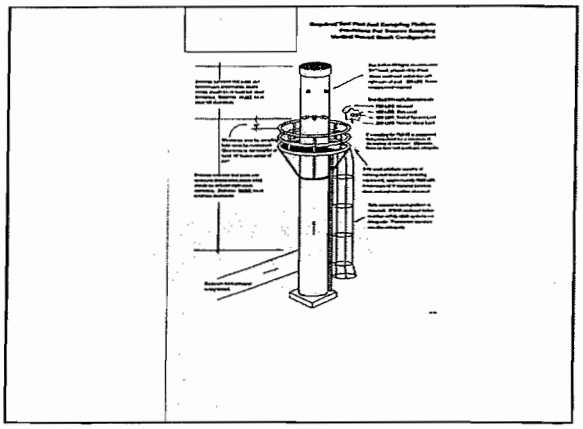
- 8 stack diameters downstream and 2 stack diameters upstream of a flow disturbance

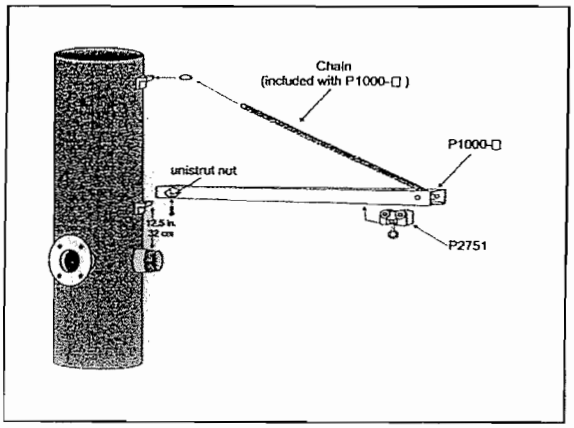
Ideal Siting Criteria

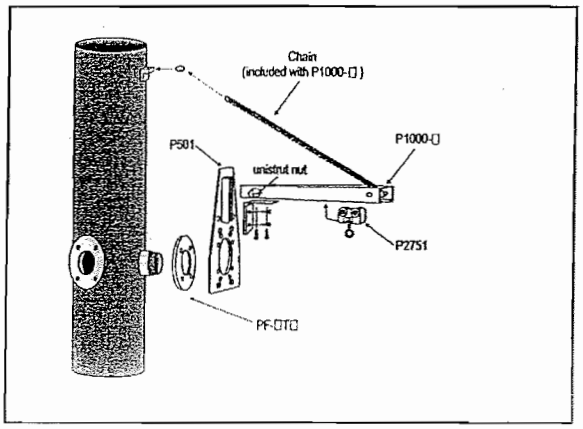


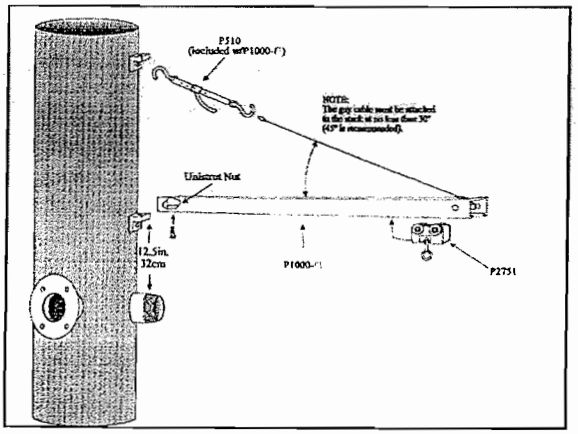
Port is downstream of A
Port is upstream of B

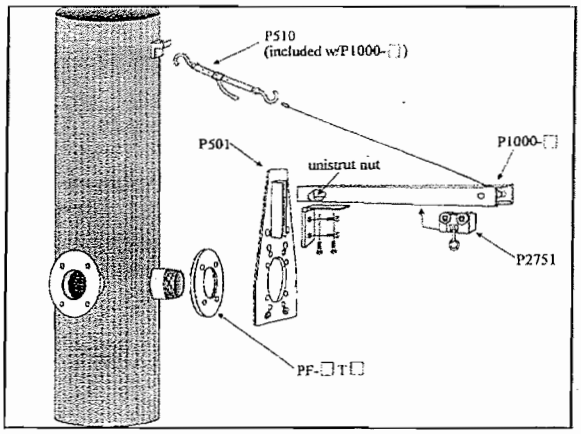


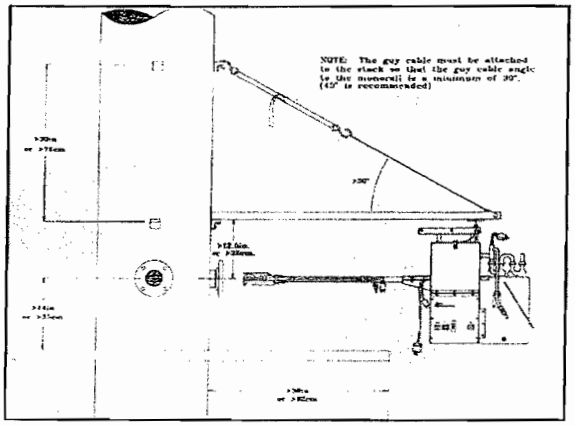


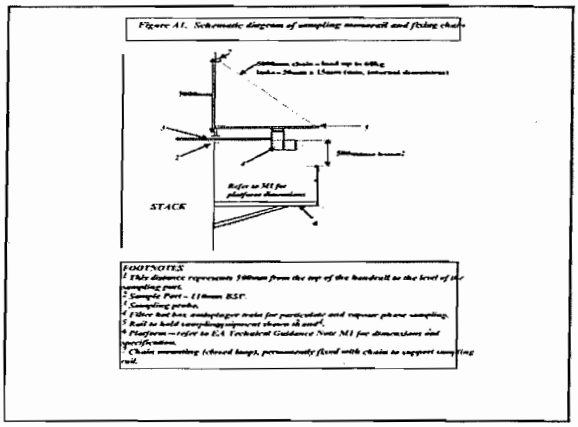

Chain
(included with P1000-□)
P1000-□
unistrut nut
12.5 in.
32 cm
P2751

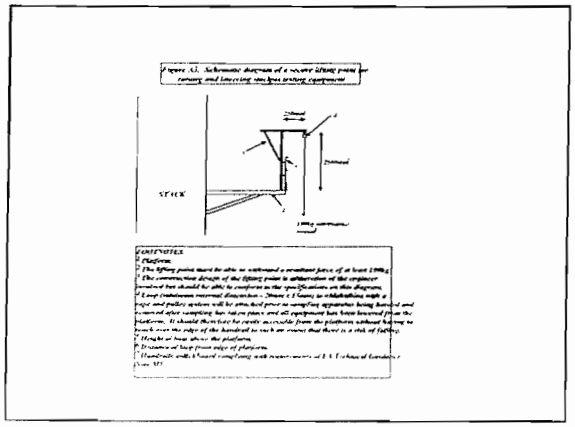

Chain
(included with P1000-□)
P501
P1000-□
unistrut nut
P2751
PF-□T□

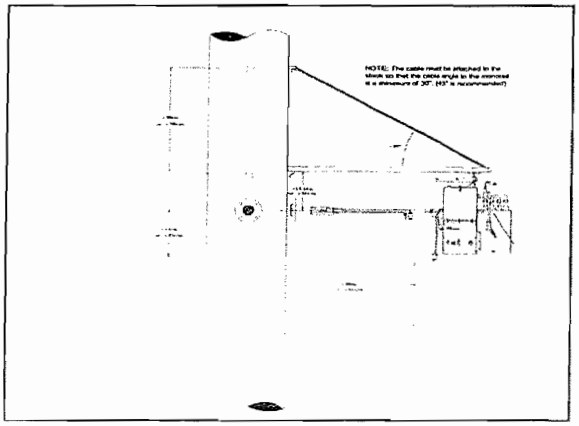

P510
(included w/P1000-□)
Unistrut Nut
12.5in.
32cm
P2751

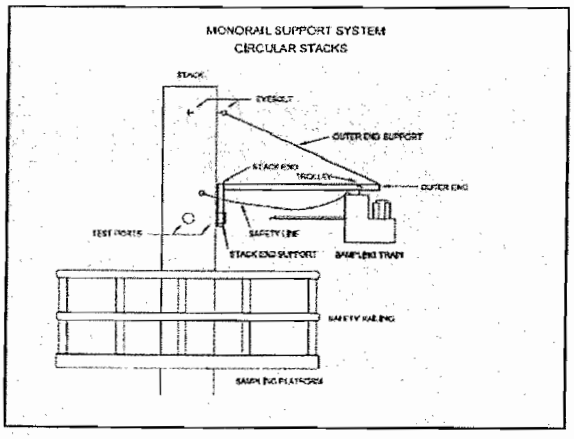

P510
(included w/P1000-□)
P501
P1000-□
unistrut nut
P2751
PF-□T□

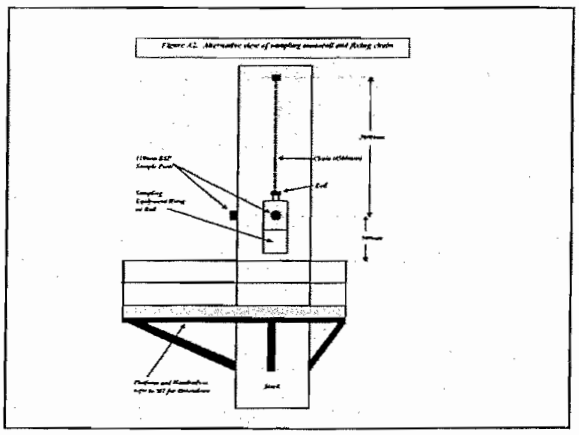

NOTE: The guy cable must be attached to the stack so that the guy cable angle to the monorail is a minimum of 30°. (45° is recommended)

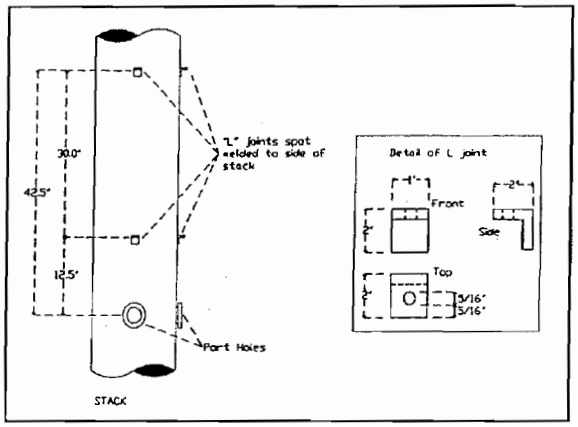

STACK

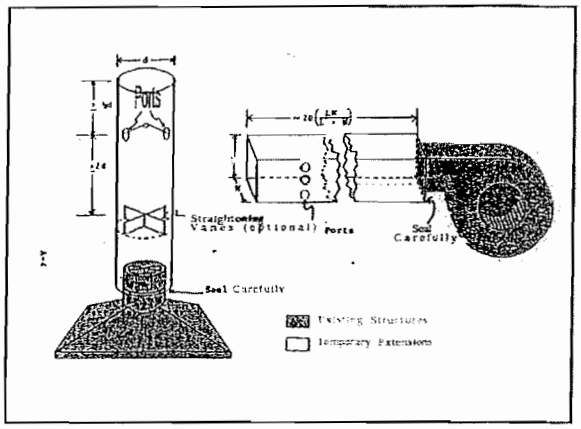

STACK

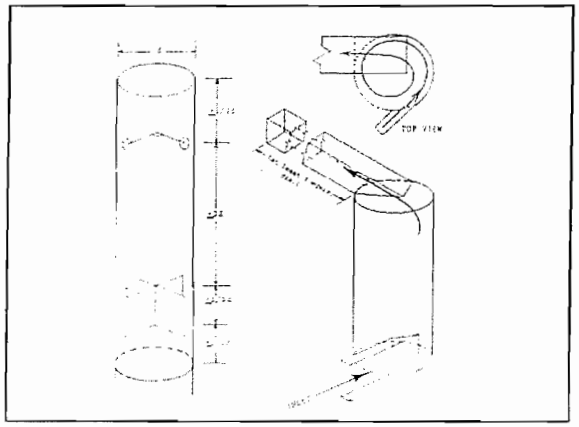


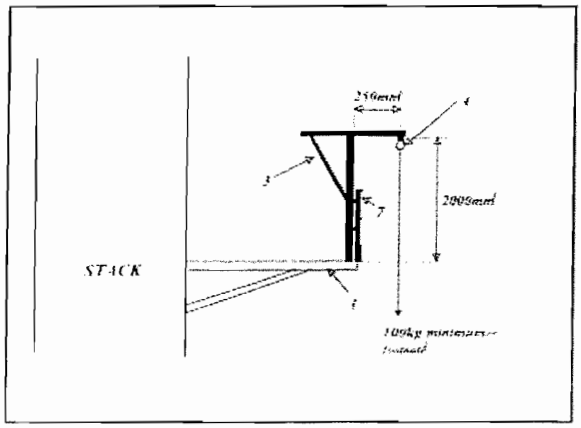

MONORAIL SUPPORT SYSTEM
CIRCULAR STACKS
STACK
EYEBOLT
OUTER END SUPPORT
STACK END TROLLEY
OUTER END
TEST PORTS
SAFETY LINE
STACK END SUPPORT
SAMPLING TRAIN
SAFETY RAILING
SAMPLING PLATFORM

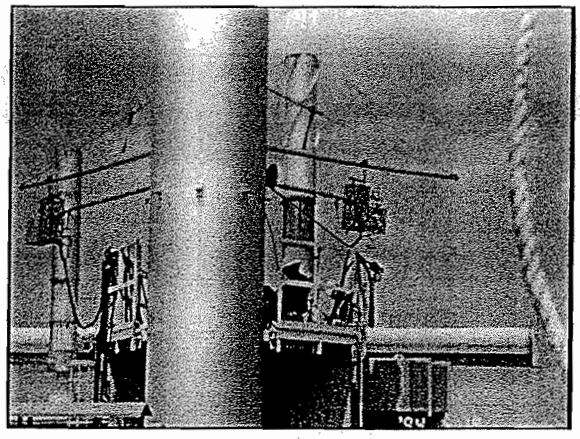


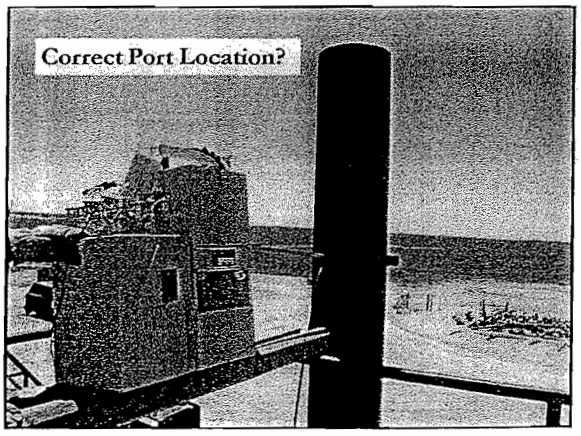

"L" Joints spot welded to side of stack
Detail of L joint
Front
Side
Top
3/16"
3/16"
Port Holes
STACK

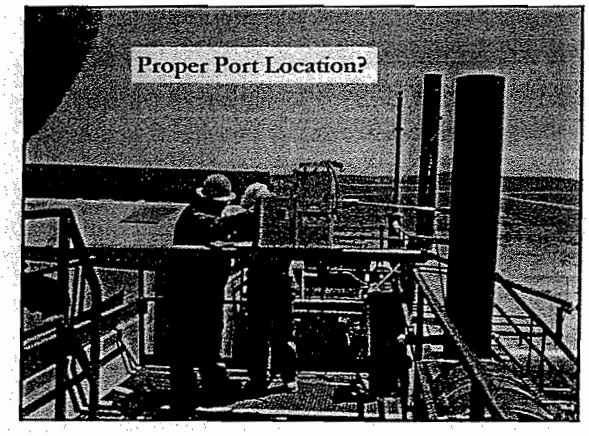

PORTS
Straightening Vanes (optional)
Ports
Seal Carefully
Seal Carefully
Existing Structures
Temporary Extensions




STACK




Correct Port Location?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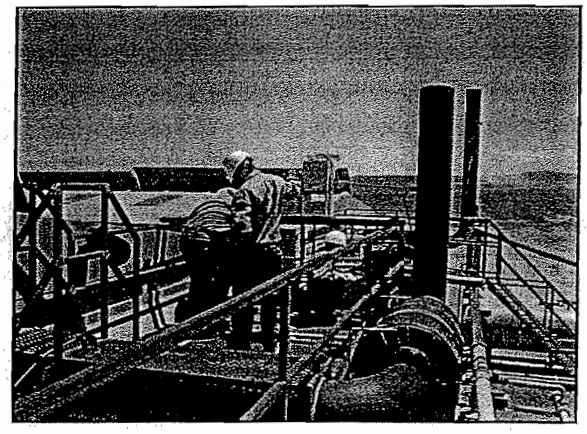
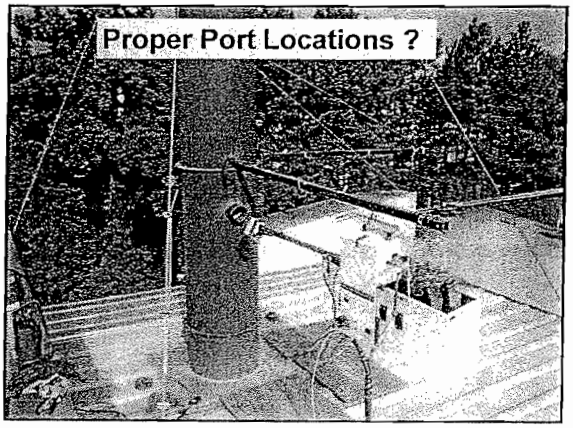
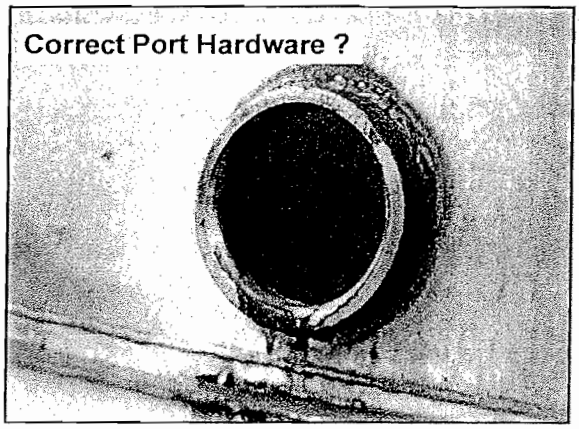
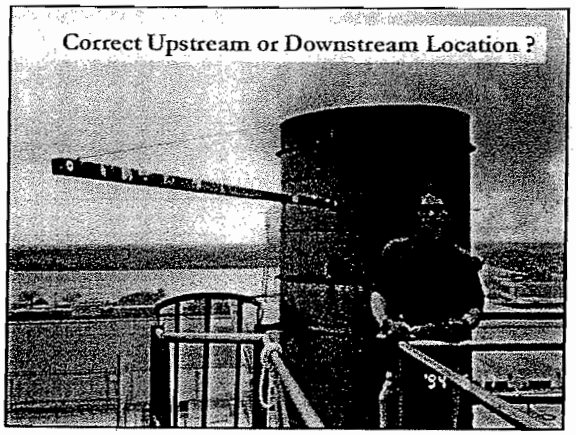
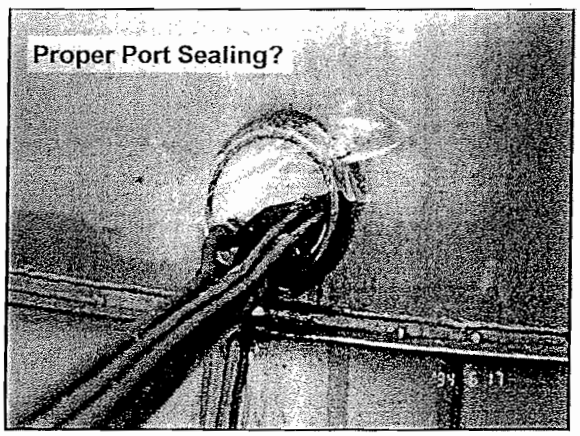
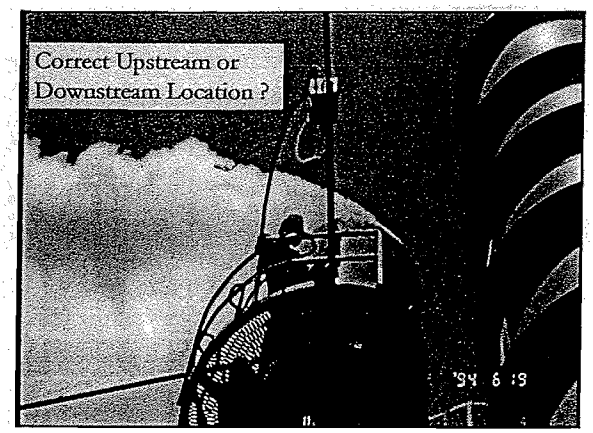


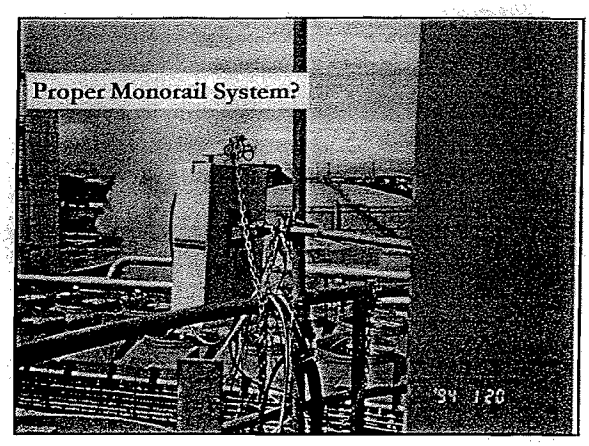

Proper Port Locations ?


Correct Port Hardware ?

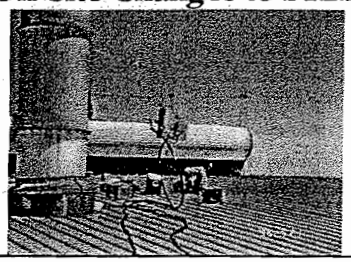

Correct Upstream or Downstream Location ?

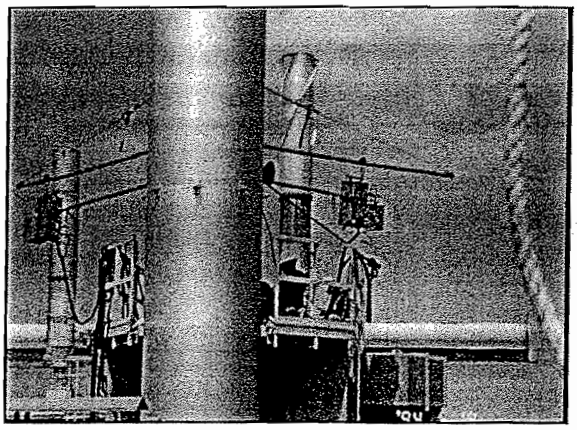

Proper Port Sealing?

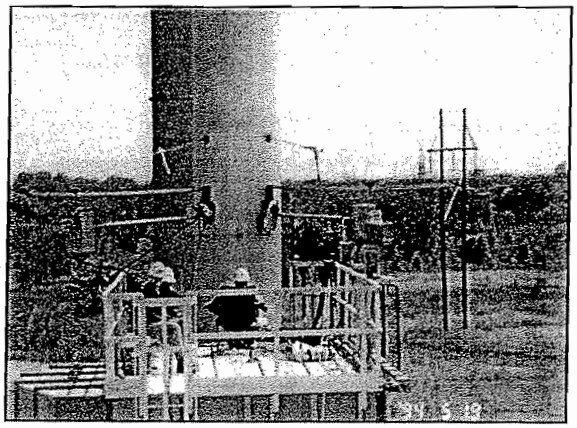

Correct Upstream or
Downstream Location ?

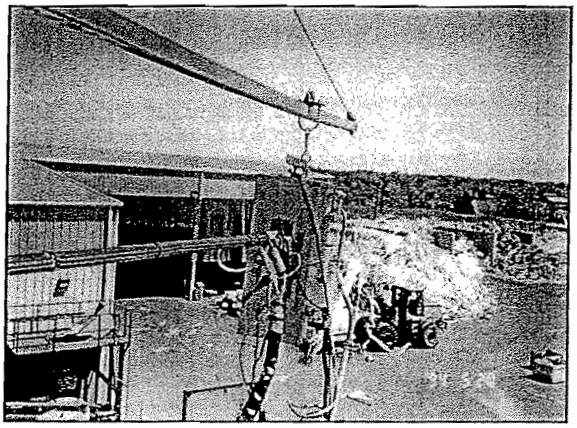

Proper Monorail System?

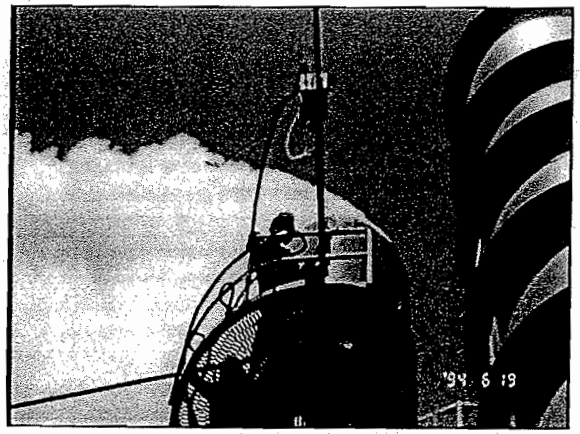
U.S. EPA APTI
Compliance Test and Source Test Observation
On-Site Changes to FRMs











On-site Request for Changes to FRMs

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

Bias Concept

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

Changes to On-site FRMs

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

Example of Minor Changes

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

Changes to On-site FRMs

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

Major Changes

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

Major Changes

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

Requesting Party Responsibility

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

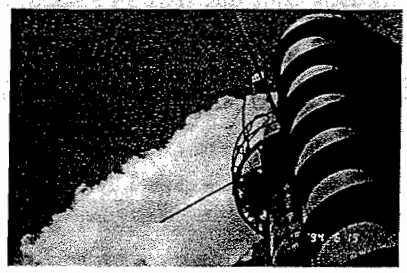
Example of Guidelines

(See Resource CD, Session 6)

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

Compliance Test and Source Test Observation

Stack Testing Special Topics:



Compliance Test and Source Test Observation

Stack Testing Special Topics:

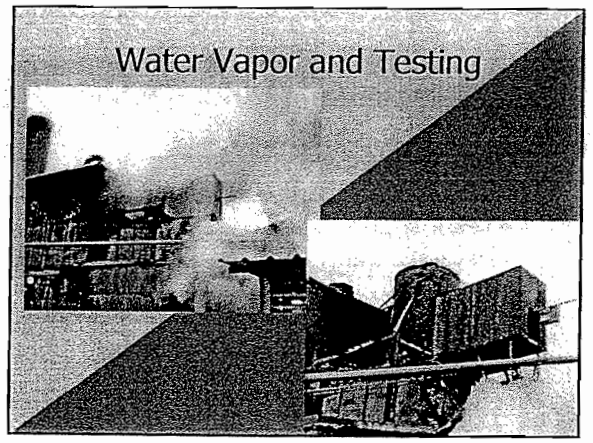
- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

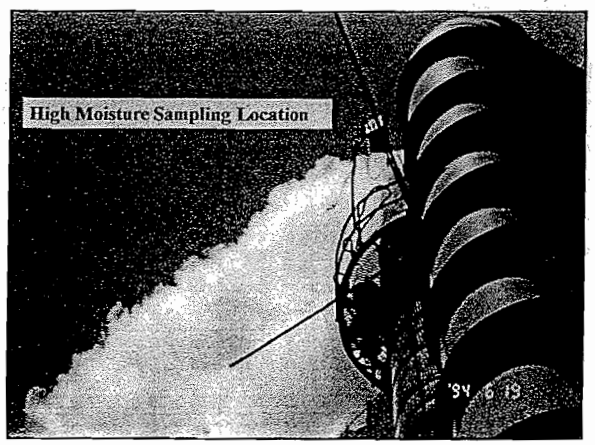
Typical Sources With High Moisture Content In Stack

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

The Problem

- High moisture in stack gas causes pitot tube to plug, thus poor Δp readings (i.e., velocity measurements)
- Problems with maintaining isokinetic sampling rate (i.e., $\Delta H = k\Delta p$)
- Water droplets on filter increasing pressure drop and effecting isokinetics
- Dilution of impinger solutions thus effecting collection efficiency of analytes
- Condensation in pitot tube sample lines





The Problem: FRM 5 Isokinetic Rate Equation

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

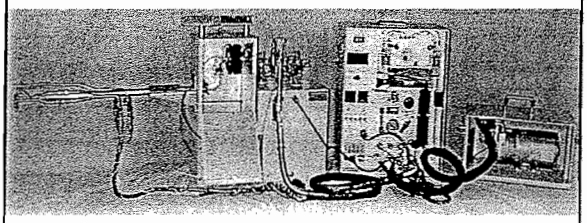
High Moisture Error

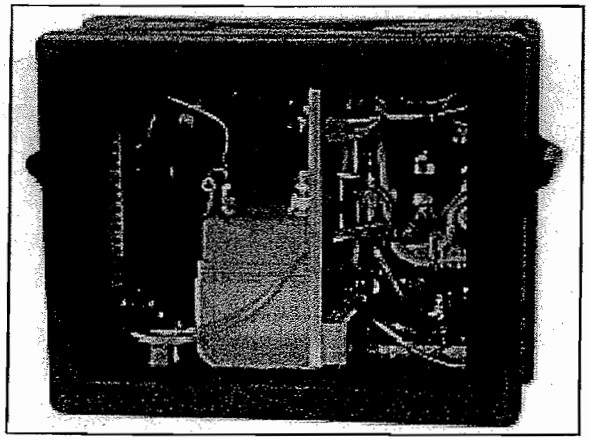
- With low moisture (i.e., <15 %), the error is rather small
- However, with high moisture (i.e., > 15 %, the error becomes small
- Typically, for every 1 % error in moisture determination reflects a 1 % error in isokinetics

Sampling Problems With High Moisture Stacks

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

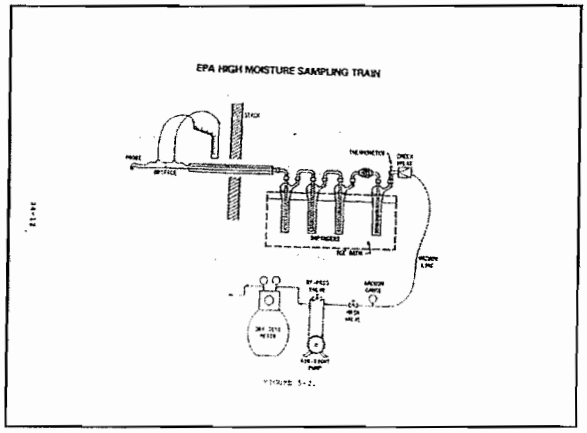
What Approaches Can Be Taken To Sample Under High Moisture Situations?





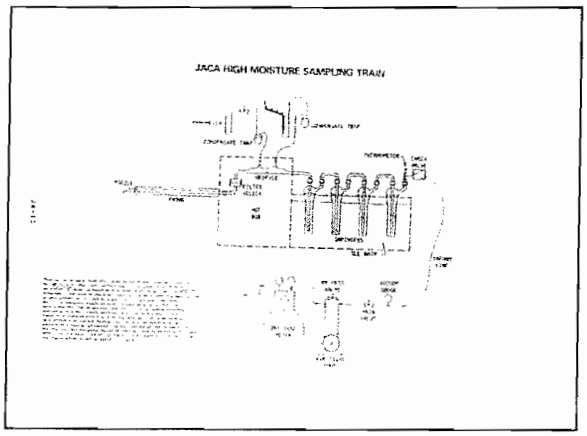
General Solution #1 (Placement of Orifice Meter In Stack)

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



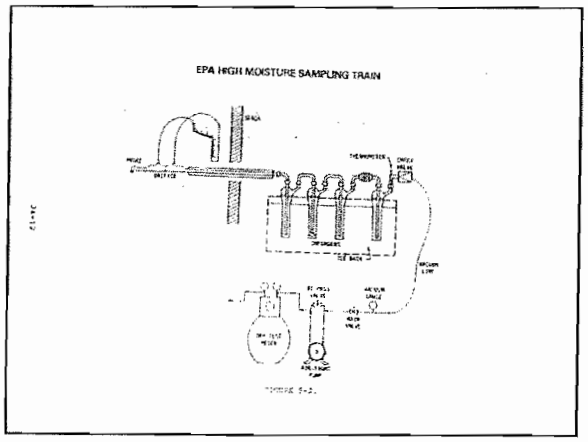
General Solution #2 (Placement of Orifice Meter In Heated Filter Box)

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



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

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



General Solution #4 (Consultant's Approach)

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

General Solution #5

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

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

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

Problems Common To All Three Approaches

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

General Solutions

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

Compliance Test and Source Test Observation

Stack Testing Special Topics:

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

Stack Testing At High Pressure Sources

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

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

- Port Leakage
- Pressure Measurement Difficulties
- Sample Losses

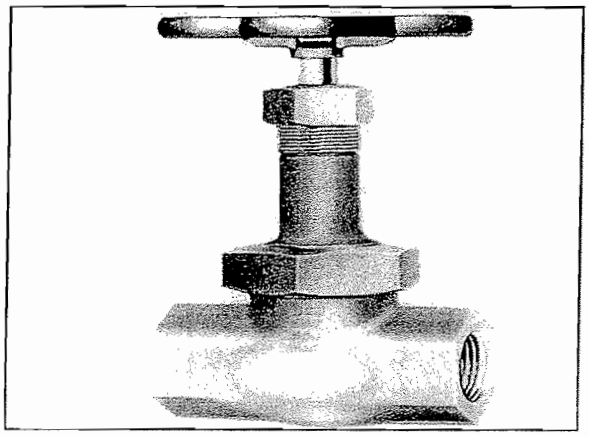
Port Leakage

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

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

Minimizing Port Leakage

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



Pressure Measurement Difficulties

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

Overcoming Pressure Measurement Difficulties

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

Sample Losses Can Occur

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

Sample Losses Can Occur

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

Preventing Sample Losses

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

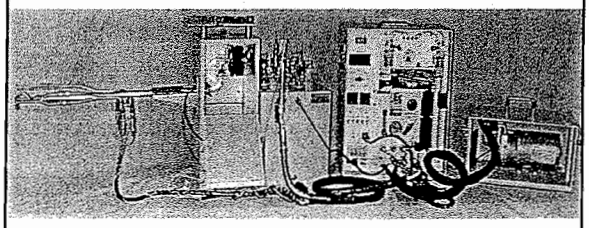
Preventing Sample Losses

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

Compliance Test and Source Test Observation

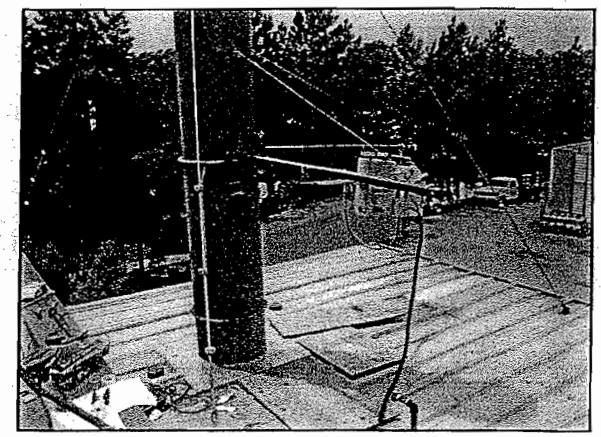
Stack Testing Special Topics:

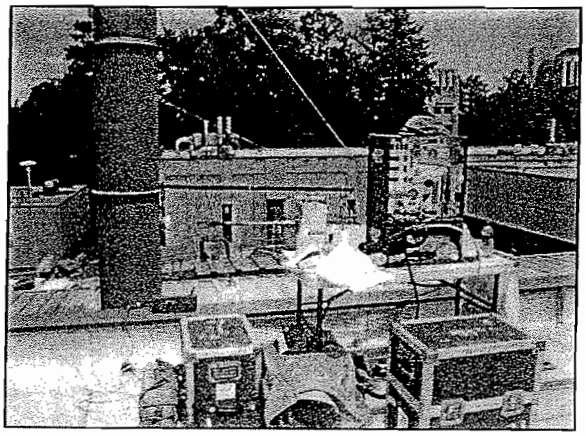
- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

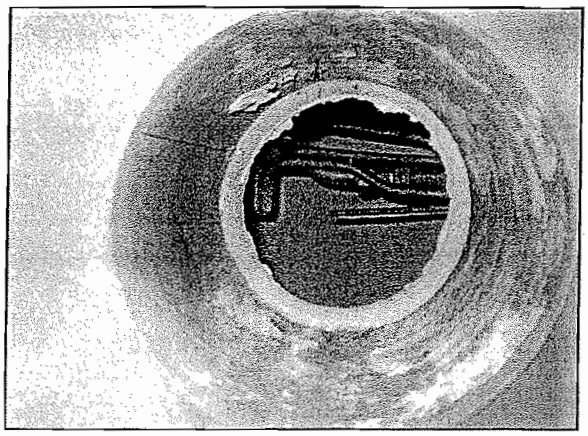


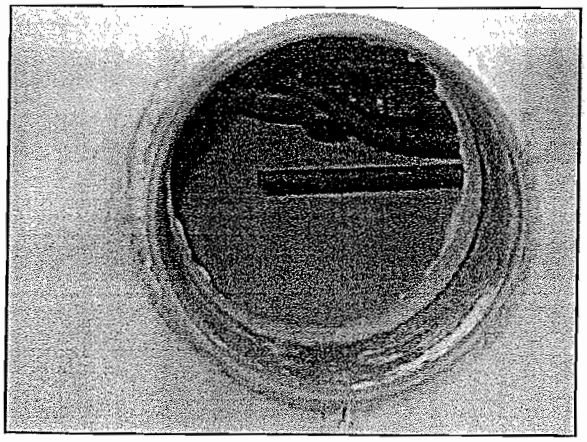
Typical Sources With High Temperature Stack

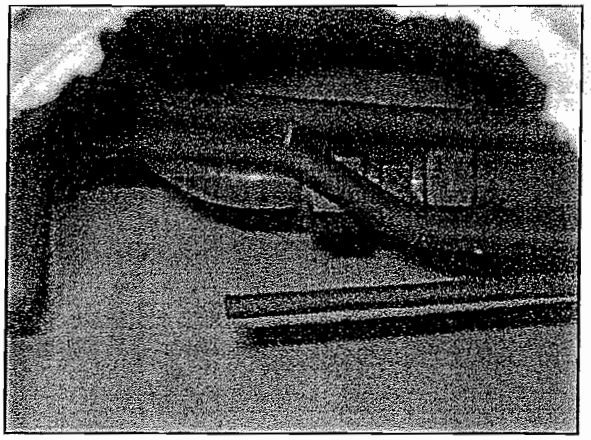
- Gas Turbines
- Municipal Incinerators
- Glass Furnaces
- Other Sources

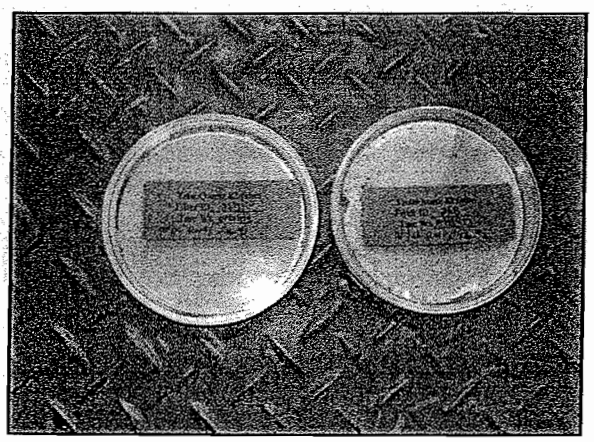


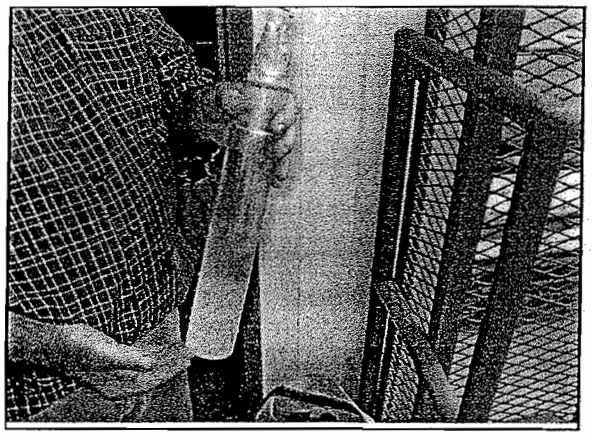


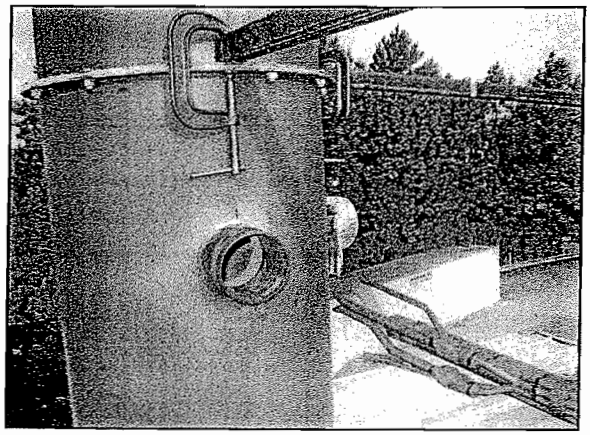


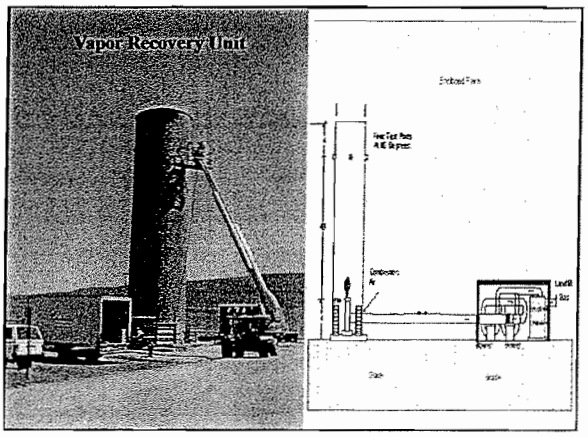


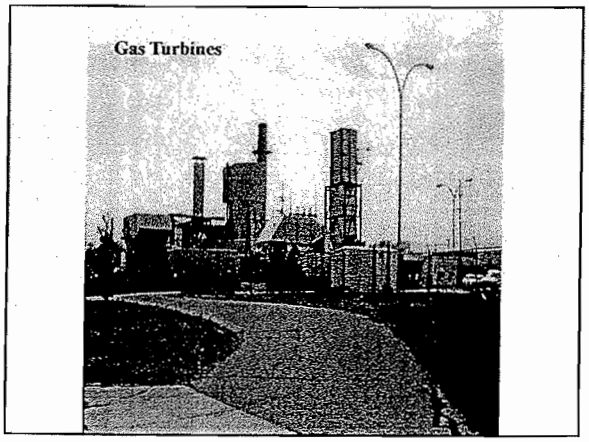


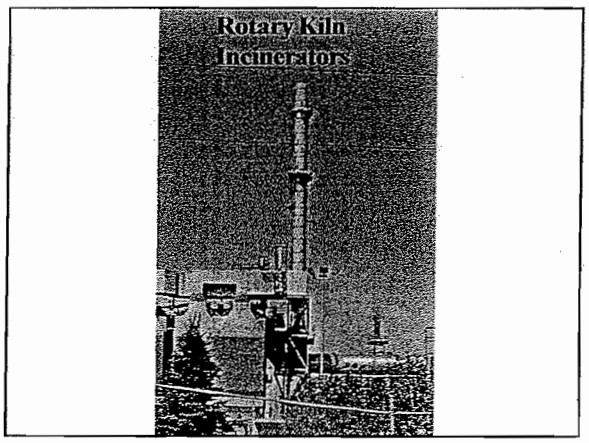


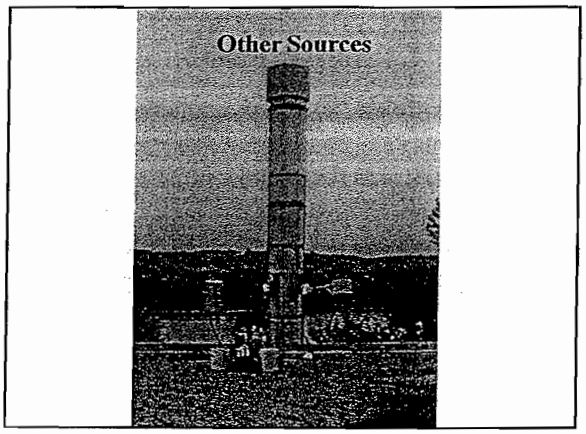





Vapor Recovery Unit


Gas Turbines


Rotary Kiln
Incinerators



The Problem

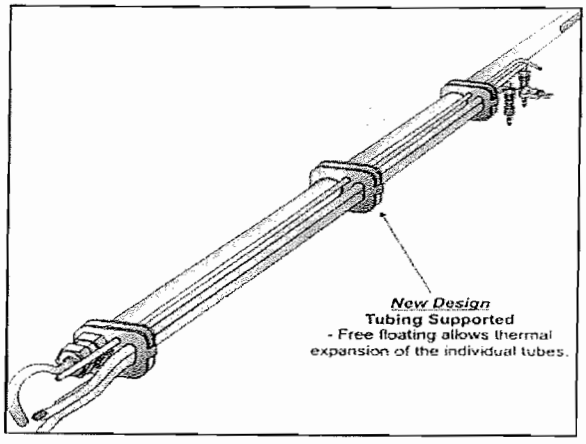
- **High stack temperatures causes problems with obtaining proper leak check of sampling system and safety problems**
- **Problems with achieving airtight seal between nozzle and probe liner**
- **Breakage of glass probe liner due to different coefficients of thermal expansion between probe liner and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

Stack Temperatures

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

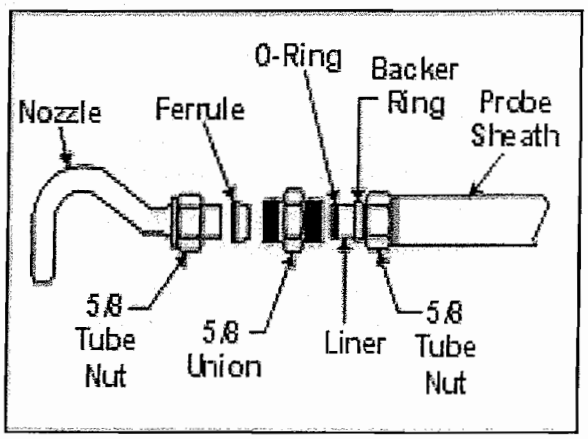
Maximum Temperature of Various Materials

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



Sampling Problems

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



Sampling Problems

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

Solution #1 (Construction of High Temperature Probes)

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

Solution #2 (Construction of High Temperature Probes)

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

Use of Probe Cooling Techniques (Advantages)

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

Use of Probe Cooling Techniques (Disadvantages)

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

Use of Quartz Probe (Advantages)

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

Use of Quartz Probe (Disadvantages)

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

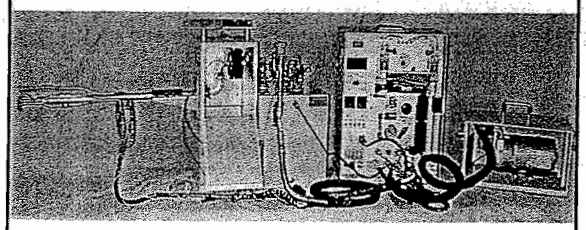
Miscellaneous Sampling Problems

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

Compliance Test and Source Test Observation

Stack Testing Special Topics:

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



Velocity Measurement

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

Federal Reference Method 2 Average Velocity Over Cross-Section

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

Average Stack Gas Dry Volumetric Flow Rate

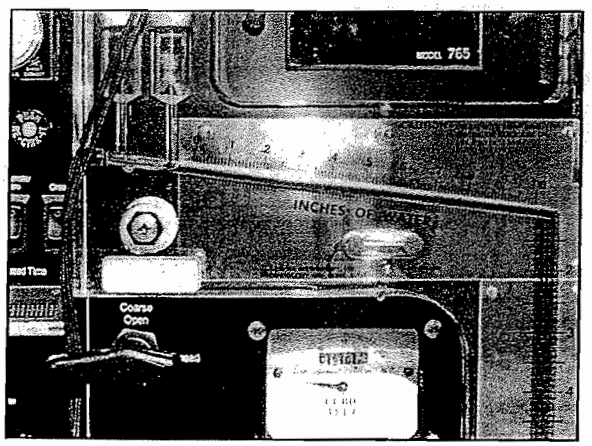
$$Q_{std} = 3600 \left(1 - B_{ws(avg)}\right) v_{s(avg)} A \frac{T_{std}}{T_{s(avg)}} \frac{P_s}{P_{std}}$$

The Problem

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

The Problem

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



Federal Reference Method 2 Guidelines

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

Federal Reference Method 2 Guidelines

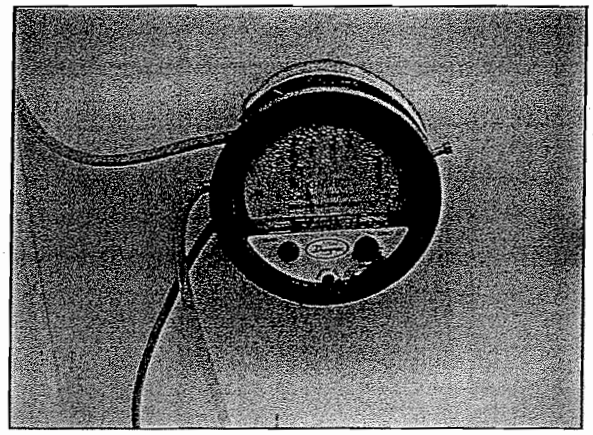
- As an alternative to criteria (1) through (3) above, the following equation may be used to determine the necessity of using a more sensitive differential pressure gauge. If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

Determination of Sensitivity of Pressure Gauge

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

Using Magnehelic Gauges Etc.

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



Alternative Approaches for Low Velocity Measurements

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

Techniques For Measurement of Low Flows

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

Techniques For Measurement of Low Flows

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

Other Low Flow Techniques

- Venturi Meters
- Orifice Meters
- Mass Flow Meters

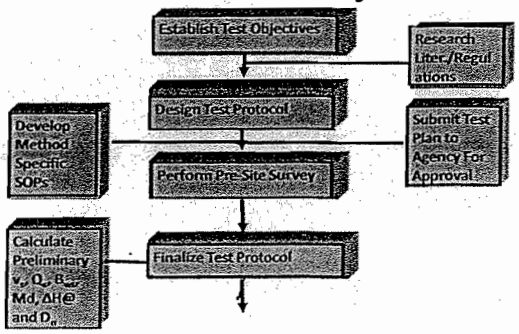
Compliance Test and Source Test Observation

Stack Testing Special Topics:

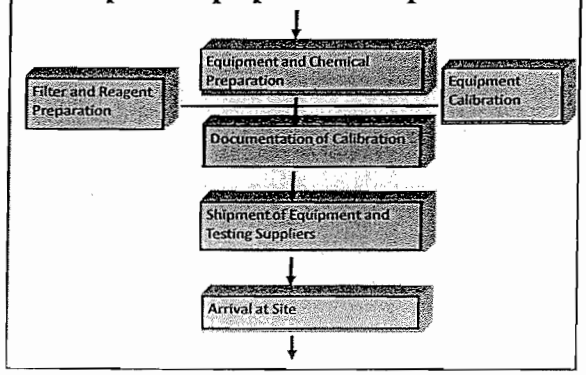
- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

U.S. EPA APTI
Compliance Test and Source Test Observation
The Emission Test Report and Review

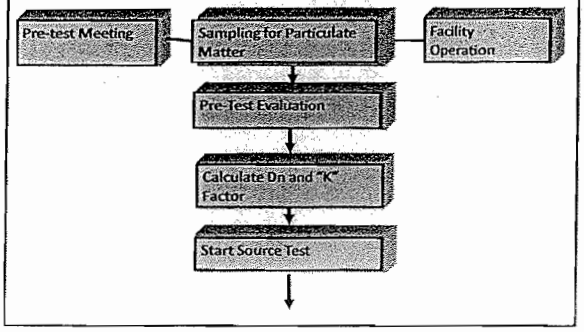
Step 1: Objectives, Protocols and Pre-site Survey



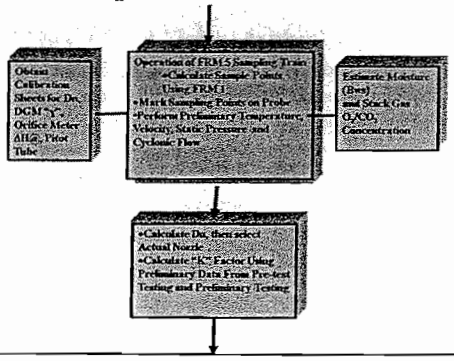
Step 2: Equipment Preparation



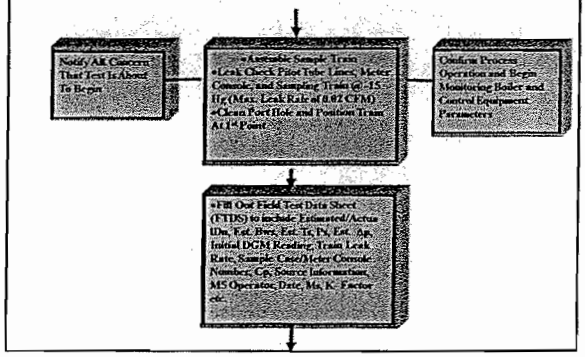
Step 3: Pre-test Conference and Evaluation

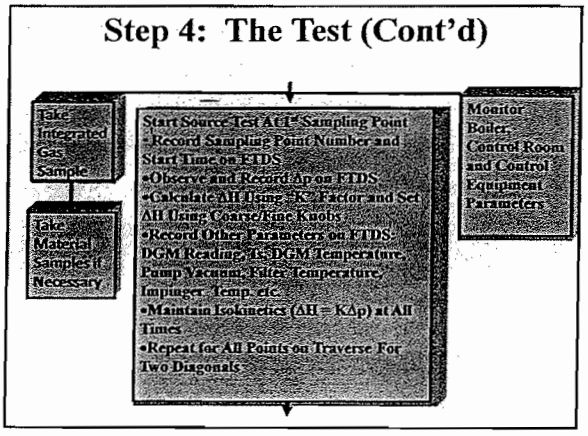


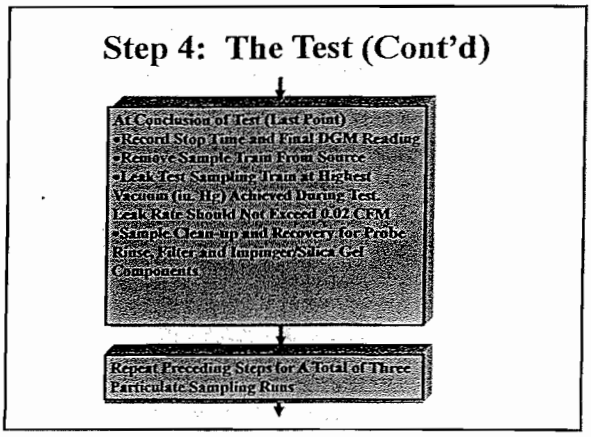
Step 4: The Test

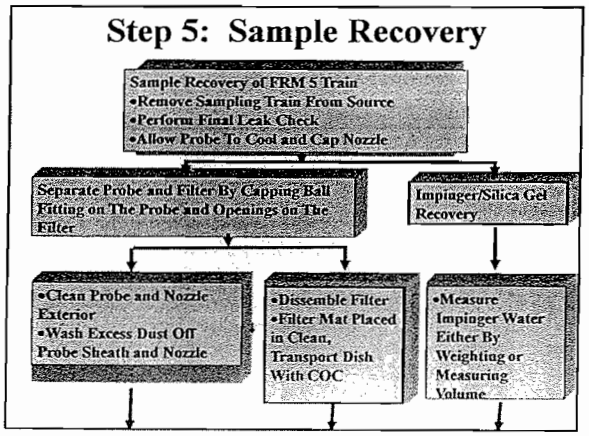


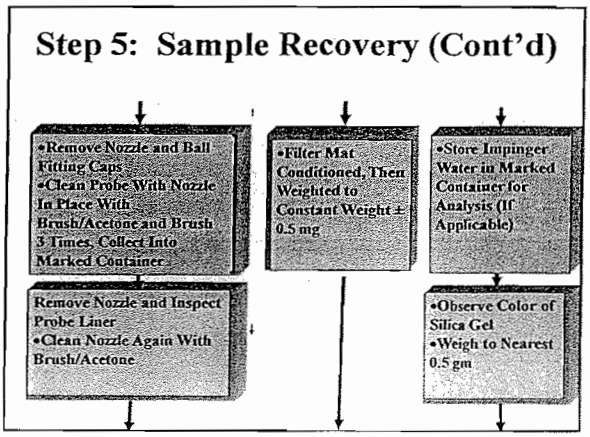
Step 4: The Test

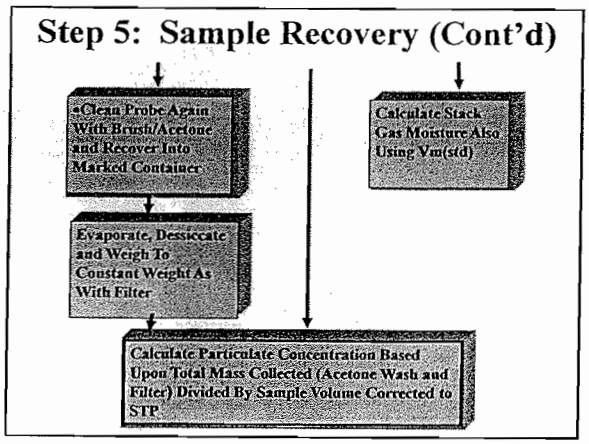












Emission Test Report

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

Emission Test Report Guideline Document

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

"Preparation and Review of Emission Test Reports"

Purpose of GD-043

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

Purpose of GD-043

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

Emission Test Report

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

Emission Test Report

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

Section 1: Summary of Test Program and Results

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

Section 1: Summary of Test Program

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

Section 3: Summary and Discussion of Test Results

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

Emission Test Report

Summary of Results

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

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

Run Number		Run 1	Run 2	Run 3	Average
Identification	Symbol/Units				
Volumetric Flow Rate Data					
Avg. Stack Gas Velocity	V_s, ft/sec	33.52	39.59	39.13	37.41
Stack Gas Cross Sect Area	A_s, ft²	1.58	1.58	1.58	1.58
Actual Stack Gas Flow	Q_{as}, acfm	3179	3745	3700	3541
Dry Std Stack Gas Flow	Q_{sd}, dscfm	760	864	856	827
Stack Gas Moisture Content	B_{ws}, %	10.4	12.5	11.4	11.4
Stack Gas Oxygen (O_2)	%	10.9	12.2	12.2	11.8
Stack Gas Carbon Dioxide (CO_2)	%	9.0	7.0	7.0	7.7
Stack Gas Nitrogen (N_2)	%	80.1	80.8	80.8	80.6
Stack Gas Temperature, (T_s)	°F	1499.4	1534.9	1543.5	1522.6
Percent of Isokinetic Rate	I, %	96.4	96.9	96.8	96.4
EPA Allowed % I[2]	I, %	90-110	90-110	90-110	90-110
Process Data					
Waste Charge Rate - Average	P, lbs/hr	97.6	129.2	128.4	135.4
Emission Rate Data					
Total Mass of Particles	m_n, mg	31.7	28.2	21.9	29.9
Stack Particulate Conc.	c_s, g/dscf	0.001	0.001	0.001	0.001
	c_s, gr/dscf	0.015	0.010	0.008	0.011
Particulate Emission Rate	E, kg/hr	0.431	0.024	0.020	0.025
	E, lbs/hr	0.968	0.053	0.044	0.055
Allowable Emission Rate[3]	E, lbs/hr	0.195	0.258	0.259	0.237

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

Jerry G. Williams and Sons Federal Reference Method 5 Test Results[1], December 19-20, 2006

Run Number		Run 1	Run 2	Run 3	Average
Identification	Symbol/Units				
Volumetric Flow Rate Data					
Avg. Stack Gas Velocity	V_s, ft/sec	22.43	26.17	28.23	25.61
Stack Gas Cross Sect Area	A_s, ft²	4.75	4.75	4.75	4.75
Actual Stack Gas Flow	Q_{as}, acfm	6387	7452	8041	7293
Dry Std Stack Gas Flow	Q_{sd}, dscfm	3627	4133	4558	4099
Stack Gas Moisture Content	B_{ws}, %	20.5	23.0	27.0	23.5
Percent of Isokinetic Rate	I, %	92.8	98.9	98.8	96.8
EPA Allowed % I[2]	I, %	90-110	90-110	90-110	90-110
Emission Rate Data					
Total Mass of Particles	m_n, mg	149.5	180.5	167.6	165.9
Stack Particulate Conc.	c_s, g/dscf	0.006	0.006	0.005	0.006
	c_s, gr/dscf	0.100	0.098	0.083	0.094
Particulate Emission Rate	E, kg/hr	1.40	1.58	1.48	1.49
	E, lbs/hr	3.1	3.5	3.3	3.3
	E, lbs/mmBtu	0.20	0.19	0.18	0.19
NC Air Permit Rate	E, lbs/mmBtu	0.49	0.49	0.49	0.49

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

[2] As specified in 10CFR60, Appendix A, Federal Reference Method 5, Section 6.12: "If 90 percent ≤ I ≤ 110 percent, the results are acceptable."

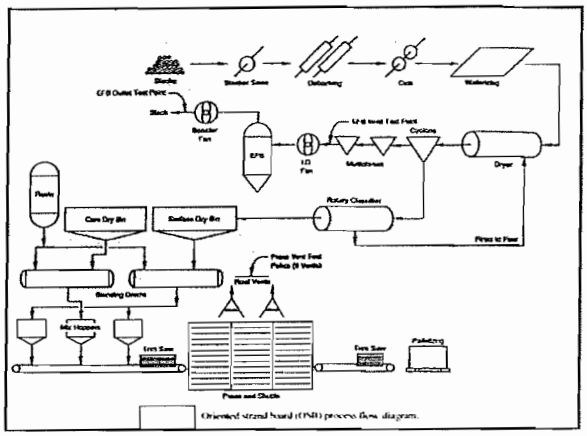
VOLUMETRIC FLOW RATE DATA

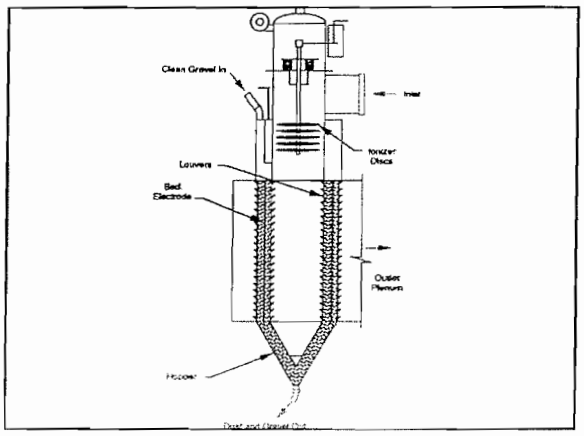
RUN NO.	FLOW RATE, dscmh				TEMPERATURE, °F			MOISTURE, %H2O			ORSAT, %	
	M5/202	30011	M315	Average	M5/202	30011	M315	M5/202	30011	M315	O_2	CO_2
1-1	54.506	54.834		54.669	225	223		23.3	23.5		10.6	8.6
1-2	56.864	54.130		54.130[1]	224	225		22.7	24.9		10.5	8.4
1-3	52.502	54.874		55.192	224	225		22.5	23.7		10.9	8.5
Avg	54.957	54.113			224	223		23.5	24.4		10.8	8.5
2-1	51.054	54.871	55.342	55.106[2]	227	225	227	23.2	22.5	23.8	10.6	8.2
2-2	52.485	55.853	55.153	56.435[2]	222	223	226	24.2	23.4	24.0	10.3	8.5
2-3	52.368	55.165	57.063	56.114[2]	227	225	227	23.4	22.9	24.0	10.8	8.6
Avg	51.969	55.280	55.153		225	225	227	23.2	22.9	23.9	10.6	8.7
3-1		32.163		32.163		111			2.2			
3-2		31.324		31.324		132			2.5			
3-3		39.067		39.067		133			2.1			
Avg		34.851				125			2.3			

[1] Does not include M5/202 run.
[2] Does not include M5/202 runs.

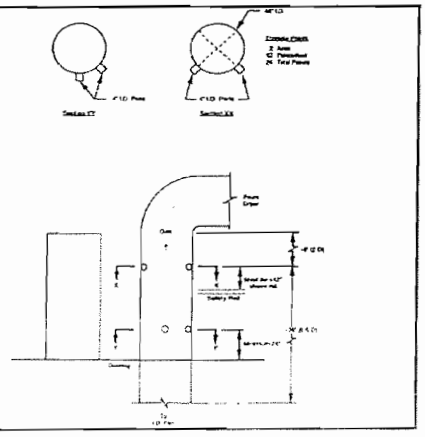
Section 2: Plant and Sampling Location

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

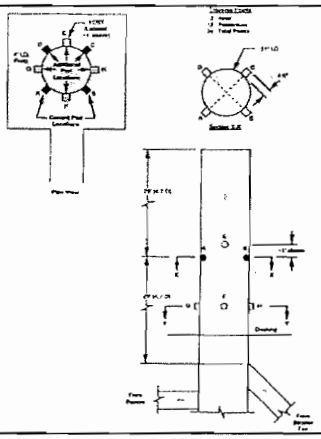




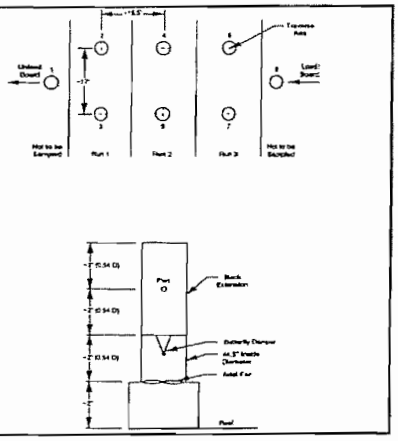
Schematic of Unit 1 Inlet Sampling Location



Schematic of Unit 1 Outlet Stack Sampling Location



Press Vents Sampling Location Configuration and Testing Scheme



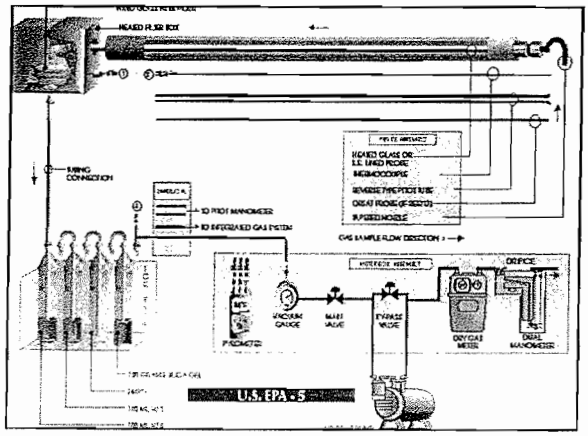
Section 4: Sampling and Analytical Procedures

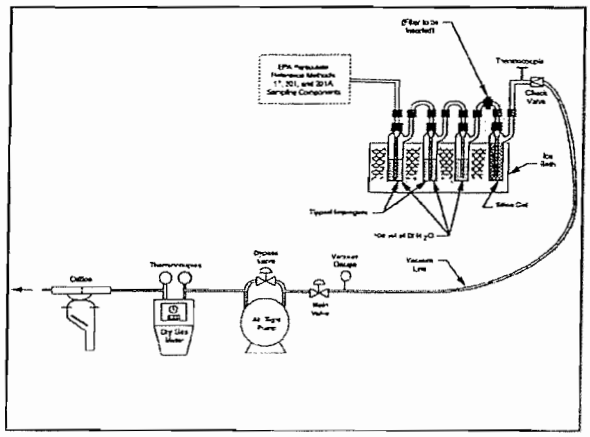
- Test Methods Discussion
- Process Test Methods Discussion

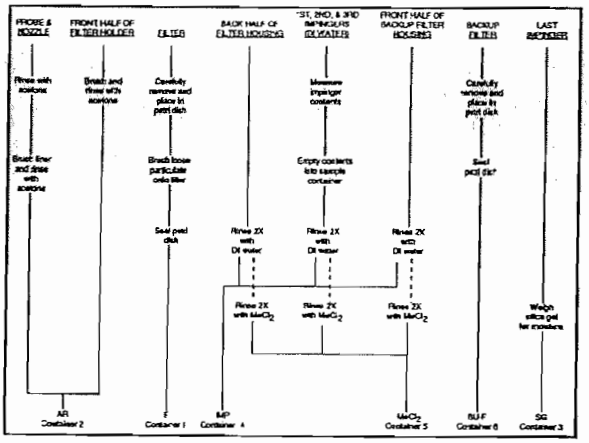
Emission Test Report

Test Methodology

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



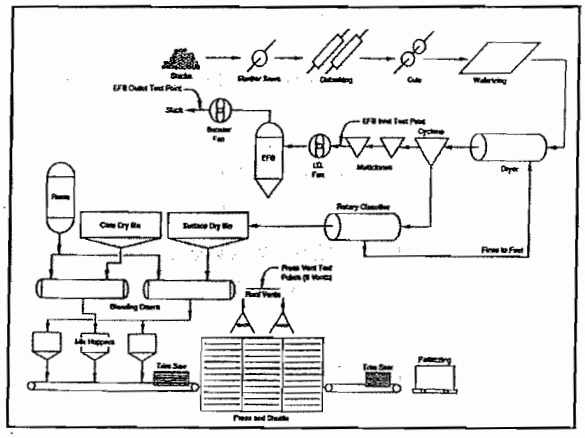




Emission Test Report

Process Description

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



Section #5: Internal QA/QC

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

Emission Test Report

Results

- Summary of data
- Charts and tables
- Example calculations

Westerne College Pathological Incinerator Federal Reference Method 5 Test Results

Run Number		Run 1	Run 2	Run 3	Average
Identification	Symbol / Units				
Volumetric Flow Rate Data					
Avg. Stack Gas Velocity	V_s, ft/sec	32.52	39.59	39.13	37.41
Stack Gas Cross Sect Area	A_s, ft²	1.58	1.58	1.58	1.58
Actual Stack Gas Flow	Q_{act}, acfm	3170	3745	3700	3538
Dry Std Stack Gas Flow	Q_{sd}, dscfm	765	864	856	828
Stack Gas Moisture Content	B_{ws}, %	10.8	12.5	11.4	11.6
Stack Gas Oxygen (O_2)	%	10.9	12.2	12.2	11.8
Stack Gas Carbon Dioxide (CO_2)	%	9.0	7.0	7.0	7.7
Stack Gas Nitrogen (N_2)	%	80.1	80.8	80.8	80.6
Stack Gas Temperature (T_s)	°F	1499.4	1524.9	1493.5	1572.6
Percent of Isokinetic Rate	I_s, %	96.4	96.9	96.8	96.4
EPA Allowed, 96-110	I_s, %	96-110	96-110	96-110	96-110
Process Data					
Waste Charge Rate - Average	F, lbs/hr	97.6	129.2	129.4	135.4
Emission Rate Data					
Total Mass of Particles	m_n, mg	37.7	28.2	23.9	29.9
Stack Particulate Conc.	c_s, g/dscf	0.001	0.001	0.001	0.001
	c_s, gr/dscf	0.015	0.010	0.008	0.011
Particulate Emission Rate	E, kg/hr	0.031	0.024	0.020	0.025
	E, lbs/hr	0.068	0.053	0.044	0.055
Allowable Emission Rate*	E, lbs/hr	0.195	0.258	0.259	0.237

Emission Test Report

Appendix

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

Emission Test Report Review

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

Emission Test Report Review

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

Emission Test Report Review

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

Reviewing Stack Test Report

- Section 6.12 of FRM 5 states:

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

Basic Approach to Reviewing

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

Step 1

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

Step 2

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

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

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

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

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

Step 2 (cont'd)

- Case 2 (I Is Less Than 90 Percent)

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

Step 2 (cont'd)

- Case 3 (I Is Greater Than 110 Percent)

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

Step 2 (cont'd)

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

Step 2 (cont'd)

- Case 2 (I Is Greater Than 110 Percent)

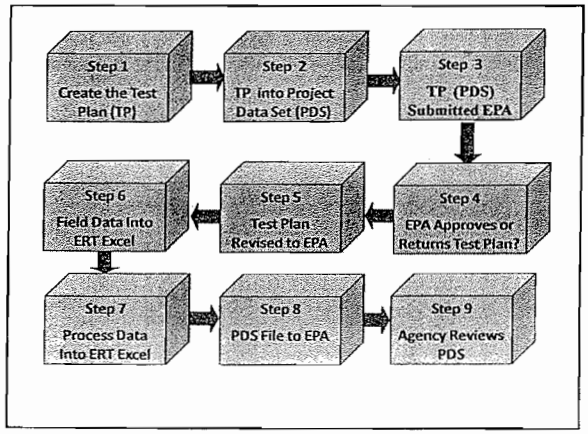
Situation 2 (cont'd): On the other hand, if the adjusted E exceeds the standard, a retest should be done.

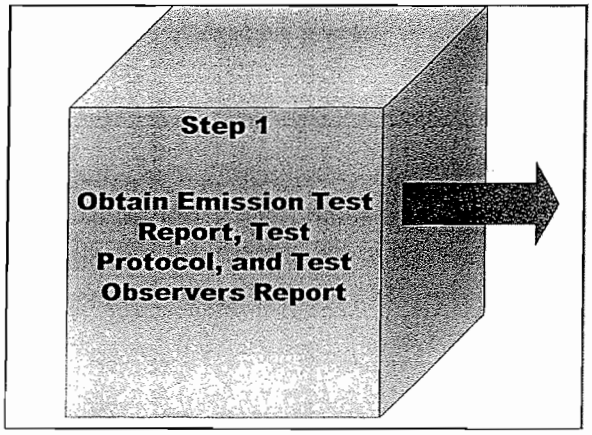
Summary of Acceptance

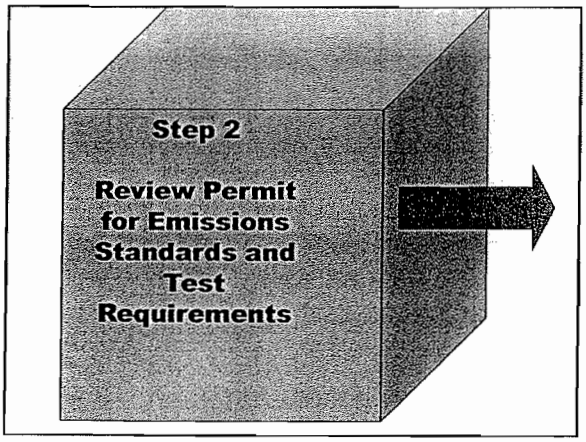
Case	I	Category	Decision
1	90-110 %		Accepted
2	< 90 %	E = < Em. St.	Accepted
		C_s (I/100) = E_{adj} > Em. Std.	Accepted
		C_s (I/100) = E_{adj} < Em. Std.	Retest

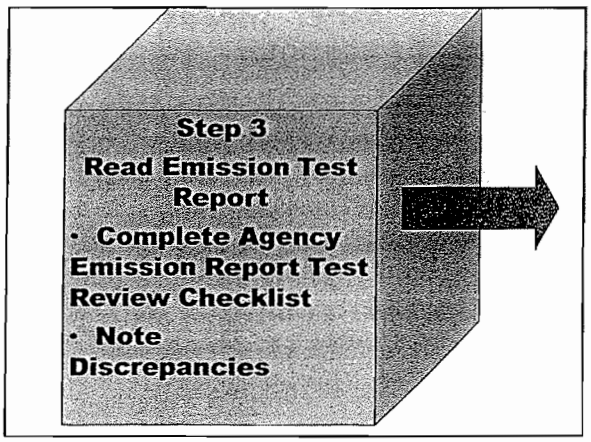
Summary of Acceptance

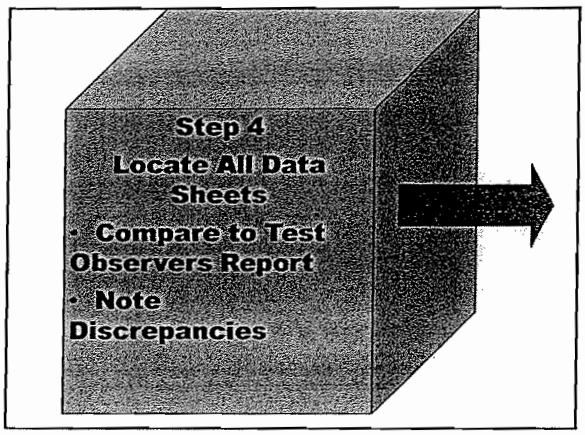
Case	I	Category	Decision
3	> 110 %	E > Em. St.	Accept
		C_s (I/100) = E_{adj} < Em. Std.	Accept
		C_s (I/100) = E_{adj} > Em. Std.	Retest

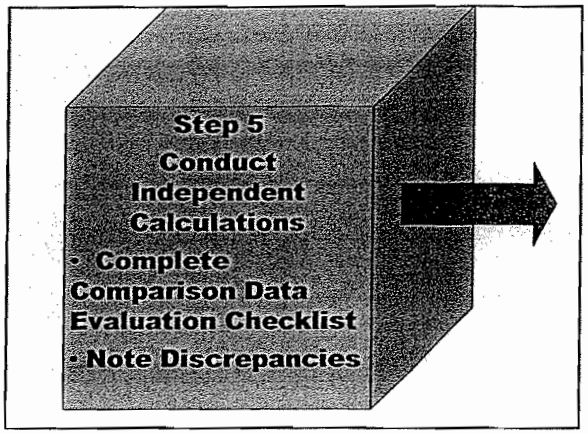


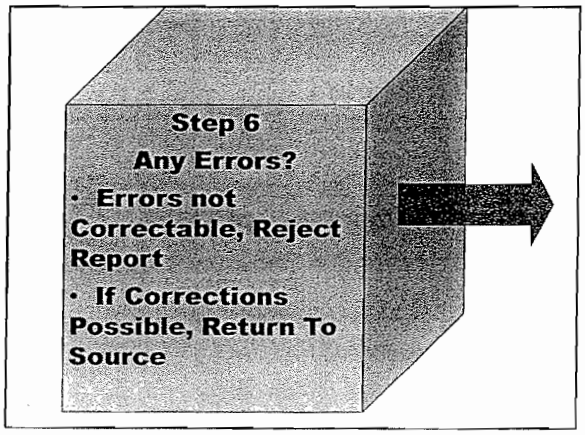


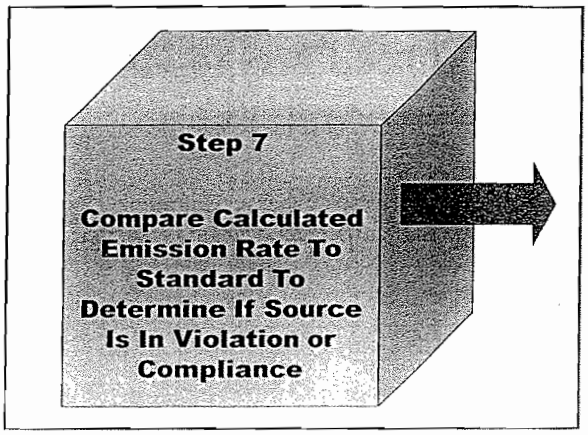


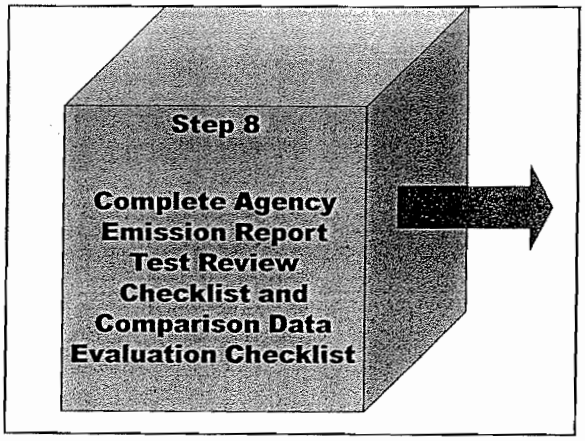


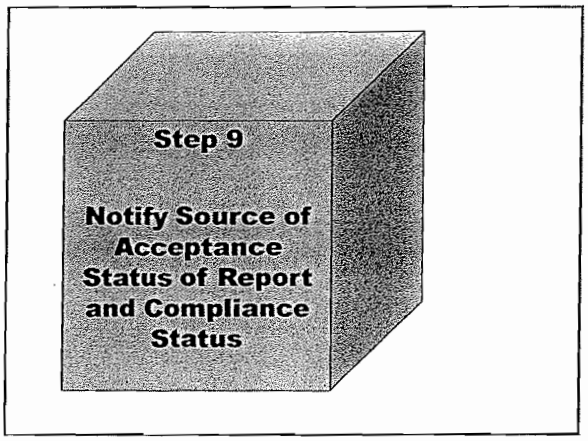

Step 4
Locate All Data Sheets
• Compare to Test Observers Report
• Note Discrepancies

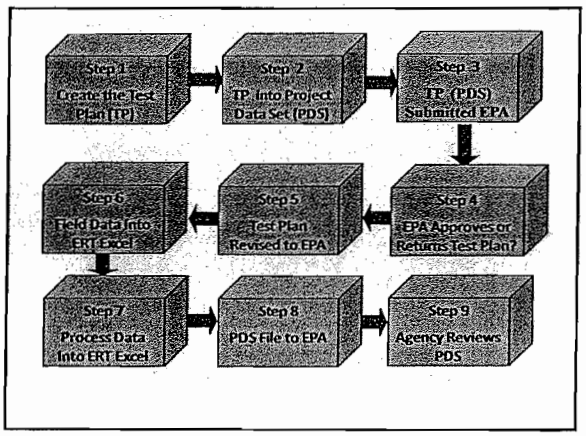

Step 5
Conduct Independent Calculations
• Complete Comparison Data Evaluation Checklist
• Note Discrepancies


Step 6
Any Errors?
• Errors not Correctable, Reject Report
• If Corrections Possible, Return To Source


Step 7
Compare Calculated Emission Rate To Standard To Determine If Source Is In Violation or Compliance


Step 8
Complete Agency Emission Report Test Review Checklist and Comparison Data Evaluation Checklist


Step 9
Notify Source of Acceptance Status of Report and Compliance Status



EPA's Electronic Reporting Tool

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

Three Parts to ERT Application

#1: The Application
#2: The Project Data Set
#3: An Excel Spreadsheet

ERT Users Guide

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

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

U.S. EPA APTI
Compliance Test and Source Test Observation
F-Factors and Units of the Standard

Emission Standards for Sources

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

Concentration of Stack Gas (c_s)

Can be expressed in:

- ppm
- g/dscm
- gr/dscf

For example:

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

0.04 gr/dscf <=> 90 mg/dscm

Pollutant Mass Rate (pmr)

Can be expressed in:

- lb/hr
- g/hr

Pollutant Mass Rate (pmr)

$$\text{pmr} = \text{Concentration} \times \text{Stack gas volumetric flow rate}$$

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

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

Emission Rate (E)

Can be expressed in:

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

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

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

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

For example:

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

Particulate emissions limited to 0.03 lb/10^6 Btu.

Process Weight Rate (E)

Can be expressed in:

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

For Example:

The NSPS for sulfuric acid plants is:

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

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

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

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

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

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

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

Method 19

F Factor Methods

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

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

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

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

Dilution correction term is dimensionless.

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

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

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

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

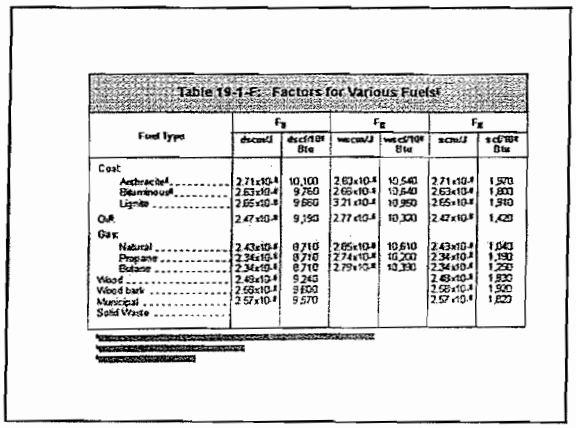


Table 19.1-5. Factors for Various Fuels[a]

Fuel type	F_d		F_c		F_h	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal						
Anthracite[b]	2.71x10^{-7}	10,100	2.63x10^{-7}	10,540	2.71x10^{-7}	1,570
Bituminous[c]	2.63x10^{-7}	9,780	2.65x10^{-7}	10,640	2.63x10^{-7}	1,800
Lignite	2.65x10^{-7}	9,860	3.21 x10^{-7}	10,950	2.65x10^{-7}	1,910
Oil	2.47 x10^{-7}	9,190	2.77 x10^{-7}	10,320	2.47x10^{-7}	1,420
Gas						
Natural	2.43x10^{-7}	8,710	2.85x10^{-7}	10,610	2.43x10^{-7}	1,040
Propane	2.34x10^{-7}	8,710	2.74x10^{-7}	10,200	2.34x10^{-7}	1,190
Butane	2.34x10^{-7}	8,710	2.79x10^{-7}	10,390	2.34x10^{-7}	1,250
Wood	2.48x10^{-7}	9,240			2.48x10^{-7}	1,830
Wood bark	2.56x10^{-7}	9,600			2.56x10^{-7}	1,900
Municipal Solid Waste	2.57x10^{-7}	9,570			2.57 x10^{-7}	1,820

U.S. EPA APTI

Compliance Test and Source Test Observation

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

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

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

Test Methods Identification

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

What Is Formaldehyde?

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

Sources of Formaldehyde?

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

Mineral Wool Process

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

Mineral Wool Process

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

Questions to Ask In Selecting A Method

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

Questions to Ask

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

Questions to Ask

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

Questions to Ask

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

Questions to Ask

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

History of Formaldehyde

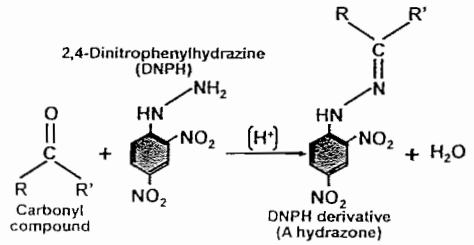
- 1990 EPA Ambient Air Method (EPA/600/3-90/005)
  - Constant Rate Sampling: DNPH Cartridges
  - Constant Rate Sampling: DNPH Impingers
  - EPA's Compendium of Methods
    - Indoor Compendium
    - Organic Compendium

Compendia

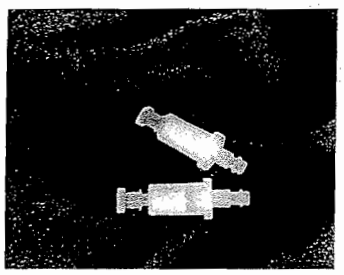
- Indoor (IP-1 through IP-10)
  - EPA-600/4-90-010
- Inorganic (I0-1 through IO-5)
  - EPA-625/R-96/010a
- Organic-Second Edition (TO-1 through TO-17)
  - EPA-625/R-96/010b

Compendium Method TO-11A

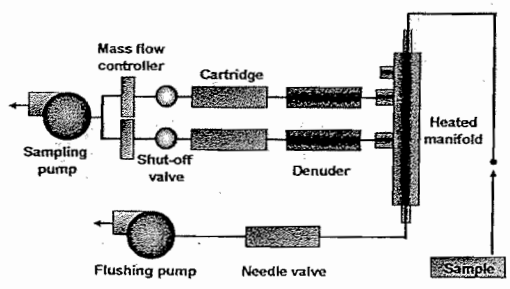
Derivatization Reaction



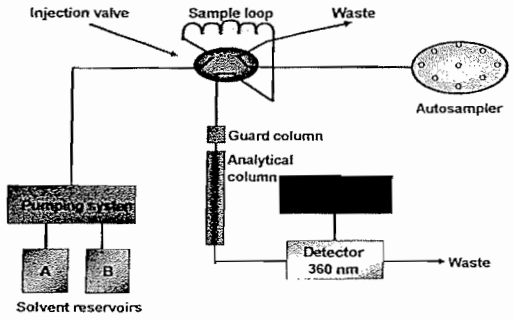
Example of Commercially Available DNPH-Cartridge



Example of Dual-port Carbonyl Sampler

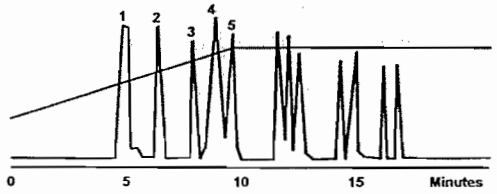


Basic HPLC System



HPLC Chromatogram

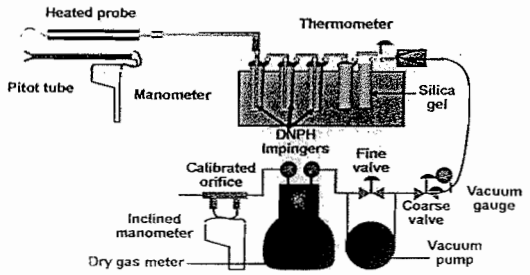
1 Formaldehyde
2 Acetaldehyde
3 Acetone
4 Acrolein
5 Propionaldehyde



History of Formaldehyde

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

SW-846, Method 0011 Sampling Train

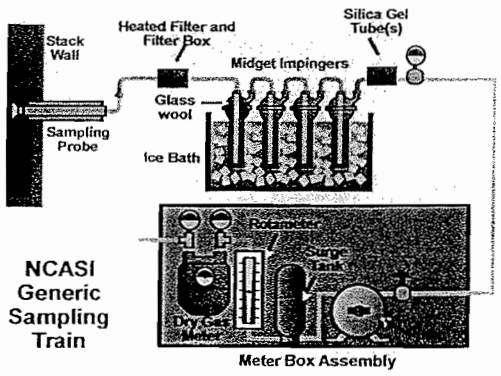


BIF Formaldehyde Method (SW846, Method 0011)

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

History of Formaldehyde

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



NCASI Generic Sampling Train

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

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

History of Formaldehyde

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

Applicability

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

Applicability

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

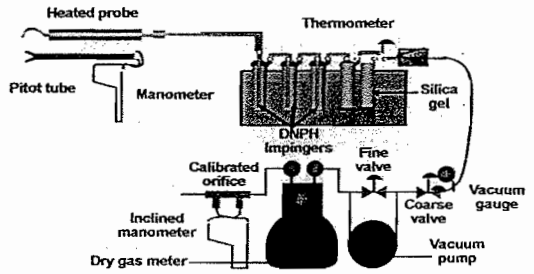
Principle FRM 316

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

FRM 316 Sampling Train

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

FRM 316 Sampling Train



FRM 316 Principle

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

FRM 316 Principle

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

FRM 316 Principle

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

FRM 316 Objective

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

FRM 316 Interferences

- Sulfites
- Cyanides

FRM 316 Sample Nozzle

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

FRM 316 Sample Nozzle

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

FRM 316 Sample Nozzle

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

FRM 316 Pitot Tube

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

FRM 316 Pitot Tube

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

FRM 316 Pitot Tube

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

FRM 316 Sampling Probe

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

FRM 316 Sampling Probe

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

FRM 316 Sampling Probe

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

FRM 316 Sampling Probe

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

FRM 316 Impinger System

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

FRM 316 Impinger System

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

FRM 316 Impinger System

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

FRM 316 Umbilical Cord

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

FRM 316 Meter Console Desirable Features

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

FRM 316 Meter Console Desirable Features

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

FRM 316 Meter Console Required Calibrations

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

FRM 316 Isokinetic Rate Equation

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

FRM 316 Isokinetic Rate Equation (Simplified)

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

FRM 316 Causes for not Meeting 100% Isokinetics

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

FRM 316 Causes for not Meeting 100% Isokinetics

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

Difficulty in Maintaining Isokinetics

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

FRM 316 Pre-test Preparation

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

FRM 316 Pre-test Preparation

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

FRM 316 Sampling

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

FRM 316 Sampling

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

FRM 316 Sampling

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

FRM 316 Leak Check

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

FRM 316 Sample Recovery

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

FRM 316 Sample Recovery

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

FRM 316 Sample Recovery

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

FRM 316 Sample Recovery

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

FRM 316 Analysis

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

FRM 316 Analysis

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

FRM 316 Post-test Calibration Requirements

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

FRM 316 Post-test Calibration Requirements

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

FRM 316 Other Components Needing Calibration

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

FRM 316 Audit Vial

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

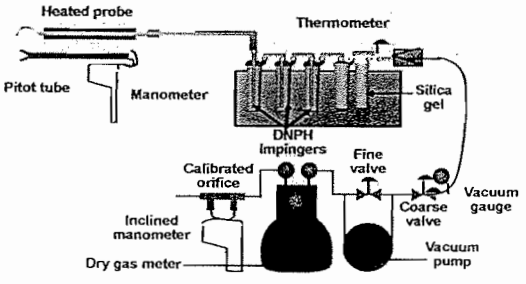
FRM 316 Audit Vial

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

SW-846, Method 0011

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

SW-846, Method 0011 Sampling Train

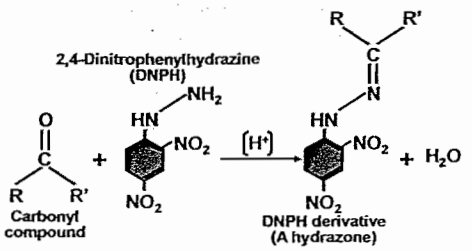


SW-846, Method 0011

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

Method 0010 Reaction

Derivatization Reaction



SW-846, Method 0011 Analyte List

- Formaldehyde
- Acetaldehyde
- Acrolein
- Acetone
- Propionaldehyde
- Crotonaldehyde
- Butyraldehyde
- Benzaldehyde

SW-846, Method 0011 Analyte List

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

Allegheny Particleboard Tests

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

Yorktowne Department Tests

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

Yorktown Department Tests

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

Wood-Mode Department Tests

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

Wood-Mode Department Tests (Contd)

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

Testing at MDF Plants (BIF Method 0011)

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

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

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

Issues of Concern

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

FRM 318 Extractive FTIR Method for Measurement of Emissions from Mineral Wool and Wool Fiberglass Industries

- See FTIR Video

EPA's FTIR Support

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

EPA's FTIR Support

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

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

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

Test Methods Identification

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

FRM 13A or 13B Applicability

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

Summary of Method

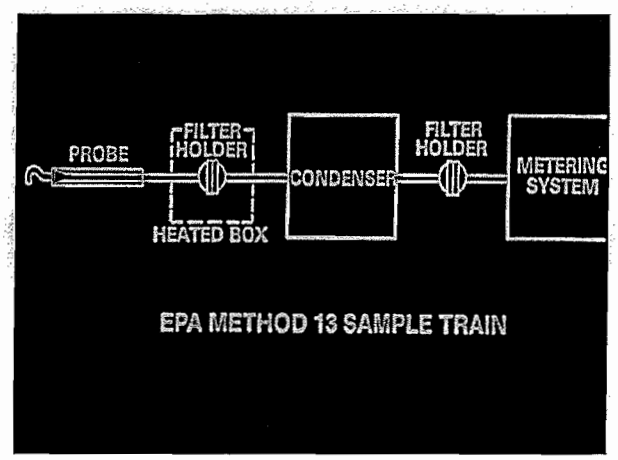
- FRM 5 sample train with Stainless steel or glass nozzle and probe liner
- Filter temperature maintained @ 248°F and interchangeable
- Particulate fluorides caught on filter while gaseous fluorides caught in impingers
- Analysis by SPADNS zirconium lake colorimetric @ 570 nm for FRM 13A

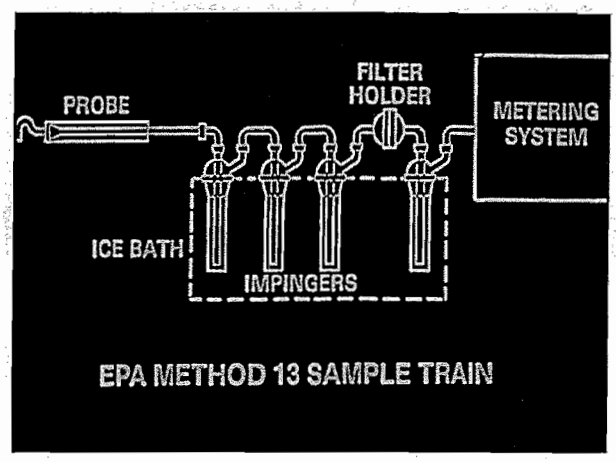
FRM 13A or 13B Design Requirements

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

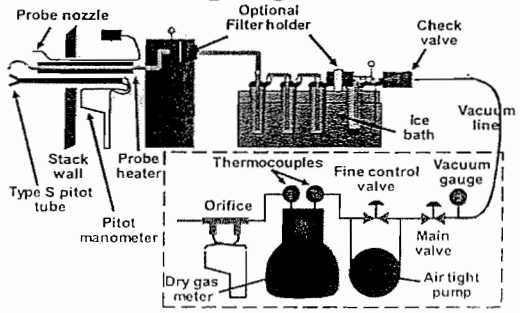
FRM 13A or 13B Sampling Train

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





FRM 13A or 13B Sampling Train



FRM 13A or 13B Sample Recovery

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

FRM 13A Sample Preparation

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

FRM 13A Sample Preparation

- Containers #2: Treated same as Container #1

FRM 13A Analysis Preparation

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

FRM 13A Sample Analysis

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

FRM 13A Sample Analysis

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

FRM 13A Analysis Interferences

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

FRM 13B Sample Analysis

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

FRM 13B Sample Analysis

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

FRM 13A or 13B Operational Requirements

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

FRM 13A or 13B Operational Requirements

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

FRM 13A or 13B Impinger Arrangement

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

FRM 13A or 13B Operation

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

FRM 13A or 13B Operation

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

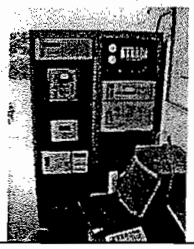
FRM 13A or 13B Key Points

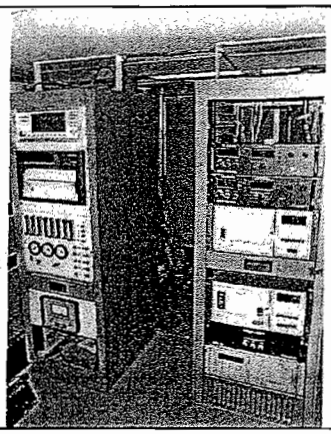
- All active sample train components can be made of glass or stainless steel (no mention of Teflon components)
- All active sample train components must be cleaned

FRM 13A or 13B Key Points

- EPA audit vial available for quality control evaluation

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





Applicability

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

Principle

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

How the Method Works

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

How the Method Works

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

Eight Major Points

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

Eight Major Points

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

Eight Major Points

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

Interesting Points

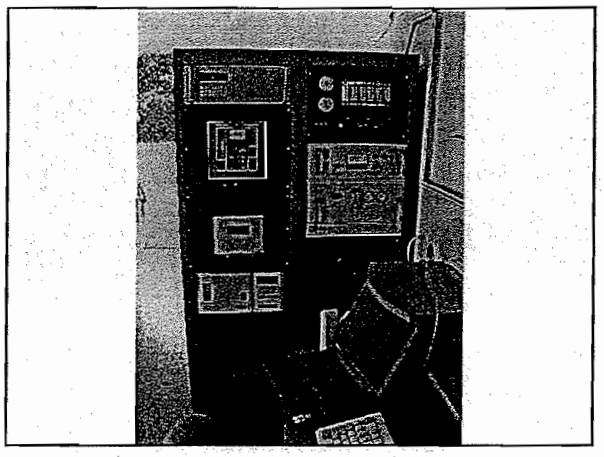
- Perform Calibration Curve: High (80-100% span), Mid (40-60% span), Zero (<0.25% span)
- Calibration Gas Certification: Protocol 1 or Method 6 (3 Runs/1 L/min), 5%

Interesting Points

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

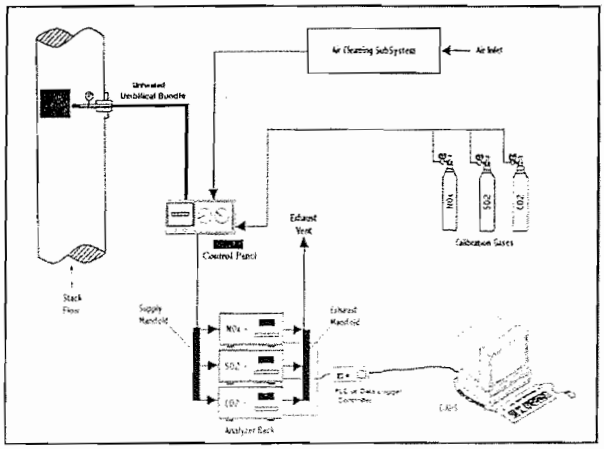
Interesting Points

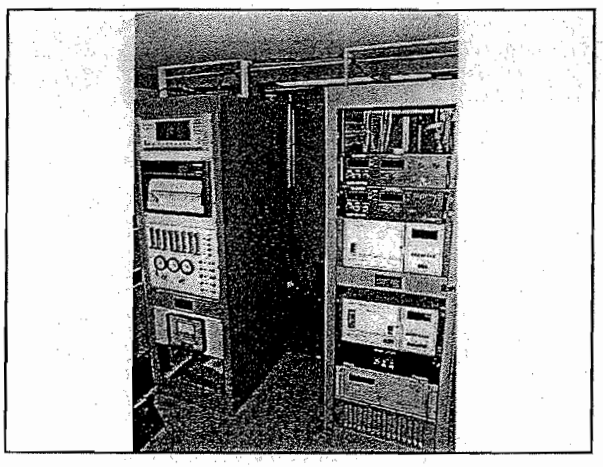
- Sampling system bias test done before and after test, then average, and apply value to emission data to correct
- Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span; May not reject if pass bias check!

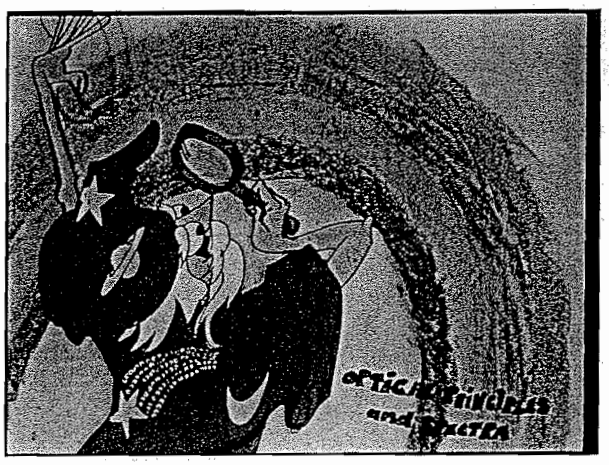


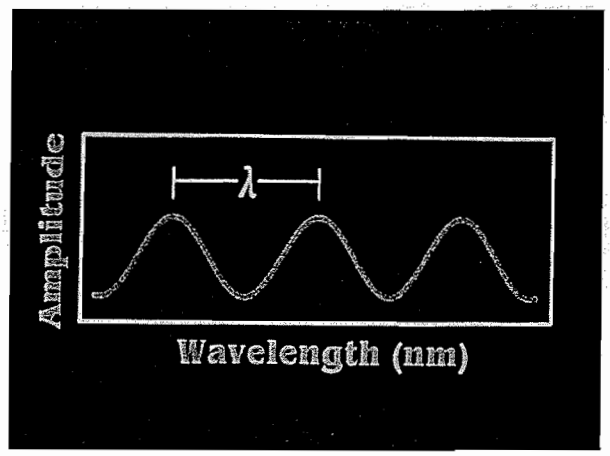
Method 6C
Only Analytical Techniques Allowed Now!

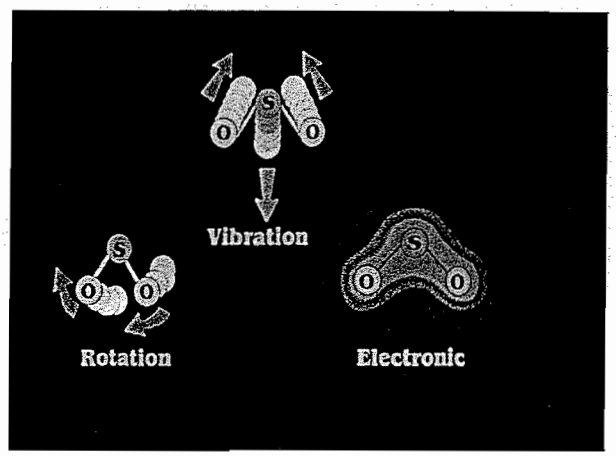
- Ultraviolet Absorption (UV)
- Nondispersive Infrared (NDIR)
- Fluorescence

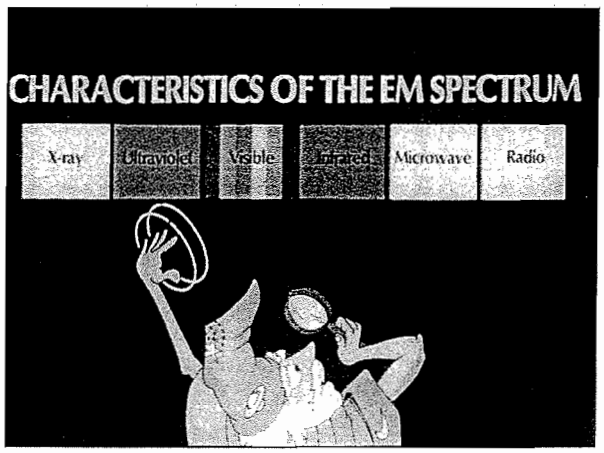


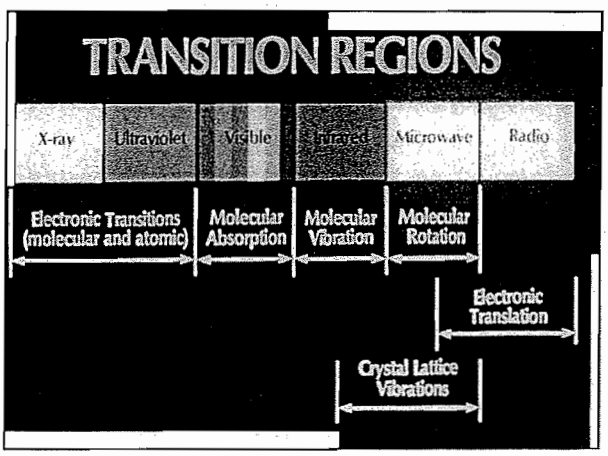


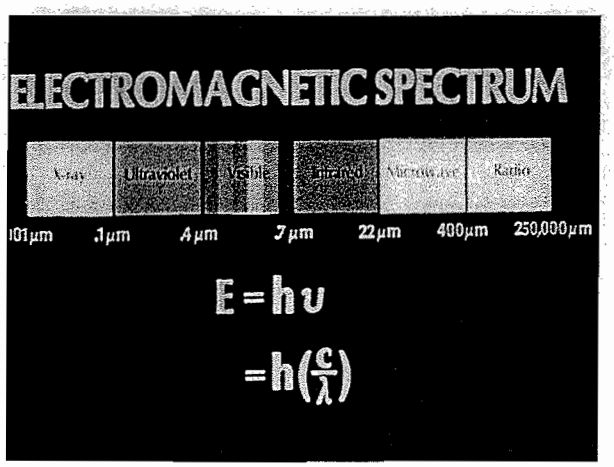


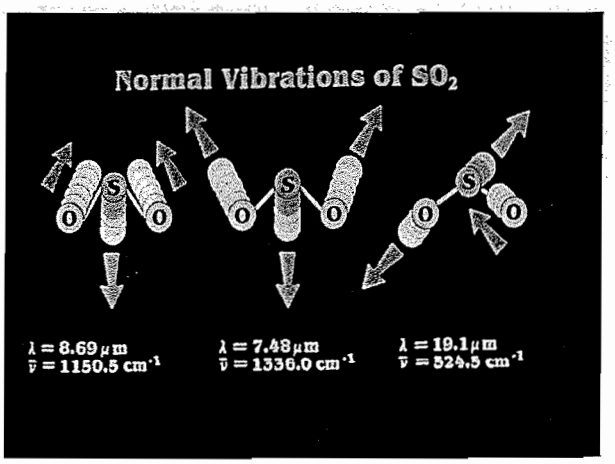

Amplitude
λ
Wavelength (nm)

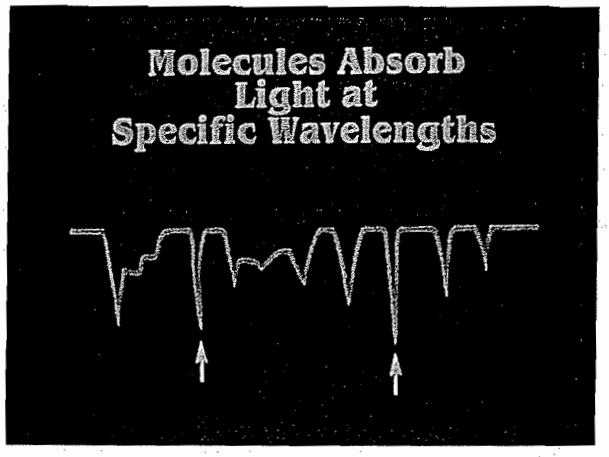

Vibration
Rotation
Electronic

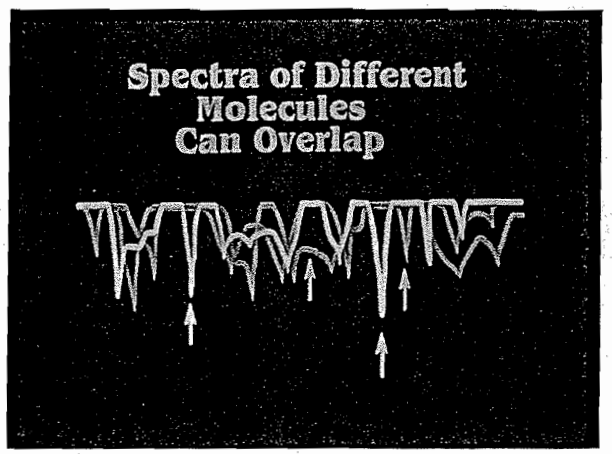

CHARACTERISTICS OF THE EM SPECTRUM
X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio

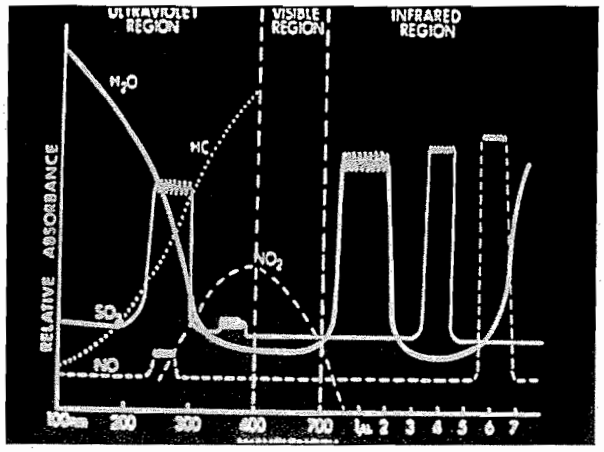

TRANSITION REGIONS
X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio
Electronic Transitions (molecular and atomic)
Molecular Absorption
Molecular Vibration
Molecular Rotation
Electronic Translation
Crystal Lattice Vibrations

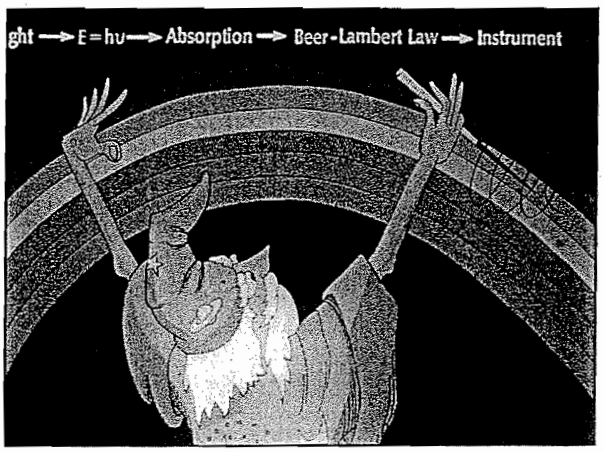

ELECTROMAGNETIC SPECTRUM
X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio
.01μm
.1μm
4μm
7μm
22μm
400μm
250,000μm
E = hυ
= h(c/λ)

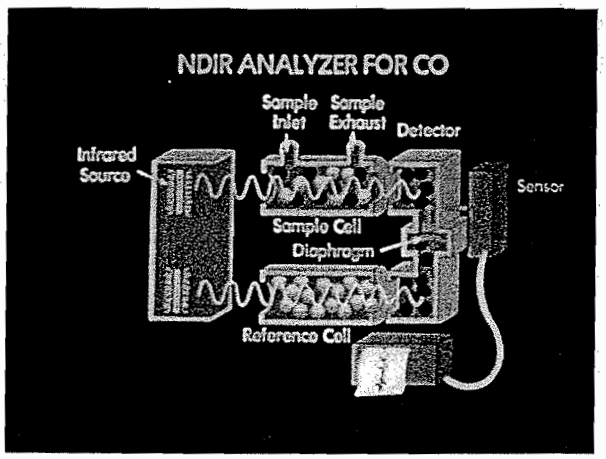

Normal Vibrations of SO2
λ = 8.69 μm
ῡ = 1150.5 cm-1
λ = 7.48 μm
ῡ = 1336.0 cm-1
λ = 19.1 μm
ῡ = 524.5 cm-1

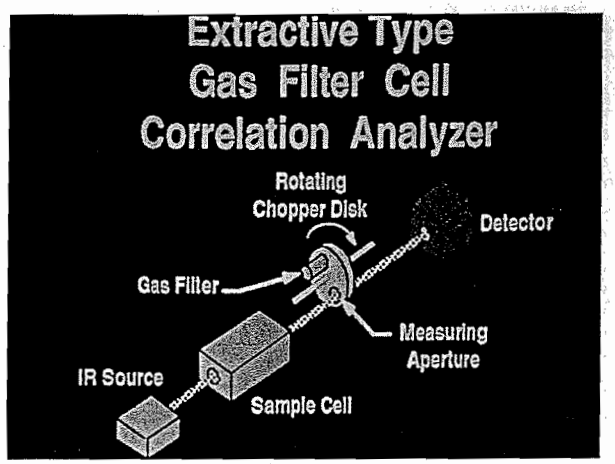

Molecules Absorb
Light at
Specific Wavelengths

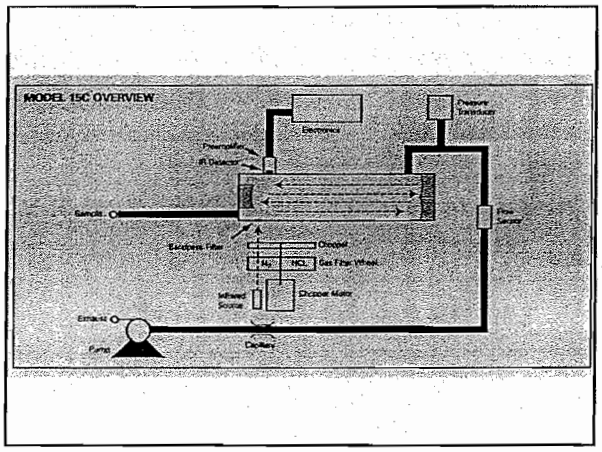

Spectra of Different
Molecules
Can Overlap

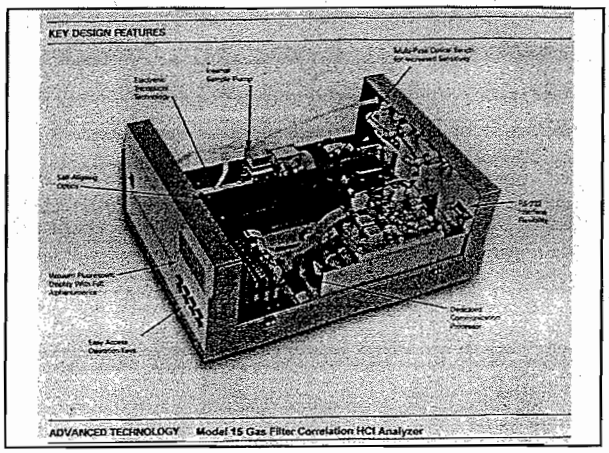

ULTRAVIOLET REGION
VISIBLE REGION
INFRARED REGION
RELATIVE ABSORBANCE
H2O
HC
NO2
SO2
NO
100nm
200
300
400
700
1
2
3
4
5
6
7

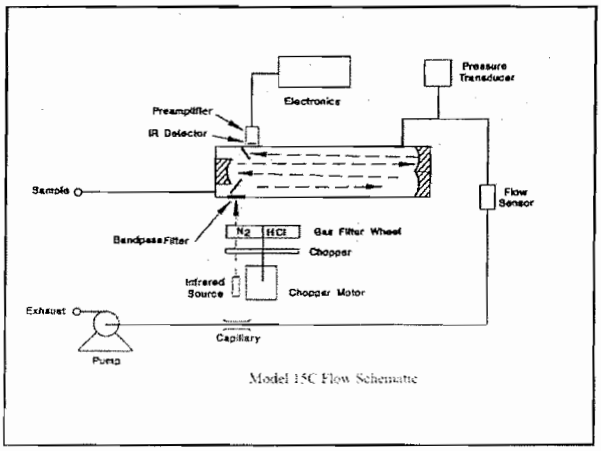

ght → E = hν → Absorption → Beer-Lambert Law → Instrument


NDIR ANALYZER FOR CO
Sample Inlet
Sample Exhaust
Detector
Infrared Source
Sensor
Sample Cell
Diaphragm
Reference Cell

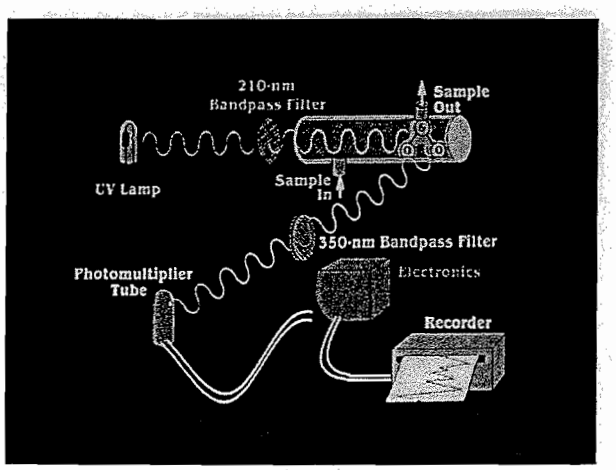

Extractive Type
Gas Filter Cell
Correlation Analyzer
Rotating Chopper Disk
Detector
Gas Filter
Measuring Aperture
IR Source
Sample Cell

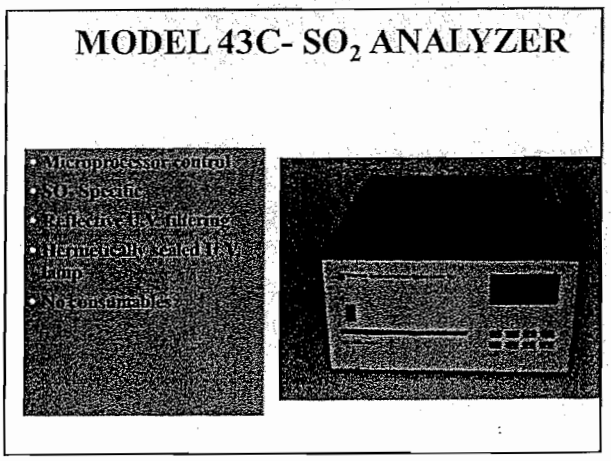






Model 15C Flow Schematic





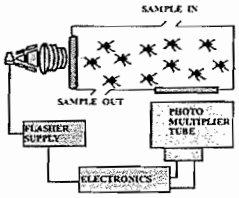
MODEL 43C-SO2 Analyzer

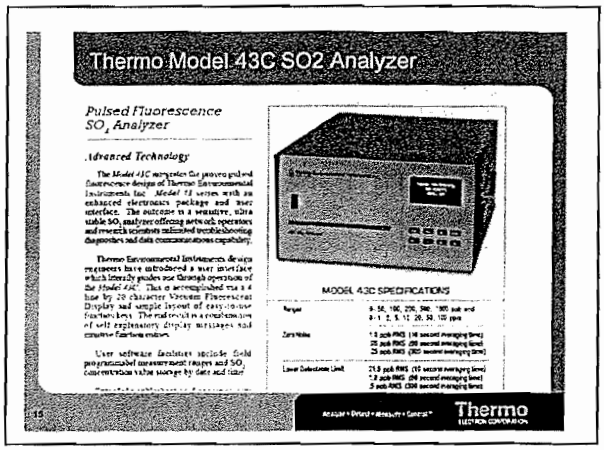
$SO_2 + h\nu_1 \xrightarrow{I_a} SO_2^*$

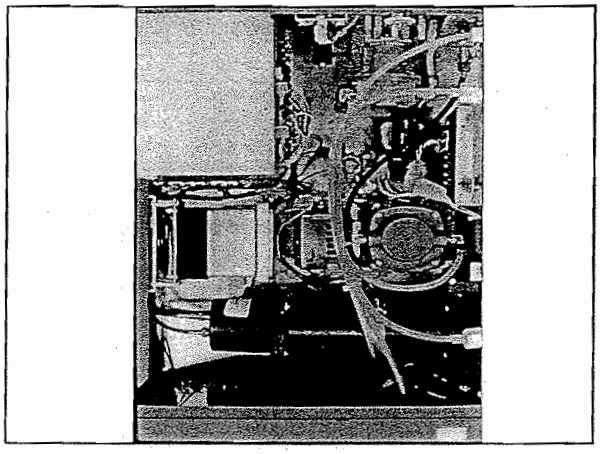
$SO_2^* \xrightarrow{K_f} SO_2 + h\nu_2$

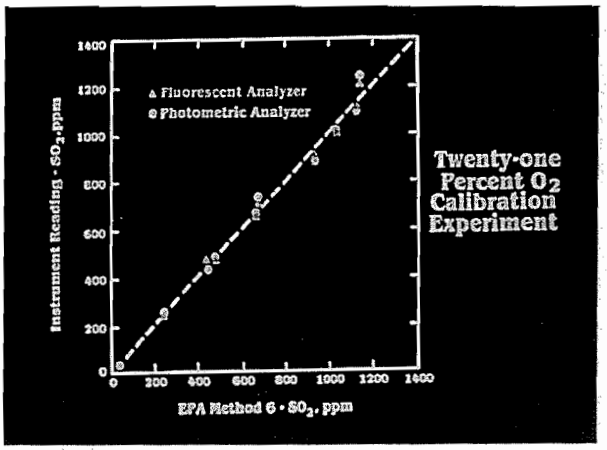
$I_a = I_o[I-e^{-(ax(SO_2))}]$

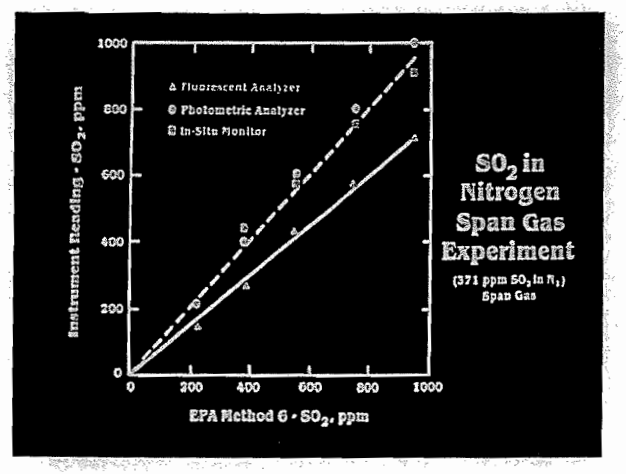
$I_f \propto I_o ax(SO_2)$ or $K(SO_2)$











HOW IS NO MEASURED?

Chemiluminescence Technique

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

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

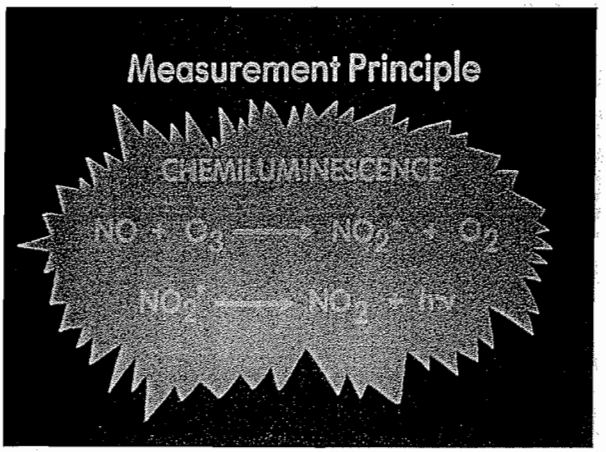
Intensity of emitted light is proportional to NO concentration

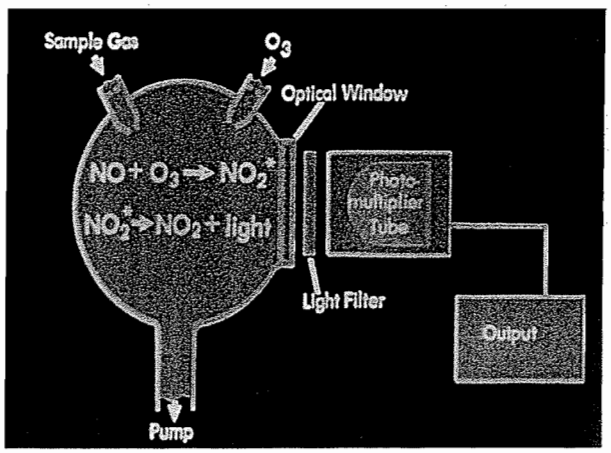
Chemiluminescent

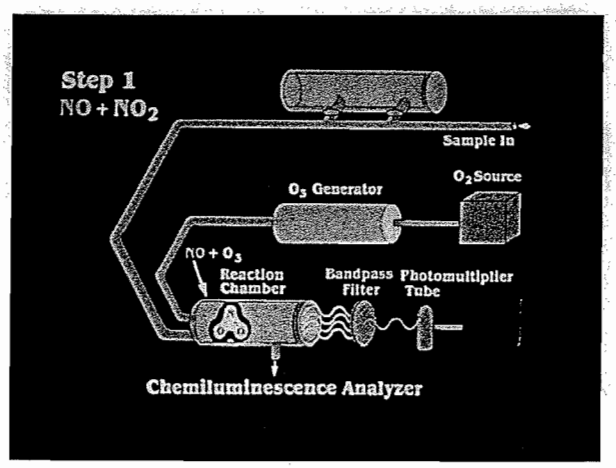
Reduction of NO_2 to NO

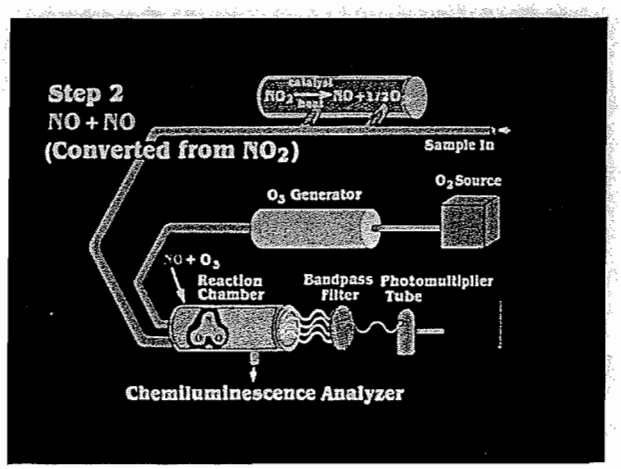
$3\,NO_2 + Mo \longrightarrow 3\,NO + MoO_3$

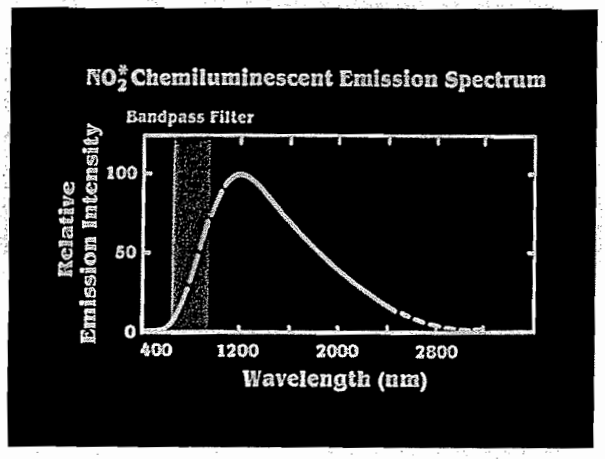
A molybdenum catalyst, heated to ~325°C, is used to Convert NO_2 to NO

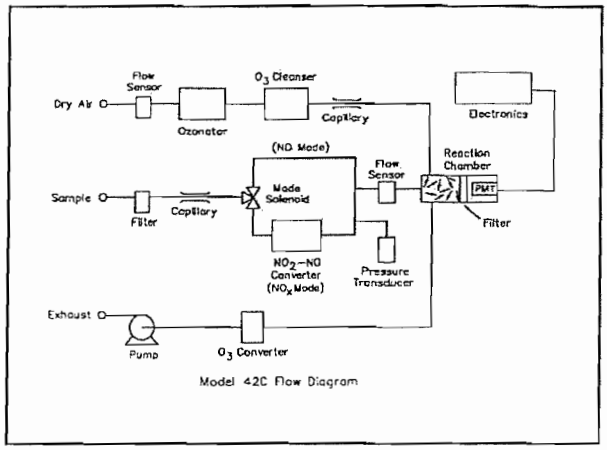


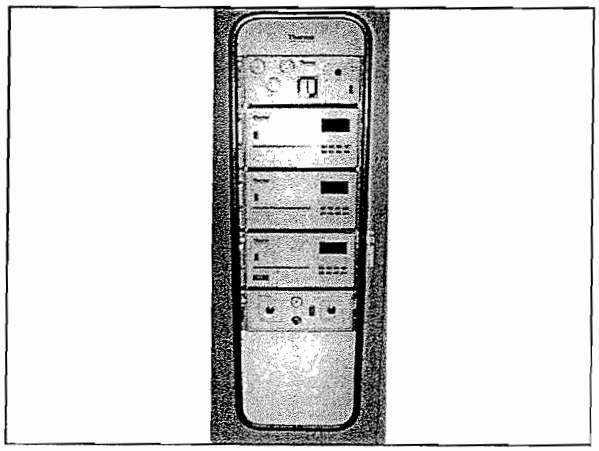


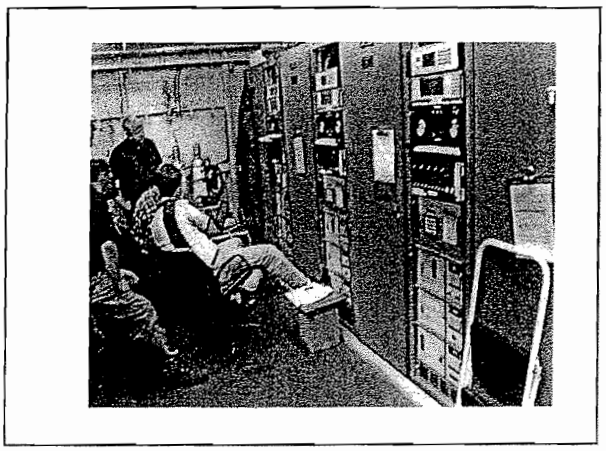












Analytical Range

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

Performance Specifications

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

Performance Specifications

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

Calibration Gases

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

Calibration Gases

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

For Fluorscence-based Analyzers

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

Measurement System Performance Test Procedures

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

Recommended Sampling System Design Criteria

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

Recommended Sampling System Design Criteria

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

Recommended Particulate Removal

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

Sample Handling

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

Moisture Removal Condensers

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

Moisture Removal Condensers

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

Other Methods of Lowering Sample Dew Point

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

Injecting Calibration Gases Into the Sampling system

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

Three Suggested Ways to Introduce Calibration Gases

- Straight Tee
- Closed Loop
- Closed Loop with Vent

Calibration Gas Introduction - Straight Tee

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

Calibration Gas Introduction - Closed Loop

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

Calibration Gas Introduction - Closed Loop with Vent

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

Leak Check

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

Analyzer Calibration Error

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

Sampling System Bias Check

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

Emission Testing

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

Sampling Procedures

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

If System Exceeds Bias Specifications

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

If System Meets Bias Specification

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

If System Exceeds Zero or Calibration Drift Limits

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

Data Recording

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

Emission Calculations

- Data corrected for errors observed in calibration error bias checks

Interference Check

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

Known SO_2 Analyzer Interferences

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

Known SO_2 Analyzer Interferences

- Fluorescence analyzers suffer from quenching effects from CO_2 and O_2

Sampling in the Presence of Ammonia

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

Sampling in the Presence of Ammonia

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

Alternative Techniques for Method 6C

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

Dilution Probes for Method 6C

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

Dilution Probes for Method 6C

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

Calibration Gas Dilution Systems

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

Calibration Gas Dilution Systems

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

Method 7E - NO_x

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

Method 7E - Ammonia (NH_3) Interference Problems

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

Method 7E - High NO_2/NO Ratio in Sample

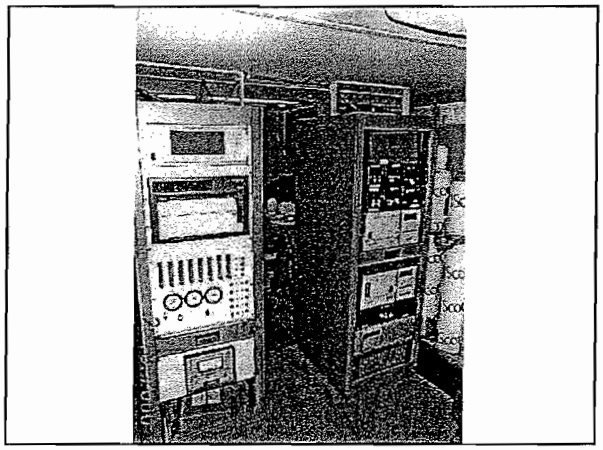
- NO_2 is readily absorbed by the sampling system, causing low bias
- Most NO_x calibration gases contain little NO_2

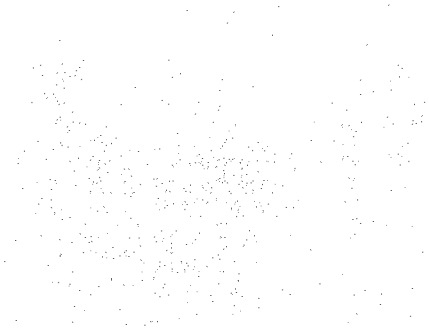
Method 7E - High NO_2/NO Ratio in Sample

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

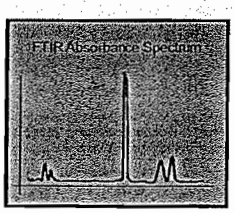
Method 3A - O_2 and CO_2

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





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



FRM 320

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 Sampling Types

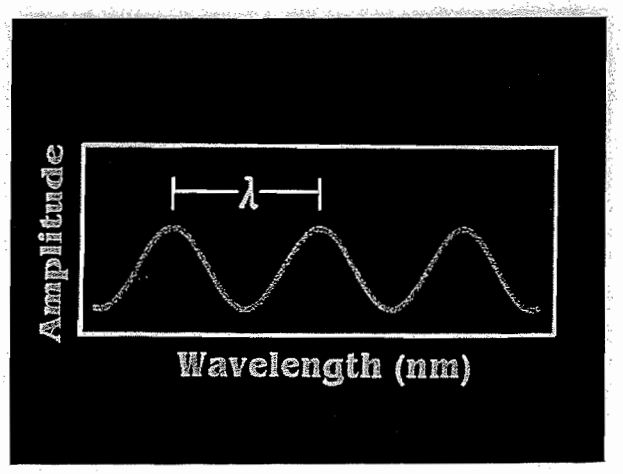
- Screening
- Emission Test
- Validation

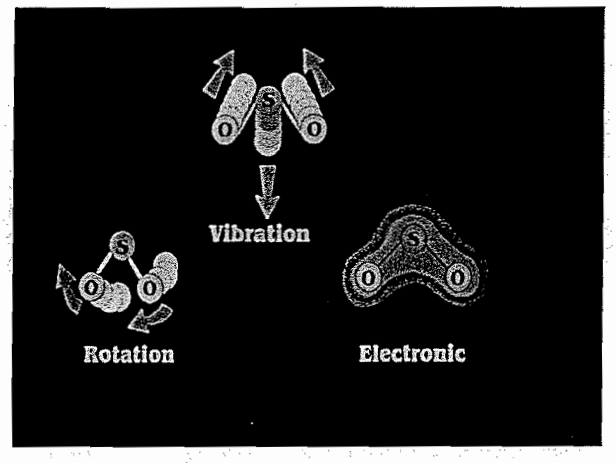
FRM 320 (cont'd)

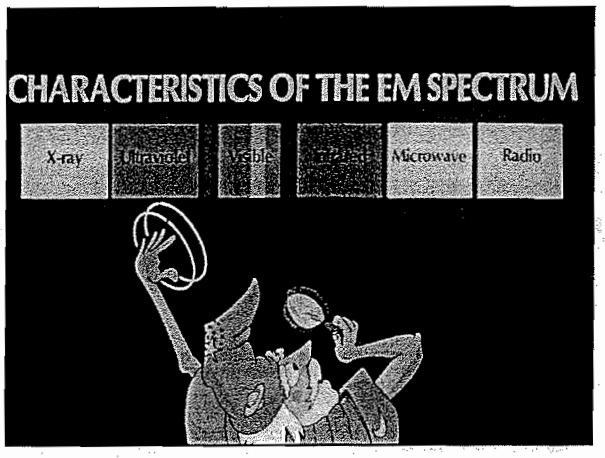
- Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy
  - System involves typical CEM probe and pump to extract the sample to the FTIR analytical bench
  - An IR spectra of the sample is digitized from the FTIR gas cell
  - "Reference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

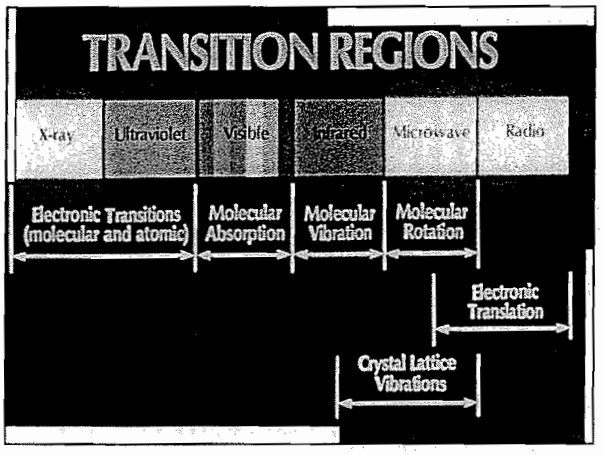
FRM 320

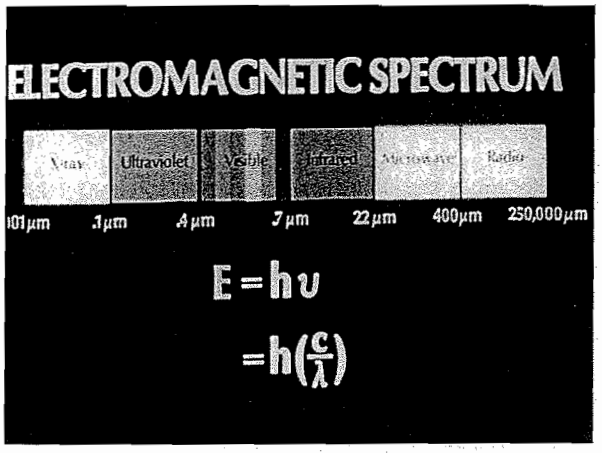
- *"...This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm^{-1} (25 to 2.5 um). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which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

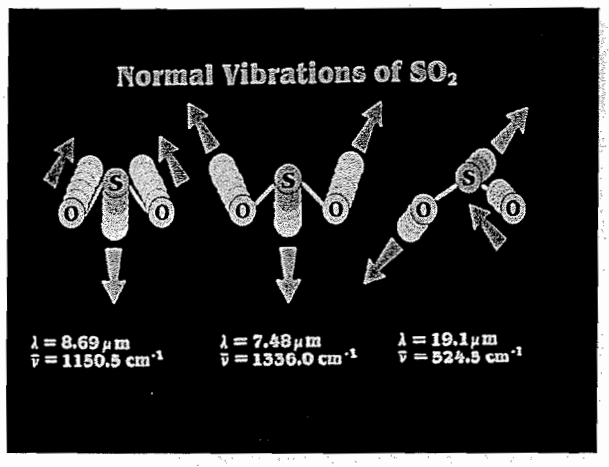


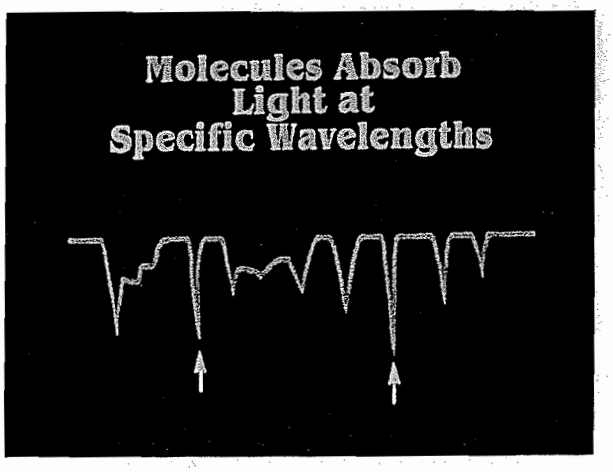

Vibration
Rotation
Electronic

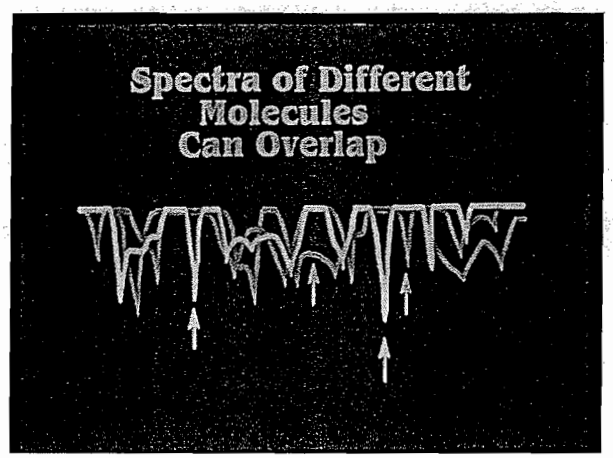

CHARACTERISTICS OF THE EM SPECTRUM
X-ray
Microwave
Radio

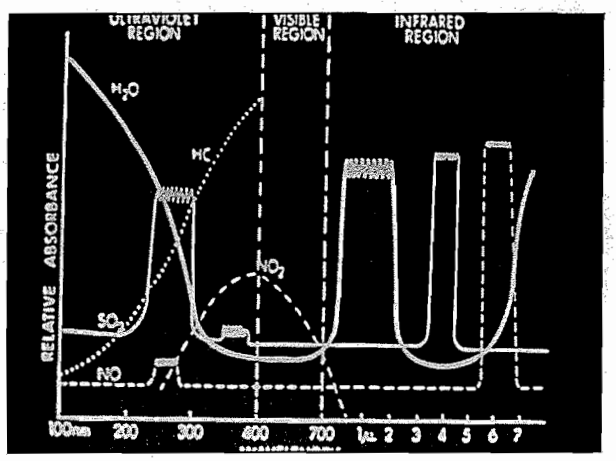

TRANSITION REGIONS
X-ray
Ultraviolet
Visible
Infrared
Microwave
Radio
Electronic Transitions (molecular and atomic)
Molecular Absorption
Molecular Vibration
Molecular Rotation
Electronic Translation
Crystal Lattice Vibrations

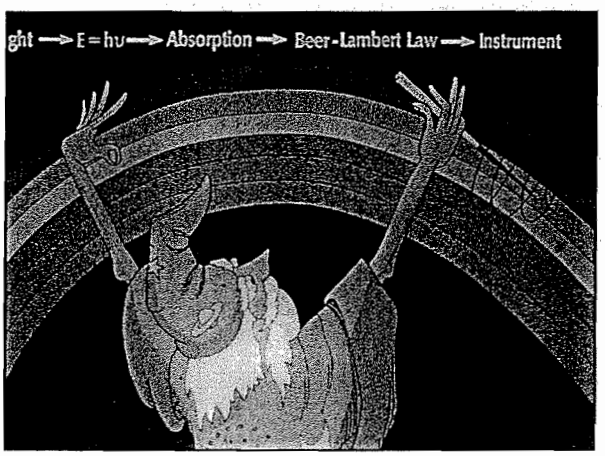

ELECTROMAGNETIC SPECTRUM
Ultraviolet
Visible
Infrared
Radio
.1μm
.4μm
.7μm
22μm
400μm
250,000μm
E = hυ
= h(c/λ)


Normal Vibrations of SO2
λ = 8.69 μm
ν̄ = 1150.5 cm-1
λ = 7.48 μm
ν̄ = 1336.0 cm-1
λ = 19.1 μm
ν̄ = 524.5 cm-1


Molecules Absorb Light at Specific Wavelengths







Beer-Lambert Law

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

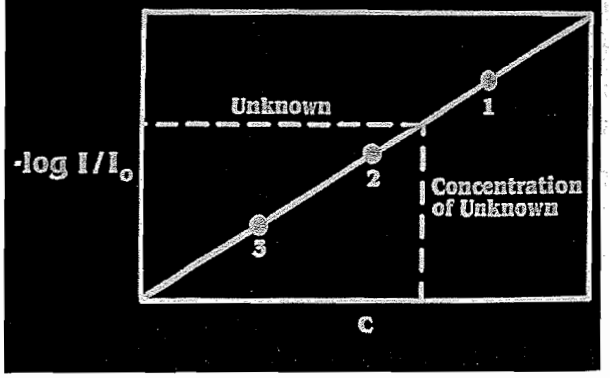
- I = intensity of radiation through the sample
- I_o = intensity of radiation with $c = 0$ or $\alpha = 0$
- α = absorption coefficient
- c = gas concentration
- ℓ = pathlength of radiation through the gas

From Beer-Lambert Law:

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

Direct Relationship

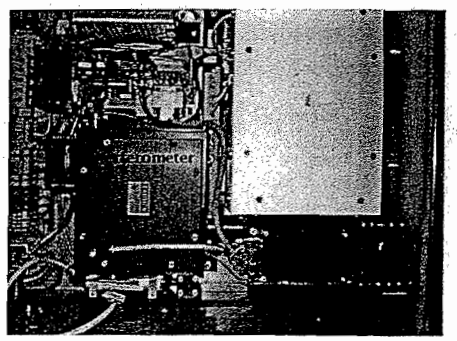
Calibrating a Spectrometer



INFRARED BAND CENTERS OF SOME COMMON GASES

Gas	Band Center (μm)	Wave Number (cm⁻¹)
NO	5.0-5.5	1800-2000
NO_2	5.5-20	500-1800
SO	9-14	700-1250

FTIR Interferometer Cell



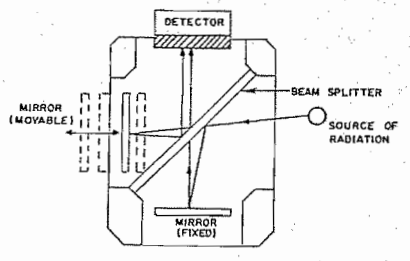
Operation of the FTIR Spectrometer

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

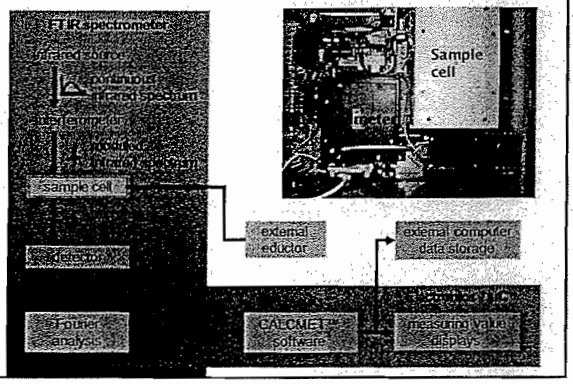
Operation of the FTIR Spectrometer

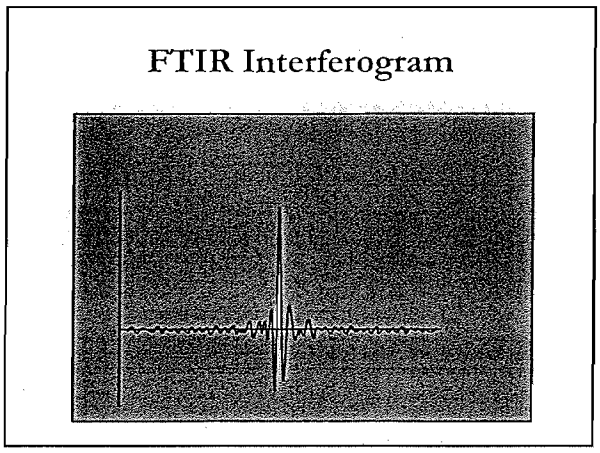
- This produces the interferogram
- The interferogram is generated by the interferometer modulating the infrared beam as the moving mirror is translated
- The modulated frequencies depend on the wavelength of the incident radiation and the velocity of the moving mirror
- The interferogram is produced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

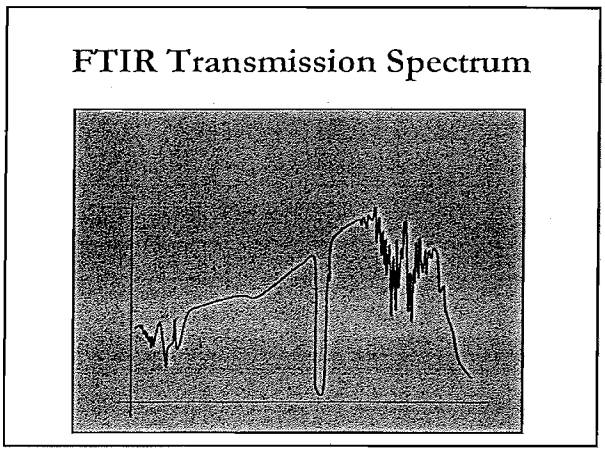
Operation of the FTIR Mirror

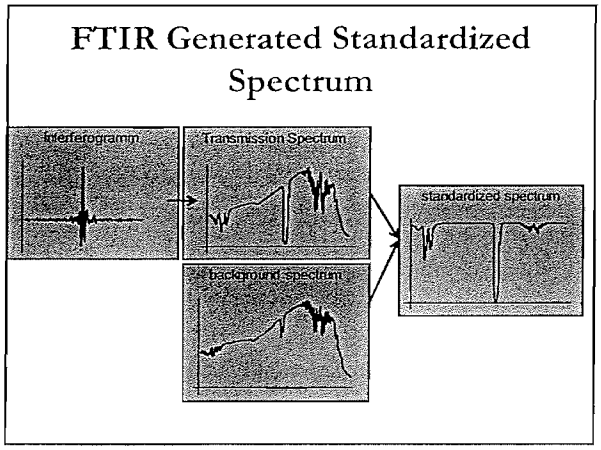


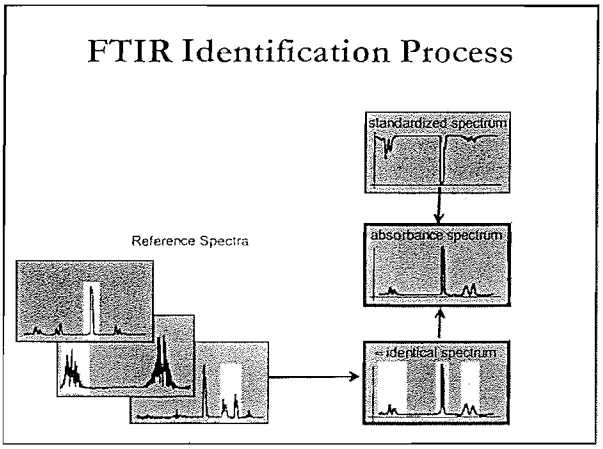
How "Gasmet-USA™" FTIR works

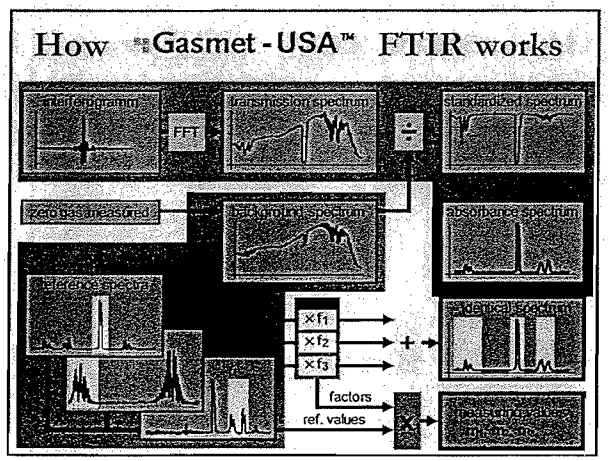



FTIR Interferogram


FTIR Transmission Spectrum


FTIR Generated Standardized Spectrum
interferogramm
Transmission Spectrum
background spectrum
standardized spectrum


FTIR Identification Process
standardized spectrum
Reference Spectra
absorbance spectrum
identical spectrum


How Gasmet - USA™ FTIR works
interferogramm
FFT
transmission spectrum
standardized spectrum
background spectrum
absorbance spectrum
identical spectrum
×f1
×f2
×f3
factors
ref. values

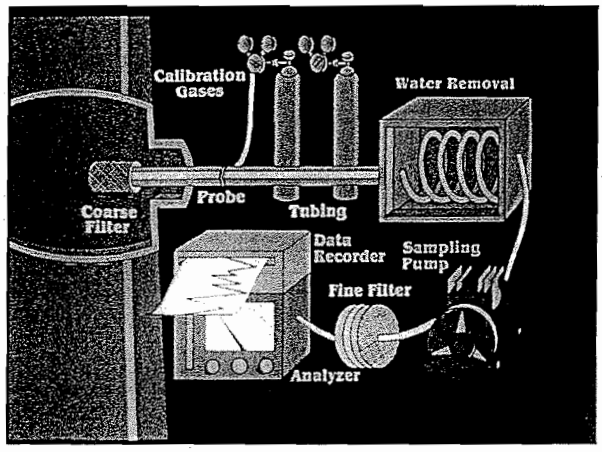

EXTRACTIVE MONITORS

Components of FRM 320

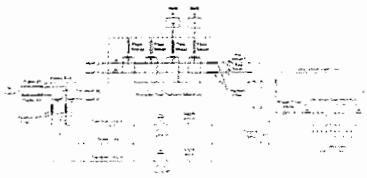
- Sample probe: Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating.
- Particulate filter: A glass wool plug inserted at the probe tip and a filter to remove particulate matter.
- Heat trace sample line: Heated sufficiently to prevent condensation.

Components of FRM 320

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



FRM 320 Extractive FTIR Sampling System



Sampling and Analysis Procedures

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

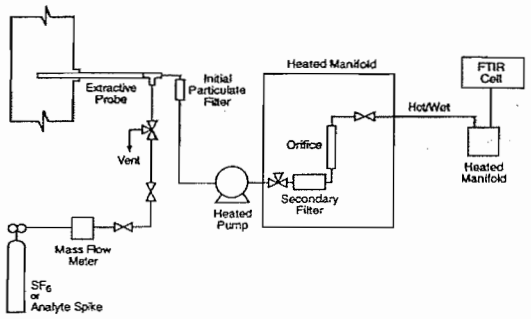
Sampling and Analysis Procedures

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

Sampling and Analysis Procedures

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

FRM 320 FTIR Sampling/Spiking Configuration



Sampling and Analysis Procedures

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

FRM 320 QA Activities

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

FRM 320 QA Activities

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

$$B = S_m - CS$$

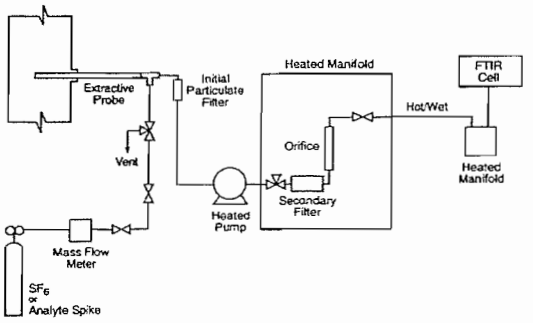
Where:

B = Bias at spike level

S_m = Mean concentration of the analyte spiked samples

CS = Expected concentration of the spiked samples

FRM 320 FTIR Sampling/Spiking Configuration



FRM 320 QA Activities

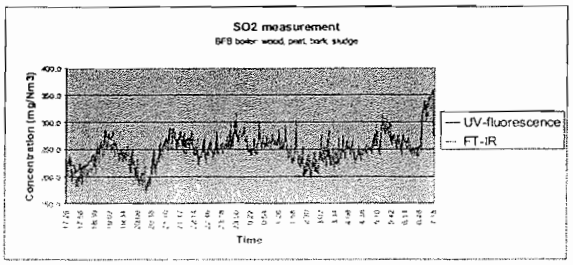
- Method Validation Procedure (Section 13)-
  - Use Method 301 to evaluate statistical significance of the bias.
  - If bias is significant ($0.7 \leq CF \leq 1.3$), then develop a correction factor (CF) is calculated and emission results are multiplied by the CF for final analyte concentration.
  -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

FRM 320 Interferences

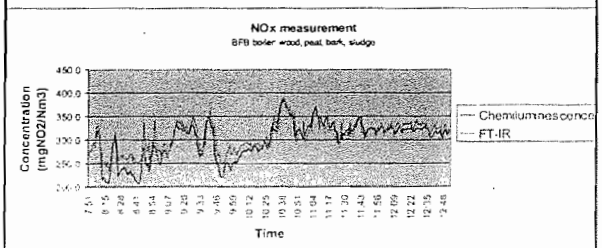
- Analytical Interferences (Background and Sampling)
  - Background interference occurs when unexpected change in background spectra from dirt on lenses, changes in detector sensitivity, changes in infrared source etc. This requires a new background to be generated.
  - Spectral interferences from mostly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

GASMET CEMS APPLICATIONS

Gasmet CEMS and reference measurements:

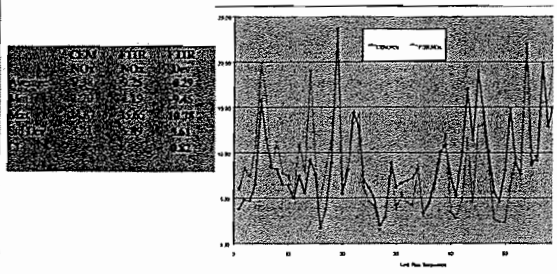


GASMET CEMS APPLICATIONS



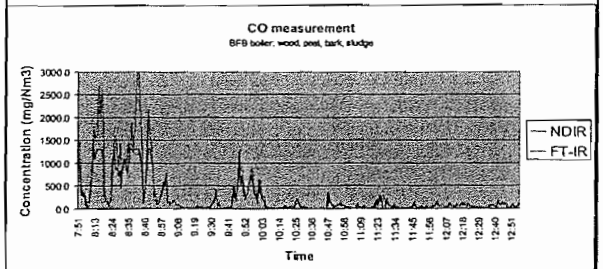
Austin Energy Sandhill

Unit #1 Demonstration Results

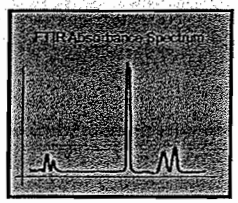


GASMET CEMS APPLICATIONS

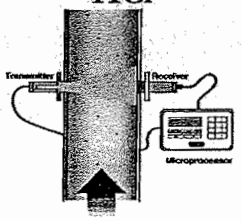
Gasmet CEMS and reference measurements:



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

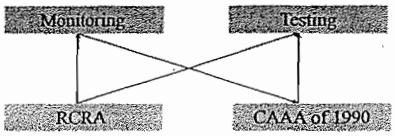


U.S. EPA APTI
Compliance Test and Source Test Observation
CEMs for Hg, PM, Multi-metals, and HCl



Why is EPA Requiring Development of New CEMS?

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



Emission Standards for Existing Incinerators

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

Implications of MACT Standards

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

CAAA of 1990 MACT

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

Monitoring Hierarchy (Three Tiered Approach)

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

What Are the Drivers To Use CEMS?

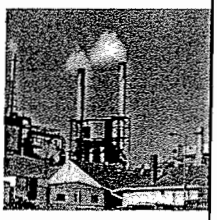
- CEM Emphasis in Draft MACT Regulations
  - Hg, PM, THC, CEMS Required
  - Metal, HCl, and Cl_2 CEMS Optional
  - No VOC, SVOC CEMS Proposed
- CEMS Provide Stakeholder and Regulatory Assurance
- CEM Data Can Be Used For System Optimization
- CEM Technologies Are New and Changing…

Use of CEMS

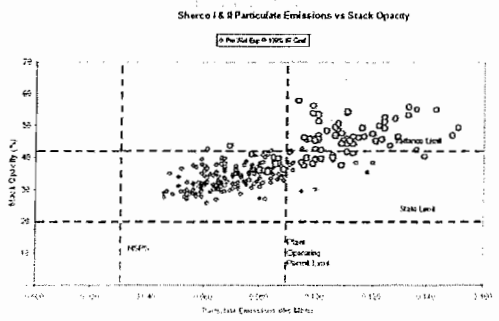
HAP	CEM Available
HCl/Cl_2	Yes
PM	Yes
Hg	Yes?
SVM (Pb, Cd)	Yes??
LVM (Sb, As, Be, Cr)	Yes??
Dioxin/Furan	No
Other Toxic Organics (PIC's)	CO/THC-Yes

Why are PM CEMs Important?

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



Opacity vs PM Emission Conc.

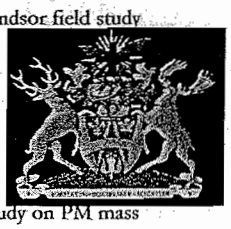


Historical Perspective

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

Historical Perspective (B)

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



- 1980 – Last EPA funded study on PM mass concentration monitor

Historical Perspective (C)

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

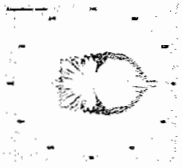
- 1997 – EPA OSWER NODA
  - Second proposed PS-11 in December 1997

Historical Perspective (D)

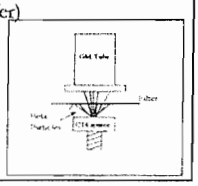
- 1999 – EPA OAQPS EMC does field study

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

Types of PM CEM

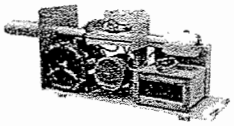


- Light scatter
  - Forward, side, backward
- Beta Gauge
- Probe Electrification (charge transfer)
- Light Extinction (opacity)
- Optical Scintillation



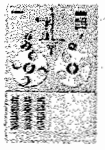
Typical Light Scatter PM CEMs

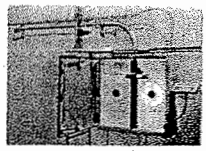
- Sigrist KTNR & CTNR
- Durag DR-300-40
- ESC P5
- Sick RM210, FW 100, FWE 200
- Grimm Technology 6300
- Teledyne ML 300E

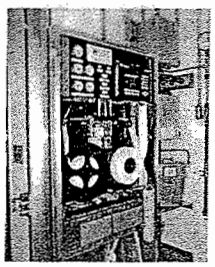


Beta Attenuation PM CEMs

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

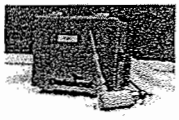


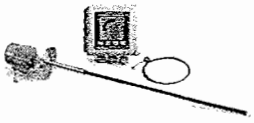




Probe Electrification

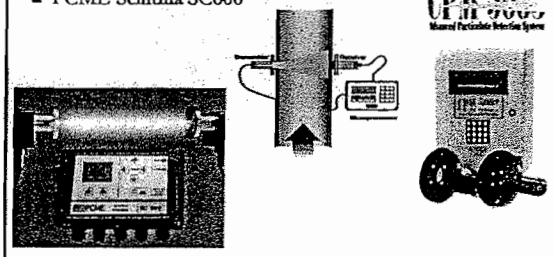
- PCME DustAlert
- Auburn Triboguard
- Codel StakGard
- DataTest 201LP
- FilterSense ProFLOW





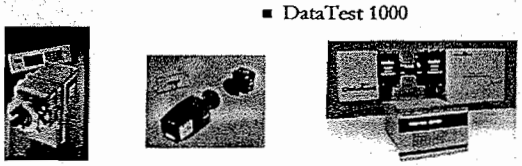
Optical Scintillation

- BHA CPM 5000
- PCME Scintilla SC600



Recent Opacity CEMs

- Land Combustion 4500
- Durag DR-280 and 290
- KVB Enertec MIP
- ML/USI 560
- Rosemount OPM 2000R
- Phoenix OPAC 20/20
- Sick OMD41
- TECO 440
- DataTest 1000



Light Scatter Adv./Disadv.

- Easy to install
- Low maintenance
- Sensitive to low PM concentration
- Not restricted to visible light spectrum
- Low price $10-15,000
- Effective after FF or multi-stage APC
- Measures secondary properties of PM
- Adversely affected by
  - Particle size, density, shape change
- IR light better than visible light
- Measures liquid drops as PM; can't be used after a scrubber
- Must correlate output to RM measurements

Beta Gauge Adv./Disadv.

- Direct measure of PM concentration
- Not affected by particle characteristic changes – use at multi-fuel fired boilers
- Designed to work in wet stack applications – use after scrubber
- Lower cost of ownership
- More difficult to install
- Sample extraction and transport must be done properly
- Expensive $50-75,000

Probe Electrification Adv./Disadv.

- Simple to install
- Sensitive to low PM concentration
- Inexpensive <$5,000
- Effective as bag leak detectors
- Adversely affected by
  - Particle charge (don't use after an ESP)
  - Particle size and velocity changes
- Measures liquid drops as PM; can't be used after a scrubber
- Difficult to correlate to mass emissions

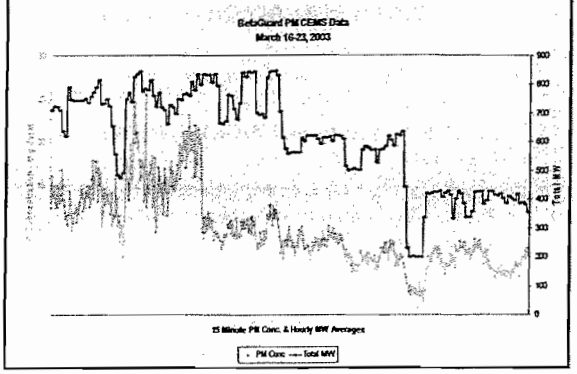
Opacity Adv./Disadv.

- 10,000+ already installed
- Measures opacity
- Measures attenuation of light
- Adversely affected by
  - Particle size, shape, density changes
- Restricted to 500-600nm by PS-1
- Measures liquid drops as PM
- Not sensitive to low PM concentration <20mg/m3
- Cost more than a light scatter PM CEM
- Correlation to mass conc. not linear

Optical Scintillation Adv./Disadv.

- Easy to install
- Low maintenance
- Not affected by dust buildup on windows or misalignment
- Low price $10,000
- Not sensitive to low PM concentration
- Doesn't detect particles < ~ 2μm
- Adversely affected by particle density change
- Measures liquid drops as PM
- Must correlate output to RM measurements

BetaGuard PM Data



CEMS For PM

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

CEMS For Total Mercury

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

CEMS For HCl

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

CEMS For Cl_2

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

CEMS For Multi-Metals

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

CEMS For Organic Compounds

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

PM CEMS

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

PM CEMS Beta Attenuation Vendors

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

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

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

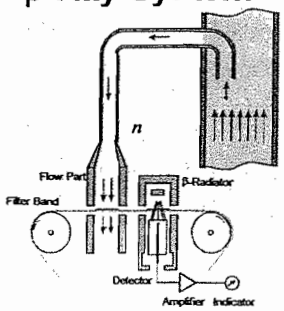
PM CEMS Scintillation Vendors

- BHA Group CPM 5000
- PCME Scintilla SC 600

PM CEMS Other Vendors

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

β-Ray-System



Type: β-Ray

Method: Extractive/Dynamic/Isokinetic

Measurement Value: mg/m³ Dust Concentration

Calibration in mg/m³ possible: yes (VDI 2066) / required

Dependent Values: V/V_0 Isokinetic Measurement required

Isokinetic Measurement: Required

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

Approvals: TÜV / no EPA (opacity required)

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

Dependent Values: V/V_0 Isokinetic Measurement required

Isokinetic Measurement: Required

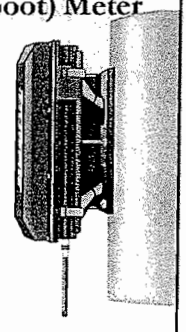
Wet Stack Application: Yes (additional Condensor and Dryer required)

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

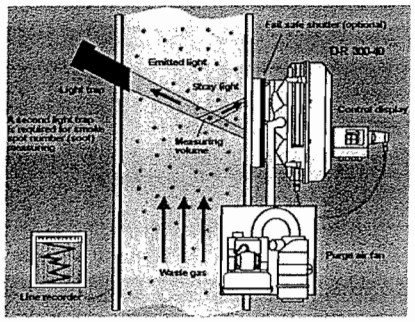
Investment Approx. US$ 60,000.- (100,000.- for wet stacks)

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

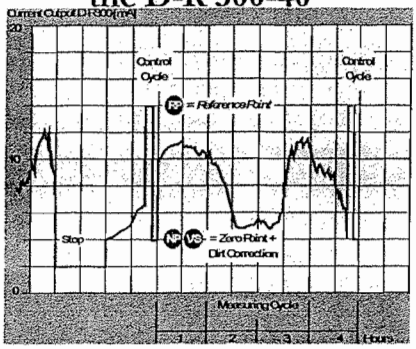
- In-situ measuring directly in the flue gas flow
- Digital evaluation of the measuring signals
- High-performance microprocessor technique and software
- Automatic system tests and correction of measuring values
- Autocalibration in 4-h-cycles
- Optics and electronics in a hermetically sealed housing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



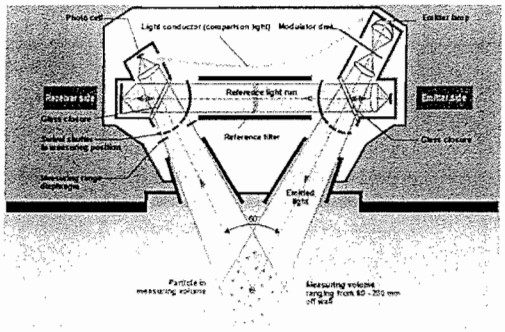
D-R 300 System Components



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



D-R 300 Optics Diagram

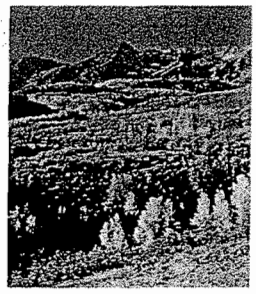


PM Instruments Demonstrated

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

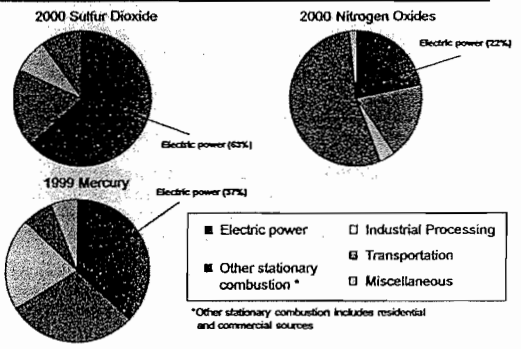
PM CEM User Assessment

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

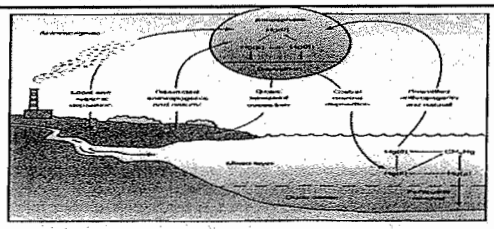


Reducing Power Plant Air Toxics Emissions: Addressing Mercury under Section 112 of the Clean Air Act

Power Sector Emissions



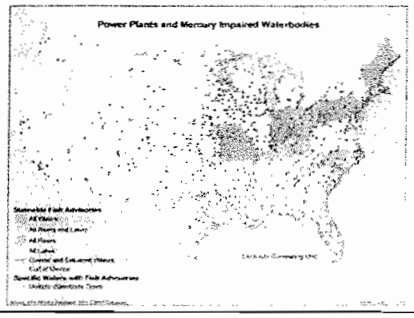
Mercury Deposition is a Nationwide Issue



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

Challenges: Mercury Deposition Impacts

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



Overview of Section 112 MACT Standards

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

Clean Air Act Section 112 - Governs All MACT Rules

- "Emission control achieved in practice by the best controlled sources" establishes 'floor' for new sources
- Average of the top performing 12 percent for existing sources defines the floor emission limit
  - Cost cannot be considered in establishing floor. Can be considered in evaluating whether controls beyond the floor are appropriate
- Allows for subcategories
- Emissions standard applicable to each source
  - Requires compliance within 3 years, with possible 1-year extension
- Section 112 does not allow trading between facilities to meet the standard
  - Averaging among units at a given facility can be considered

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

- **1990 Amendments required**
  - Study of hazards to public health of HAP emissions from electric utility steam generating units
  - Determination on whether regulation necessary and appropriate
  - Study to have been done by November 1993
- **1990 Amendments also required**
  - Study of mercury emissions from all sources
- **Initiated data collection for mercury**
  - 1999 Information Collection Request (ICR)
  - 112(n)(1)(A) determination delayed until ICR completed
- **National Academy of Science (NAS) report on methylmercury**
  - Mandated by Congress
  - Released in July 2000
    - Confirmed EPA's RfD for methylmercury (0.1 µg/kg/day)

Summary of Utility MACT Determination

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

Control Technologies for Power Plant Mercury Emissions

- From 1999 data, approximately 1/3 of the mercury in coal was being captured as a 'co-benefit' of SO_2 or NO_x control – not intentionally as mercury control
  - Capture by existing equipment ranges from 0 to >95%
  - Capture dependent on coal type
  - Capture dependent on installed air pollution control device
- Activated carbon injection - ACI - (and other new technologies) and optimization of existing technologies could greatly enhance mercury capture and control
  - Full-scale demonstrations completed that quantify removal rates for ACI for bituminous and subbituminous coals
    - Test durations range from a few hours to less than 2 weeks
    - Intermittent removals up to 90% demonstrated; continuous removals averaged approximately 80%
  - No full-scale ACI facility in operation

Other Utility HAP Issues

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

Public Outreach/Participation

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

Issues for Utility MACT

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

Summary

- Under settlement agreement, MACT rule must be proposed on or before December 15, 2003
  - Promulgation: December 15, 2004
  - Compliance: December 17, 2007
- Public comment period will follow publication in the Federal Register
- Public Hearings will undoubtedly be requested
  - Single hearing?
  - Multiple hearings in different parts of the country?

Source Monitoring for Hg

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

Source Monitoring for Mercury

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

CEMS For Hg Monitoring

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

Summary of Testing

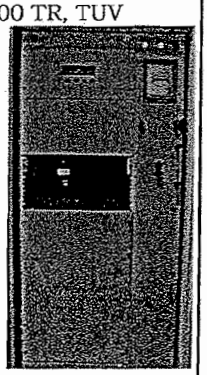
Test No.	Total Hg	Elemental Hg	Speciated Hg
1	20.3	18.7	1.6
2	23.2	1.0	22.2
3	16.1	3.1	13.0
4	21.9	2.5	19.4
5	16.0	6.4	9.6
6	18.8	7.3	11.5

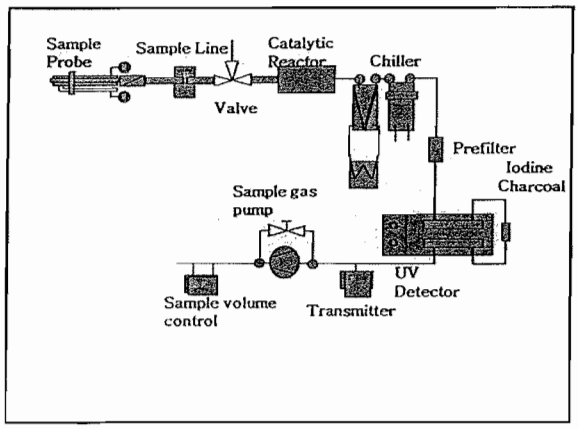
Mercury CEMS

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

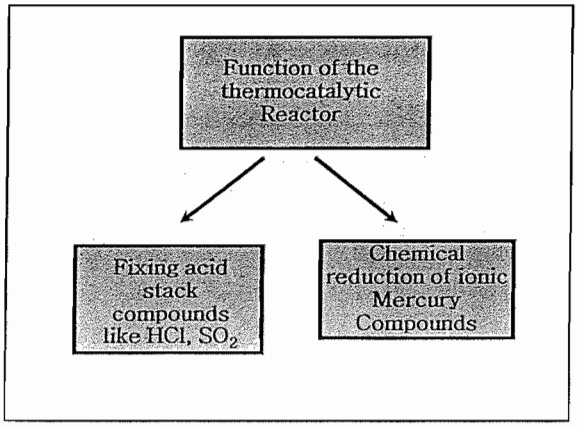
Total Mercury CEM HM 1400 TR, TUV

Maintenance cycle: 3 Month
Measuring range : 0~45 to 0~2000 μg/Nm^3
Lowest detection limit:0,5 μg/Nm^3
Sample treatment : Thermocatalytic
Signal output : 4~20 mA, μg / Nm^3 dry
Controller : Omron PLC
Remote control : via DMS 500 or DMS 285
Failure control: Memory stored
Interference : None
Detector : Dual Beam Photometer
Sample probe : M & C, SP 2000

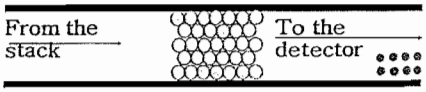




Thermocatalytic Reactor



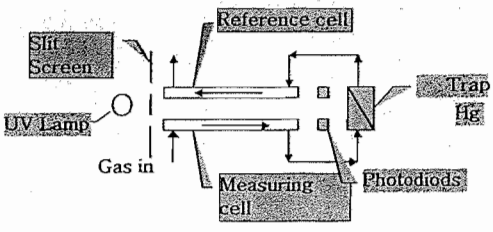
The way how the reactor works



- SO_2
- HCl
- NO
- x

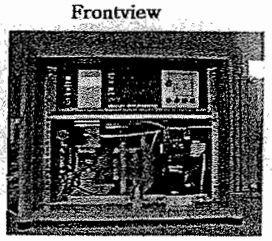
- Hg^{n+}, ionic Mercury
- Hg^0, elemental Mercury

The Dual Beam UV Detector

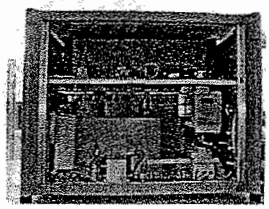


The Portable Version

Frontview



Rear View



Project Overview

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

Phase III Test Design

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

Test Conditions

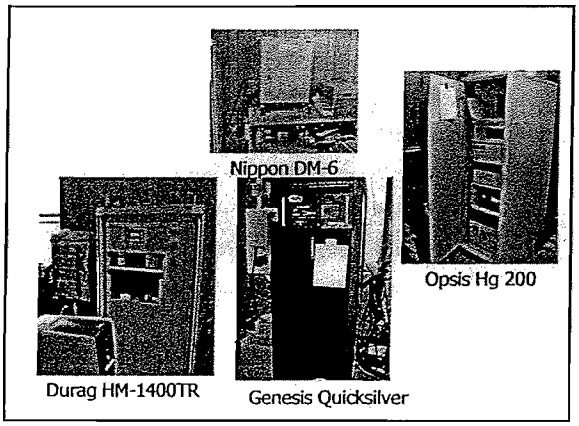
- 600 MW coal-fired power plant (2 yr old)
- Powder River Basin coal
- NH_3 injection, SCR, spray dryer, fabric filter
- 2-6 ug/m^3 mercury (expected)
- 1-10 ug/m^3 mercury (observed)
- 35-50 ppm SO_2

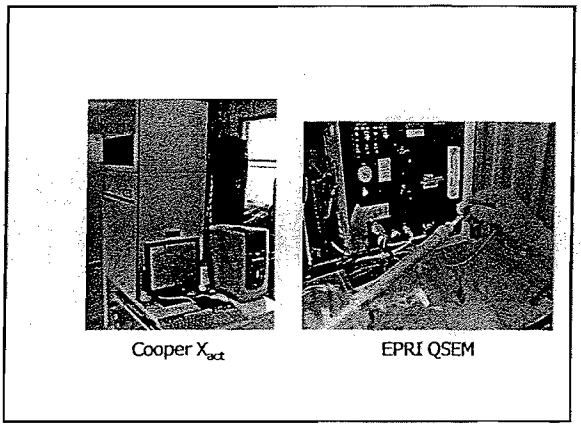
CEMS Selection

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

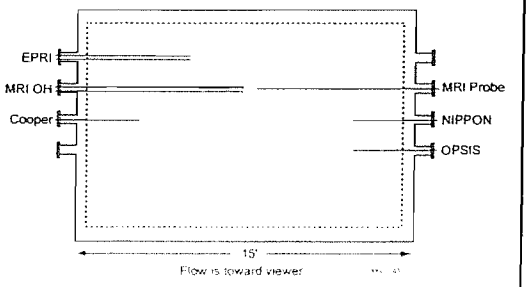
Systems Evaluated

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



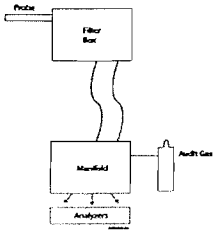


Sampling Configuration



MRI Sampling System Configuration

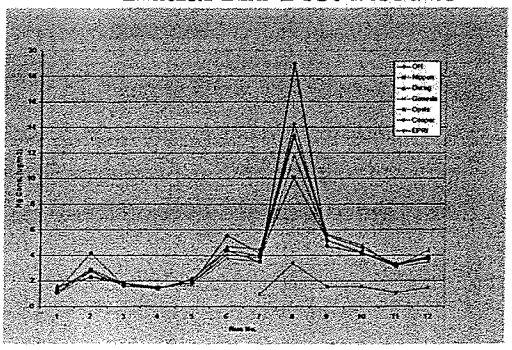
- Heated probe, filter
- Heated sample line
- Heated manifold
- Teflon PFA
- 360°F (300°F probe)
- Flowrate 5-10 lpm
- Connected to Durag, Genesis, Cooper X_{act} (Nippon, OPSIS on own separate lines)



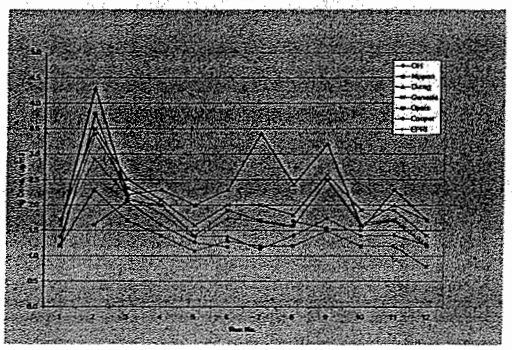
Audit Gas Checks

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

Initial RA Test Results



Final RA Test Results



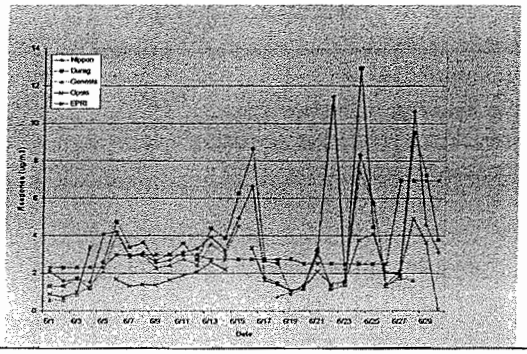
Relative Accuracy Results

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

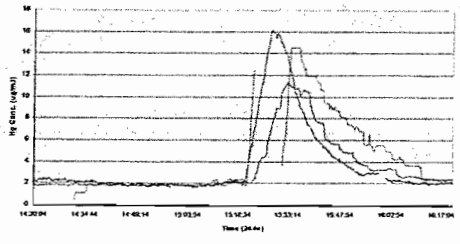
Long-term CEMS Operations

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

CEMS Daily Averages - June



'Transients' in Hg Concentration



Summary Observations

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

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

CEMS For Hg Conclusions

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

Source Monitoring for HCl/Cl_2

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

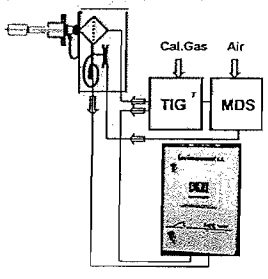
Acid Gas CEMS Monitoring Technologies

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

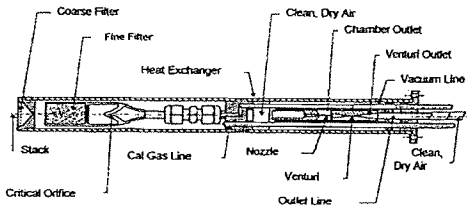
Acid Gas CEMS Vendors (IR/GFC)

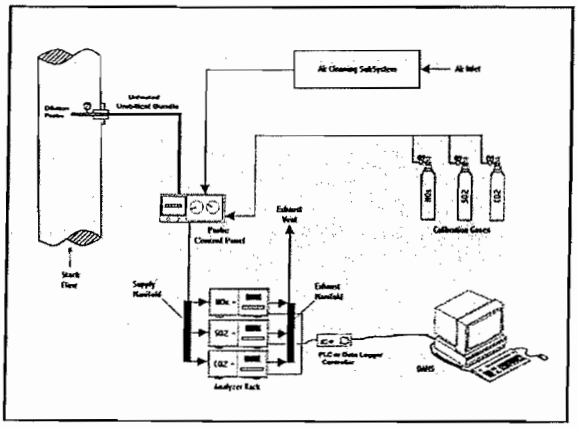
- Altech Environment USA (Environment SA)
  - Extractive/In-Situ/IR/GFC
- Air Instruments and Measurements (AIM)
  - Extractive/In-Situ/IR/GFC
- Thermo Environmental
  - In-Situ/Dilution Probe/IR/GFC

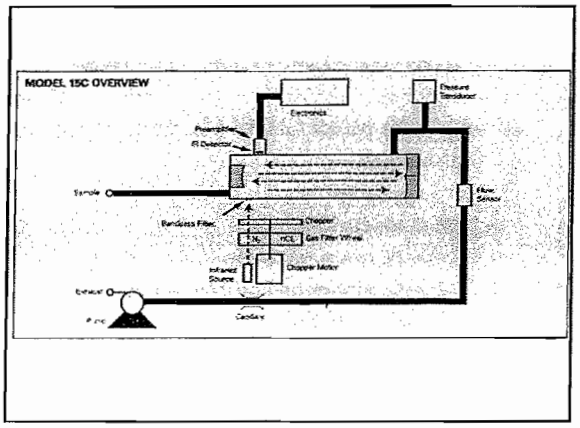
Environment SA MIR 9000 Ext/IR/GFC

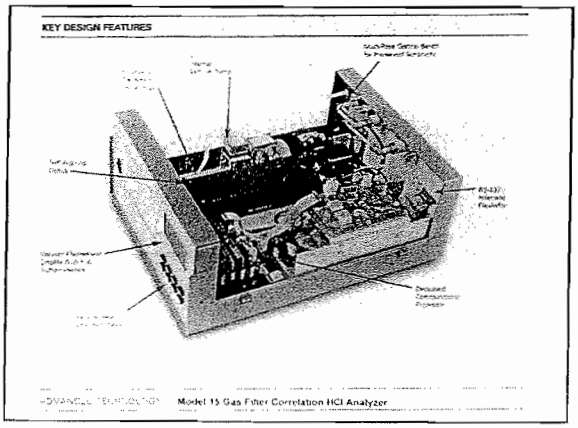


- High temp probe
- Perm. sampling
- Rem. control cable:
- Auto. Cal.
- Air dryer
- MIR9000 (IR/GFC)
- SO_2, NO, NO_2, CO, CO_2, HCl, HF









Acid Gas CEMS Vendors (Ion Selective Electrode Based)

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

Acid Gas CEMS Vendors (Ion Mobility Spectroscopy)

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

Acid Gas CEMS Vendors (UV/FTIR Spectroscopy Based)

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

Multi-Metals (MM) CEMS

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

Multi-Metal CEM Summary

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

Current Detection Limits (ug/m^3)

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

Current Detection Limits (ug/m^3)

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

Current Detection Limits (ug/m^3)

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

General Technology Evaluation

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

Conclusions

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