United States
Environmental
Protection Agency

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

EPA XXX/X-XX-XXX
May 2023

EPA's APTI

Course #450/468

Monitoring Compliance Test And Source Test Observation

Student Workbook

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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 #450/#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, jwinberrv@mindspring.com , 919-467-2785, was awarded the contract to update EPA's APTI Course #450/#468. Mr. Winberry is the author of this Student Workbook (SW) 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 #450/#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 #450/#468

Monitoring Compliance Test and Source Test Observation

Student Workbook (SW)

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The updated Course #450/#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 #450/#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 #450/#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 each of the Sessions and lessons presented in APT! Course #450/#468.

I. Background

Over the last several years, public awareness of air pollution and its sources has increased steadily. Specifically, since the passage of the Clean Air Act Amendments (the Act) of 1990 and the implementation of EPA's maximum achievable control technology (MACT) program, more emphasis has been placed on local, State, and Federal agencies to keep the public informed on health effects of various air pollutants and their levels of exposure. This awareness has required industry to become accountable for air pollution emissions as part of their source's compliance strategy and regulatory agencies to become knowledgeable of the methodology used to quantify reported emissions.

Traditionally, air pollution control agencies require all sources to quantitate their emissions in order to demonstrate compliance. To insure that the source test methods utilized to demonstrate compliance are performed according to EPA guidelines, regulatory agencies observe stack test to document compliance with the methodology. This has meant that sources must know how to properly sample and report emissions using EPA reference methods and that regulatory agencies must know how to properly observe these test to insure that reliable and accurate data is gathered and reported.

In addition, with the passage of the Act and Title IV, Acid Rain, those fossil-fueled-fired-steam generators (FFFSG) covered must report emissions in units of pollutant mass rate (pmr) as part of EPA's emission trading program. This required the installation and certification of velocity monitors if the continuous emission monitoring system (CEMS) data was to be used as part of EPA's market base-trading program. These new regulatory requirements have now required Agency personnel to know how to observe and verify the proper use and implementation of Federal Reference Methods 2F, 2G, and 2H in certification of the velocity CEMS as part of a source's market base-trading emission program.

Consequently, the Act has required regional, state, and local air pollution control agencies to better understand the stack test methodologies that are used to quantitate air pollution emissions from industrial sources. Agencies see a need to provide training to it's personnel on how to properly observe stack test used to meet regulatory compliance for criteria and hazardous air pollutants (HAPs).

II. Course Objective

The objective of EPA's APTI Course #450/#468 is to provide Agency personnel the needed background information, checklist, and guidance associated with EPA methodologies involving stack test for characterizing and quantifying criteria and HAPs from industrial sources. This course will address Federal Reference Methods (FRMs)1-5 (isokinetic stack testing and stack test basics), FRMs 2F, 2G, and 2H (velocity), stack testing for volatile organic compounds (FRMs 18, 25, 25A/B), SO_2 (FRMs 6, 6A, and 8), NOx (FRMs 7, 7C), dioxin/furans and PCBs (FRM 23), heavy metals (FRM 29), and instrumental (FRMs 3A, 6C, and 7E).

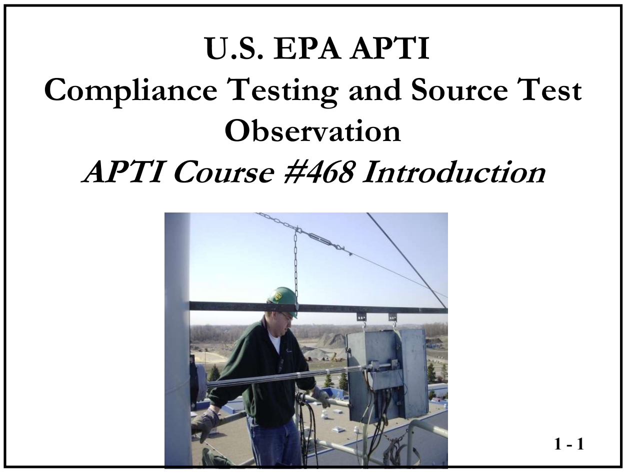
The course will present standardized stack test methodology for sampling and analysis of air pollutants as identified in the Code of Federal Regulations (CFR), Part 60, Appendix A. In addition, information will be presented on EPA's stack test monitoring programs associated with PM-10 (Methods 201 A/B) and condensable particulate (Method 202) monitoring from CFR 51 Subpart M. Specific source test checklists will be demonstrated during the presentation for each test methodology as part of the course. Participants will learn how to use the checklist in performing source test observations, how to observe mandated QA/QC requirements associated with each methodology, and how to use source test databases available to the air pollution scientist.

At the end of this course, the agency personnel will gain an understanding of the unique source test methods used to accurately characterize air pollutant emissions from industrial sources. The agency personnel will learn about EPA's programs that require characterization of air pollutants from industrial sources utilizing FRMs.

III. Course Manuals

Course presentations and videos will be supported by four manuals. They are:

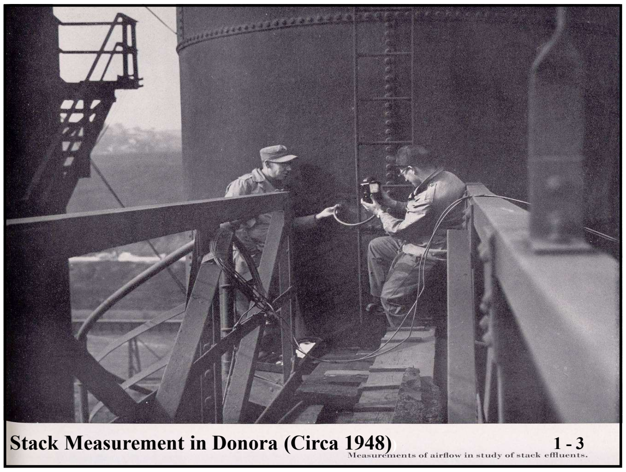
- **#468 Student Workbook (Hard Copy):** The updated Student Workbook (SW) contains copies of selected slides from each of the lecture presentations, and **Agency Inspector Checklist.**
- **#468 Stack Test Manual (Flash Drive):** The Stack Test Manual contains full copies of selected stack test sampling and analytical methods found in the CFR, Part 60, Appendix A, and SW-846, Standard Methods.
- **Apex Instruments Federal Reference Method 5 Operational Manual:** The Federal Reference Method 5 Operation Manual is a document describing specifically the construction and operation of Federal Reference Method 5 stack testing sampling train. **http://www.apexinst.com/cms/wp-content/uploads/2015/03/Model-500-Series-Manual-Method-5.pdf**.



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

Compliance Testing and Source Test Observation

IDEM: Air Compliance: Stack Tests (in.gov)

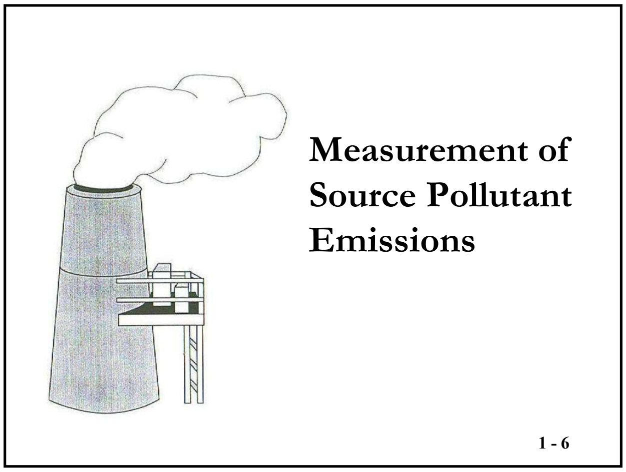


Stack Measurement in Donora (Circa 1948)

Measurements of airflow in study of stack effluents.

Source Sampling At a Scrap Metal Dryer Circa 1970's

Source Sampling At a Scrap Metal Dryer Circa 1970's



Measurement of Source Pollutant Emissions

Measurement Methods of Source Pollutant Emissions

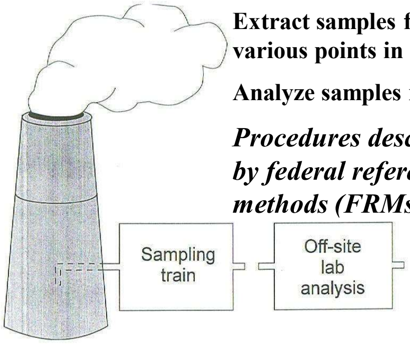
1. Stack testing
   - Manual methods
   - Instrumental methods
2. Continuous Emission monitoring
   - Instrumental methods
3. Remote Sensing

Manual Sampling

Extract samples from various points in stack.

Analyze samples in lab.

Procedures described by federal reference methods (FRMs)



Manual vs. Instrumental

Manual

Anything related to PM and some gases

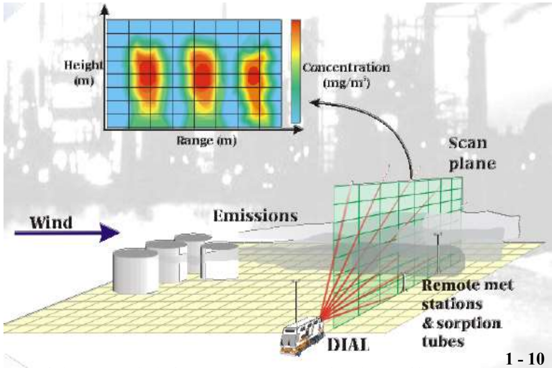
- **PM**
- **PM_{10}**
- **Metals**
- **Semi-volatile**
- **Organisms**
- **HCL & H2SO4**

Instrumental

Anything related to gases

- **NO_X**
- **SO_2**
- **CO**
- **Opacity**
- **Volatile Organics**
- **O_2**
- **CO_2**
- **VOC**
- **H_2S**

Remote Sensing



EPA Handbook: Optical and Remote Sensing for Measurement and Monitoring of Emissions Flux of Gases and Particulate Matter

EPA Manual Federal Reference Methods (FRMs)

Used for source compliance testing

Describe actual testing procedure

Found in Code of Federal Regulations

Agency's Purpose for Stack Testing

Compliance Evaluation

Regulatory Support

Emission Inventory

Method Development

Certify CEM's

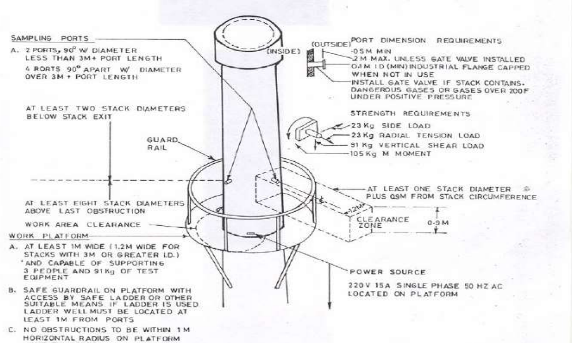
Industry's Purpose for Stack Testing

Determine Control Device Efficiency
Evaluate process operation
Design new process and equipment
Demonstrate compliance

Types of Emission Points Tested

Stacks
Process vents
Building exhausts
Tank emissions
Fugitive emissions

Typical Sampling Point Provisions



Four H's of Source Testing

High -- up to 300 feet
Hot -- stacks up to 2000
Heavy -- sampling equipment
Hazardous -- noxious gases

Source Testing a Wet Mill Corn Dryer

Something Source Testers use a lot of?

Types of Emissions Tested

Particulate matter (Total PM; PM_{10} ;$PM_{2.5}$)

Inorganic gases

Organic gases and vapors

Combinations of solids and gases

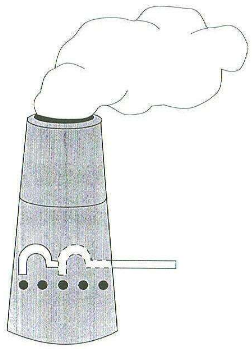
Where Methods are Found

U.S. EPA test methods (CFR)

State Implementation Plans (SIPs) and regulations

Industrial and trade associations, Publications

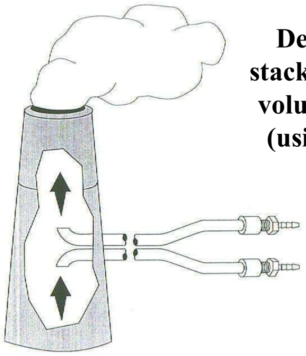
http://www.epa.gov/emc/



Method 1

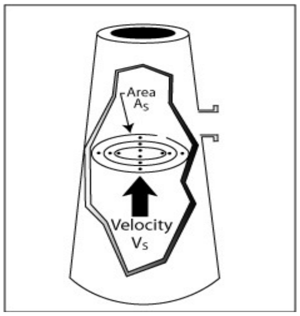
Selection of sampling traverse points

Method 2



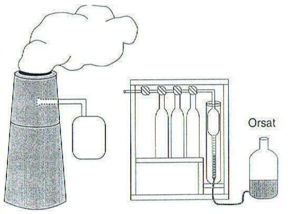
Determination of stack gas velocity and volumetric flow rate (using Type S pitot tube)

Distributed Sampling Points



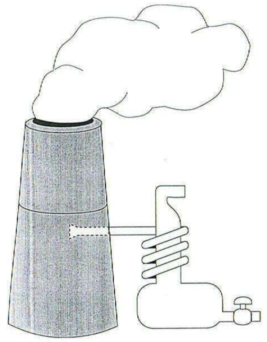
Method 3

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



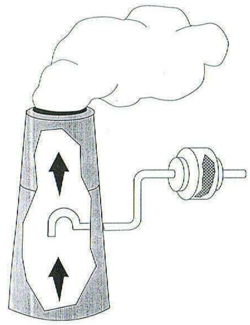
Method 4

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



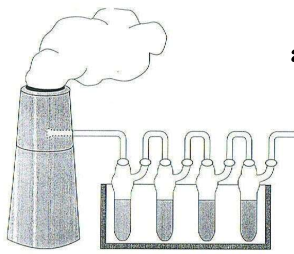
Method 5

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



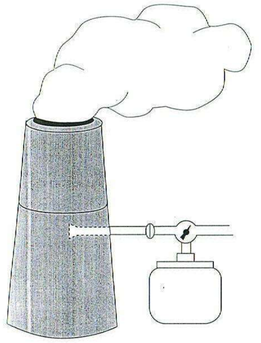
Method 6

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



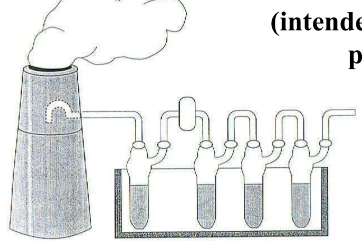
Method 7

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 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

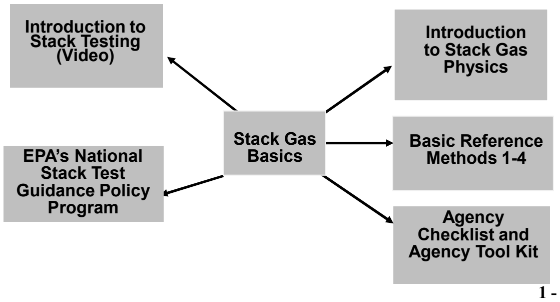
Instruct Agency personnel in the proper observation and measurement techniques for quantifying particulate and gaseous stack emissions

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



Stack Gas Basics

Introduction to Stack Testing (Video)

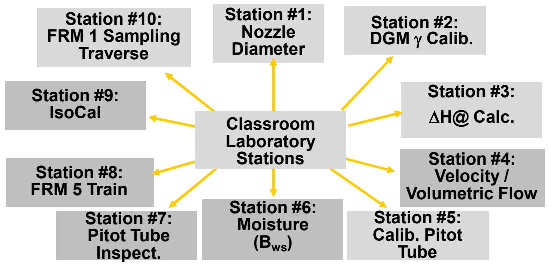
EPA's National Stack Test Guidance Policy Program

Introduction to Stack Gas Physics

Basic Reference Methods 1-4

Agency Checklist and Agency Tool Kit

What We Will Cover



Classroom Laboratory Stations

Station #1: Nozzle Diameter

Station #2: DGM γ Calib.

Station #3: ΔH@ Calc.

Station #4: Velocity / Volumetric Flow

Station #5: Calib. Pitot Tube

Station #6: Moisture (B_{ws})

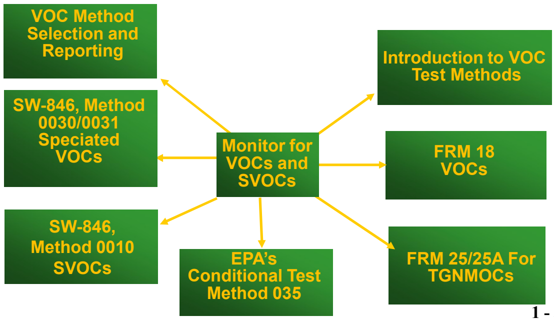
Station #7: Pitot Tube Inspect.

Station #8: FRM 5 Train

Station #9: IsoCal

Station #10: FRM 1 Sampling Traverse

What We Will Cover



Monitor for VOCs and SVOCs

VOC Method Selection and Reporting

Introduction to VOC Test Methods

SW-846, Method 0030/0031 Speciated VOCs

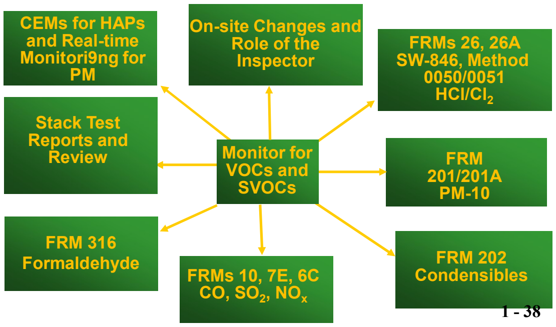
FRM 18 VOCs

SW-846, Method 0010 SVOCs

EPA’s Conditional Test Method 035

FRM 25/25A For TGNMOCs

What We Will Cover



Monitor for VOCs and SVOCs

CEMs for HAPs and Real-time Monitori9ng for PM

On-site Changes and Role of the Inspector

FRMs 26, 26A SW-846, Method 0050/0051 HCl/Cl$_2$

Stack Test Reports and Review

FRM 201/201A PM-10

FRM 316 Formaldehyde

FRMs 10, 7E, 6C CO, SO$_2$, NO$_x$

FRM 202 Condensibles

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

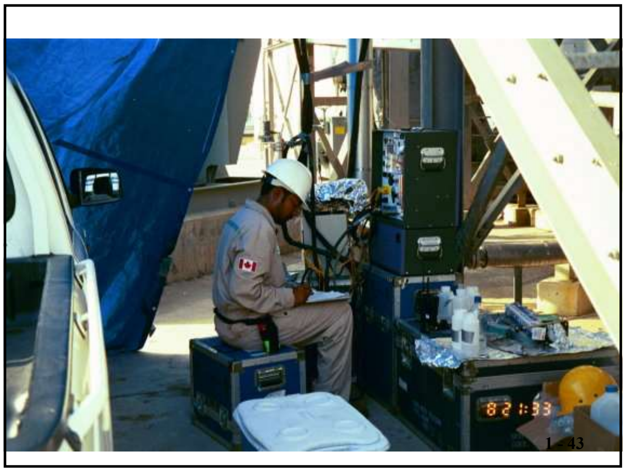
Federal Register containing FRM 1-5

Course CD- Contains Over 90 Stack Testing Entries

Role of the Inspector?

Regulatory Science vs. Measurement Science

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



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?

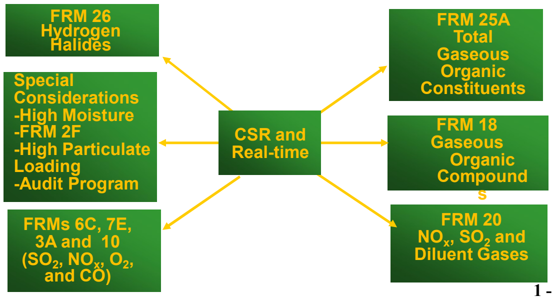
https://www.govinfo.gov/content/pkg/FR-2009-07-22/pdf/E9-17402.pdf
https://www.govinfo.gov/content/pkg/FR-1997-10-06/pdf/97-26443.pdf
https://www.epa.gov/sites/production/files/2016-02/documents/flexible_approaches_to_environmental_measurement_-_reaffirmed_112015.pdf

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 stricter than the EPA program?

Constant Sampling Rate (CSR) and Real-time Methods



CSR and Real-time

FRM 26 Hydrogen Halides

Special Considerations
-High Moisture
-FRM 2F
-High Particulate Loading
-Audit Program

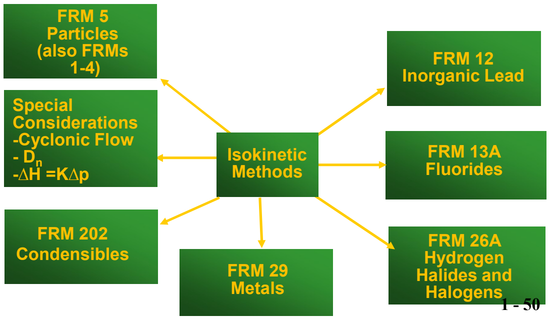
FRMs 6C, 7E, 3A and 10 (SO_2, NO_x, O_2, and CO)

FRM 25A Total Gaseous Organic Constituents

FRM 18 Gaseous Organic Compounds

FRM 20 NO_x, SO_2 and Diluent Gases

Isokinetic Sampling Rate Methods



Isokinetic Methods

FRM 5 Particles (also FRMs 1-4)

Special Considerations
-Cyclonic Flow
- D_n
-$\Delta H = K\Delta p$

FRM 202 Condensibles

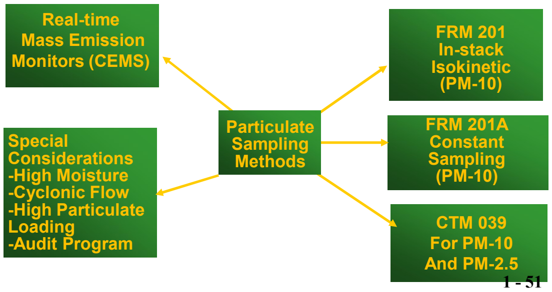
FRM 29 Metals

FRM 12 Inorganic Lead

FRM 13A Fluorides

FRM 26A Hydrogen Halides and Halogens

Particulate Sampling Methods



Particulate Sampling Methods

Real-time Mass Emission Monitors (CEMS)

Special Considerations
-High Moisture
-Cyclonic Flow
-High Particulate Loading
-Audit Program

FRM 201 In-stack Isokinetic (PM-10)

FRM 201A Constant Sampling (PM-10)

CTM 039 For PM-10 And PM-2.5

Stack Test Methods

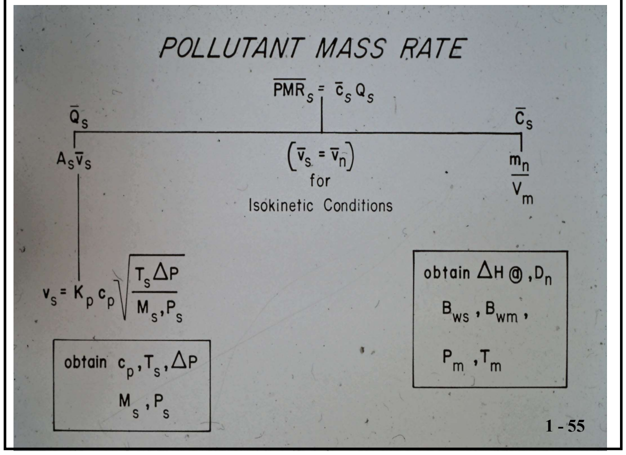
Why Develop Stack Test Methods and What is the Driving Force In The United States?

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)



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

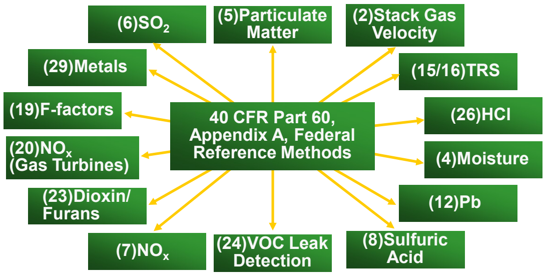
Where Do We Find the Test Methods?

www.epa.gov/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

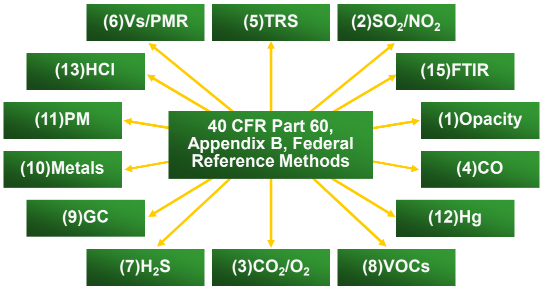

40 CFR Part 60, Appendix A, Federal Reference Methods
(6)SO_2
(5)Particulate Matter
(2)Stack Gas Velocity
(15/16)TRS
(26)HCl
(4)Moisture
(12)Pb
(8)Sulfuric Acid
(24)VOC Leak Detection
(7)NO_x
(23)Dioxin/ Furans
(20)NO_x (Gas Turbines)
(19)F-factors
(29)Metals

Regulations

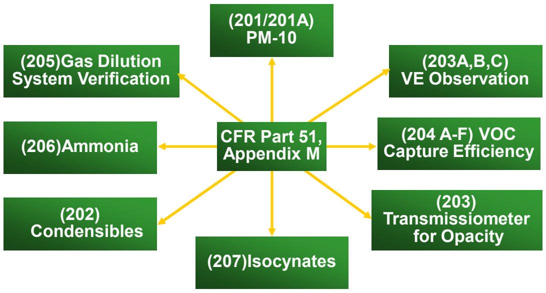
40 CFR Part 60, Appendix B
Performance Specification Test (PST) Methods (00 Series)

40 CFR Part 51, Appendix M
State Implementation Plan (SIP) Methods (200 Series)

Performance Specification Test (PSTs)-00 Series


40 CFR Part 60, Appendix B, Federal Reference Methods
(6)Vs/PMR
(5)TRS
(2)SO_2/NO_2
(15)FTIR
(1)Opacity
(4)CO
(12)Hg
(8)VOCs
(3)CO_2/O_2
(7)H_2S
(9)GC
(10)Metals
(11)PM
(13)HCl

State Implementation Plan (SIP)-200 Series

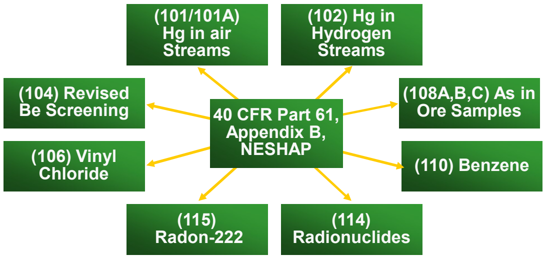

CFR Part 51, Appendix M
(201/201A) PM-10
(203A,B,C) VE Observation
(204 A-F) VOC Capture Efficiency
(203) Transmissiometer for Opacity
(207)Isocynates
(202) Condensibles
(206)Ammonia
(205)Gas Dilution System Verification

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)

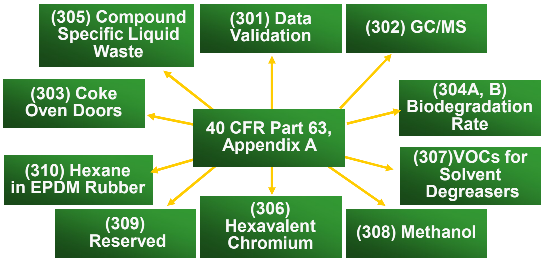
National Emission Standards For Hazardous Air Pollutants (NESHAPs)- 100 Series



40 CFR Part 61, Appendix B, NESHAP

- (101/101A) Hg in air Streams
- (102) Hg in Hydrogen Streams
- (104) Revised Be Screening
- (108A,B,C) As in Ore Samples
- (106) Vinyl Chloride
- (110) Benzene
- (115) Radon-222
- (114) Radionuclides

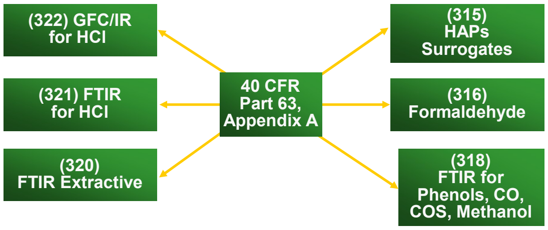
Maximum Achievable Control Technology (MACT)-300 Series



40 CFR Part 63, Appendix A

- (305) Compound Specific Liquid Waste
- (301) Data Validation
- (302) GC/MS
- (303) Coke Oven Doors
- (304A, B) Biodegradation Rate
- (310) Hexane in EPDM Rubber
- (307)VOCs for Solvent Degreasers
- (309) Reserved
- (306) Hexavalent Chromium
- (308) Methanol

Maximum Achievable Control Technology (MACT)-300 Series



40 CFR Part 63, Appendix A

- (322) GFC/IR for HCl
- (315) HAPs Surrogates
- (321) FTIR for HCl
- (316) Formaldehyde
- (320) FTIR Extractive
- (318) FTIR for Phenols, CO, COS, Methanol

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 " Approved Alternative"

Compliance Methods for specific applications with approval from EPA

Categories

Category C:
"Conditional Methods" evaluated by EPA; methods may be used by state/local in conjunction with federal enforcement; must be "Alternative Method" to be used as meeting 40 CFR Parts 60, 61, and 63

Categories

Category D: Methods which may be useful in limited applications until more supporting information is provided; "gap filling" methods (Preliminary Methods)

Categories

Category E: "Idea Box" contain method concepts intended to promote information exchange

These methods generally have had no EPA review or analysis

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)

Example Category Stack Test Methods

Category E (Idea Box):
Sampling and analysis for phosgene emissions from stationary sources

All categories of methods found on

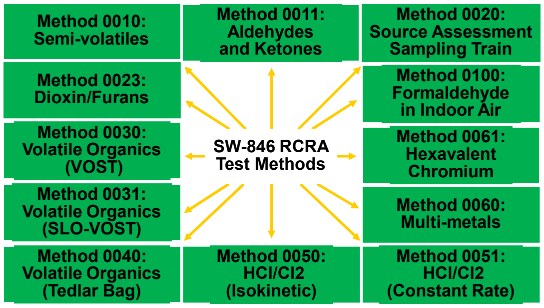
www.epa.gov/emc/tmethods.html

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



SW-846 RCRA Test Methods

Method 0010: Semi-volatiles

Method 0011: Aldehydes and Ketones

Method 0020: Source Assessment Sampling Train

Method 0023: Dioxin/Furans

Method 0100: Formaldehyde in Indoor Air

Method 0030: Volatile Organics (VOST)

Method 0061: Hexavalent Chromium

Method 0031: Volatile Organics (SLO-VOST)

Method 0060: Multi-metals

Method 0040: Volatile Organics (Tedlar Bag)

Method 0050: HCl/Cl2 (Isokinetic)

Method 0051: HCl/Cl2 (Constant Rate)

How Do We Define HAPs

CAAA of 1990, Title III now contains a list of 188 HAPs containing both organic and inorganic analytes

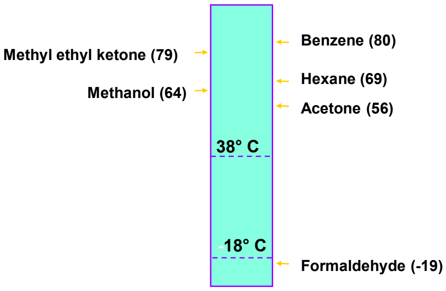
Defining the 188 HAPs according to

- Vapor Pressure (in mm Hg at 25°C)
- Boiling Point Temperature (°C)

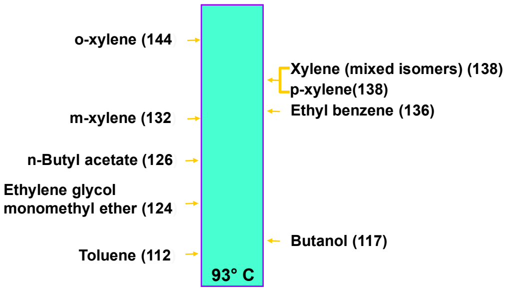
General Classification of VOCs

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

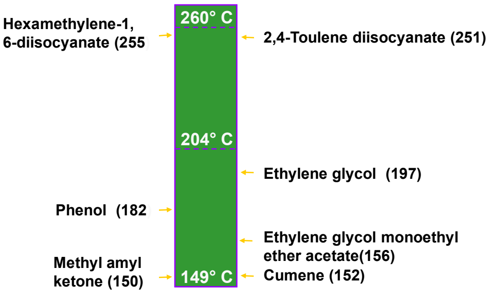
Boiling Points of Volatile Organic Compounds



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
- Expand upon CMS and HPV policy
- 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

Background of National Testing Guidance

- Interim Guidance: February 2, 2004
- Final Guidance: September 30, 2005
- Subsequent rulemaking to allow for extensions in testing deadlines in Force Majeure events effective August 9, 2006
  - Parts 60, 61, 63 of General Provisions amended May 16, 2007
  - Consolidated Federal Air Rule (GP Part 65) amended August 27, 2007
- Guidance issuance: April 27, 2009

Definition

- Definition and "Scope of Guidance" sections clarify guidance applies only to tests conducted for <u>compliance</u> 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

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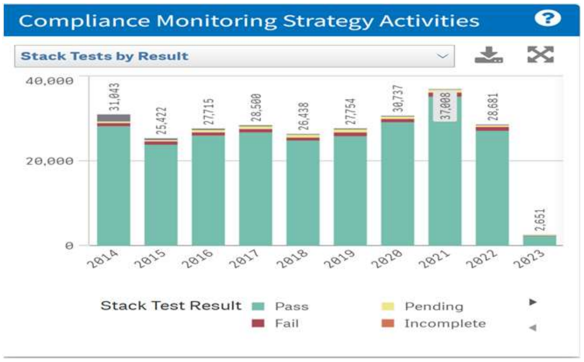
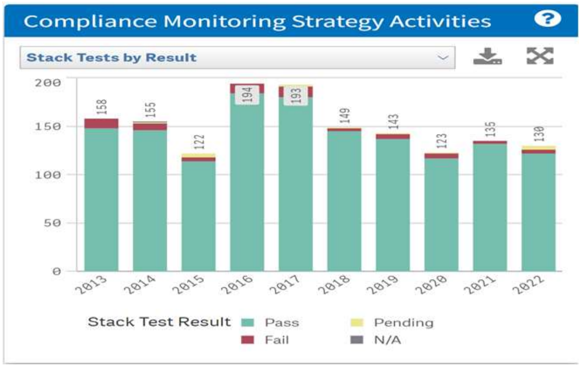
*States/EPA have until 12/1 to report FY '08 data

Analyze Trends: State Air Dashboard

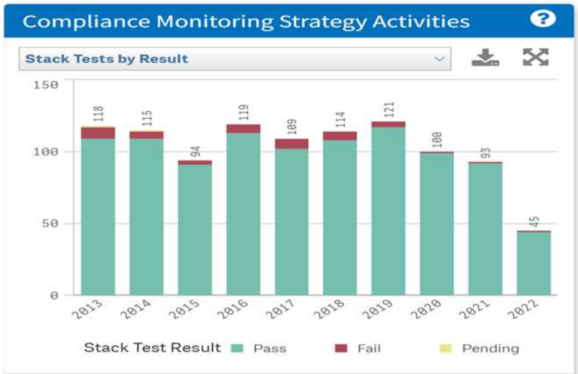


https://echo.epa.gov/trends/comparative-maps-dashboards/state-air-dashboard

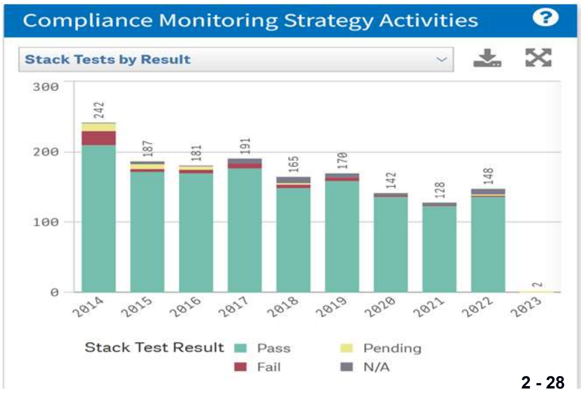
Illinois CMS Stack Tests



New York CMS Stack Tests

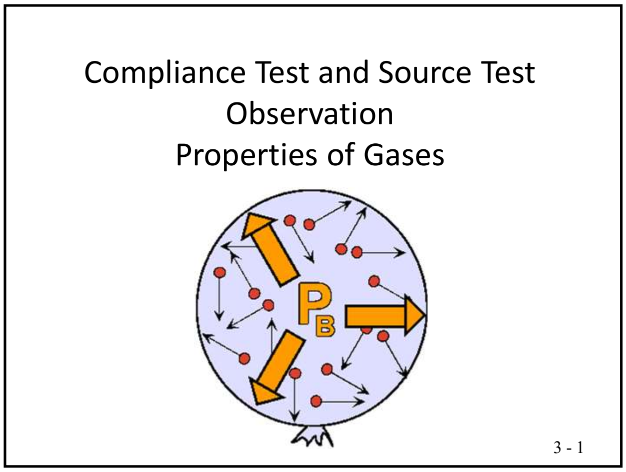


Alaska CMS Stack Tests



Additional Information

- Robert Lischinsky
  lischinsky.robert@epa.gov
  202-564-2628
- Internet Address:
  https://echo.epa.gov/trends/comparative-maps-dashboards/state-air-dashboard?state=IL&view=activity



Compliance Test and Source Test Observation
Properties of Gases

Properties of Gases

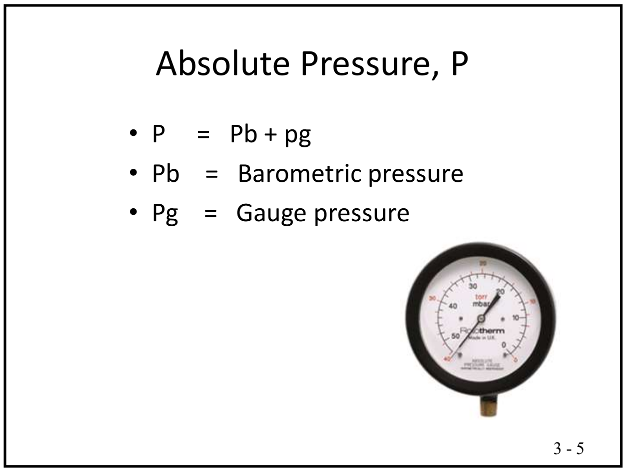
- Temperature
- Pressure
- Atomic Weight
- Molecular Weight and Moles
- Avogadro's Number
- Ideal Gas Law
- Moving Gases

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 = Pb + pg
- Pb = Barometric pressure
- Pg = Gauge pressure

Units of Pressure

- in. Hg
- mmHg
- in. H2O
- Atmospheres
- Torr
- pascals

1 Atmosphere =

29.92	in. Hg
39.90	ft H2O
14.70	lbs/in.2
760	mmHg
1	torr

EPA Standard Pressure and Temperature

- Pstd = 29.92 in. Hg
- Tstd = 20° C or 68° F

for source testing

Atomic Weight

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

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

Molecular Weight, M

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

MW of CO

12 + 16 = 28

n = number of moles
1 mole =

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

or

in grams (g-mole)

1 mole of CO = 28 grams

1 gram-mole =

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

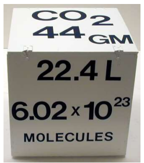
1 mole = Avogadro's Number worth of molecules

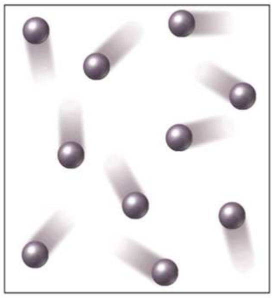
(6.023×10^{23})

Occupies

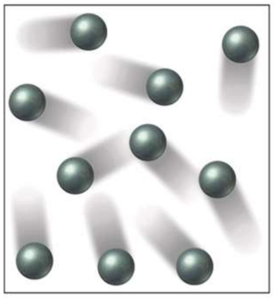
22.4 L

At O° C and 1 atmosphere





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

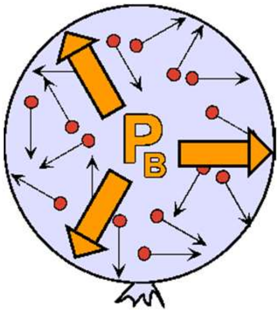


1 mol xenon at STP
Volume = 22.4 L
Mass = 131.3 g

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:

$$R = 21.85 \left\{ \frac{(in.Hg)(ft^3)}{(lb - mol)(°R)} \right\}$$

Correcting Volume to Standard Conditions

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

$$V_{std\,(standard)} = nR\,\frac{T_{std}}{P_{std}}$$

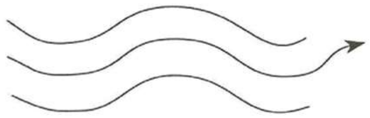
Dividing top by bottom gives

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

Properties of Moving Gases

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

Velocity



V_s = ft/sec or ft/hr

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

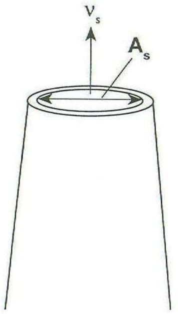
Determined by Method 2 using the
Type S pitot tube

The Pitot Tube Equation

$$v_s = K_p C_p \left(\frac{\sum_{i=1}^{n}\sqrt{\Delta p}}{n}\right)_{avg}\sqrt{\frac{T_{s(abavg)}}{P_s M_s}}$$

USEAP Method 2, Eq. 2-7

Volumetric Flow Rate



$$\boxed{Q_s = V_s A_s}$$

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

or

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

Isokinetic Sampling

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

FRM 5 Isokinetic Rate Equation

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

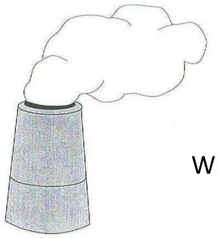
$$\%I_{final} = \frac{100\ T_{s(avg)} \left[K_3 V_{lc} + \left(\frac{V_{m(avg)}}{T_{m(avg)}} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60\ \theta\ V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

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

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

Pollutant Mass Rate (pmr)



$$\boxed{pmr = c_S Q_S}$$

Where: c_S = the pollutant concentration

Concentration, c_S

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

Units: g/m3 , lbs/ft3 , gr/ft3, ppm

Note : 7000 grains (gr) = 1 lb

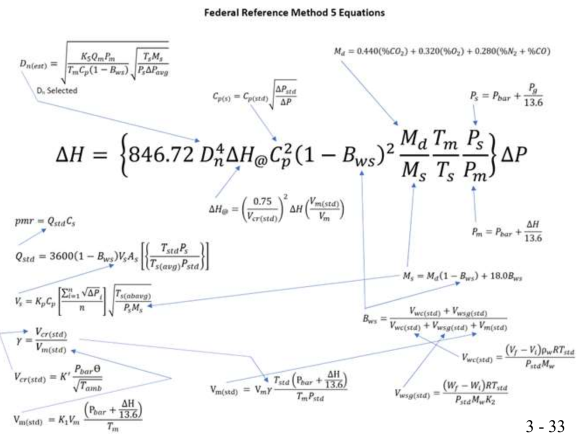
pmrS = c_s Q_s

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

Emission Rate
(Combustion Sources)

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

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



Federal Reference Method 5 Equations

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

D_n Selected

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$$

$$C_{p(s)} = C_{p(std)}\sqrt{\frac{\Delta P_{std}}{\Delta P}}$$

$$P_s = P_{bar} + \frac{P_g}{13.6}$$

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

$$\Delta H_@ = \left(\frac{0.75}{V_{cr(std)}}\right)^2 \Delta H \left(\frac{V_{m(std)}}{V_m}\right)$$

$$pmr = Q_{std} C_s$$

$$P_m = P_{bar} + \frac{\Delta H}{13.6}$$

$$Q_{std} = 3600(1 - B_{ws}) V_s A_s \left[\left\{\frac{T_{std} P_s}{T_{s(avg)} P_{std}}\right\}\right]$$

$$M_s = M_d(1 - B_{ws}) + 18.0 B_{ws}$$

$$V_s = K_p C_p \left[\frac{\sum_{i=1}^{n}\sqrt{\Delta P}_i}{n}\right]\sqrt{\frac{T_{s(abavg)}}{P_s M_s}}$$

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

$$\gamma = \frac{V_{cr(std)}}{V_{m(std)}}$$

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

$$V_{cr(std)} = K' \frac{P_{bar}\Theta}{\sqrt{T_{amb}}}$$

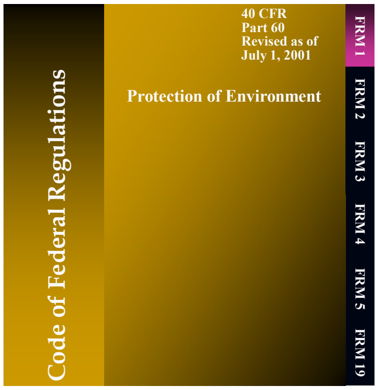
$$V_{m(std)} = V_m \gamma \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}}$$

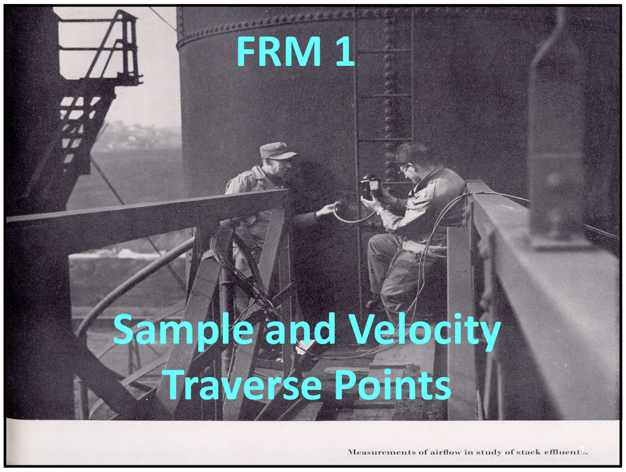
$$V_{wsg(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w K_2}$$

$$V_{m(std)} = K_1 V_m \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m}$$

Compliance Test and Source Test Observation

FRM 1: Sampling/Velocity Traverse Points





FRM 1

Sample and Velocity Traverse Points

Measurements of airflow in study of stack effluents.

FRM 1 History

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

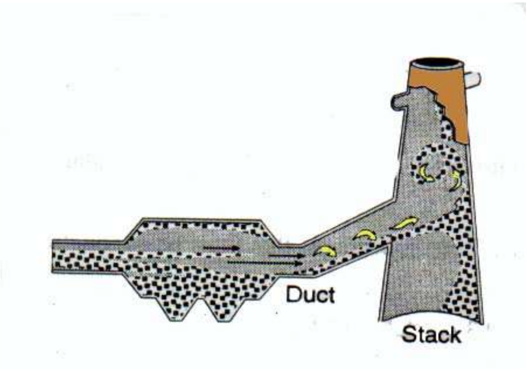
FRM 1

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

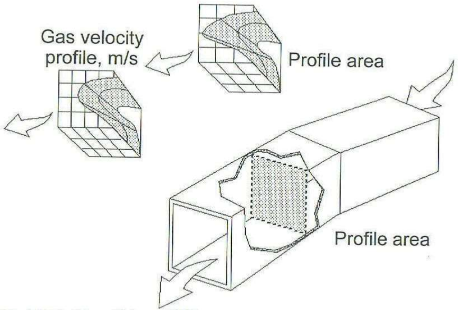
FRM 1 Basic Principle

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

FRM 1 Sampling Site Locations

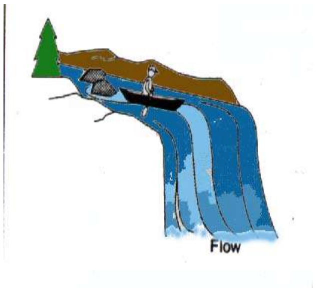


Particle mass concentration profile, mg/m^3

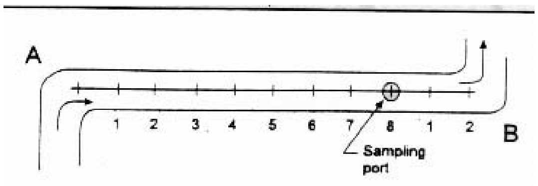


Source: Adapted from Buhne, 1977

FRM 1 Siting Criteria



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 11.1.2)

FRM 1 Flow Disturbance

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

Stack Extensions Required

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

Sampling Location

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

FRM 1 Siting Criteria

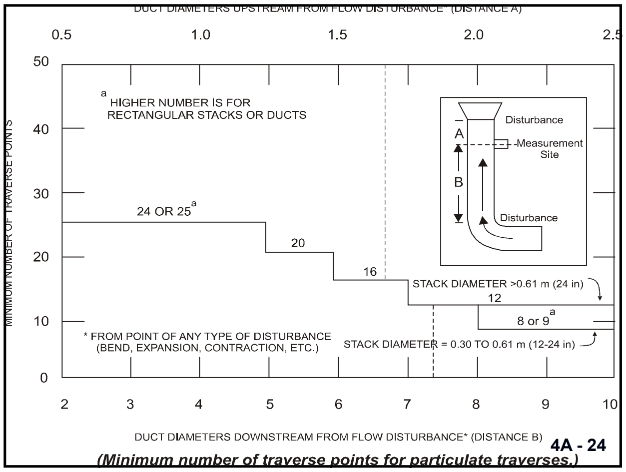
- At 8 duct diameters downstream and 2 duct diameters upstream of a flow disturbance, the siting criteria states
  - Velocity head profile is assumed to resemble laminar flow

FRM 1 Siting Criteria

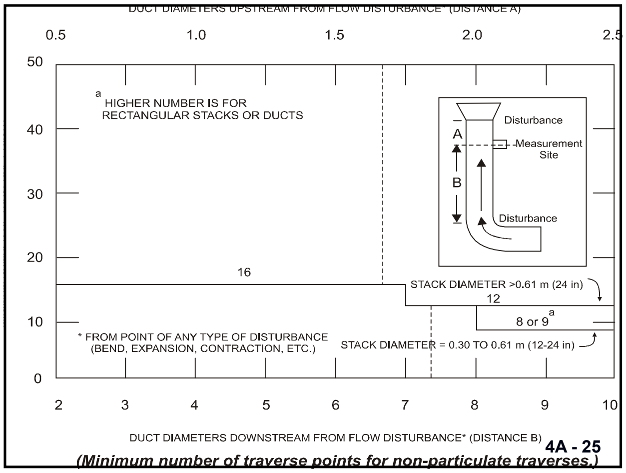
- The minimum number of sampling points can be used
  - 8 or 9 for 12-24 in. stacks
  - 12 for > 24 in. stacks

FRM 1 Siting Guidance

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



(Minimum number of traverse points for particulate traverses.)



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

FRM 1 Equal Areas

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

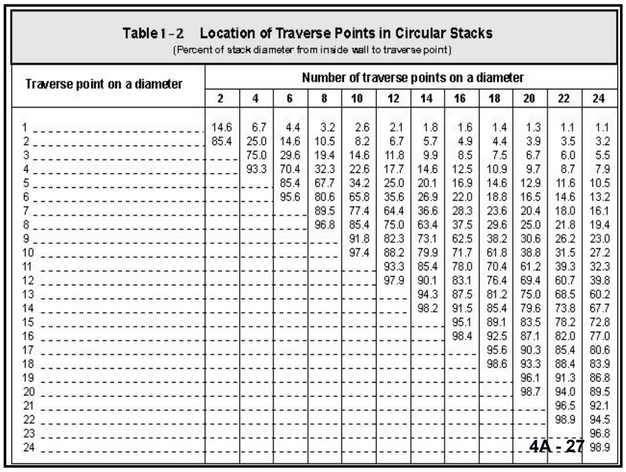


Table 1-2 Location of Traverse Points in Circular Stacks

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

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

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

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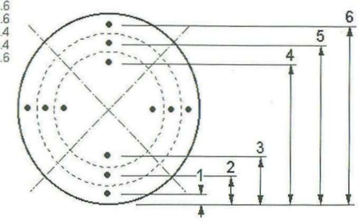
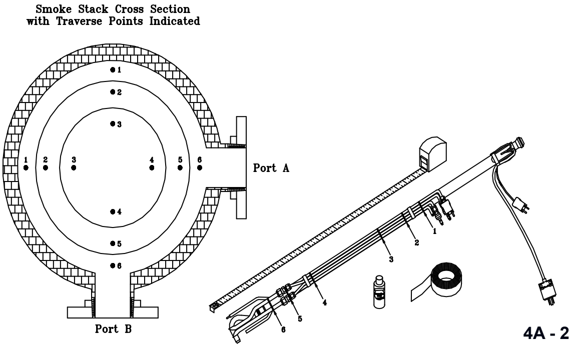




FRM 1 Location of Traverse Points

- 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

FRM 1 Diameter Equivalent Formula for Rectangular Ducts

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

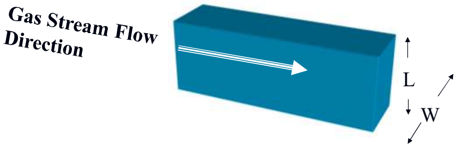
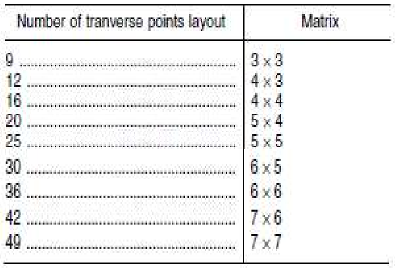
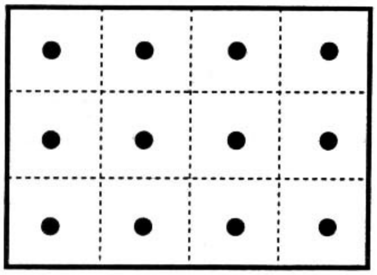


Table 1–1 Cross-section Layout For Rectangular Stacks 40CFR Part 60 Appendix A



Number of tranverse points layout	Matrix
9	3 × 3
12	4 × 3
16	4 × 4
20	5 × 4
25	5 × 5
30	6 × 5
36	6 × 6
42	7 × 6
49	7 × 7

Rectangular Duct (3 X 4)



Section 11.4.1

- In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined.

FRM 1 Verification or Absence of Cyclonic Flow

- Cyclonic flow may exist (Section 1.1)
  - 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.)

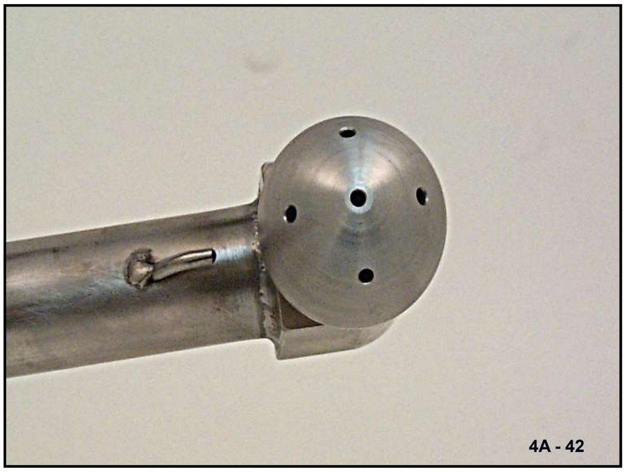
- Equipment
  - Manometer
  - Type S pitot tube/level indicator
- Procedure
  - “Null” reading; O.K.
  - Determine delta p if not “null”
  - Acceptance avg. Δp < 20 degrees

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

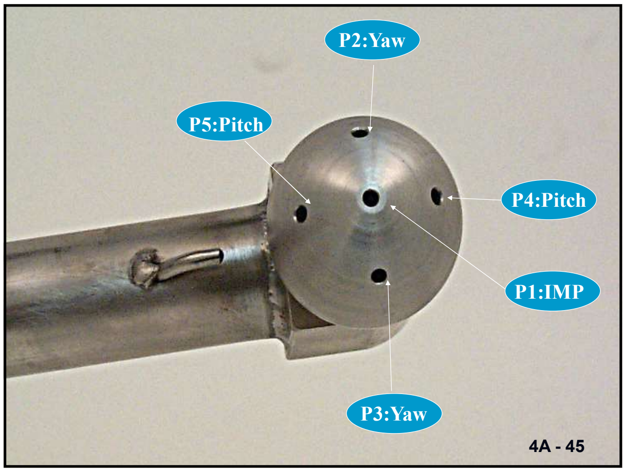
Method 2F Equipment

- 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

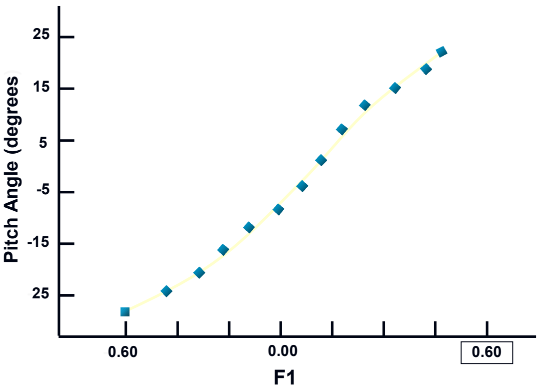
- Position probe at traverse point and verify position of "scribe line."
- Pre leak check
- Record yaw and pitch angles at each traverse point
- Calculate resultant angle
- Post leak check

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. 11.2.1.1)
- Minimum number of traverse points (Sec. 11.2.1.1)
- For particle sampling, one diameter in plane of bend (Sec. 11.3.1.2)

Major Points in FRM 1

- Relocation of traverse points (Sec. 11.3.2.1)
- Definition of cyclonic flow (Sec. 11.4.1)
- Verification of absence of cyclonic flow (Sec. 11.4)

Major Points in FRM 1

- Alternative Measurement Site Location (Sec. 11.5)
  - Directional flow sensor and resultant angle (Sec. 6.1.1)
  - Post leak check required at 3 in. water (Sec. 11.5.3.1)

Major Points in FRM 1

- Alternative Measurement Site Location (Sec. 11.5) Continued
  - Calculate resultant angle at each traverse point (Sec. 11.5.1)
  - Calibration of directional flow sensor (Sec. 11.5.4)

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

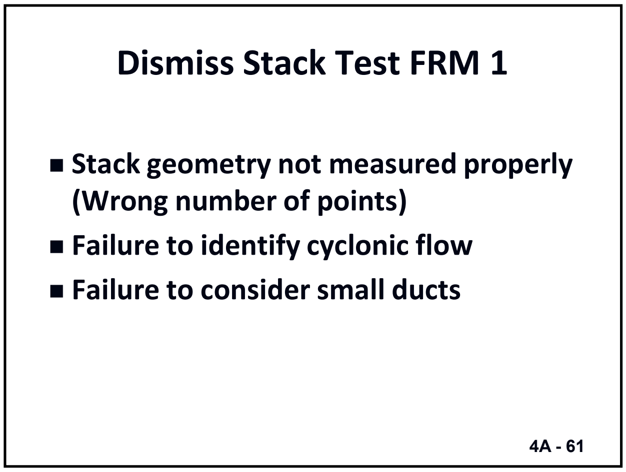
- Measure the stack diameter from each sampling port and average values
- Find in-stack restrictions by using gloved hand and visual inspection of internal area
- Don’t forget to take into consideration the nipple of the stack or inner lining in calculations

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 pipe coupling (nipple) diameter to calculated traverse points
- “White-out” is an excellent tool for marking probe

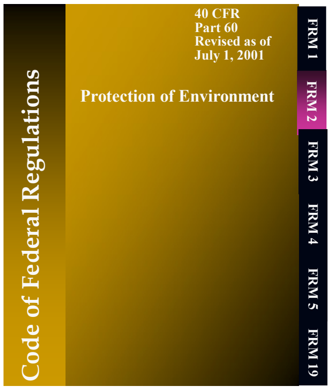


Dismiss Stack Test FRM 1

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

Compliance Test and Source Test Observation

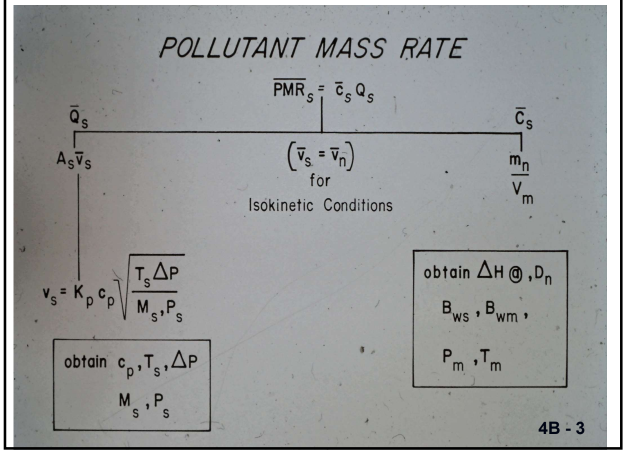
FRM 2: Stack Gas Velocity



Code of Federal Regulations

40 CFR
Part 60
Revised as of
July 1, 2001

Protection of Environment



POLLUTANT MASS RATE

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

$\bar{Q}_s$

$A_s \bar{v}_s$

$(\bar{v}_s = \bar{v}_n)$
for
Isokinetic Conditions

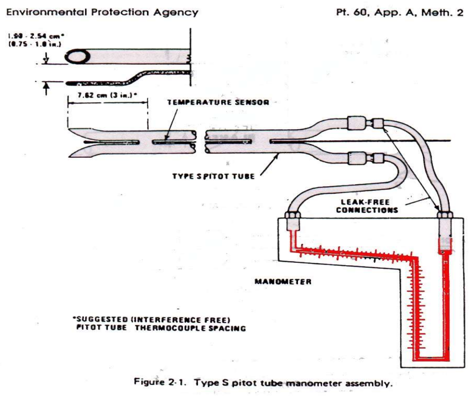
$\bar{C}_s$

$\frac{m_n}{V_m}$

$$v_s = K_p c_p \sqrt{\frac{T_s \Delta P}{M_s, P_s}}$$

obtain $c_p, T_s, \Delta P$
M_s, P_s

obtain $\Delta H@, D_n$
$B_{ws}, B_{wm},$
P_m, T_m

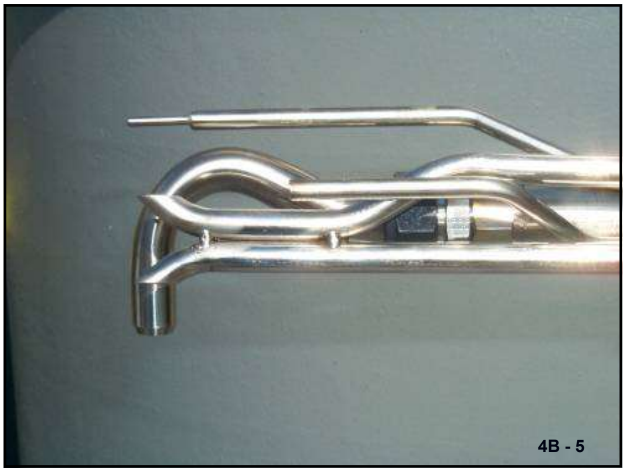


Environmental Protection Agency

Pt. 60, App. A, Meth. 2

*SUGGESTED (INTERFERENCE FREE) PITOT TUBE THERMOCOUPLE SPACING

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



FRM 2

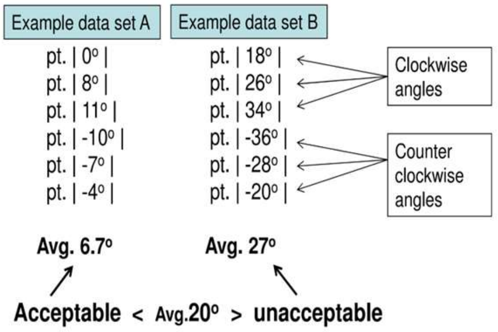
- This method is applicable for measurement of the average velocity of a gas stream
- The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube

FRM 2 History

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

Can't Use FRM 2

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



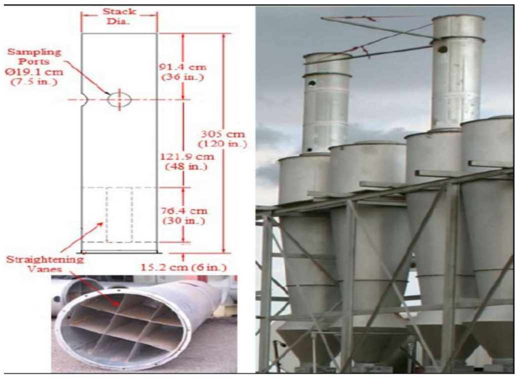
Example data set A	Example data set B
pt. | 0° |	pt. | 18° |
pt. | 8° |	pt. | 26° |
pt. | 11° |	pt. | 34° |
pt. | -10° |	pt. | -36° |
pt. | -7° |	pt. | -28° |
pt. | -4° |	pt. | -20° |
Avg. 6.7°	Avg. 27°

Clockwise angles

Counter clockwise angles

Acceptable < Avg.20° > unacceptable

Stack Modifications Due to Cyclonic Flow



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:
  - Δp>0.05 " water, then 0-10 " manometer adequate
  - Δp<0.05 " water, then use manometer with 0.005 /division (i.e., micro-manometer)
  - Δp<0.01 "water, then use high sensitivity transducer such as Hasting Thermo Probe

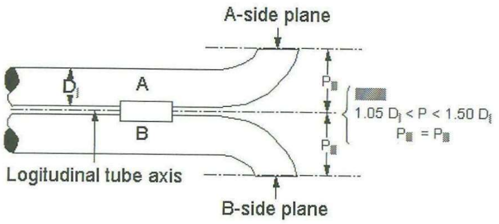
Interference-Free Component Arrangement

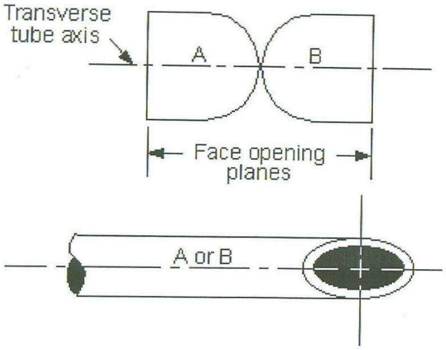
- Pitot tube distance to nozzle: >3/4 inches for ½ nozzles
- Center of nozzle and pitot tube opening aligned
- Thermocouple location to pitot tube > ¾ inch for 3 inches
- Back-recess thermo. > 2 inches
- Gas sampling assembly > 3 inches from pitot tube

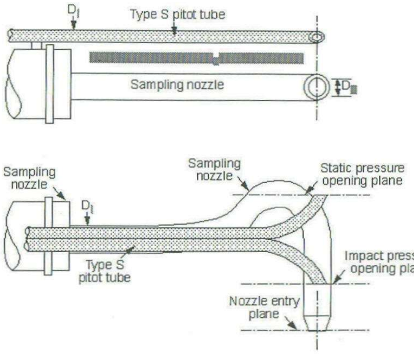
Type S Pitot Tube

Design criteria for assigning

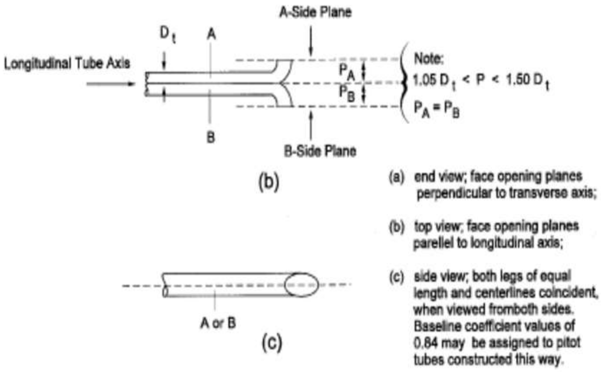
$C_p = 0.84$







- Properly Constructed S-type Pitot Tube

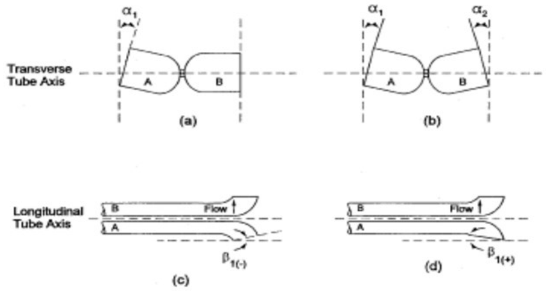


(a) end view; face opening planes perpendicular to transverse axis;

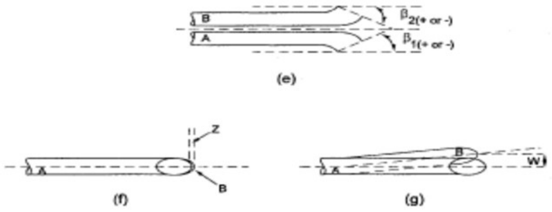
(b) top view; face opening planes parellel to longitudinal axis;

(c) side view; both legs of equal length and centerlines coincident, when viewed fromboth sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

- Types of face opening mis-alignments that can result from field use or improper construction of type S pitot tubes



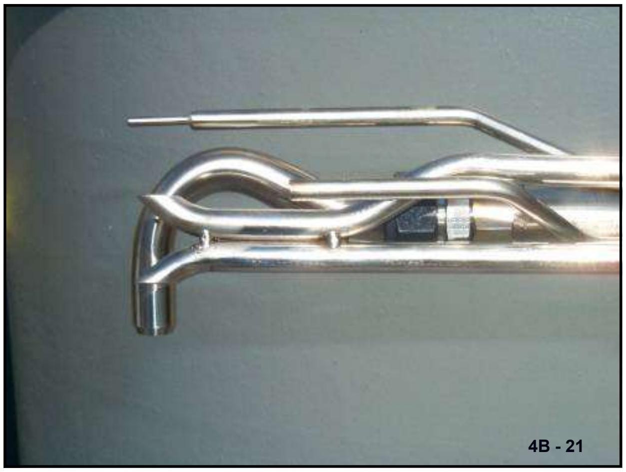
Types of face opening mis-alignments that can result from field use or improper construction of type S pitot tubes (cont.)

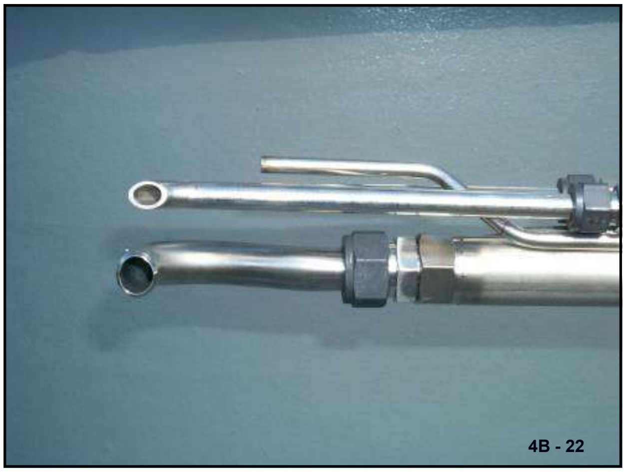


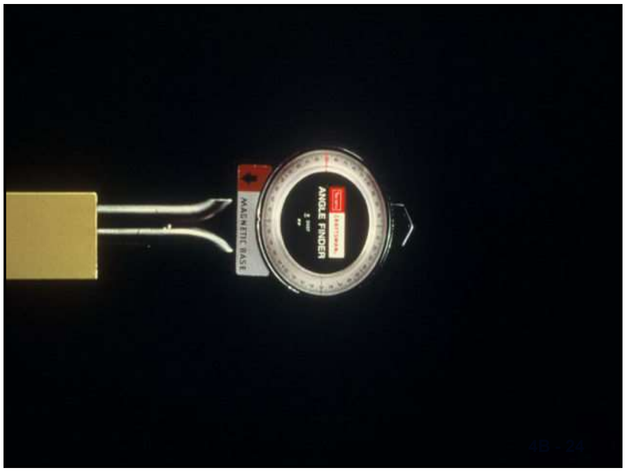
The types of face-opening misalignment shown above will not affect the baseline value of $C_{p(s)}$ so long as α_1 and $\alpha_2 \le 10°$, β_1 and $\beta_2 \le 5°$, $z \le$ 0.32 cm (1/8 in.), and $w \le$ 0.08 cm (1/32 in.) (Reference 11.0 in Section 16.0)

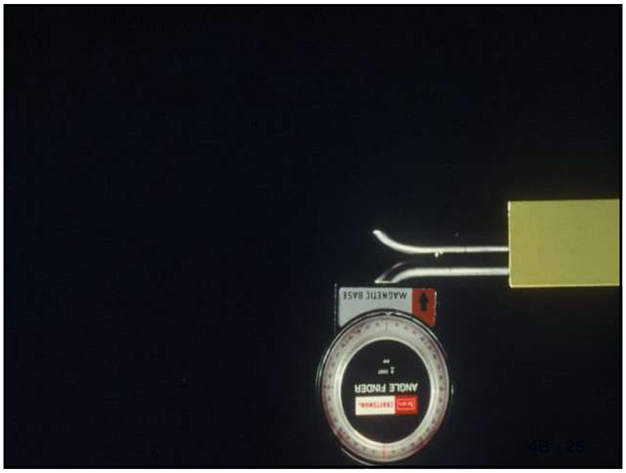
Verification of Geometry of Type S Pitot Tube To Assign 0.84

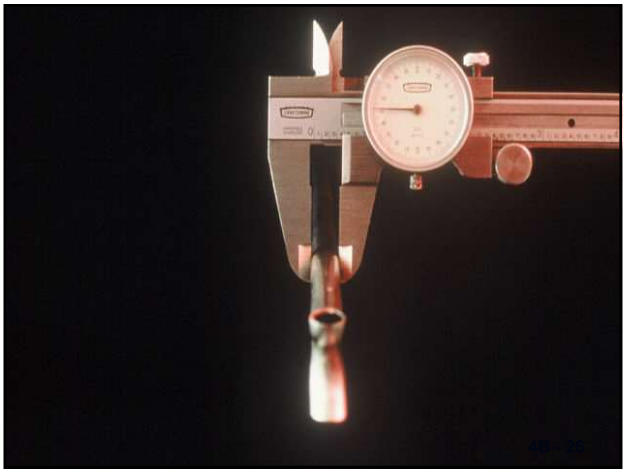
- α 1 and 2 (+/- 10 degrees)
- β 1 and 2 (+/- 5 degrees)
- Z = </= 0.125 inches
- W = </= 0.031 inches
- P_a and P_b 0.263 to 0.375
- D_t = 0.188 to 0.375

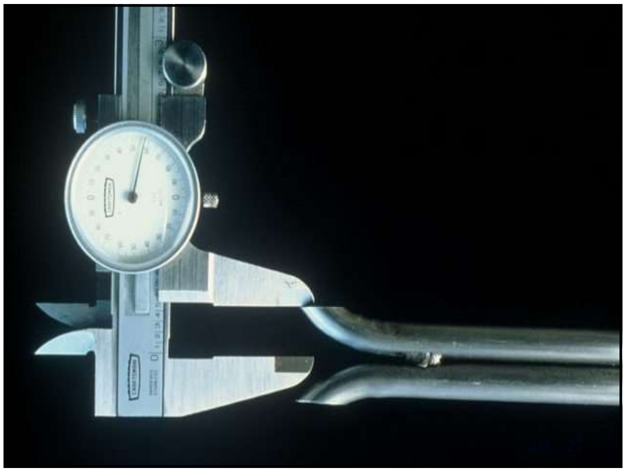




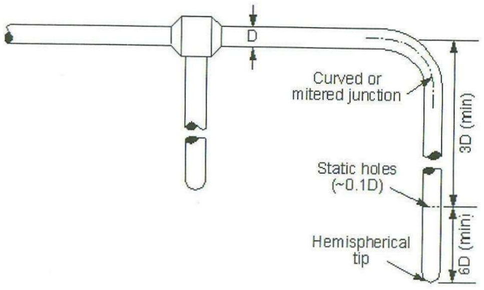


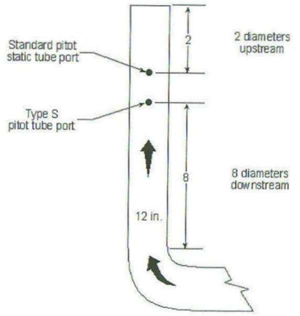






Type S Pitot Tube Calibrate Using a Standard Pitot Tube and Wind Tunnel

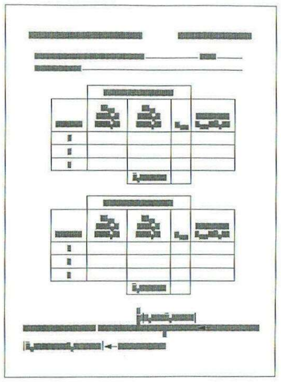




Pitot Tube Calibration Equation

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

Pitot Tube Calibration Data Sheet



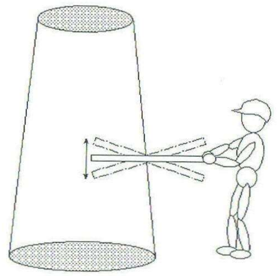
Velocity Measurement Procedures

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.

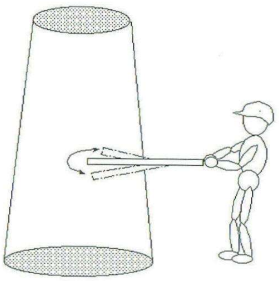
Velocity *(cont.)*

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.

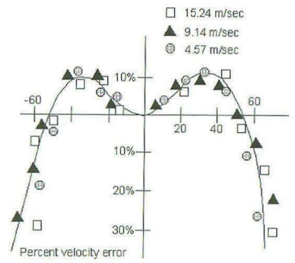
Pitch Angle



Yaw Angle



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



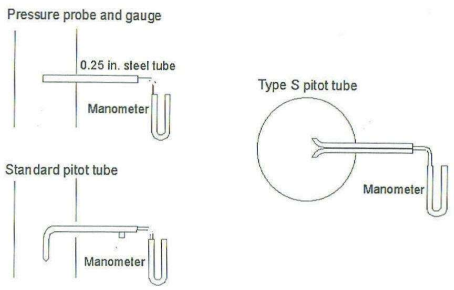
Federal Reference Method 2 Average Velocity Over Cross-Section Area of Stack

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

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

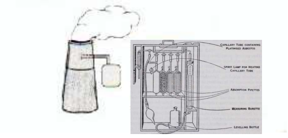
- Pitot tube leak check at 3 “ water failed
- Pitot tube geometry not to specifications
- Pitot tube orientation during test not proper

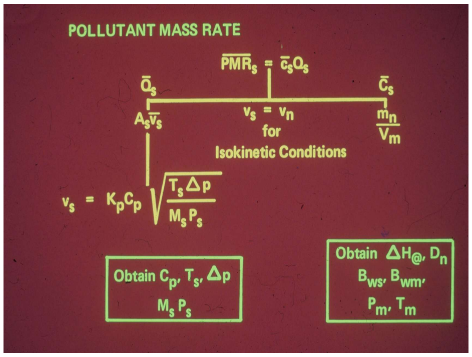
U.S. EPA APTI
Compliance Test and
Source Test Observation

Stack Test Basic Continued

Method 3

Determination of the dry molecular weight of flue gas
(using Orsat apparatus measuring %0_2, %CO_2, and %CO)





POLLUTANT MASS RATE

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

$\bar{Q}_s$

$A_s \bar{v}_s$

$v_s = v_n$
for
Isokinetic Conditions

$\bar{C}_s$

$\frac{m_n}{V_m}$

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

Obtain C_p, T_s, Δp
M_s P_s

Obtain $\Delta H_@$, D_n
B_{ws}, B_{wm},
P_m, T_m

Federal Reference Method 3 History

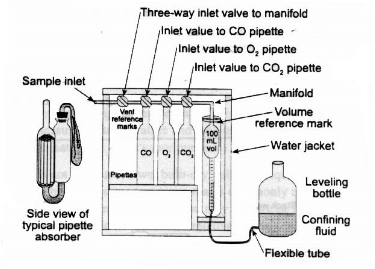
• 1970FRM 3	Promulgated
• 1986FRM 3A	Instrumental
• 1990FRM 3B	Orsat for Correction Factor and Excess Air (F_o- Factor)
• 1996FRM 3C	Landfill Gas

Federal Reference Method 3

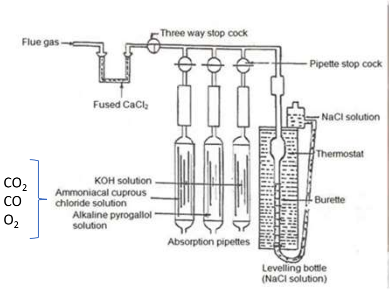
- Gas analysis: measuring percent of O_2 and percent of CO_2 to determine the dry molecular weight of the flue gas (using Orsat Apparatus)

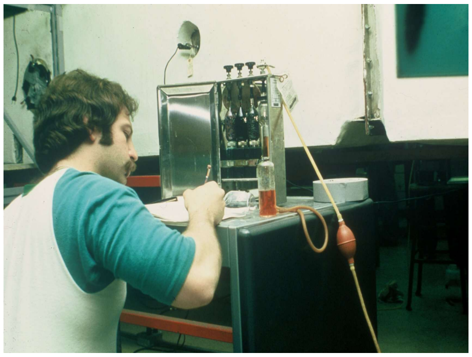
Orsat Analyzer

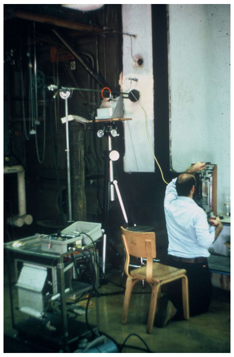
Oxidation
Reduction
Selective
Absorption
Technique



Orsat Analyzer







Fyrite Gas Analyzer

FRM 3 Sampling Techniques

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

Single-Point Grab Sampling Train

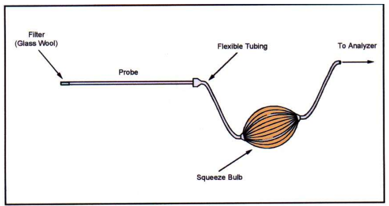


Figure 3-1. Grab-Sampling Train.

Single-Point Integrated Sampling Train

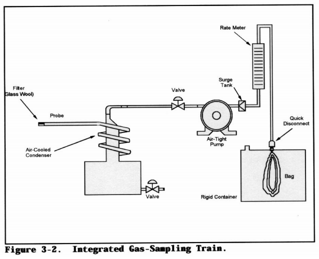
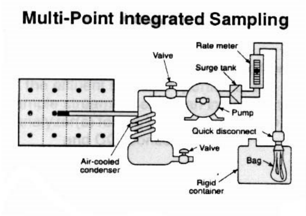


Figure 3-2. Integrated Gas-Sampling Train.

Multi-point Integrated Sampling Train



Multi-Point Continuous Integrated Sampling

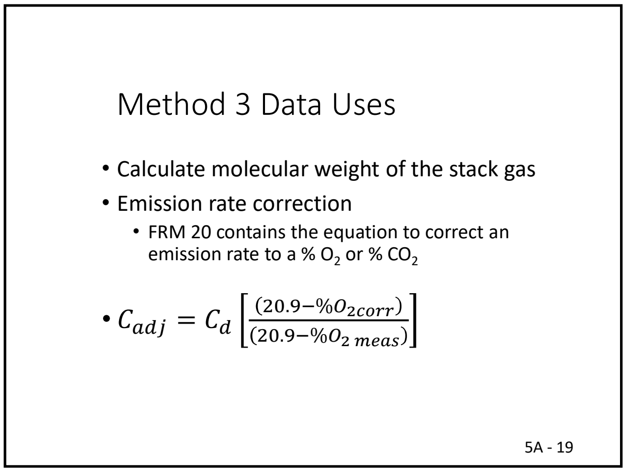
- Particulate sample and variations
- Modified Method 5 sampling
- VOST sampling
- For concentrations given to specific conditions (i.e., 12 % CO_2, 6 % O_2)
- For emission rate calculations (F-factor)
- For molecular weight determination

FRM 3 Calculation

- **Dry Molecular Weight Equation**

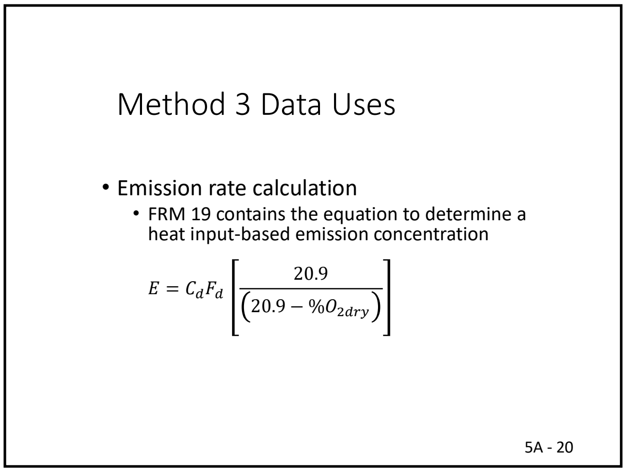
$$M_d = 0.44(\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO)$$

Where: M_d = dry molecular weight
$\%CO_2$ = present CO_2 by volume (dry basis)
$\%O_2$ = present O_2 by volume (dry basis)
%CO = present CO by volume (dry basis)
$\%N_2$ = present 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



Method 3 Data Uses

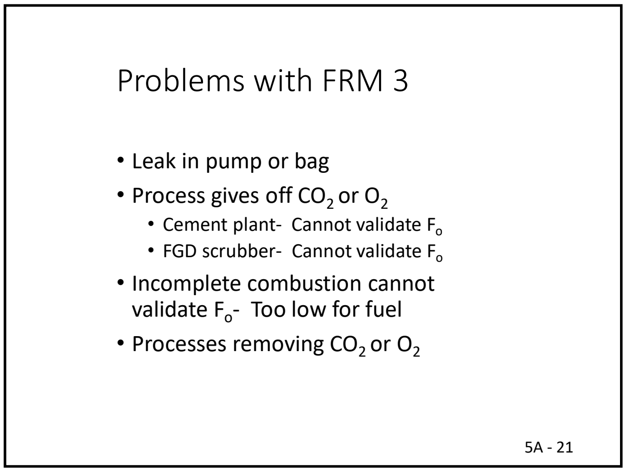
- Calculate molecular weight of the stack gas
- Emission rate correction
  - FRM 20 contains the equation to correct an emission rate to a % O_2 or % CO_2
- $C_{adj} = C_d \left[\frac{(20.9 - \%O_{2corr})}{(20.9 - \%O_{2\,meas})}\right]$



Method 3 Data Uses

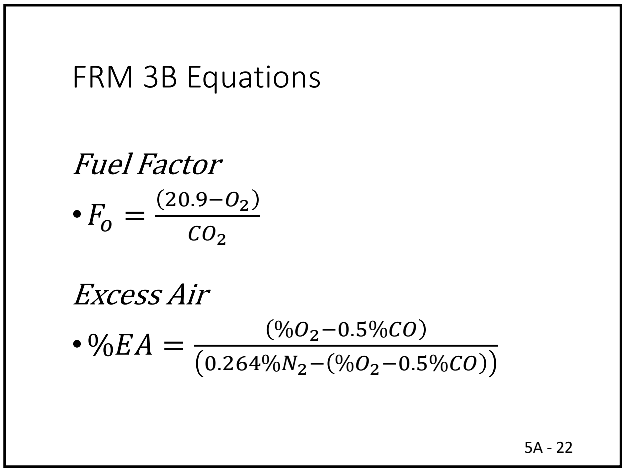
- Emission rate calculation
  - FRM 19 contains the equation to determine a heat input-based emission concentration

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



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



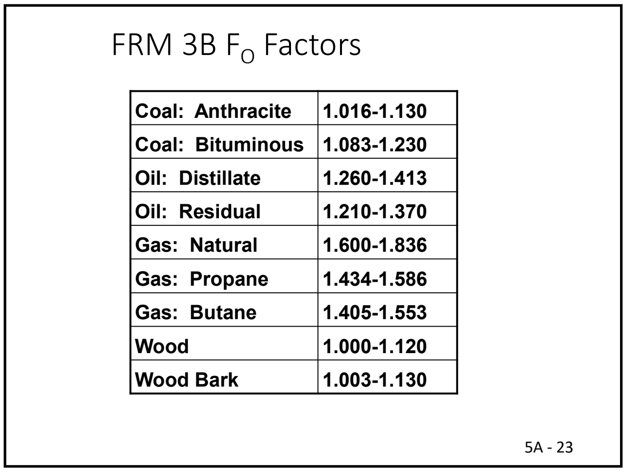
FRM 3B Equations

Fuel Factor

- $F_o = \frac{(20.9 - O_2)}{CO_2}$

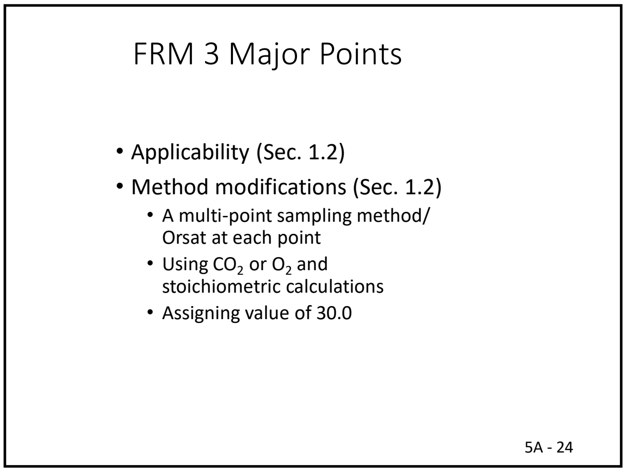
Excess Air

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



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 (Sec. 1.2)
- Method modifications (Sec. 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. 6.2.6)
- Sampling point in the stack for single point grab (Sec. 8.1)
- Multi-point integration (Sec. 8.3): >24 in. 12 Pts; <24 in. 8 Pts

FRM 3 Major Points

- Sampling at constant rate and same time as FRM 5 (Sec. 8.2.5)
- Analysis time 8 hours (Sec. 8.2.4)
- Leak-check Orsat (Section 11.5)
- F_o Factor (Method 3B)
- Can't use Fyrite (Method 3B)
- Triplicate trials

FRM 3 Inspector Tools

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

FRM 3 Tips

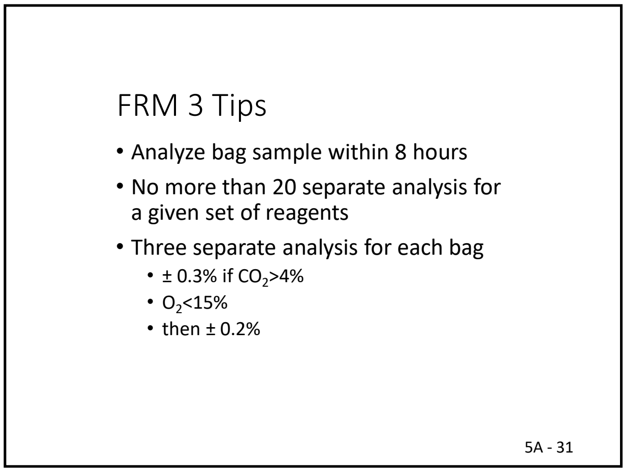
- Don't forget to take into account correction for altitude location of sampling port (0.1 in./100 ft)
- Stack gas pressure also requires determination of stack static pressure (P_g): $P_g/13.6$

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.)

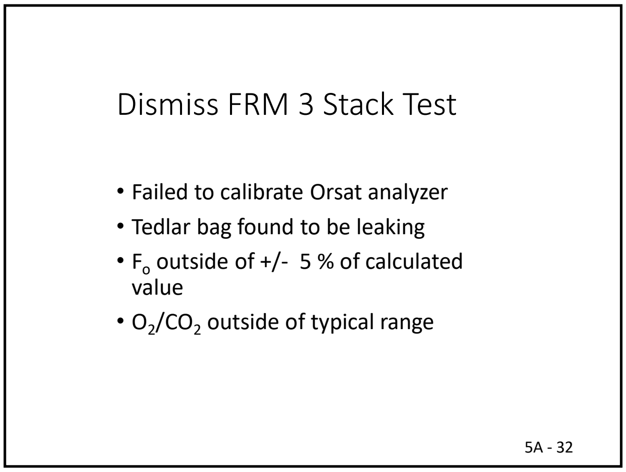
FRM 3 Tips

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



FRM 3 Tips

- Analyze bag sample within 8 hours
- No more than 20 separate analysis for a given set of reagents
- Three separate analysis for each bag
  - ± 0.3% if CO_2>4%
  - O_2<15%
  - then ± 0.2%

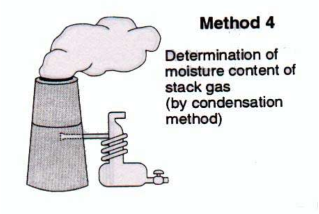


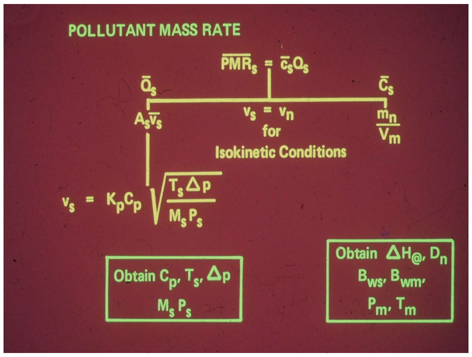
Dismiss FRM 3 Stack Test

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

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

Stack Test Basic Continued





POLLUTANT MASS RATE

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

$\bar{Q}_s$

$A_s \bar{v}_s$

$v_s = v_n$ for Isokinetic Conditions

$\bar{C}_s$

$\frac{m_n}{V_m}$

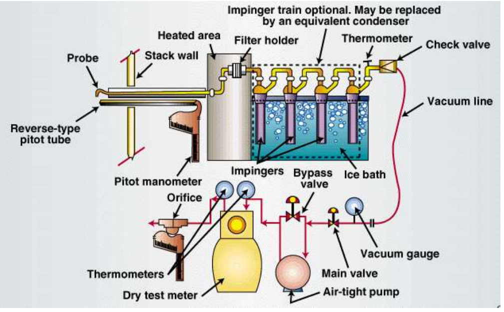
$v_s = K_p C_p \sqrt{\frac{T_s \Delta p}{M_s P_s}}$

Obtain C_p, T_s, Δp, M_s P_s

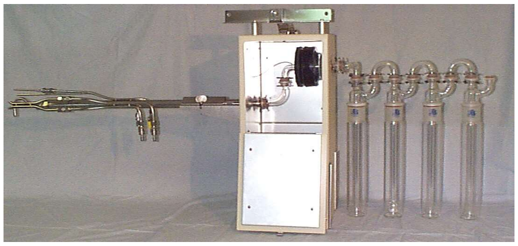
Obtain $\Delta H_@$, D_n, B_{ws}, B_{wm}, P_m, T_m

Two Methods in FRM 4

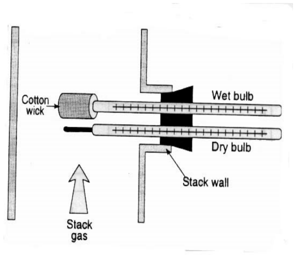
- Reference method
  (FRM 5 Condenser Methodology)
- Approximate Methodology
  - FRM 6 Impingers
  - Wet Bulb/Dry Bulb
  - Nomographs



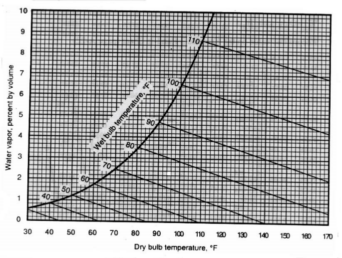
Federal Reference Method 4



Wet Bulb/Dry Bulb



Psychrometric Chart



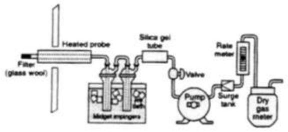
Psychrometric chart expressing volume of water vapor by percent

Calculating % Moisture Under Saturated Gas Stream

$$\%H_2O = \frac{10^{\left(6.691-\left(\frac{3144}{(T_S+390.86)}\right)\right)}}{(P_S \times 100)}$$

FRM 4 Approximate Method Sampling Train

Moisture Sampling Train - Approximation Method



Bws = Proportion of water vapor in the gas stream.

(by volume)

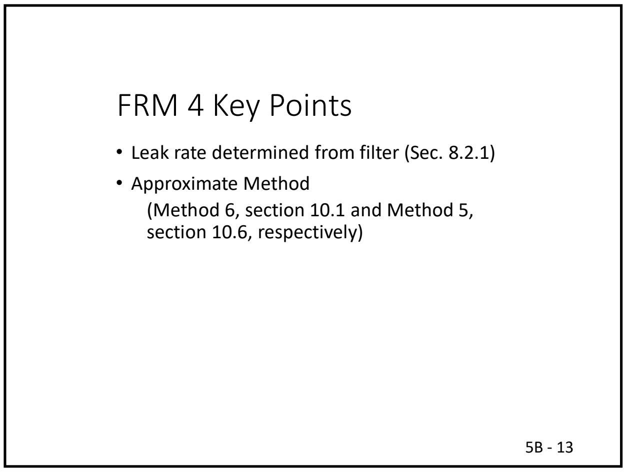
$$B_{ws} = \frac{V_{wc(std)}}{V_{m(std)} + V_{wc(std)}}$$

FRM 4 Key Points

- Reference Method: Condenser Approach (Sec. 8.1)
- Approximation Method: Method 6 impingers, wet bulb/dry bulb, charts (Sec. 6.1.1.2)
- Saturated gas streams may give questionable results (Sec. 4.1)

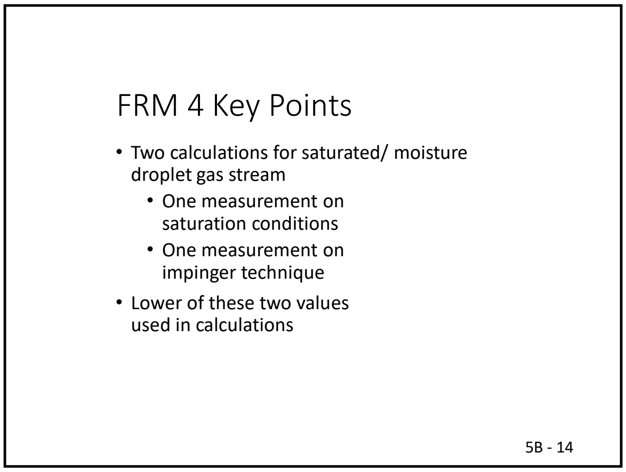
FRM 4 Key Points

- Design of train (Method 5, sec. 6.1.1.8)
- Number of traverse points (sec. 8.1.1.1)
- Minimum sample vol. (21 scf) and sampling rate (0.75 cfm) (Sec. 8.1.1.2)
- Sampling at a "constant sampling rate" (Sec. 6.1.4)



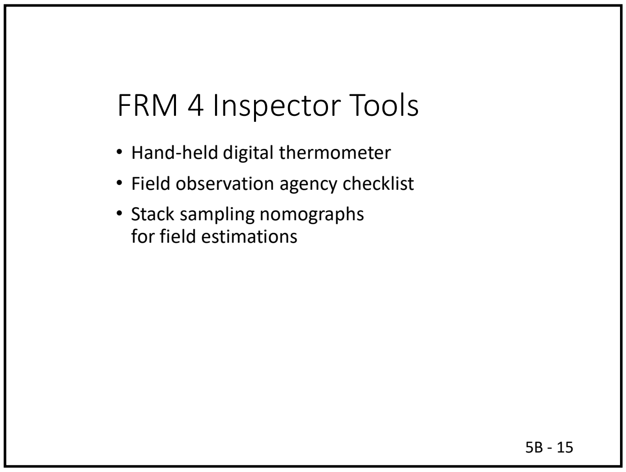
FRM 4 Key Points

- Leak rate determined from filter (Sec. 8.2.1)
- Approximate Method
  (Method 6, section 10.1 and Method 5, section 10.6, respectively)



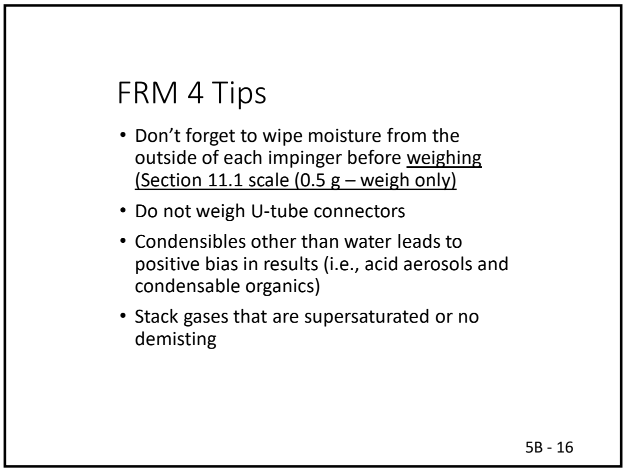
FRM 4 Key Points

- 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



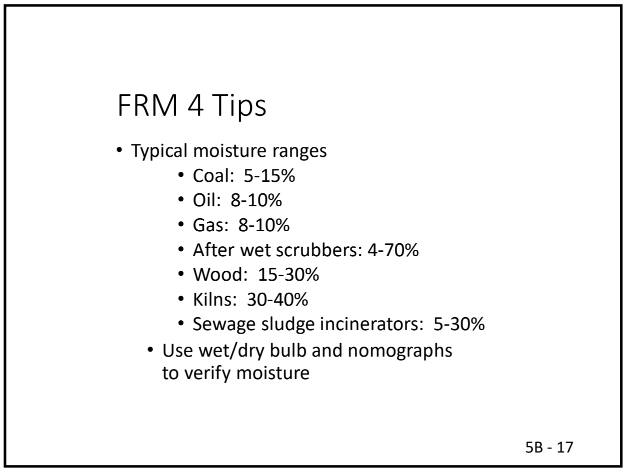
FRM 4 Inspector Tools

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



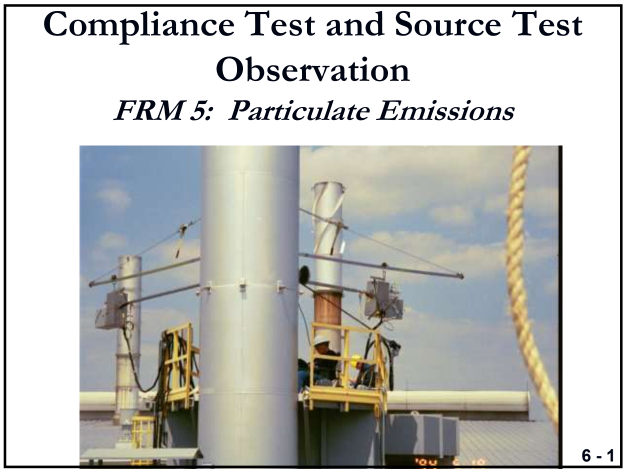
FRM 4 Tips

- Don’t forget to wipe moisture from the outside of each impinger before weighing (Section 11.1 scale (0.5 g – weigh only)
- 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



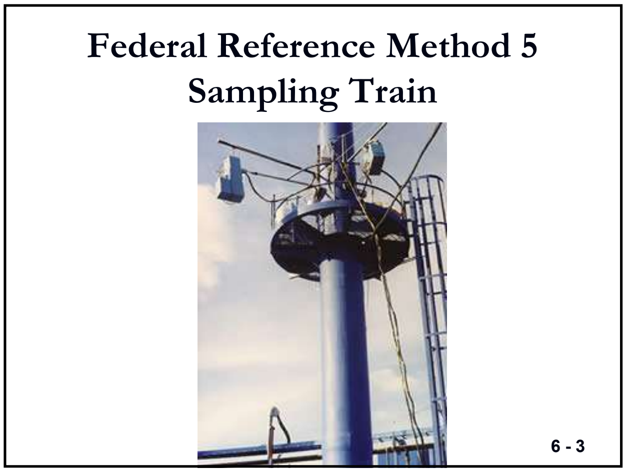
FRM 4 Tips

- 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

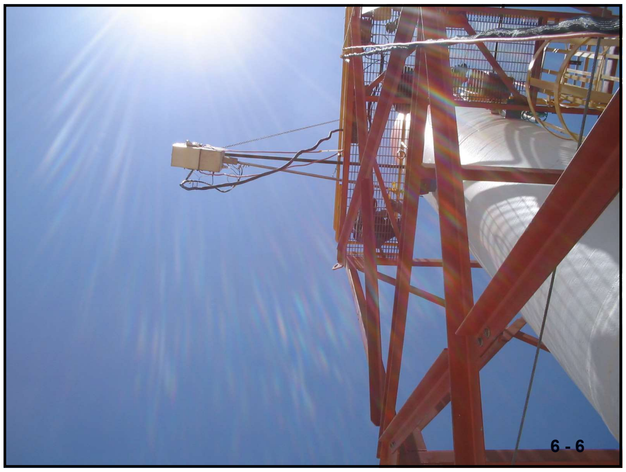


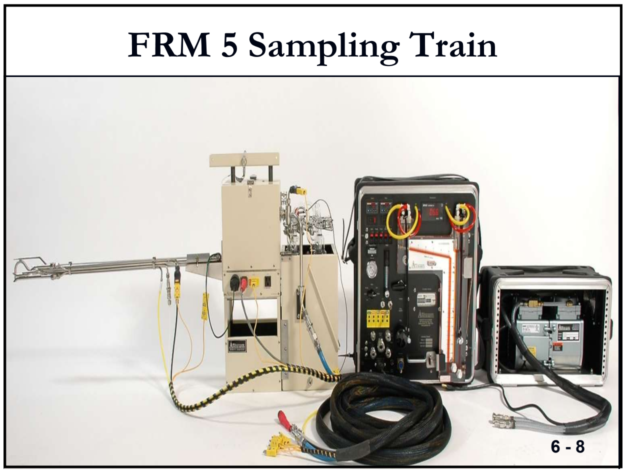
Compliance Test and Source Test Observation

FRM 5: Particulate Emissions

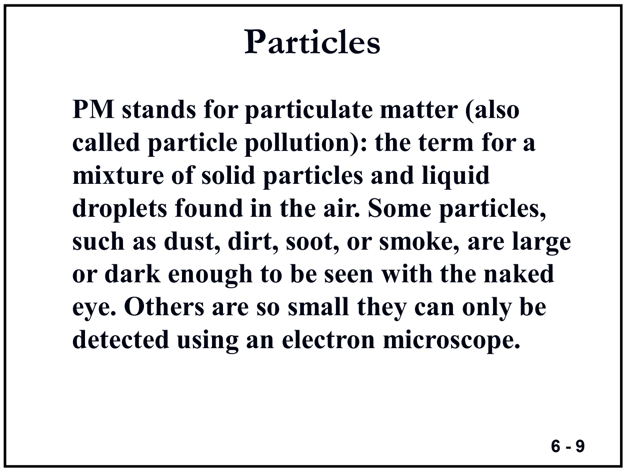


Federal Reference Method 5 Sampling Train



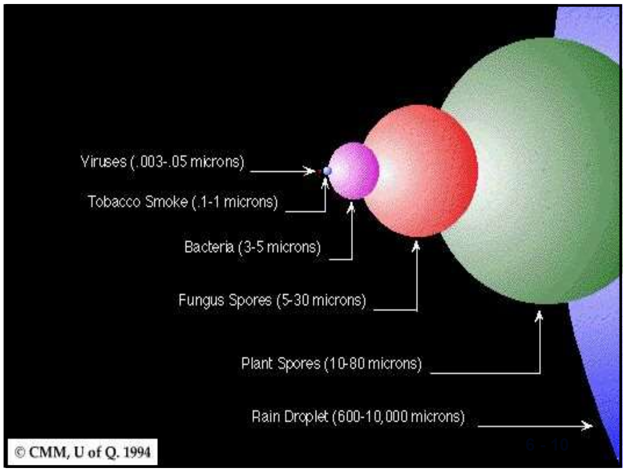


FRM 5 Sampling Train

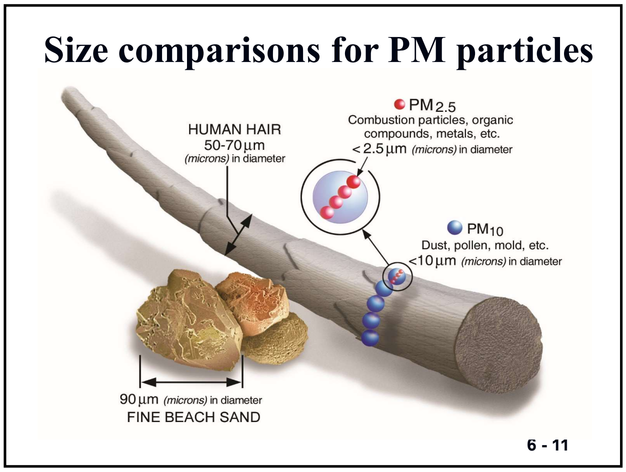


Particles

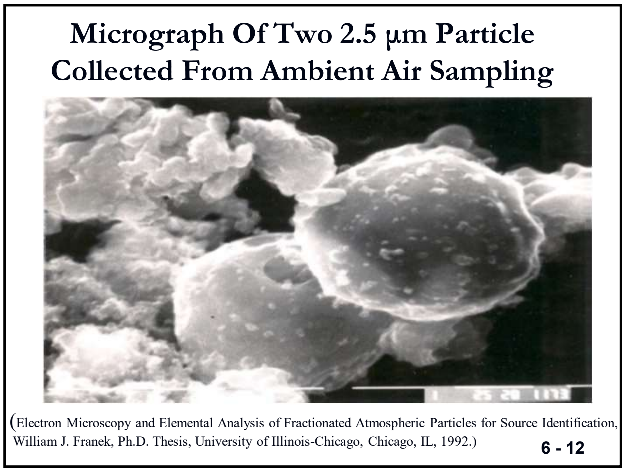
PM stands for particulate matter (also called particle pollution): the term for a mixture of solid particles and liquid droplets found in the air. Some particles, such as dust, dirt, soot, or smoke, are large or dark enough to be seen with the naked eye. Others are so small they can only be detected using an electron microscope.



© CMM, U of Q. 1994



Size comparisons for PM particles



Micrograph Of Two 2.5 µm Particle Collected From Ambient Air Sampling

(Electron Microscopy and Elemental Analysis of Fractionated Atmospheric Particles for Source Identification, William J. Franek, Ph.D. Thesis, University of Illinois-Chicago, Chicago, IL, 1992.)

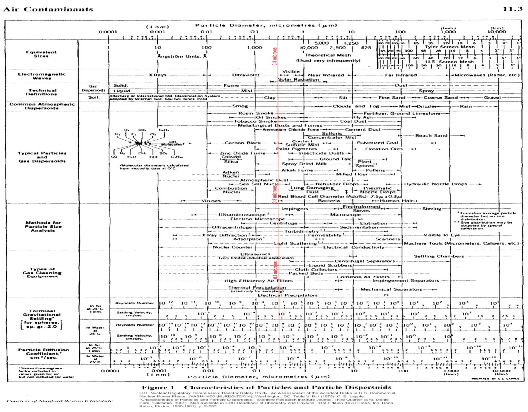
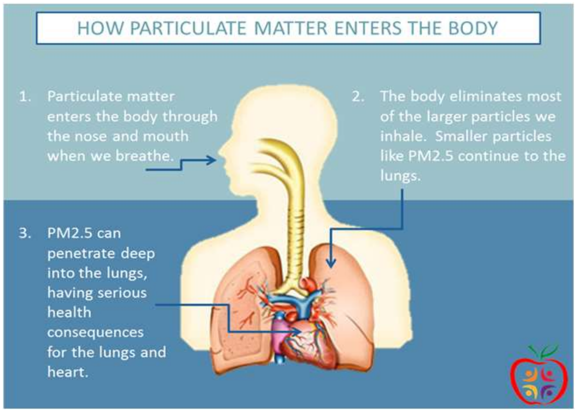


Figure 1 Characteristics of Particles and Particle Dispersoids

Courtesy of Stanford Research Institute

HOW PARTICULATE MATTER ENTERS THE BODY



1. Particulate matter enters the body through the nose and mouth when we breathe.
2. The body eliminates most of the larger particles we inhale. Smaller particles like PM2.5 continue to the lungs.
3. PM2.5 can penetrate deep into the lungs, having serious health consequences for the lungs and heart.

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 for Source Emissions?

- 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 rinses 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%)

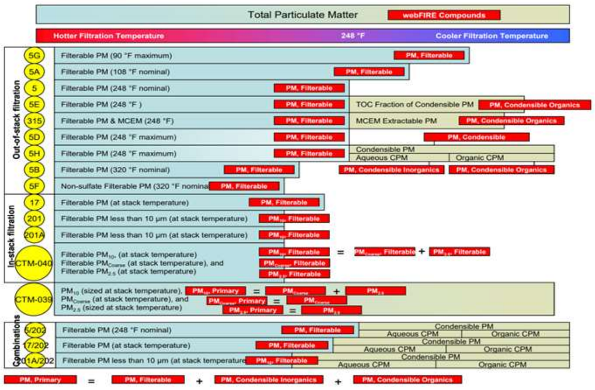


Figure 2-1: PM Methods and *WebFIRE* PM Fractions Cross-reference.

Emission Generation Categories

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

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

- Emits 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

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

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
  - $\Delta H = K \, \Delta p$

Simplified Isokinetic Rate Equation

$$\Delta H = K \, \Delta P$$

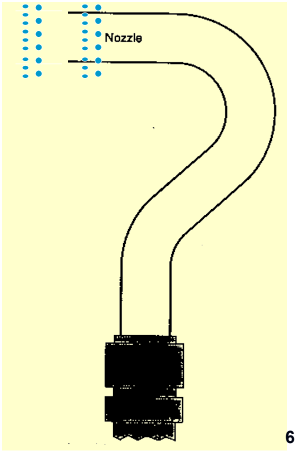
Isokinetic Sampling and Bias

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

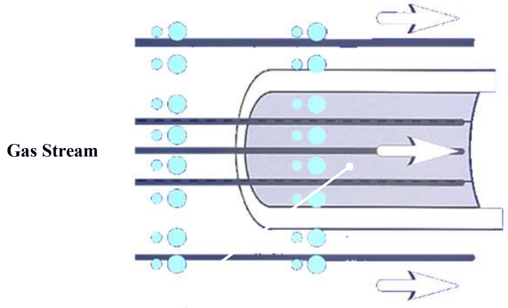
Isokinetic Sampling and Bias

- 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

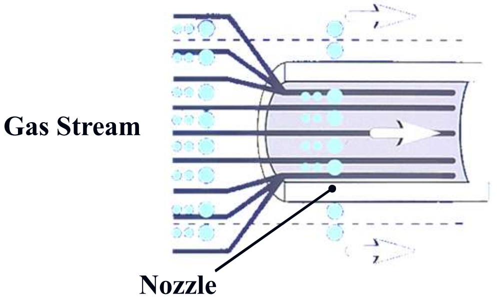


Isokinetic Sampling (100%)



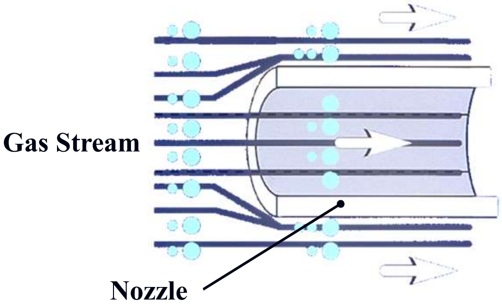
Vs=Vn

Over Isokinetic Sampling (200%)

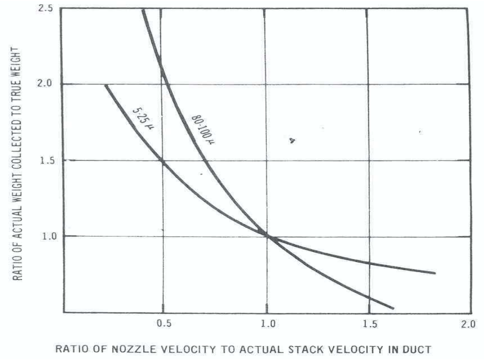


$V_s = \frac{1}{2} V_n$

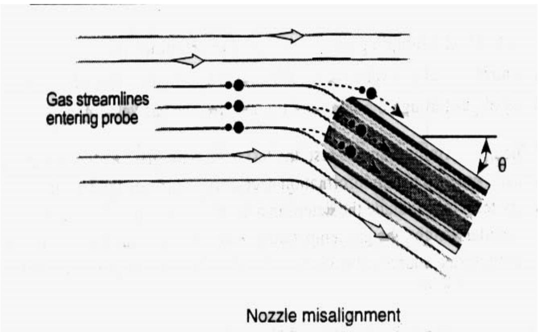
Under Isokinetic Sampling (50%)



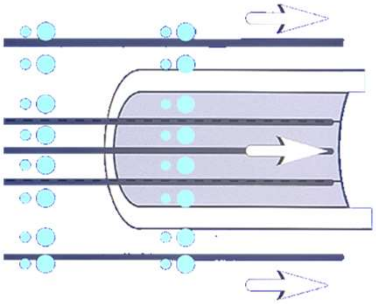
$V_s = 2V_n$



Nozzle Misalignment



$\Delta H = K\Delta p$



$V_s = V_n$

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

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

$$I_{final} = \frac{100 \, T_{s(avg)} \left[K_4 V_{1c} + \left(\frac{V_{m(avg)} \, \gamma}{T_{m(avg)}} \right) P_{bar} + \frac{\Delta H}{13.6} \right]}{60 \, \theta \, V_{s(avg)} P_s A_n}$$

FRM 5 Isokinetic Rate Equation (Simplified)

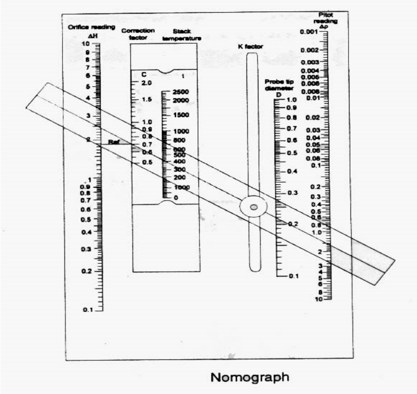
$$D_{n(est)} = \sqrt{\frac{0.0358 \, Q_m P_m}{T_m C_p \, (1 - B_{ws(est)})} \sqrt{\frac{T_s M_s}{P_s \, \Delta p_{est}}}}$$

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

FRM 5 Isokinetic Rate Equation

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

FRM 5 Nomograph



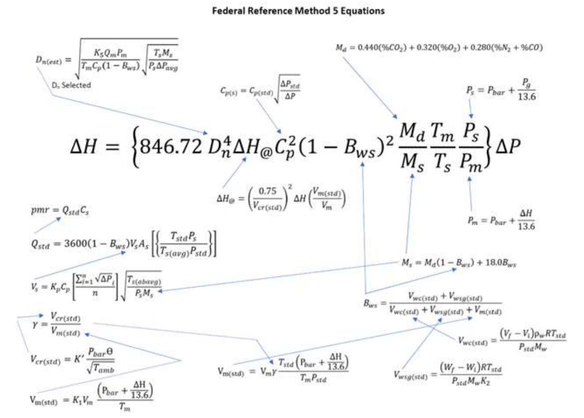
FRM 5 Isokinetic Rate Equation

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

FRM 5 Operation

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

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



Federal Reference Method 5 Equations

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

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

Dₙ Selected

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta P_{std}}{\Delta P}}$$

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$$

$$P_s = P_{bar} + \frac{P_g}{13.6}$$

$$\Delta H_{@} = \left(\frac{0.75}{V_{cr(std)}}\right)^2 \Delta H \left(\frac{V_{m(std)}}{V_m}\right)$$

$$P_m = P_{bar} + \frac{\Delta H}{13.6}$$

$$pmr = Q_{std} C_s$$

$$Q_{std} = 3600(1 - B_{ws}) V_s A_s \left[\left\{\frac{T_{std} P_s}{T_{s(avg)} P_{std}}\right\}\right]$$

$$M_s = M_d(1 - B_{ws}) + 18.0 B_{ws}$$

$$V_s = K_p C_p \left[\frac{\sum_{i=1}^{n} \sqrt{\Delta P_i}}{n}\right] \sqrt{\frac{T_{s(abavg)}}{P_s M_s}}$$

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

$$\gamma = \frac{V_{cr(std)}}{V_{m(std)}}$$

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

$$V_{cr(std)} = K' \frac{P_{bar}\Theta}{\sqrt{T_{amb}}}$$

$$V_{m(std)} = V_m \gamma \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}}$$

$$V_{wsg(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w K_2}$$

$$V_{m(std)} = K_1 V_m \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m}$$

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

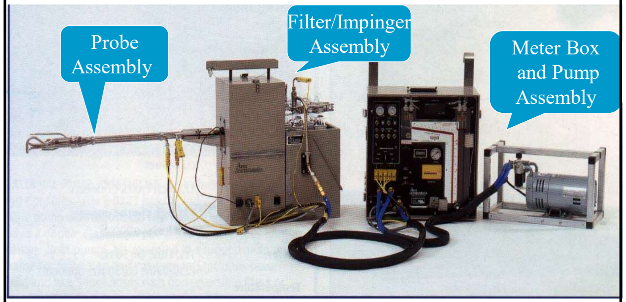
Difficulty in Maintaining Isokinetics

- 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

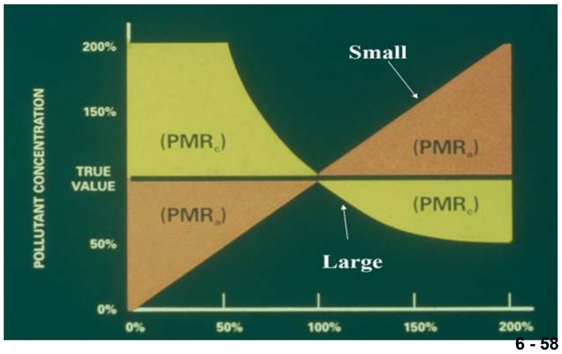
FRM 5 Sampling Train



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)

Percent Isokinetic vs: Pollutant Concentration



Errors in pmr Calculations Using FRM 5

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

What Are the Significant Errors With FRM 5?

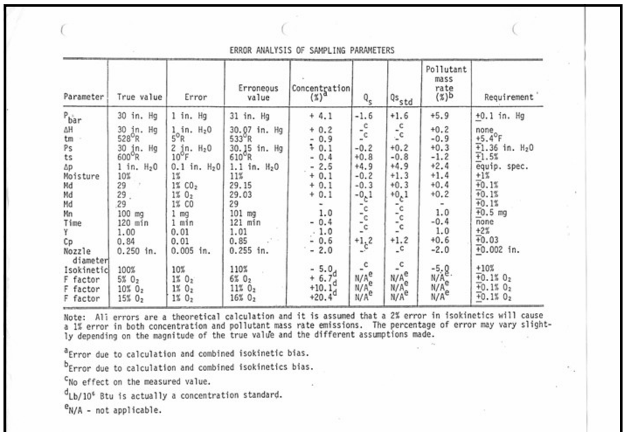
- Before obtaining the answer, the tester or observer needs to know three things to determine what is important in significant errors with FRM 5:
  - What is the data to be used for (i.e., proof of compliance, proof of violation, engineering evaluation etc.)?

What Are the Significant Errors With FRM 5?

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

Source Compliance

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



ERROR ANALYSIS OF SAMPLING PARAMETERS

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

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

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

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

[c] No effect on the measured value.

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

[e] N/A - not applicable.

Example #1 (Stack Temperature)

- Asphalt plant with concentration standard of 0.04 gr/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 0.01
  - Therefore, 6 % bias high error
  - May want to reject test!

FRM 5 Principle

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

FRM Method 5 Limits

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

FRM 5

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

FRM Method 5 Limits

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

Required Sampling

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

Example

Given the following information use the isokinetic ΔH equation to find a K factor for setting isokinetic rate through the sampling train:

$Q_m = 0.75$ *CFM*
$\Delta H_@ = 1.85$
Pitot tube $C_p = 0.85$
$t_m = 80°F$
$P_m = 30.0$ *in. Hg*
$P_s = 29.6$ *in. Hg*
$B_{wm} = 0$
$B_{ws} = 0.12$
$t_s = 280°F$
$M_d = 29$ *lb/lb-mole*
Average $\Delta p = 0.80$ *in.* H_2O

You will need to find M_s then solve the equations for nozzle diameter and K.

Example Problem (cont.)

Ans:

$$M_s = M_d(1-B_{ws}) + 18\ B_{ws}$$

$$M_s = 29\ (1-.12) + 18\ (.12) = 27.7$$

$$D_n = \sqrt{\left(\frac{0.0357\ Q_m P_m}{T_m C_p}\right) \frac{1}{(1-B_{ws})} \sqrt{\frac{T_s M_s}{P_s \overline{\Delta p}}}}$$

$$= \sqrt{\frac{(0.0357)\ (.75)\ \ (30.0)}{(540)\ (.85)} \frac{1}{.88} \sqrt{\frac{(740)\ 27.7}{(29.6)\ (.80)}}}$$

$$= \quad .241$$

Example Problem (cont.)

choose .25" nozzle

then

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

$$= \left\{846.72\,(.25)^4\, 1.85(.85)^2(.88)^2 \frac{29}{27.7}\left(\frac{540}{740}\right)\left(\frac{29.6}{30.0}\right)\right\} \Delta p$$

$$= 2.59\,\Delta p$$

$$\Delta H = 2.59\,\Delta p$$

Example Problem (cont.)

What do you do if Δp = 1.0
.80
.60

Say if moving probe from traverse point to traverse point – get new Δp's at each point, calculate and set new ΔH's at each point.

How do you set the ΔH?

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**

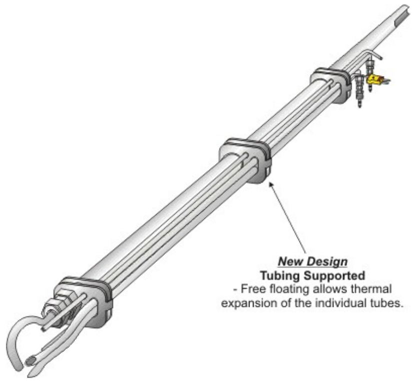
Sampling Train Components

- 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



New Design
Tubing Supported
- Free floating allows thermal expansion of the individual tubes.

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**

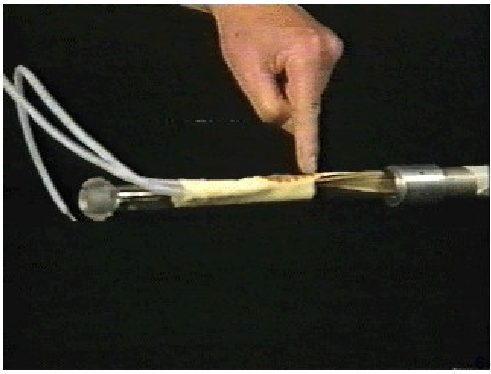
FRM 5 Sampling Probe

- 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

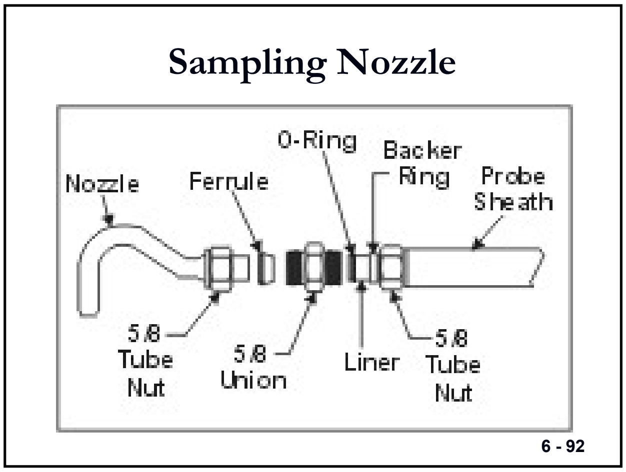
FRM 5 Sample Nozzle

- 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

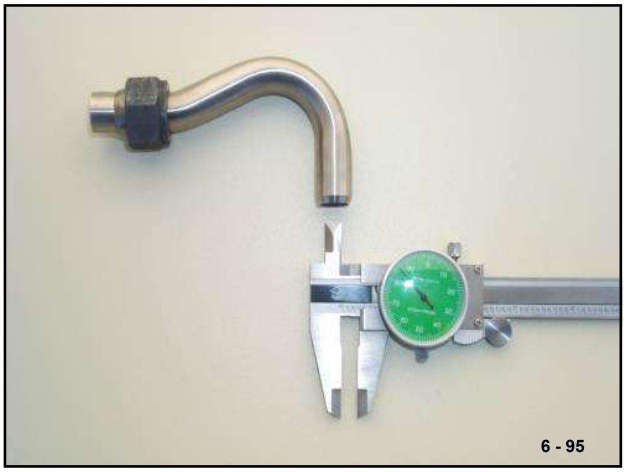
FRM 5 Sample Nozzle

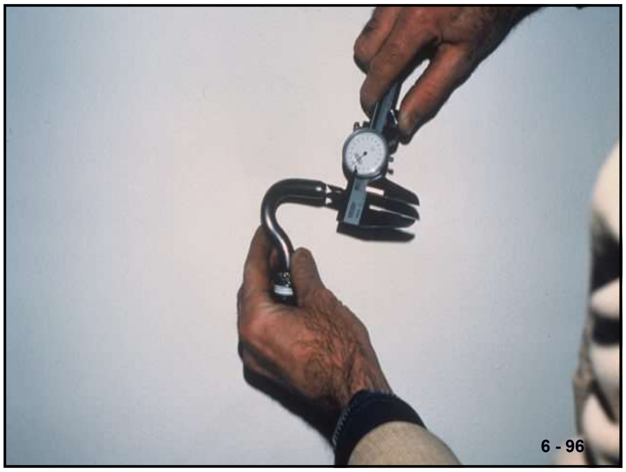
- **Range of nozzles (0.32-1.27 cm ID)**
  - **Nozzle must be calibrated**
  - **Measure 3 readings using micrometer (take average)**
  - **Low/high readings not exceed 0.004 inches**

FRM 5 Sampling Nozzle



Sampling Nozzle





FRM 5 Sample Nozzle

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

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

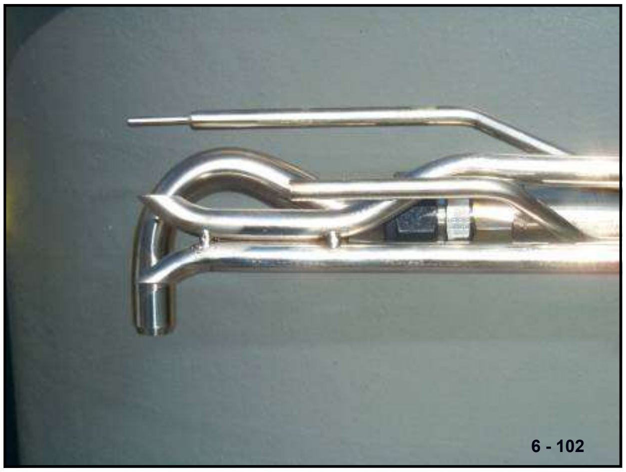
FRM 5 Isokinetic Rate Equation (Simplified)

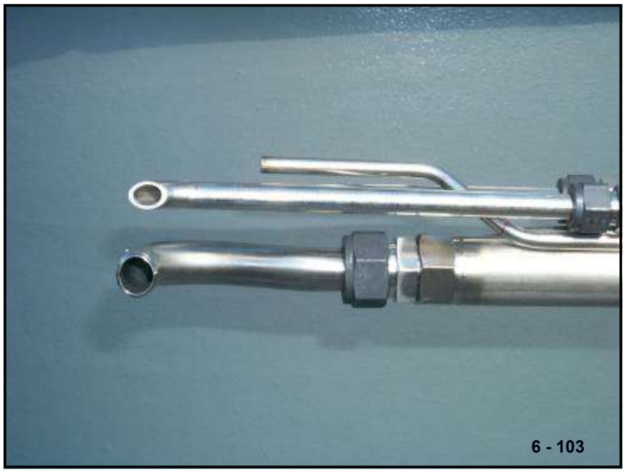
$$D_{n(est)} = \sqrt{\frac{0.0358\ Q_m P_m}{T_m C_p\ (1 - B_{ws(est)})} \sqrt{\frac{T_s M_s}{P_s\, \Delta p_{est}}}}$$

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

FRM 5 Nozzle/Pitot Tube/Thermocouple Orientation

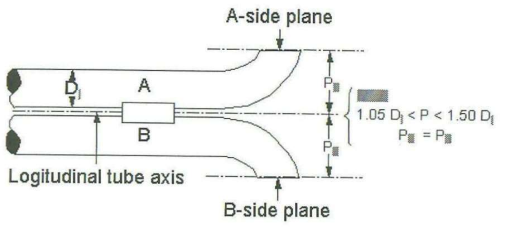
- **Must meet certain design and configuration specifications**
- **Inspect during each test to verify orientation**

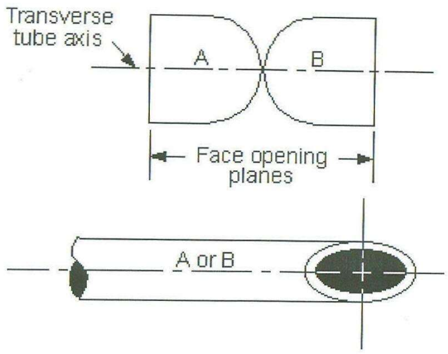


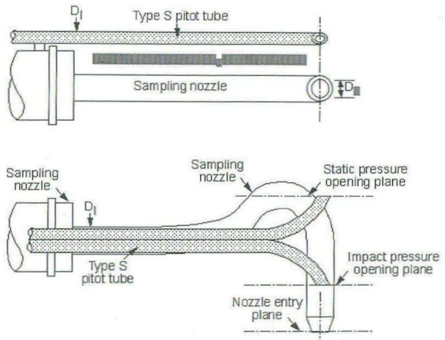


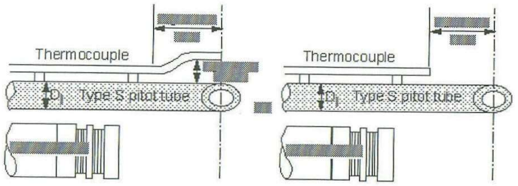
Type S Pitot Tube

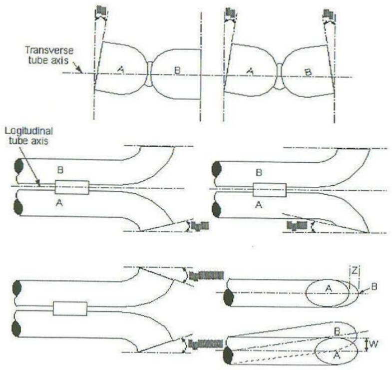
Design criteria for assigning











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

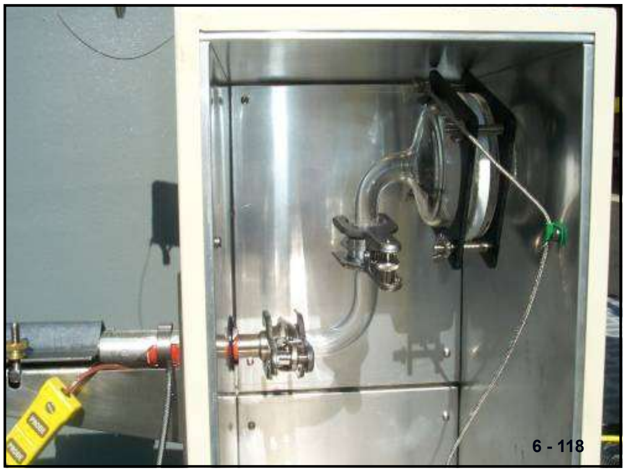
The Sample Box

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**



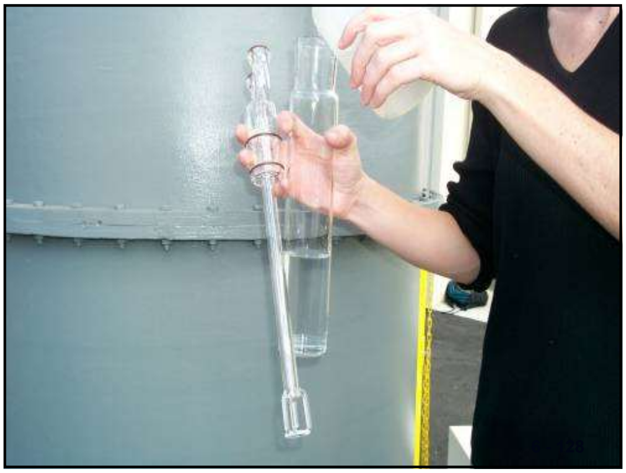
FRM 5 Heated Filter Box Desired Features

- 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%

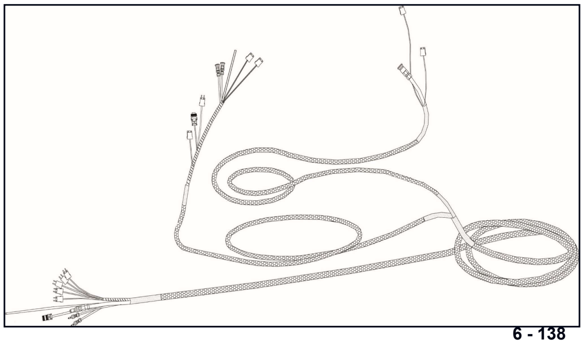
Sampling Train Components

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

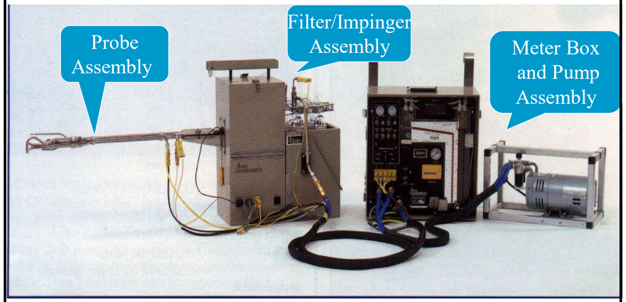
The Umbilical Line

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

FRM 5 Transfer Line



FRM 5 Sampling Train



Sampling Train Components

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

The Meter Box

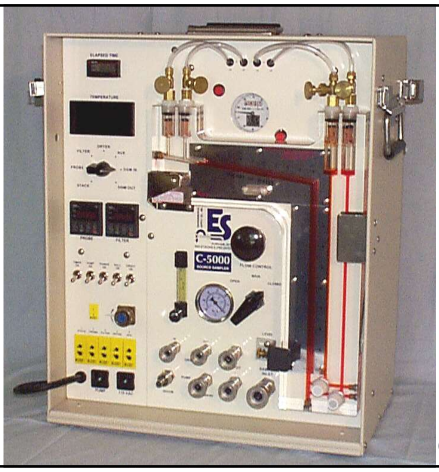
- **Pump**
- **Dry gas meter**
- **Inclined manometer for Δp and ΔH readings**
- **Flow control valves**
- **Ports for integrated gas sampling**

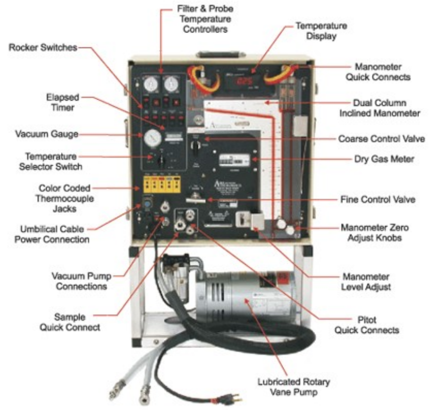
FRM 5 Meter Console Desirable Features

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

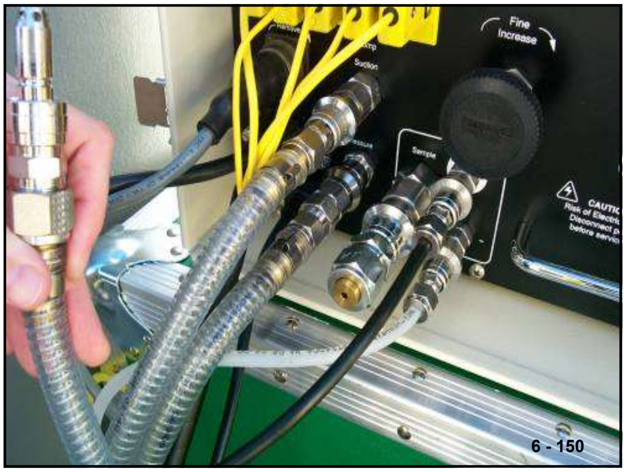
FRM 5 Meter Console Desirable Features

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



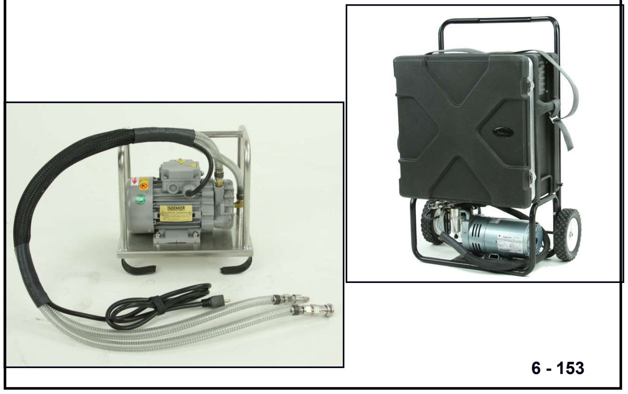


FRM 5 Dry Gas Meter

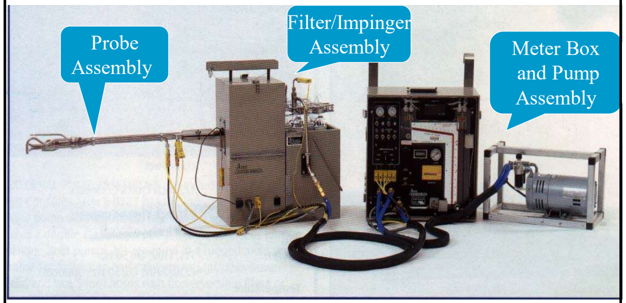


FRM 5 Digital Meter Box

FRM 5 Sampling Pump



FRM 5 Sampling Train

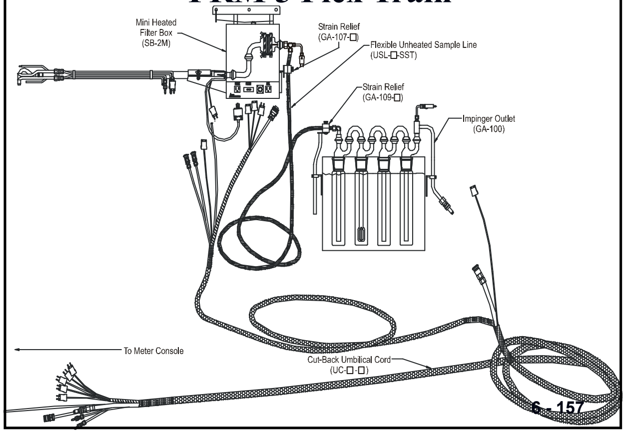


Errors in pmr Calculations Using FRM 5

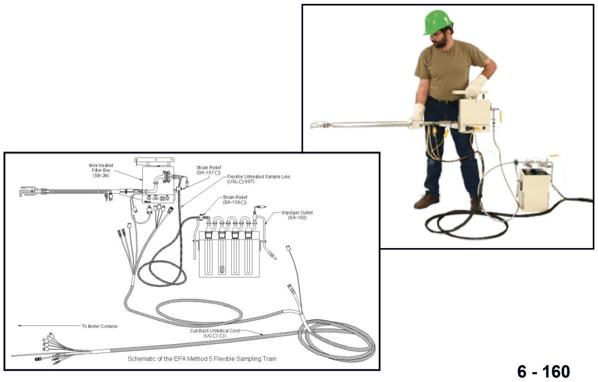
- T_s: 1.4 %
- DGM: 1.0 %
- P_s: 0.4 %
- P_m: 0.4 %
- P_b: 0.2 %
- B_{ws}: 1.0 % Affects % Iso
- Δ H: 5.0 %
- D_n: 1.0 %
- Delta $H_@$: 1.5 %

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

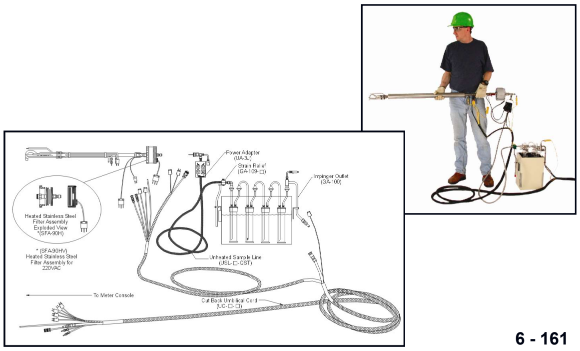
FRM 5 Flex Train



FRM 5 Flex Train



FRM 5 Compact Train



FRM 5 Recovery

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

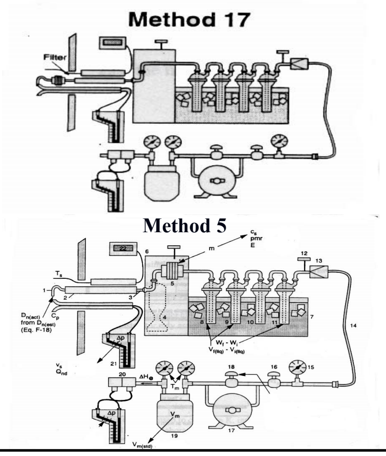
FRM 5 Recovery

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

FRM 5 Recovery

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

FRM 5 Sample Recovery Items

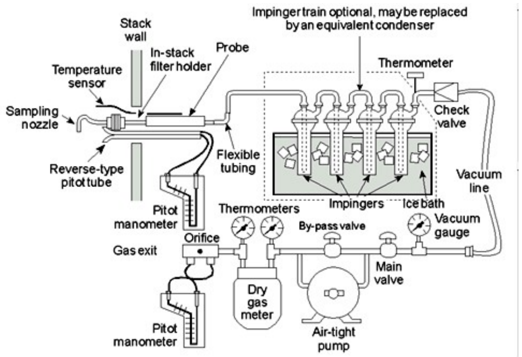


Method 17

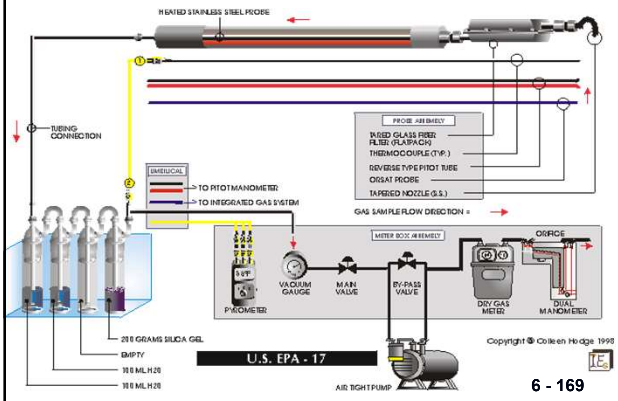
In-stack Filter
Applicability

In sources where particulate matter concentration is independent of temperature

FRM 17

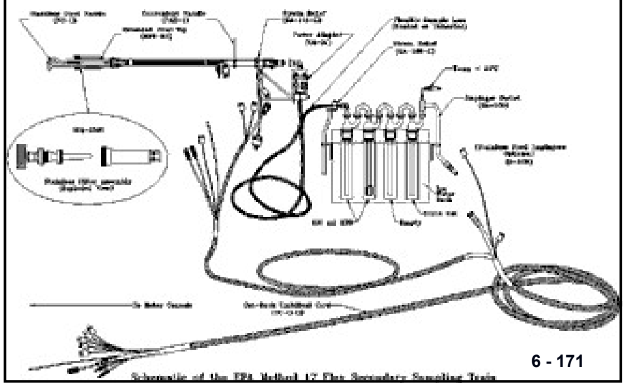


Method 17



FRM 17 In-stack Filters

FRM 17 Flex Train



Schematic of the EPA Method 17 Flex Secondary Sampling Train

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
The Source Test

The Source Test and Protocols

- Dates/Times (timeliness of the submittal?)
- Facility Information
- Unit(s) to be Tested
- Operating and Control Information
- Stack Diagram
- Methods
- Modifications
  - Listed in the method as written
  - Proposed (who has the authority to approve?)

Reviewing the Test Protocol

- Rules/Regulations
- Permits
- Previous Testing History

http://www.dep.pa.gov/BUSINESS/AIR/BAQ/BUSINESSTOPICS/SOURCETESTING/Pages/default.aspx

SOP-Test-Obs-03012019.pdf (ohio.gov)

Emission Monitoring Unit (Testing Group) | Ohio Environmental Protection Agency

Reviewing the Test Protocol

Protocol spells out the procedures to be followed by tuning the methods.

- Analyzer ranges
- Detection limits
- Sampling times
- etc.

Reviewing the Test Protocol

- Method specific tuning information
- Production Information
- Final report preparation details
- QA/QC Procedures
- **Internal stack diameter**
- **Sampling port location(s)**
  - **diagram required**
- **Location(s) relative to disturbances**
  - **must meet minimum requirements**
  - **If not > 3D traverse required**

Pre-test Meeting/Conference

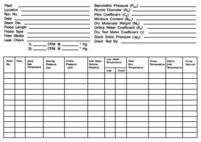
- Smoother Testing , Less Procedural Problems
- Preview facility: emissions unit and control
- Discuss Testing – request changes

Observing Testing – Be Prepared

Have a Test Protocol Handy

- PPE
- Observation Forms
- Camera (if allowed)
- Paperwork (copies)
- Methods
- Permits
- Rules

Observing Testing – Take Notes



- Field Data recorded
  - INK
  - Single-line cross out and initialed
  - Computer Entered
- Equipment ID information
- Visual inspection of nozzle, pitot tube
  - Alignment in the stack
  - Nozzle diameter

Observing Testing – Take Note

- Calibration and span gases used
- Manometers to scale
- Meter Box Values : ΔH@, γ and calibration dates
- Static and barometric pressures

Observing Testing – Take Note

- Silica Gel
- Leak checks
- Probe and nozzle clean up
- Filter
- Instrumental Methods

Observing Testing- What to be Aware of !

- Umbilical cord crimping during leak check
- Adjusting impinger connections during leak checks
- Turning off the pump during leak check
- Not using highest vacuum during leak check
- Adjusting instrument based on readings
- Fabricating data on field data sheets
- Not traversing the stack for cyclonic flow check

Types of Problems Found

- Unacceptable Sample Locations
  - Port Locations
  - Upstream & Downstream Diameters

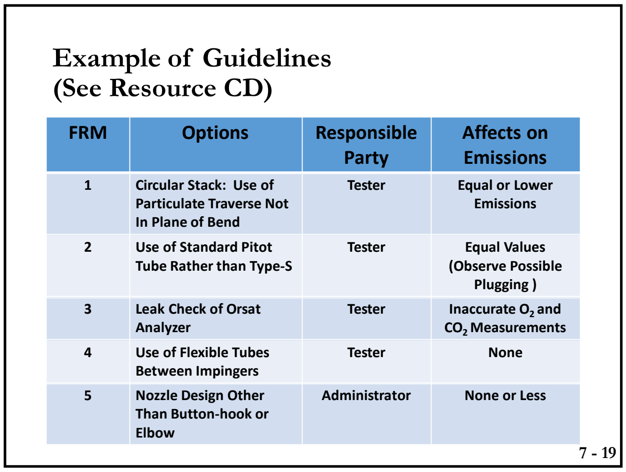
- Equipment & Electrical Needs/Limitations
  - Equipment Clearances
  - Port Diameters
  - Traversing needs (vertical)

Types of Problems Found

- <u>Equipment Errors</u>
  - Operating ranges/calibration gases
  - Poor condition or not calibrated
  - Incorrect train components
  - Improper methods

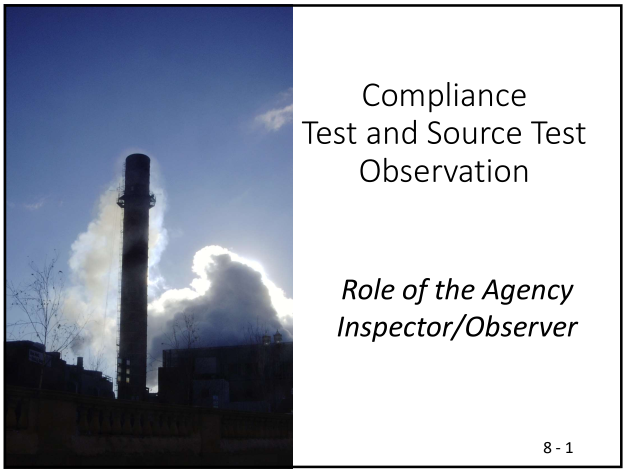
Types of Problems Found

- <u>Procedural Errors</u>
  - Cyclonic flow checks
  - Leak checks
  - Traverse points
  - Isokinetics
  - Temperatures and ice downs
  - Recovery procedures



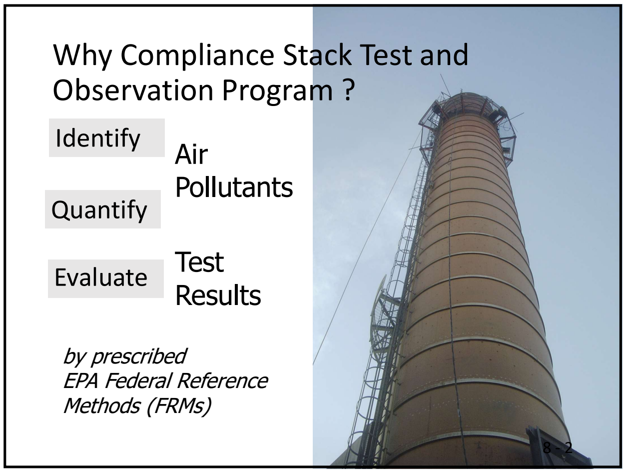
Example of Guidelines
(See Resource CD)

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

Role of the Agency Inspector/Observer



Why Compliance Stack Test and Observation Program ?

Identify
Quantify
Air Pollutants

Evaluate
Test Results

by prescribed EPA Federal Reference Methods (FRMs)

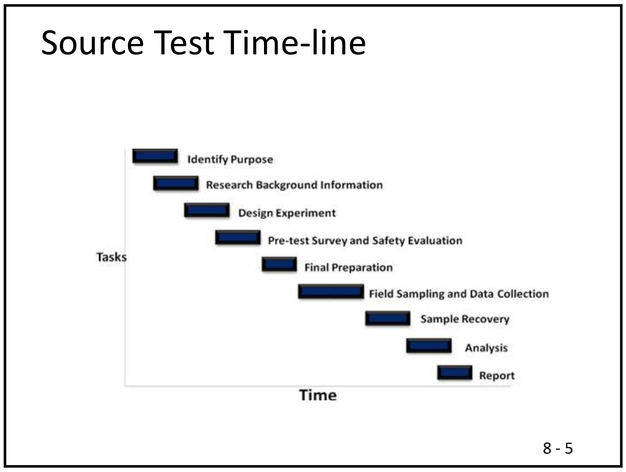
Example of Typical Industries

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

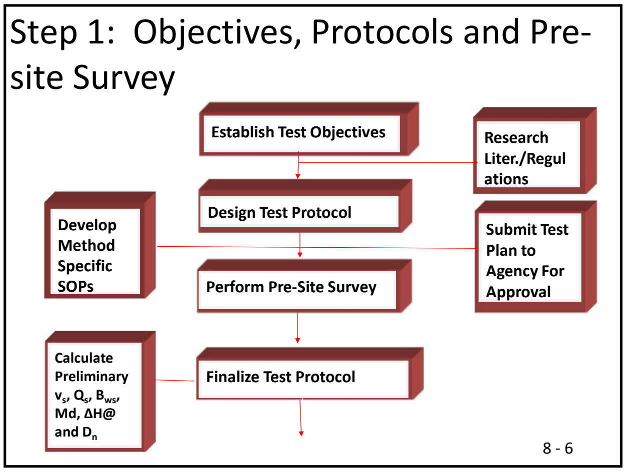
Groups Involved In A Compliance Test

- 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



Establish Test Objectives

Research Liter./Regulations

Design Test Protocol

Develop Method Specific SOPs

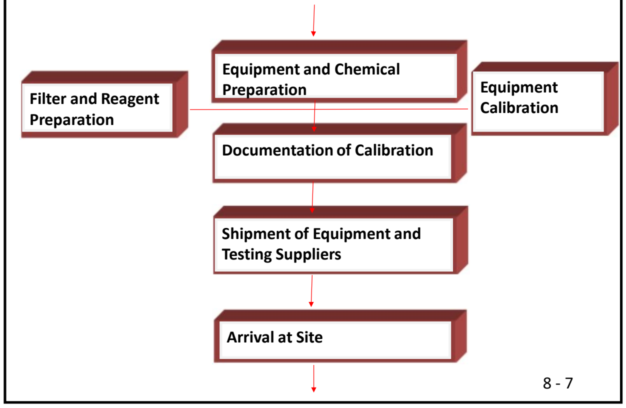
Submit Test Plan to Agency For Approval

Perform Pre-Site Survey

Calculate Preliminary v_s, Q_s, B_{ws}, Md, ΔH@ and D_n

Finalize Test Protocol

Step 2: Equipment Preparation



Equipment and Chemical Preparation

Filter and Reagent Preparation

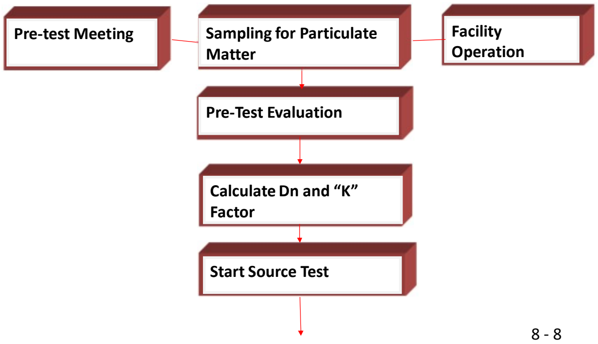
Equipment Calibration

Documentation of Calibration

Shipment of Equipment and Testing Suppliers

Arrival at Site

Step 3: Pre-test Conference and Evaluation



Pre-test Meeting

Sampling for Particulate Matter

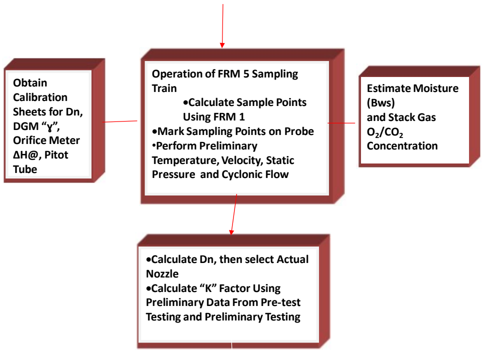
Facility Operation

Pre-Test Evaluation

Calculate Dn and “K” Factor

Start Source Test

Step 4: The Test



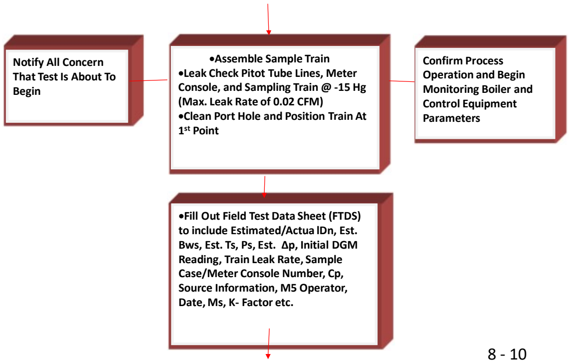
Obtain Calibration Sheets for Dn, DGM “ɣ”, Orifice Meter ΔH@, Pitot Tube

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



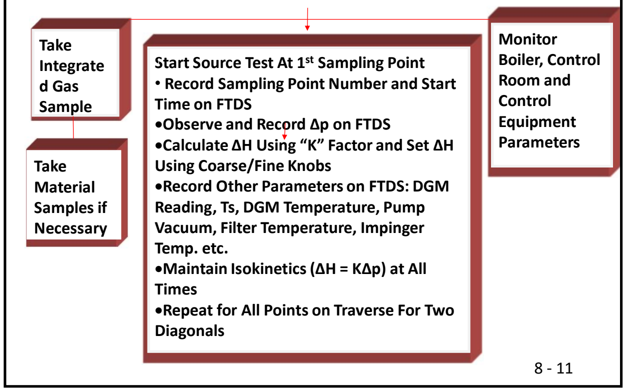
Notify All Concern That Test Is About To Begin

- 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, M5 Operator, Date, Ms, K- Factor etc.

Step 4: The Test (Cont’d)



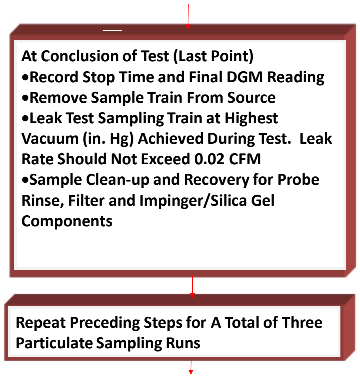
Take Integrated Gas Sample

Take Material Samples if Necessary

Start Source Test At 1st Sampling Point
- Record Sampling Point Number and Start Time on FTDS
- Observe and Record Δp on FTDS
- Calculate ΔH Using “K” Factor and Set ΔH Using Coarse/Fine Knobs
- Record Other Parameters on FTDS: DGM Reading, Ts, DGM Temperature, Pump Vacuum, Filter Temperature, Impinger Temp. etc.
- Maintain Isokinetics (ΔH = KΔp) at All Times
- Repeat for All Points on Traverse For Two Diagonals

Monitor Boiler, Control Room and Control Equipment Parameters

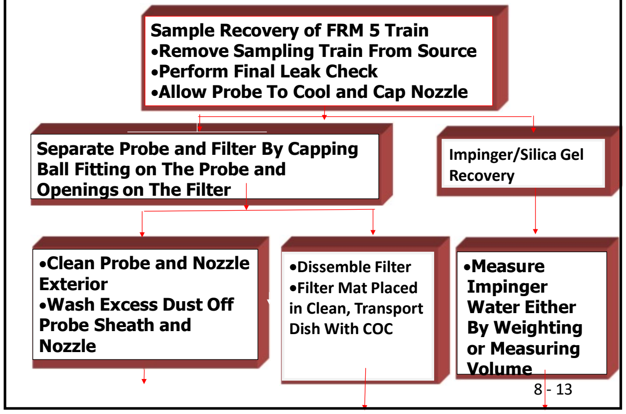
Step 4: The Test (Cont’d)



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



Sample Recovery of FRM 5 Train
- **Remove Sampling Train From Source**
- **Perform Final Leak Check**
- **Allow Probe To Cool and Cap Nozzle**

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

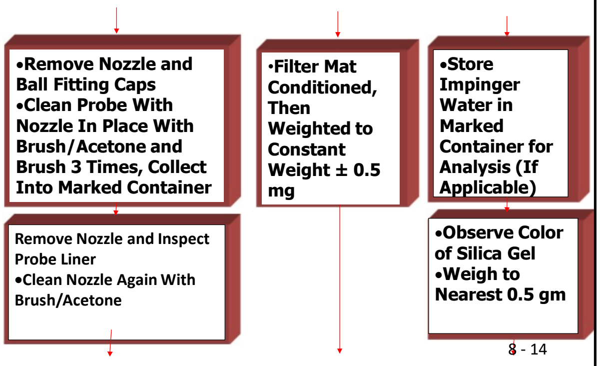
Impinger/Silica Gel Recovery

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

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

- **Measure Impinger Water Either By Weighting or Measuring Volume**

Step 5: Sample Recovery (Cont'd)



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

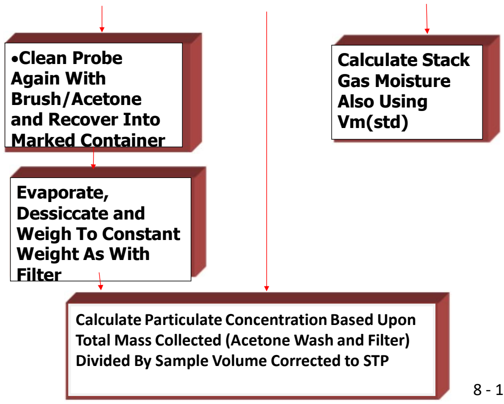
Remove Nozzle and Inspect Probe Liner
- Clean Nozzle Again With Brush/Acetone

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

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

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

Step 5: Sample Recovery (Cont'd)



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

Evaporate, Dessiccate and Weigh To Constant Weight As With Filter

Calculate Stack Gas Moisture Also Using Vm(std)

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

Function of Stack Test Observer

- *"…the principal 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

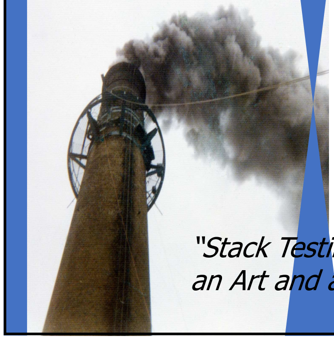
- Be Present! (Phone insp. and windshield insp. are discouraged)
- Have a Plan, Follow the Plan!
- 3-Tier Inspection
- Observations – "familiar" with 40 CFR 60, App. A, Methods 1-4,5; 1.Velocity Profile, 2.Leak Check, 3.Clean-up 4. Observer Check-list
- Operations of facility
- Sample train recovery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

Inspectors Do's and Don'ts

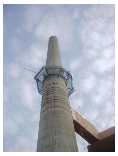
DO
- Ask intelligent questions that add value
- Become "familiar" with test methods rules and test plans
- Show Up! Presence is critical
- Be critical but reasonable
- Reward "quality testing"

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

1974 – Coal



2004 – Natural Gas



*"Stack Testing…
an Art and a Science"*

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 c**ompliance 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

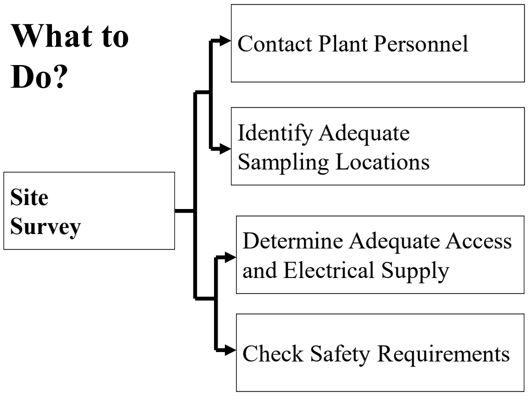
Observer Behavior

- The observer should do all within his/her 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/her 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

What to Do?



Phase 1: Preparation and Planning

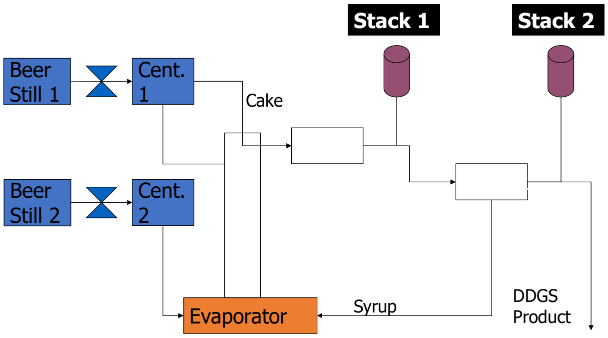
- Division of Air Quality must clarify for the plant representative and stack test team leader procedures to be followed (i.e., compliance test guidelines)
  - Identification of Federal Reference Methods (FRMs): PM, Condensibles, Filter Temp, Inorganics, Organics etc.
  - Operation level of process during 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

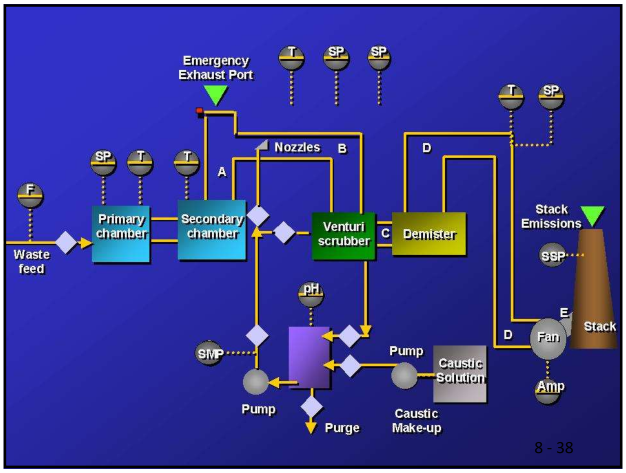


Utility of Preparing a Block-Style Flowchart

- 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?

- **Test Plan**
  - Verify Correct Test Methods For Regulated Source
  - Finalize Test Schedule
  - Review All Calibration Requirements
  - Identify Variations from Federal Reference Methods

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
  - 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

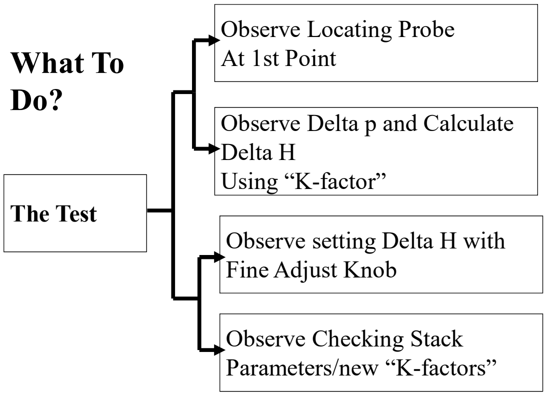
What To Do?

- **On-site Test**
  - Have Opening Pre-Test Meeting
  - Observe Equipment Setup
  - Observe Leak Checks, Preliminary Measurements, Sampling Points
  - Determine “K” Factor and Review Field Test Data Sheets

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

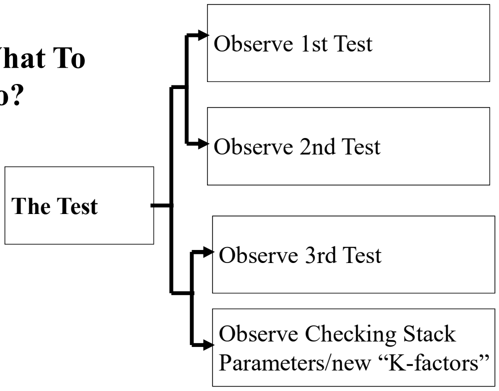
What To Do?



The Test

- Observe Locating Probe At 1st Point
- Observe Delta p and Calculate Delta H Using “K-factor”
- Observe setting Delta H with Fine Adjust Knob
- Observe Checking Stack Parameters/new “K-factors”

What To Do?



The Test

- Observe 1st Test
- Observe 2nd Test
- Observe 3rd Test
- Observe Checking Stack Parameters/new “K-factors”

Phase 2: Conducting The Test

- Observer’s Checklist
  - 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 (Δ 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

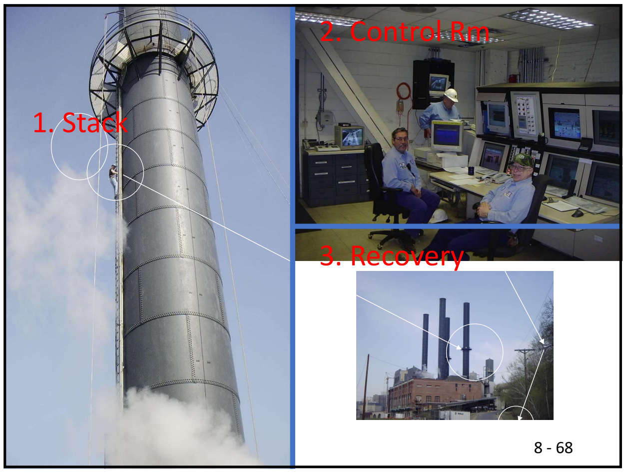
Phase 2: Conducting The Test

- 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 and then Climb

Safe Climb?

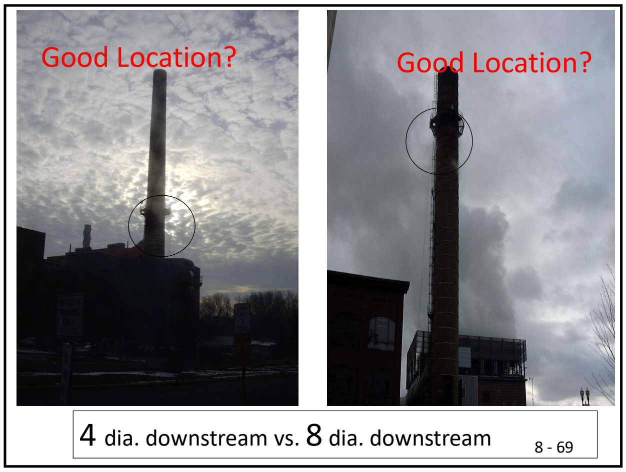
Unsafe Climb?



1. Stack

2. Control Rm

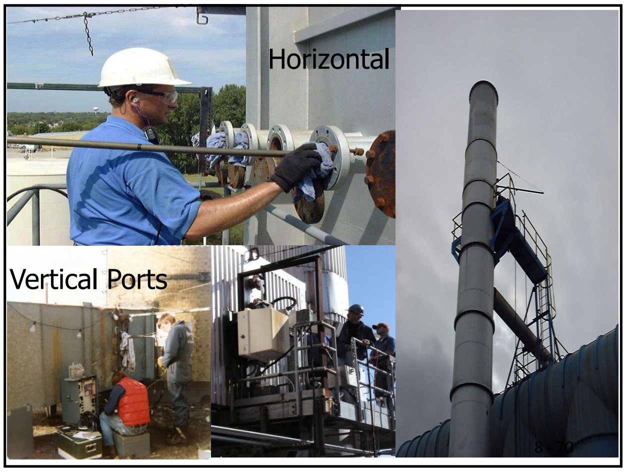
3. Recovery



Good Location?

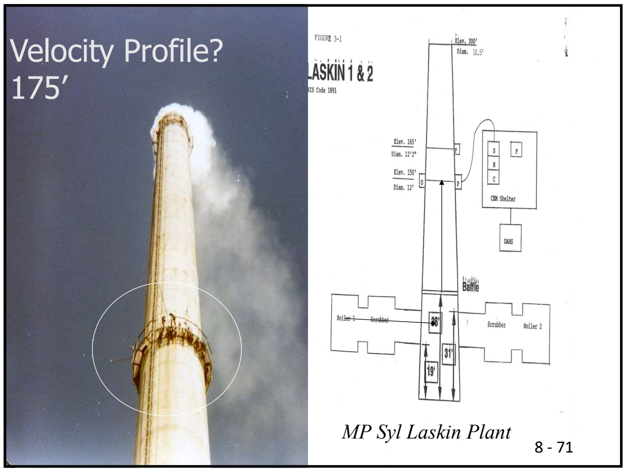
Good Location?

4 dia. downstream vs. 8 dia. downstream



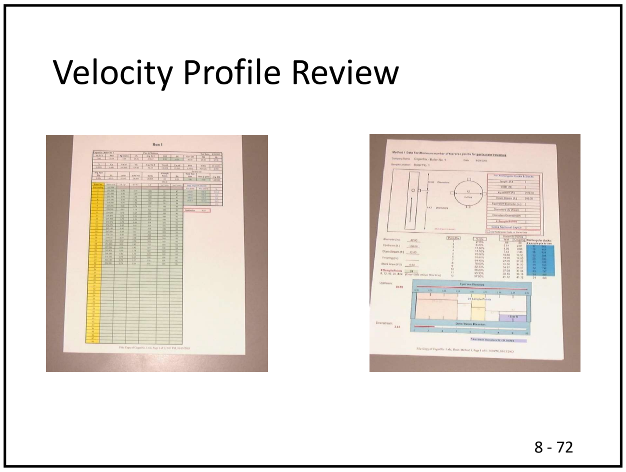
Horizontal

Vertical Ports

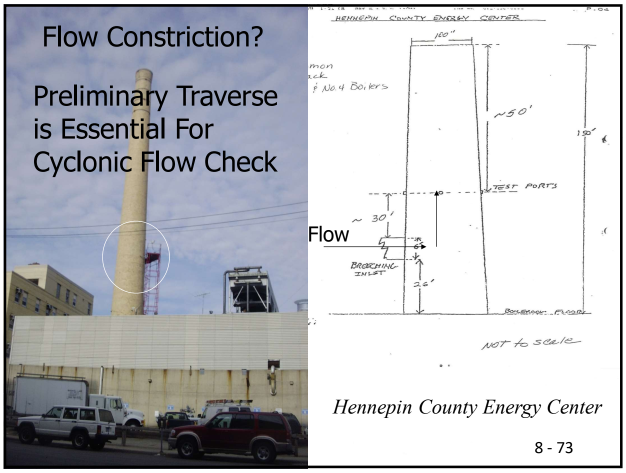


Velocity Profile?
175′

MP Syl Laskin Plant



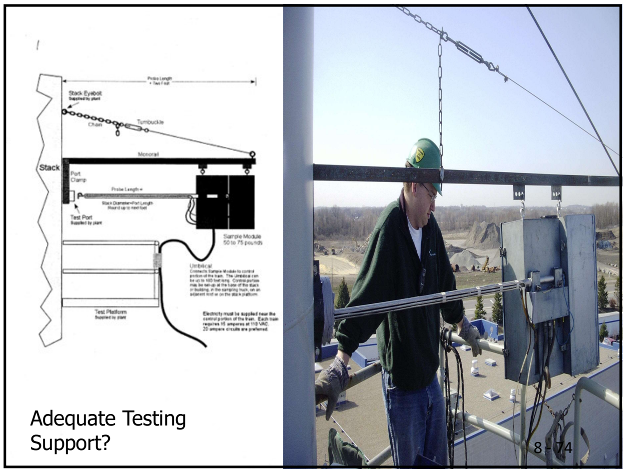
Velocity Profile Review



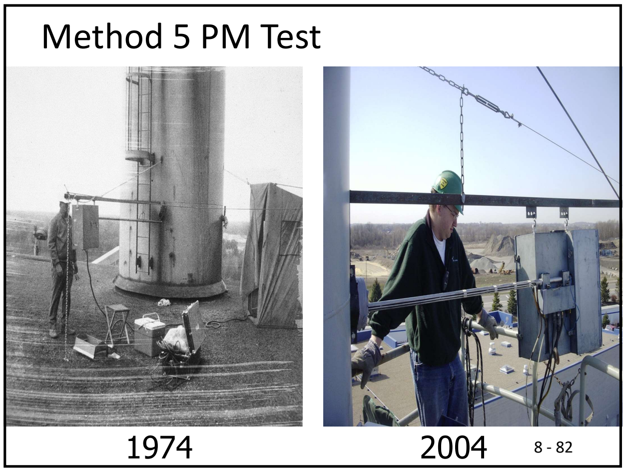
Flow Constriction?

Preliminary Traverse is Essential For Cyclonic Flow Check

Hennepin County Energy Center

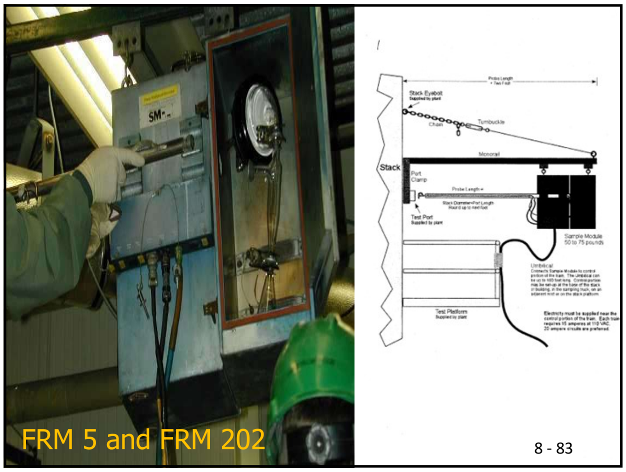


Adequate Testing Support?


Method 5 PM Test

1974

2004

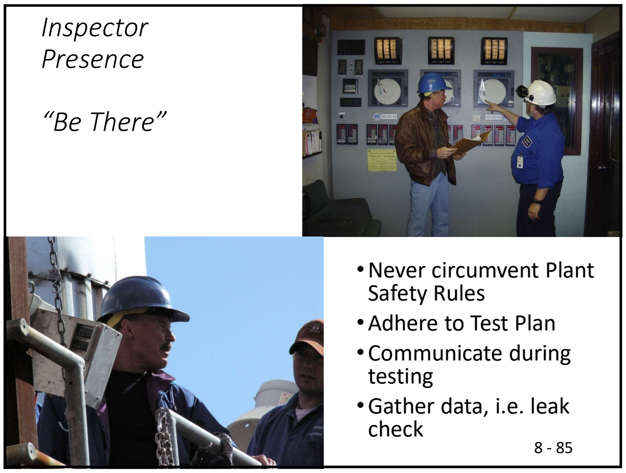


FRM 5 and FRM 202


Set up

Clean up

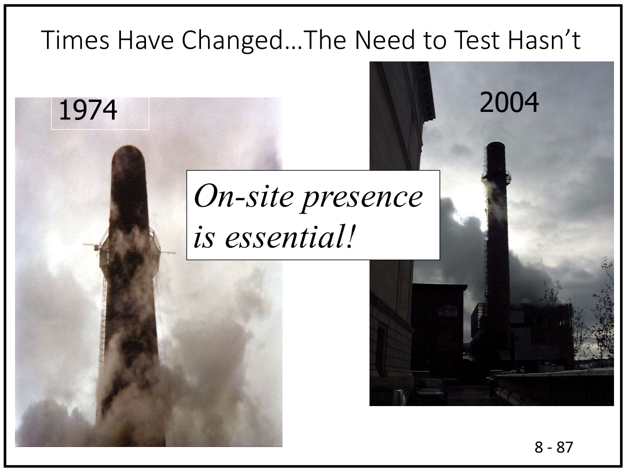
Inspector: Use Discretion



Inspector Presence

"Be There"

- Never circumvent Plant Safety Rules
- Adhere to Test Plan
- Communicate during testing
- Gather data, i.e. leak check

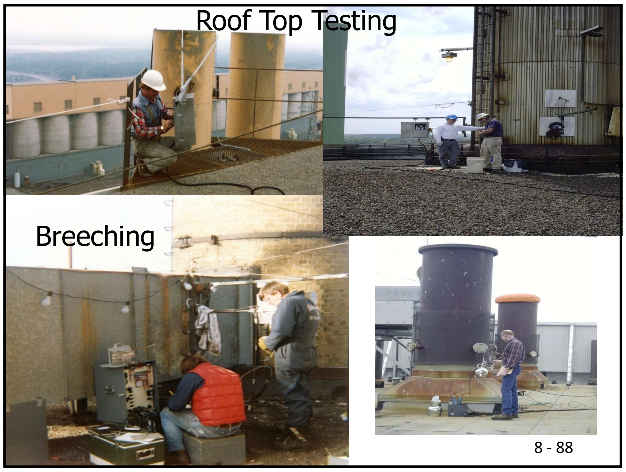


Times Have Changed…The Need to Test Hasn't

1974

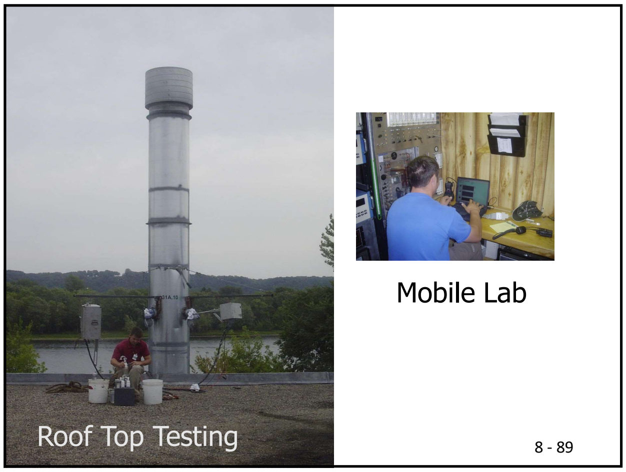
2004

On-site presence is essential!



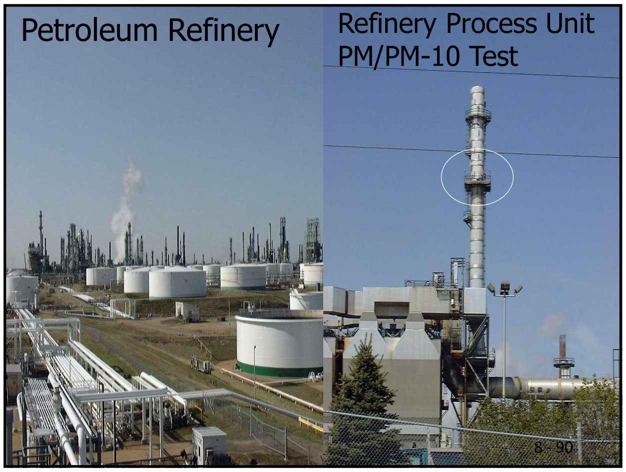
Roof Top Testing

Breeching



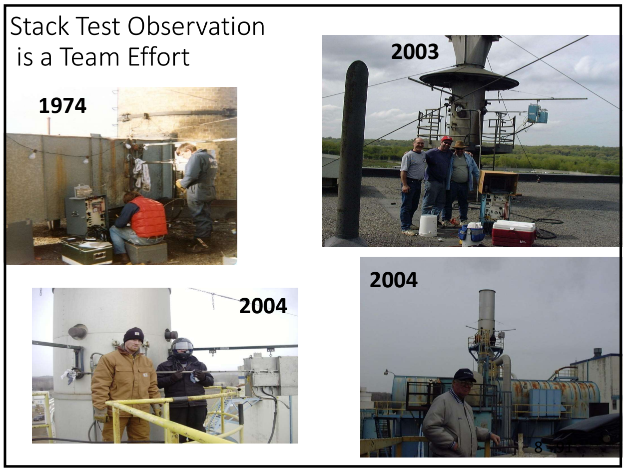
Roof Top Testing

Mobile Lab



Petroleum Refinery

Refinery Process Unit PM/PM-10 Test



Stack Test Observation is a Team Effort

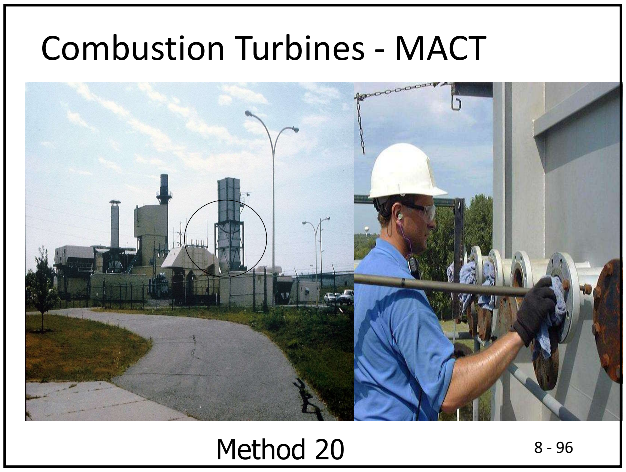
Set-Up, Leak Checks, Operations and Clean-up Essential

Proper Operations are Critical

"Study, Then Pass the Test"

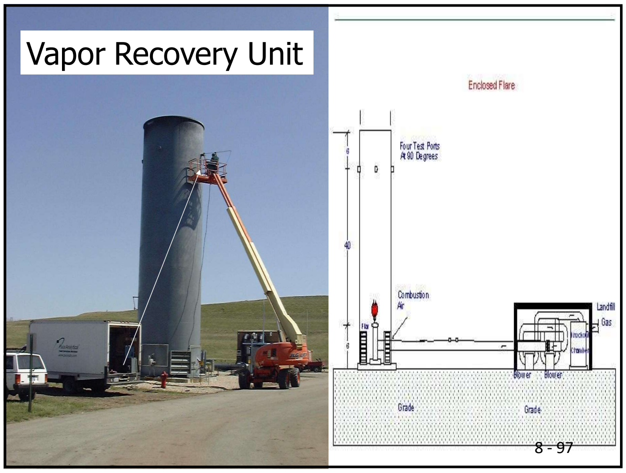
Operations - Data Acquisition, You Have To Be There!

Load, production limits and temperatures

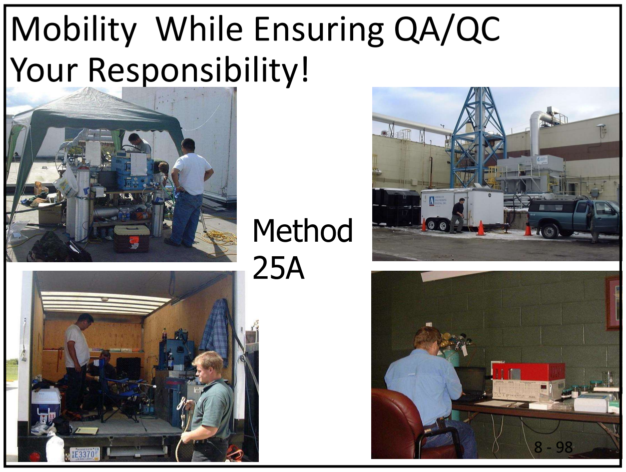


Combustion Turbines - MACT

Method 20



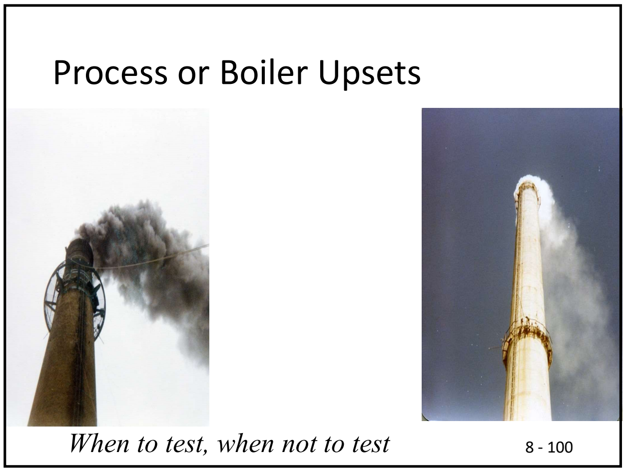
Vapor Recovery Unit



Mobility While Ensuring QA/QC
Your Responsibility!

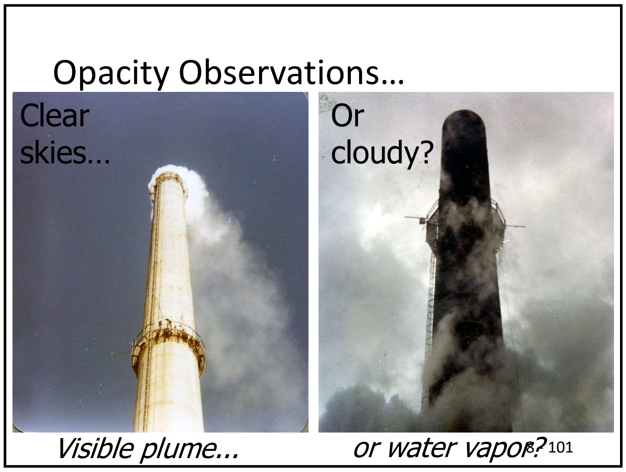
Method
25A

Mobility



Process or Boiler Upsets

When to test, when not to test



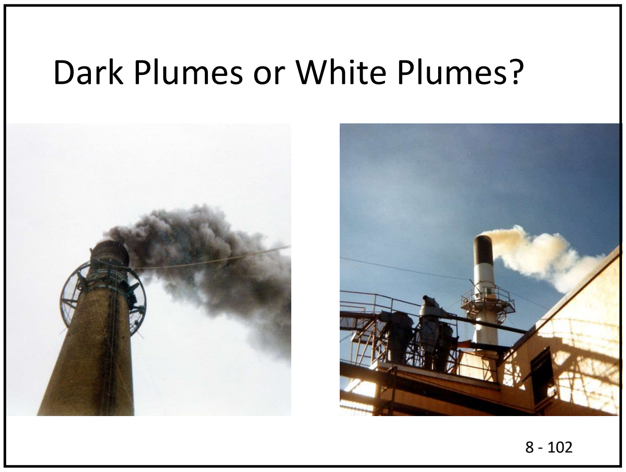
Opacity Observations…

Clear
skies…

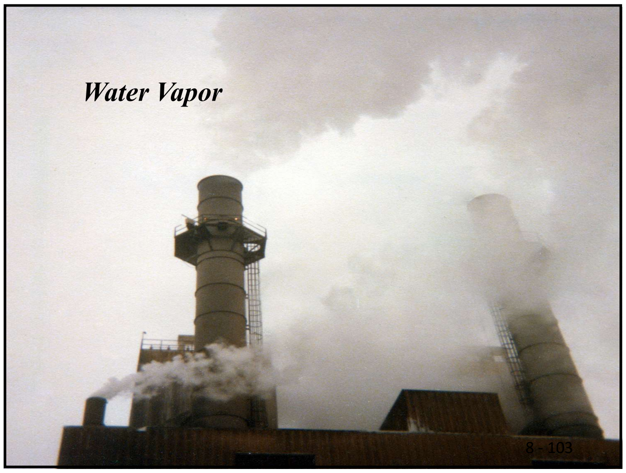
Or
cloudy?

Visible plume…

or water vapor?



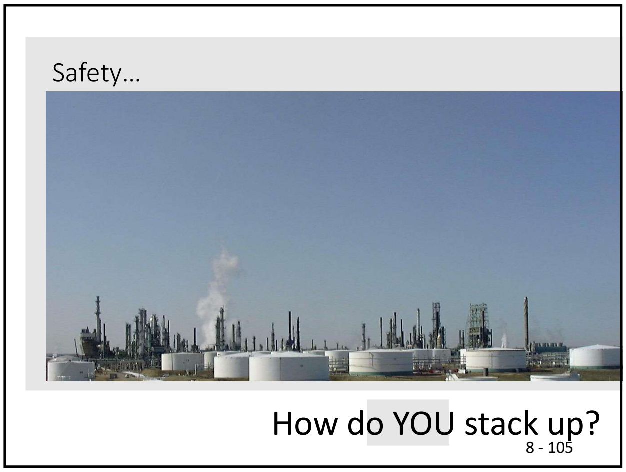
Dark Plumes or White Plumes?



Water Vapor

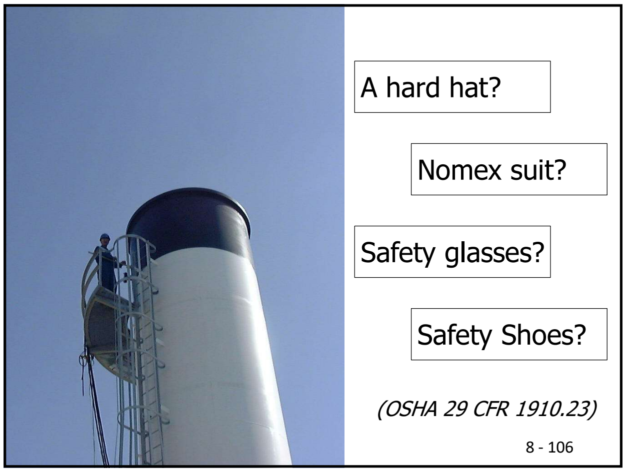
Testing Issues

- 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?



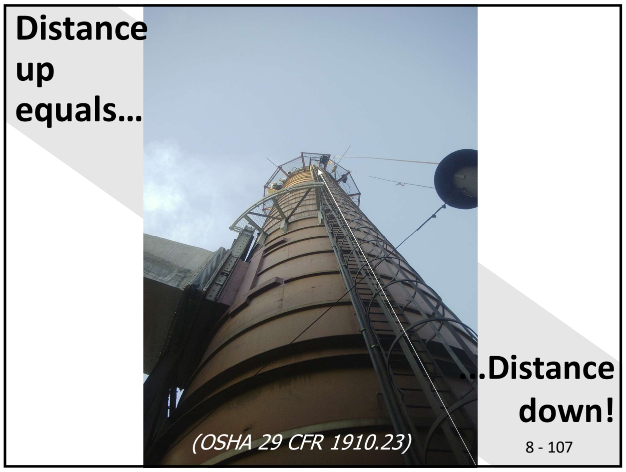
A hard hat?

Nomex suit?

Safety glasses?

Safety Shoes?

(OSHA 29 CFR 1910.23)



Distance up equals…

…Distance down!

(OSHA 29 CFR 1910.23)

Be Prepared

Buckle Up…

Hook Up…

Lock Up!

Weather is Critical

Dress Accordingly

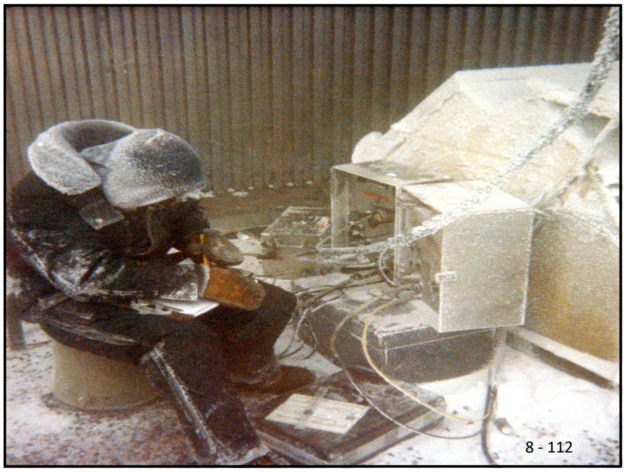
Ladder + Cable + Cage

Be safe up there!

(OSHA 29 CFR 1910.23)

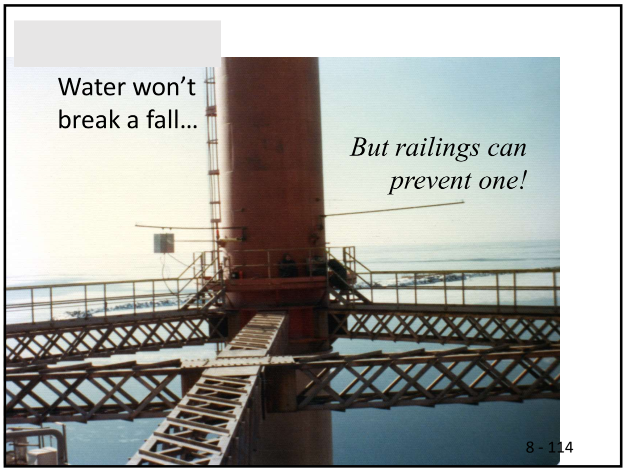
Safety…Always

Compatible and necessary!



Cold Weather Testing

Dress for it!

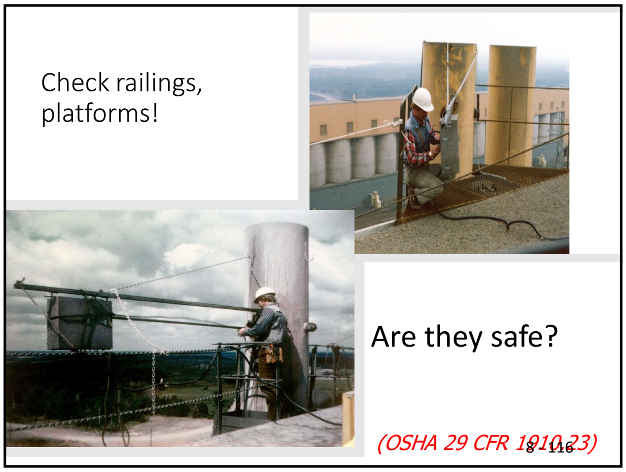


Water won’t break a fall…

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)

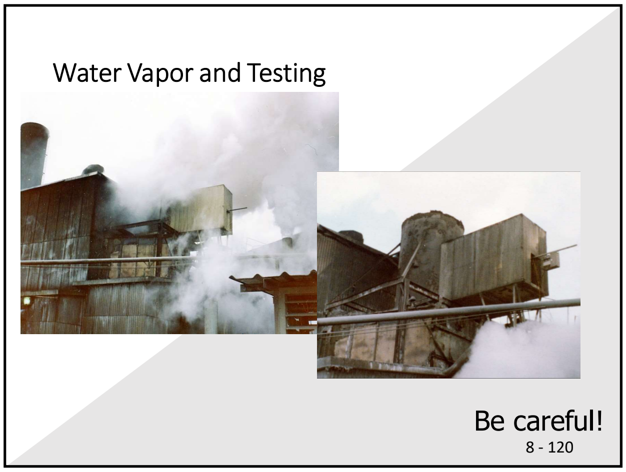

Unsafe Testing

Be careful!


Is this safe for testing?


Clear visibility…

Enhances safety!


Water Vapor and Testing

Be careful!

Communications are Essential

Make time for *SAFETY!*

Testers use Harnesses!

State inspectors should too!

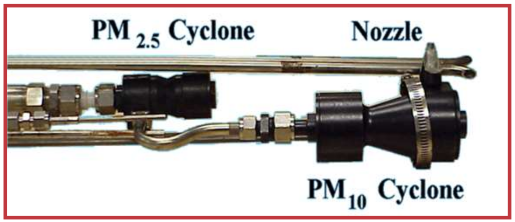
Respirators…

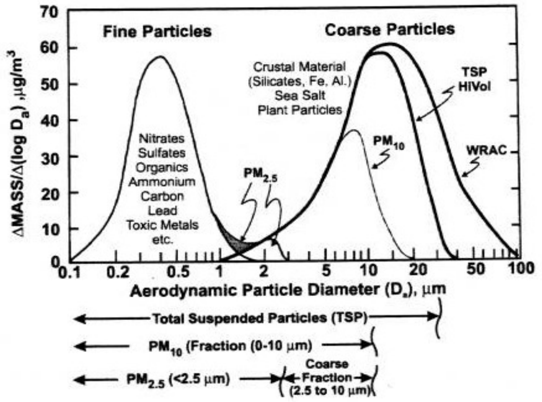
Are helpful!

Scaffolding or Ladders

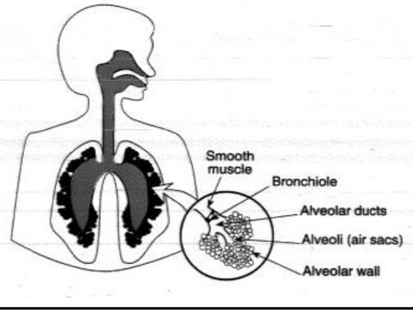
Always Buckle Up!

U.S. EPA APTI
Compliance Test and Source Test Observation
FRMs 201/201A
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

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)

- 40 CFR 51, Appendix M
- $Q_c = Q_s + Q_r$ 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

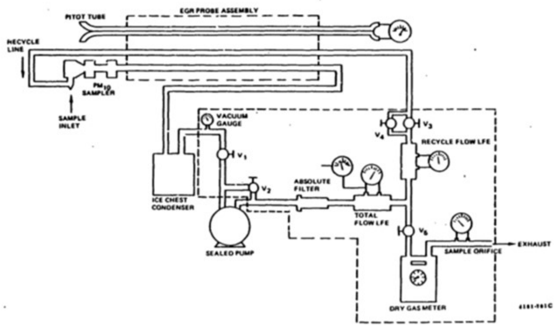
FRM 201
Exhaust Gas Recirculation (EGR)

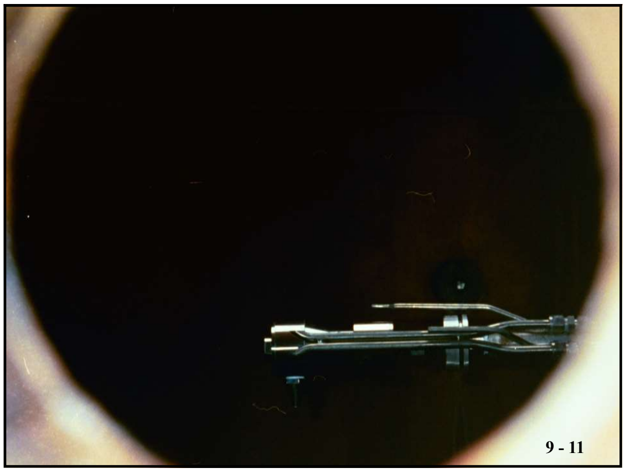
- EGR modification of FRM 5
  - Nozzle has a recycle attachment
  - The recycle gas is heated to stack temperature
  - Adds in-stack cyclone to capture PM-10
  - Delete out-of-stack filter

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

Schematic of EGR Sampling Train





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%, sample within 80 and 120 percent of isokinetic flow 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 important as FRM 5.
- Dwell time at each point is proportional to stack gas velocity. (sec. 8.7.1)
- Assume a Reynolds number N_{RE} using Equation 10 in the described CFR method and an estimated sampling rate.

FRM 201A
Constant Sampling Rate (CSR)

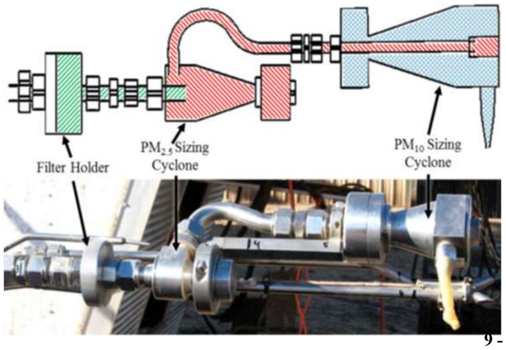
- Total catch may not be accurate as FRM 5
- Can use impactor or cyclone
- If using impactor, must be calibrated
- FRM 201A can also be used with FRM 202
- CSR is recommended if:
  - Particle sizing is desired
  - Low concentration of PM-10

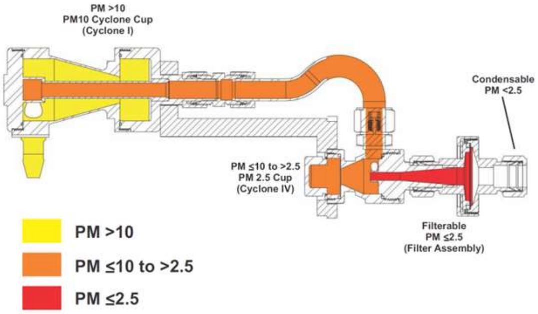
FRM 201A
Constant Sampling Rate (CSR)

- A 4-inch port should be adequate for the single PM_{10} or $PM_{2.5}$ sampling apparatus.
- A 4-inch diameter port cannot be use, in any circumstances, when the combined dimension of the cyclone and the exceeds the internal diameter of the port.

PM – 10 Sampling at Cotton Gins

EPA Method 201A PM10 and PM2.5 sizing cyclones and in-stack filter holder schematic (CFR, 2010) and photograph (▨ ≤ 2.5 µm ▨ , 10 to 2.5 µm, ▨ > 10 µm).

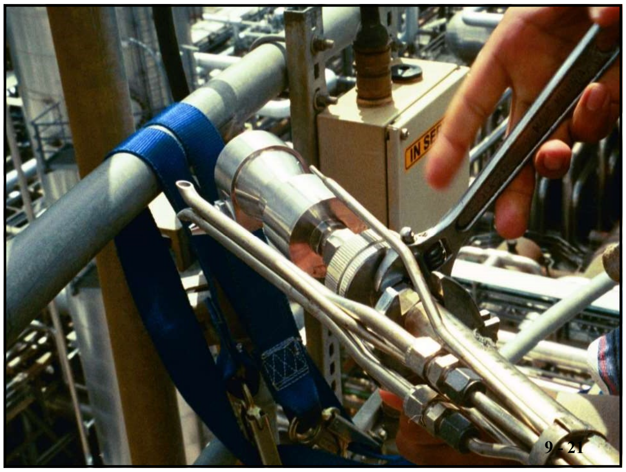


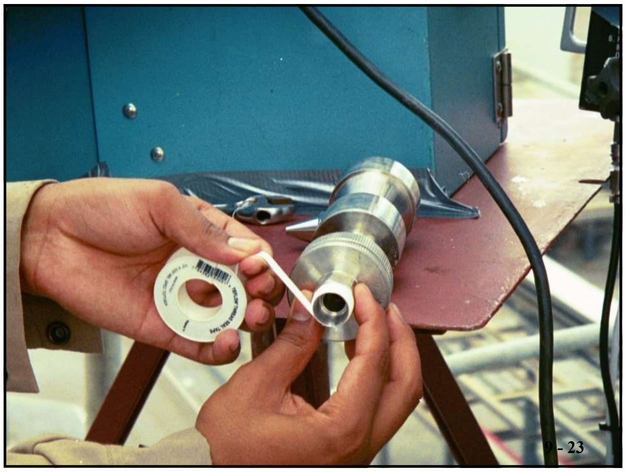


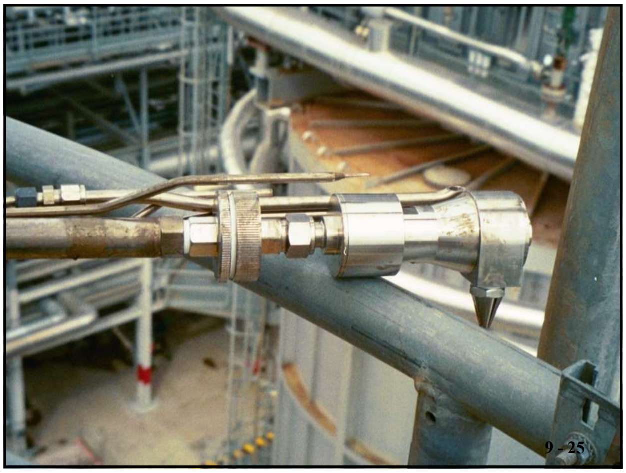
- 🟨 PM >10
- 🟧 PM ≤10 to >2.5
- 🟥 PM ≤2.5

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

FRM 201A previously 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

FRM 201A 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

FRM 201A PM-10 and PM-2.5

- Sampling train identical to FRM 201A PM-10 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

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

FRM 201A: Method for Determination of PM10/PM2.5

- Flow rate determination for cyclones determined from manufacturer’s graph

FRM 201A: 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

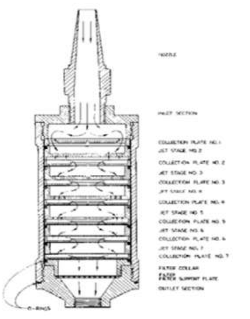
Cascade Impactors

- The following slide shows a cascade impactor sampling system that is designed for direct measurement of particle size ranges. The circular plates have different size slots or round holes that allow particles smaller than the impaction plate collection to pass through to the next plate, until they are distributed by size on all plates. These are directly weighed.
- The disadvantage for use in measuring PM from Cascade impactors is that it does not work well when the total PM catch is small.

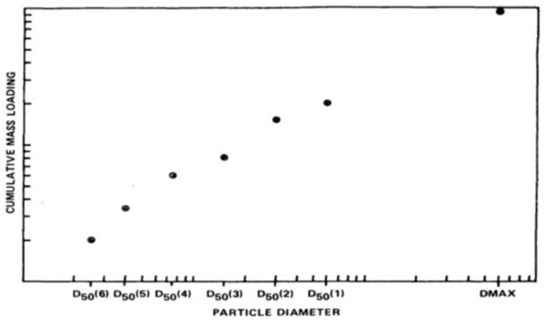
Cascade Impactors

- Another primary alternative that could be used is employing a Method 5 PM train fitted with a polycarbonate filter instead of a glass fiber (the polycarbonate filter traps PM on its surface, whereas the glass fiber allows PM to penetrate into the fiber, making it difficult to see). Selective electron microscopy is then used to count the fraction of different PM size ranges.

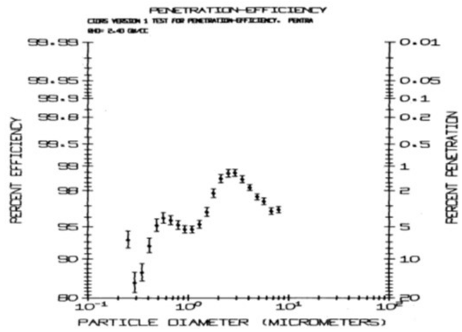
Cascade Impactors



Cumulative Size Distribution from Raw Impactor Data



Control Device Penetration Curve with Confidence Limits



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)

pmr = Concentration x Stack gas volumetric flow rate

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

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

Emission Rate (E)

Can be expressed in:

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

The emission rate, in terms of the units given in the New Source Performance Standards (NSPS), is related to concentration and mass rate in the following manner:

$$E = \frac{pmr}{Q_H} = \frac{c_S Q_S}{Q_H}$$

Where:

Qs = the stack gas volumetric flow rate (units of ft3/hr, m3/hr)

QH = the heat input rate, the rate at which combusted fuel supplies heat to the boiler or other heat utilization system (Btu/hr, Kcal/hr)

By dimensional analysis, it can be seen that the units of E in terms of pollutant mass per unit of heat input are:

- $E = \frac{\text{lb/hr}}{10^6 \text{ BTU/hr}} = \frac{(\text{lb/ft}^3)\ (\text{ft}^3\text{/hr})}{10^6 \text{ BTU/hr}} = \frac{\text{lb}}{10^6 \text{ BTU/hr}}$

For example:

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

Particulate emissions limited to 0.03 lb/10^6 Btu.

Reporting In Units Of The Standard: F Factor Methods

To obtain emission rates in units of lb/10^6 Btu, it is necessary for the source sampler to obtain the following information:

1. Pollutant concentration, c_S
   a. Pollutant mass captured
   b. Dry gas volume sampled
2. Effluent volumetric flow rate, Q_S
   a. Stack gas velocity
   b. Stack temperature
   c. Stack pressure

Reporting In Units Of The Standard: F Factor Methods

d. Dry gas composition (Orsat) %CO2, %O2, %N2
e. Moisture content

3. Heat input rate, QH
   a. Fuel input rate
   b. Proximate analysis of fuel

Process Weight Rate (E)

Can be expressed in:

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

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

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

For Example:

The NSPS for sulfuric acid plants is:

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

Concentration Corrected To Standard Conditions

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

Correcting Concentration to 12% CO_2

$$\overline{C}_{S_{12\ CO2}} = \overline{C}_S \frac{12}{\%CO_2}$$

Correcting Concentration to 6% 0_2

$$\overline{C}_{S6\%O2} = \frac{\overline{C}_S\ (20.9 - 6.0)}{20.9 - \%O_2}$$

Correcting Concentration to 3% 0_2

$$c_s\,(3\%O_2) = \frac{18c_s}{21 - \%O_2}$$

Excess Air Correction Factor

$$\%EA = \frac{\%O_2 - 0.5\%CO}{0.26\%N_2 - \%O_2 + 0.5\%CO} \times 100$$

$$c_s\,(\mathrm{corr}) = c_s \left(\frac{150}{100 + \%EA} \right)$$

Method 19

F Factor Methods

Reporting in Units of Standard: F factor Methods

- The F factor is used in calculating particulate emission levels from new stationary sources.
- It was promulgated in the October 6, 1975
- The F factor is intended to reduce the amount of data necessary to calculate particulate emissions in terms of the standard expressed as pounds per million Btu heat inputs (lb/10^6 Btu).
- An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel.

Reporting in Units of Standard: F factor Methods

- The dry F factor (Fd) includes all products of combustion less water,
- The wet F factor (Fw) includes all products of combustion, and
- The carbon F factor (Fc) includes only carbon dioxide.

Reporting in Units of Standard: F factor Methods

- All of the quantities for c_S and Q_S are obtained in a source test
- Q_H, may not be easily obtained.
- The accuracy the source fuel flow and analysis representative may be difficult to determine
- F factors are based on simple principles of combustion

Reporting in Units of Standard: F factor Methods

- **Developed to avoid many of the problems involved in the calculation of E. By using the F factors, E may be obtained from a formula such as the following:**
- **$E = c_S F_d \left(\frac{20.9}{20.9 - \%O2}\right)$**
- **Where: Fd is the dry F factor**
- **The F factor essentially replaces the ratio OS/OH and the term in brackets is merely an**

Reporting in Units of Standard: F factor Methods

- F factors are useful in calculating emissions for particulate matter.
- In their application to continuous monitoring instrumentation for gases, it is even more valuable.
- Fd factors and its variants (Fc and F_W factors) are useful in reporting continuous monitoring data in terms of lb/10^6 Btu heat input

Reporting in Units of Standard: F factor Methods

- **F factors enables the source operator to monitor only the pollutant gas concentration and the oxygen or carbon dioxide concentrations.**
- **Without this method, it would be necessary to continuously monitor stack gas velocity, temperature, fuel input rate, and so on.**
- **This would be possible, but impractical and expensive**

Reporting in Units of Standard: F factor Methods

- Before proceeding with the derivation of the F factors, it is necessary to give a few definitions used in combustion analysis, namely those for **proximate analysis, ultimate analysis,** and **gross calorific value**. The definitions generally apply to the fuel "as received" at the plant.
-

Reporting in Units of Standard: F factor Methods

- Proximate analysis is a fuel analysis procedure that expresses the principal characteristics of fuel as follows:

1. % moisture	Total 100%	5. % sulfur
2. % ash		6. Heating value (BTU/lb)
3. % volatile matter		7. Ash fusion temperature
4. % fixed carbon		

Reporting in Units of Standard: F factor Methods

- **Ultimate analysis is the determination of the exact chemical composition of the fuel. The analysis is generally given in terms of percent hydrogen, percent carbon, percent sulfur, percent nitrogen, and percent oxygen.**
- **Gross calorific value (GCV), also termed the "high heating value," is the total heat obtained from the complete combustion of a fuel, referred to a set of standard conditions. The GCV is obtained in the proximate analysis as the "heating value."**

Reporting in Units of Standard: F factor Methods

- $$\frac{Q_S}{Q_H} = (\text{correction air excess}) \frac{V_t}{GVC}$$

Dimensionally, this says

$$\frac{ft^3/hr}{BTU/hr} = \frac{ft^3}{hr}$$

Q_S and Q_H can be determined at the source. V_t is obtained from the ultimate analysis of the fuel.

Reporting in Units of Standard: F factor Methods

- **Remembering the first equation given in this lesson,**
- **$E = c_S Q_S/Q_H$**
- **and through substitution**
- $$E = \frac{c_S V_t}{GCV} \quad \frac{1}{(\text{excess air correction})}$$

The quantity Vt/GCV is then defined as the Fd factor and the following simplified equation is obtained: $E = (c_S F_D)\ 1/(\text{excess air correction})$

Reporting in Units of Standard: F factor Methods

- **For Method 5, the oxygen concentration of the source must be determined simultaneously and at the same traverse. Since the excess air correction using percent oxygen is:**
- **$(20.9 - \%\ O_2)/\ 20.9$**
- **and the equation to be used for calculating emissions for Method 5 is:**
- **$E = (c_S F_d)(20.9/20.9 - \%O_2)$**

Reporting in Units of Standard: F factor Methods

- Since there are different types of F factors (see Table below). The differences arise in the way in which the excess air corrections are determined.
- It should also be noted that the F factor method may be used with the percent O_2 and c_{ws} determined on a wet basis if the moisture content B_{ws} of the stack is known:
- $E = (c_{ws}F_d)\ ((20.9/20.9(1 - B_{ws}) - \%O_2))$
- *Note*: The subscript w stands for measurements made on a wet basis.

F Factors Table

Factor	Excess Air Units	Measurement Required for Emissions Determination	Calculations	Comments
F_d	$\frac{dscf}{10^6 Btu}$	$\%O_2$ (dry basis)	$E = c_s F_d \left[\frac{20.9}{20.9 - \%O_{2d}}\right]$	c_S determined on dry basis
F_c	$\frac{dscf}{10^6 Btu}$	$\%CO_2$ (dry or wet basis)	$E = c_s F_c \left[\frac{100}{\%CO_2}\right]$	c_S on dry or wet basis consistent with CO_2 measurement
F_w	$\frac{wscf}{10^6 Btu}$	$\%O_2$ (wet basis)	$E = c_{ws} F_w \left[\frac{20.9}{20.9\,(1 - B_{wa}) - \%O_{2w}}\right]$	The "wet" F factor, c_{ws} and $\%O_2$ on wet basis B_{wa} = average moisture content of ambient air
F_o	——	——	$F_o = \frac{20.9}{100}\frac{F_d}{F_c} = \frac{20.9 - \%O_2}{\%CO_2}$	Miscellaneous factor useful for checking Orsat data

Calculation and Tabulation of F Factors

The F_d factor method carries with it the assumption that V_t/GCV, the ratio of the quantity of dry effluent gas generated by combustion to the gross calorific value, is constant within a given category. This ratio, of course, is the F_d factor.

V_t is determined from the stoichiometry of the combustion reaction. If a hydrocarbon is burned in air, gaseous products will result; the volumes of which can be calculated. For example

$$\underset{\text{propane}}{C_3H_8} + \underset{\text{air}}{O_2 + N_2} \rightarrow \underset{\text{gases}}{CO_2\uparrow + H_2O\uparrow + N_2\uparrow}$$

For each pound of fuel undergoing perfect combustion, a known amount of gaseous products will result. Using the stoichiometric relationships resulting from chemical reactions (similar to the preceding example) and given the gross calorific value of the fuel per pound, the following relationships have been developed for the F factors.

Calculation and Tabulation of F Factors

- The F_d factor method based on the assumption that V_t/GCV, is constant within a given category.
- V_t is determined from the stoichiometry of the combustion reaction. When hydrocarbons are burned in air, gaseous products will result and the volumes can be calculated. For example,
- $C3H8 + O2 + N2 \rightarrow CO2\uparrow + H2O\uparrow + N2\uparrow$

Propane Air Combustion Gases

For each pound of fuel undergoing perfect combustion, a known amount of gaseous products will result.

Calculation and Tabulation of F Factors

$$F_d = \frac{227.0\,(\%H) + 95.7\,(\%C) + 35.4\,(\%S) + 8.6\,(\%N) - 28.5\,(\%O)}{GCV} \quad \text{(metric units)}$$

$$F_d = \frac{10^6\,[3.64\,(\%H) + 1.53\,(\%C) + 0.57\,(\%S) + 0.14\,(\%N) - 0.46\,(\%O)]}{GCV} \quad \text{(English units)}$$

$$F_c = \frac{20.0\,(\%C)}{GCV} \quad \text{(metric units)}$$

$$F_c = \frac{321 \times 10^6\,(\%C)}{GCV} \quad \text{(English units)}$$

$$F_w = \frac{347.4\,(\%H) + 95.7\,(\%C) + 35.4\,(\%S) + 8.6\,(\%N) - 28.5\,(\%O) + 13.4\,(\%H_2O)}{GCV_w}$$

$$F_d = \frac{10^6\,[5.56\,(\%H) + 1.53\,(\%C) + 0.57\,(\%S) + 0.14\,(\%N) - 0.46\,(\%O + 0.21\,(\%H_2O))]}{GCV_w}$$

Calculation and Tabulation of F Factors

If the source utilizes a combination of fossil fuels, a simple addition procedure can be used to compute the F factor.

$$F = xF_1 + yF_2 + zF_3$$

Where: x, y, z = the fraction of total heat input derived from gaseous, liquid, and solid fuels, respectively

F_1, F_2, F_3 = the value of F for gaseous, liquid, and solid fossil fuels, respectively

Calculation and Tabulation of F Factors

- **Several F factors have been calculated for various types of fossil and waste fuels. It has been found that for a given type of fuel the F factor does not vary over a significantly large range. In general, it has been reported that the Fd factor can be calculated to within a ±3% deviation and the Fc factor can be calculated to within a ±5.9% deviation. The calculated factors are given in the Table below.**

F Factors for Various Fuels

Fuel Type	F_d		F_w		F_c	
	dscm/j	dscf/10^6 Btu	wscm/j	wscf/10^6 Btu	scm/j	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminous[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	10,950	0.513×10^{-7}	1,910
Oil[3]:	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:						
Natural	2.43×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid waste						

[1] Determined at standard conditions: 20°C (68°F) and 760 mmHg (29.92 in. Hg)
[2] As classified according to ASTM D388-77
[3] Crude, residual, or distillate

Calculation and Tabulation of F Factors

- Three important points that should be made regarding application of the F factor to Method 5 are:
- 1. Only the dry F factor using percent O2 for the excess air correction may be used in the calculation. The Fc and Fw factors may not be used.

Calculation and Tabulation of F Factors

- 2. The oxygen sample is to be obtained simultaneously with the Method 5 run at the same traverse points. This essentially requires that an additional probe be placed along with the Method 5 probe and an additional pump be used to obtain an integrated bag sample over the duration of the run. However, only 12 sample points are required. If there are more than 12 traverse points determined by Method 1, an independent integrated gas sampling train could be used to traverse 12 points in the duct simultaneously with the particulate run.

Calculation and Tabulation of F Factors

- 3. The procedures in 40 CFR Part 60.46 apply to new fossil-fuel fired steam generators (new sources are those constructed or modified after August 17, 1971). For existing fossil fuel steam generators, which are regulated by state standards, the state or local regulations should be checked for application of the F factor method.
-

Other Uses for F Factors

- 1. If values for QS (the stack gas volumetric flow rate), and QH (the heat input rate), are obtained during the source test, as they often are, several cross-checks can be made by comparing various calculated F factor values with the tabulated values. Equations that can be used to do this are as follows.

Other Uses for F Factors

$$F_d\,(\mathrm{calc}) = \frac{Q_s}{Q_H}\frac{(20.9 - \%O_2)}{20.9}$$

$$F_w\,(\mathrm{calc}) = \frac{Q_{sw}}{Q_H}\frac{20.9\,(1-B_{wa}) - \%O_{2w}}{20.9}$$

$$F_c\,(\mathrm{calc}) = \frac{Q_s}{Q_H}\frac{\%CO_2}{100} = \frac{Q_{sw}}{Q_H}\frac{\%CO_{2w}}{100}$$

Other Uses for F Factors

- If after calculating Fd, Fc, or Fw, a large discrepancy exists between the calculated value and the corresponding value in the table, the original data for Qs, Q_H, and the Orsat data should be checked. This is an easy way of conducting a material balance check.
- 1. Using a tabulated value for Fd, Fc, or Fw and the data obtained during the stack test for Qs and %O2, a value of QH may be obtained from the equations.

Other Uses for F Factors

- 2. If ultimate and proximate analyses are available, they may be used to calculate an F factor using one of the equations. The calculated value can then be checked with the tabulated values and should be within 3 to 5% agreement, depending on the type of fuel and F factor.
- The F_0 factor is the ratio
- $F_0 = (20.9/100)(F_d/F_C)$
- $F_0 = (20.9 - O_2)/\%CO_2$
- A value differing from those tabulated would necessitate a recheck of the Orsat data.

Errors and Problems in the Use of F Factors

- The following factors may contribute to errors in reporting emissions by using F factors:
- Deviations in the averaged or "midpoint" F factor value itself.
- Errors in the Orsat analysis and the consequent %O2 and %CO2 values.
- Failure to have complete combustion of the fuel (complete combustion is assumed in the derivation of all of the F factor methods).
- □

Errors and Problems in the Use of F Factors

- Loss of carbon dioxide when wet scrubbers are used affecting the F_d, F_c and F_w, factors.
- Addition of carbon dioxide when lime or limestone scrubbers are used, affecting the Fc factor.
-

Errors and Problems in the Use of F Factors

- Since the F factors given are averaged values, differences in the ultimate analysis between fuel samples could easily account for the deviation. Also an error of a few percent in the oxygen concentration could cause a relatively large error in the value of E, or more importantly, could mean the difference between compliance and noncompliance. A publication by Mitchell and Midgett (1976) entitled "Field Reliability of the Orsat Analyzer," states:

Errors and Problems in the Use of F Factors

- "The results from five collaborative tests of the Orsat method indicate that the use of Orsat data to determine the molecular weight of flue gases is a valid procedure, but the use of such data routinely to convert particulate catches to such reference conditions as 12% CO2 and 50% excess air may introduce sizeable errors in the corrected particulate loading…

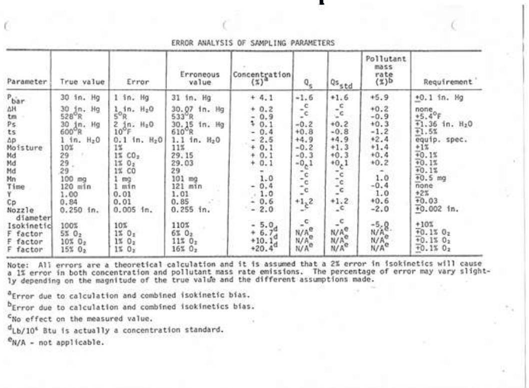
Errors and Problems in the Use of F Factors

- Complete combustion is assumed for the derivation of all F Factor Methods.
- For incomplete combustion when carbon monoxide, are present in the effluent stream, the volume of effluent gas and carbon dioxide per pound of fuel burned will differ from the values used in calculating the F Factors.
- Adjustments to the measured CO2 or O2 concentration can be made, which would minimize this error, if the % CO is determined in the flue gas.

Errors and Problems in the Use of F Factors

- **$(\%CO_2)_{adj} = \%CO_2 + \%CO$**
- **$(\%O_2)_{adj} = \%O_2 - 0.5\ \%CO$**
- With these adjustments, the error amounts to minus one-half the concentration of carbon monoxide present.
- Thus, if 1% CO (an extreme case) is %, an error of minus 0.5% is introduced. Without adjusting the CO_2 or O_2 concentration, a combustion source having 11% CO2, 1 % CO, and 6% O_2 will result in about plus 9% error for the Fc Factor Method and about plus 3% for the F_d Factor and F_w Factor Methods.

Errors in Source Sampling and F factor Examples



ERROR ANALYSIS OF SAMPLING PARAMETERS

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

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

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

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

[c] No effect on the measured value.

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

[e] N/A - not applicable.

Example F Factor Problem

- The Bradshaw Furniture Company has an industrial steam generating unit of greater than 250 x 10^6 Btu/hr heat input. The unit fires Bituminous coal and has an extractive CO_2 monitor. Recent testing showed an effluent SO_2 concentration of 750 ppm (wet basis) and 12.8 % CO_2(dry basis). The average stack moisture content is 7% H_2O.
- What is the emission rate in lb/10^6 BTU

What is the emission rate in lb/10^6 BTU

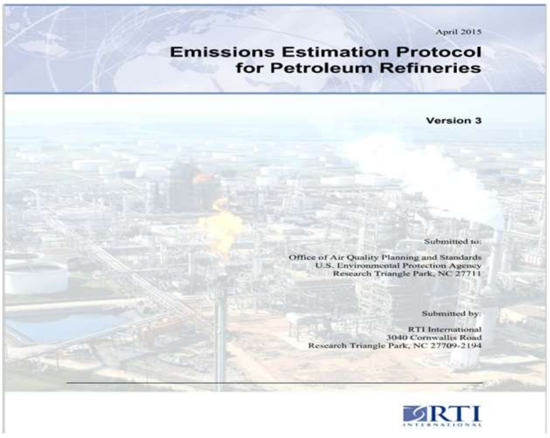
- Use F_C and convert C_{SO2} from ppm to lb/dscf

$$(750\text{ ppm}) \times \frac{10^{-6}\text{ ft}^3\text{ SO2}}{\text{ft}^3\text{ air/ppm}} \times \frac{(64\text{ lb SO2})}{\text{lb- mole}} \times \frac{(\text{lb-mole})}{392.75\text{ ft}^3} = 1.22 \times 10^{-4}\text{ lb/dscf}$$

$$1.22 \times 10^{-4}\text{ lb/dscf} \times \frac{(1\text{ ft}^3\text{ wet})}{(1 - 0.07)\text{ ft}^3\text{ dry}} = 1.31 \times 10^{-4}\text{ lb/dscf}$$

$E = C_S\, F_C\, 100/CO_2 = 1.31 \times 10^{-4}$ lb/dscf (1800 ft^3/10^6BTU) (100/12.8)

= 1.85 lb SO2/10^6BTU



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Emissions Estimation Protocol for Petroleum Refineries

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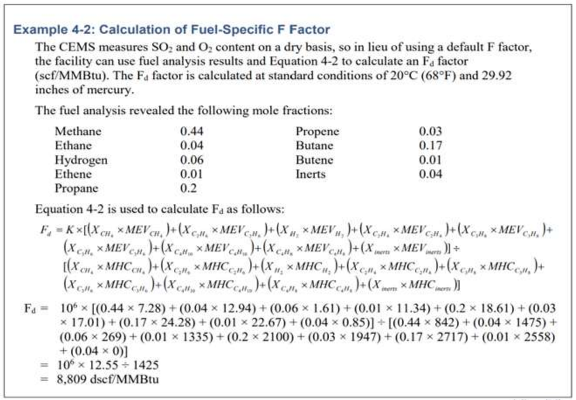


Example 4-2: Calculation of Fuel-Specific F Factor

The CEMS measures SO_2 and O_2 content on a dry basis, so in lieu of using a default F factor, the facility can use fuel analysis results and Equation 4-2 to calculate an F_d factor (scf/MMBtu). The F_d factor is calculated at standard conditions of 20°C (68°F) and 29.92 inches of mercury.

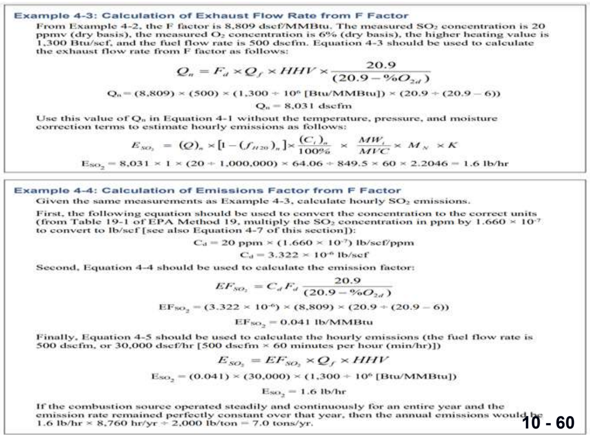
The fuel analysis revealed the following mole fractions:

Methane	0.44	Propene	0.03
Ethane	0.04	Butane	0.17
Hydrogen	0.06	Butene	0.01
Ethene	0.01	Inerts	0.04
Propane	0.2		

Equation 4-2 is used to calculate F_d as follows:

$$F_d = K \times [(X_{CH_4} \times MEV_{CH_4}) + (X_{C_2H_6} \times MEV_{C_2H_6}) + (X_{H_2} \times MEV_{H_2}) + (X_{C_2H_4} \times MEV_{C_2H_4}) + (X_{C_3H_8} \times MEV_{C_3H_8}) + (X_{C_3H_6} \times MEV_{C_3H_6}) + (X_{C_4H_{10}} \times MEV_{C_4H_{10}}) + (X_{C_4H_8} \times MEV_{C_4H_8}) + (X_{inerts} \times MEV_{inerts})] \div [(X_{CH_4} \times MHC_{CH_4}) + (X_{C_2H_6} \times MHC_{C_2H_6}) + (X_{H_2} \times MHC_{H_2}) + (X_{C_2H_4} \times MHC_{C_2H_4}) + (X_{C_3H_8} \times MHC_{C_3H_8}) + (X_{C_3H_6} \times MHC_{C_3H_6}) + (X_{C_4H_{10}} \times MHC_{C_4H_{10}}) + (X_{C_4H_8} \times MHC_{C_4H_8}) + (X_{inerts} \times MHC_{inerts})]$$

F_d = 10^6 × [(0.44 × 7.28) + (0.04 × 12.94) + (0.06 × 1.61) + (0.01 × 11.34) + (0.2 × 18.61) + (0.03 × 17.01) + (0.17 × 24.28) + (0.01 × 22.67) + (0.04 × 0.85)] ÷ [(0.44 × 842) + (0.04 × 1475) + (0.06 × 269) + (0.01 × 1335) + (0.2 × 2100) + (0.03 × 1947) + (0.17 × 2717) + (0.01 × 2558) + (0.04 × 0)]
= 10^6 × 12.55 ÷ 1425
= 8,809 dscf/MMBtu



Example 4-3: Calculation of Exhaust Flow Rate from F Factor

From Example 4-2, the F factor is 8,809 dscf/MMBtu. The measured SO_2 concentration is 20 ppmv (dry basis), the measured O_2 concentration is 6% (dry basis), the higher heating value is 1,300 Btu/scf, and the fuel flow rate is 500 dscfm. Equation 4-3 should be used to calculate the exhaust flow rate from F factor as follows:

$$Q_n = F_d \times Q_f \times HHV \times \frac{20.9}{(20.9 - \%O_{2d})}$$

$$Q_n = (8{,}809) \times (500) \times (1{,}300 \div 10^6\ [\text{Btu/MMBtu}]) \times (20.9 \div (20.9 - 6))$$

$$Q_n = 8{,}031\text{ dscfm}$$

Use this value of Q_n in Equation 4-1 without the temperature, pressure, and moisture correction terms to estimate hourly emissions as follows:

$$E_{SO_2} = (Q)_n \times [1 - (f_{H2O})_n] \times \frac{(C_i)_n}{100\%} \times \frac{MW_i}{MVC} \times M_N \times K$$

$$E_{SO_2} = 8{,}031 \times 1 \times (20 \div 1{,}000{,}000) \times 64.06 \div 849.5 \times 60 \times 2.2046 = 1.6\text{ lb/hr}$$

Example 4-4: Calculation of Emissions Factor from F Factor

Given the same measurements as Example 4-3, calculate hourly SO_2 emissions.

First, the following equation should be used to convert the concentration to the correct units (from Table 19-1 of EPA Method 19, multiply the SO_2 concentration in ppm by 1.660 × 10^{-7} to convert to lb/scf [see also Equation 4-7 of this section]):

$$C_d = 20\text{ ppm} \times (1.660 \times 10^{-7})\text{ lb/scf/ppm}$$

$$C_d = 3.322 \times 10^{-6}\text{ lb/scf}$$

Second, Equation 4-4 should be used to calculate the emission factor:

$$EF_{SO_2} = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})}$$

$$EF_{SO_2} = (3.322 \times 10^{-6}) \times (8{,}809) \times (20.9 \div (20.9 - 6))$$

$$EF_{SO_2} = 0.041\text{ lb/MMBtu}$$

Finally, Equation 4-5 should be used to calculate the hourly emissions (the fuel flow rate is 500 dscfm, or 30,000 dscf/hr [500 dscfm × 60 minutes per hour (min/hr)])

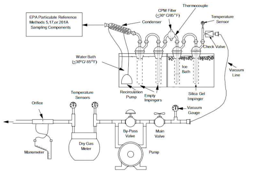
$$E_{SO_2} = EF_{SO_2} \times Q_f \times HHV$$

$$E_{SO_2} = (0.041) \times (30{,}000) \times (1{,}300 \div 10^6\ [\text{Btu/MMBtu}])$$

$$E_{SO_2} = 1.6\text{ lb/hr}$$

If the combustion source operated steadily and continuously for an entire year and the emission rate remained perfectly constant over that year, then the annual emissions would be 1.6 lb/hr × 8,760 hr/yr ÷ 2,000 lb/ton = 7.0 tons/yr.

U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 202 Condensable Particulate Matter (CPM)



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)."*

Particulate Matter (PM) Classified As Either

Filterable

(i.e., FRM 5)

Condensable

(i.e., FRM 202)

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}/$PM_{2.5}$ particulate matter using FRM 201/201A

Basic Measurement Methods for condensable PM

- 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 Condensable particulate Emissions from Stationary Sources

Basic Measurement Methods for condensable PM

- Method 315 - Particulate and Methylene Chloride Extractable Matter from Aluminum Production Facilities
- Other Test Method 37 (OTM-37): Measurement of Direct $PM_{2.5}$ and PM_{10} Emissions at Low Concentrations by Dilution Sampling (Constant Sampling Rate Procedure)

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 039 (2004): Measurement of $PM_{2.5}$ and PM_{10} Emissions by Dilution Sampling (Constant Sampling Rate Procedures)

Regulatory Background CPM

- Conditional Test Method 040 (2004): EPA proposes test method for combined PM_{10} and $PM_{2.5}$, now incorporated into Method 201/201A
- Other Test Method 37 (May 2018): Measurement of Direct $PM_{2.5}$ and PM_{10} Emissions at Low Concentrations by Dilution Sampling (Constant Sampling Rate Procedure)

Condensable Particulate Matter

- Condensable 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

Historical Measurement Methods for CPM

- Condensable 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 condensable particulate matter (i.e., the back half of the FRM 5 sampling train, including water and organic soluble extractions)

Recent History

- Pre - PM_{10} & $PM_{2.5}$ NAAQS
  - Recognized condensable PM impact
    - Dust 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 Condensable Test Method?

- New NAAQS for particulate matter ($PM_{2.5}$)
- New emission inventories required
- More comprehensive emission factors required

Why A Condensable Test Method?

- More comprehensive test methods are 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 Condensable PM

Ammonia
HCl
HF
Sulfates
Nitrates
Organics
Chlorides

List of Precursors Reactions to Condensable PM

Condensable 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 Form Condensable PM

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 Condensable PM simultaneously

Condensable 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, Dioxins/Furans, 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

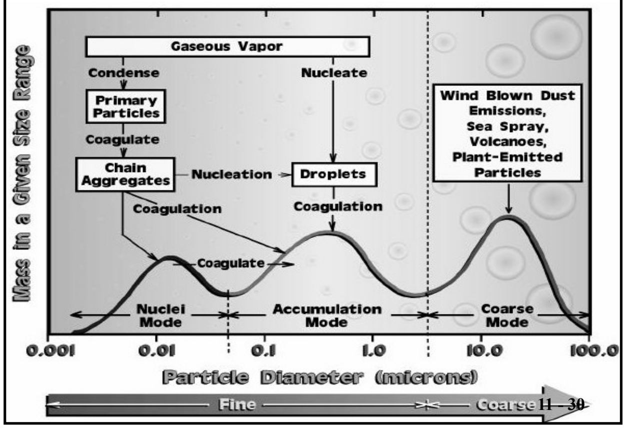
Issues to Consider for CPM

- 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

Size Distribution and Sources of Atmospheric Particles.



Biases from Condensable PM

Positive

- Some condensable PM that are not intended to be regulated condense below stack temperature and are collected on heated filter

Biases from Condensable PM

Negative

- Some condensable PM that are to be regulated do not condense at filter temperature and pass through the filter and are not counted

Steps to Handle Condensable PM

- Determine if condensable PM are to be regulated by applicable emission regulations
- Design proper sampling and analytical procedures to match intention of the regulation

Cautions on Condensable 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 Condensable Sampling Techniques

- Although temperature is major parameter for collection of condensable PM, several other factors can greatly affect condensable PM (i.e., moisture content, dilution air, presence of other compounds)

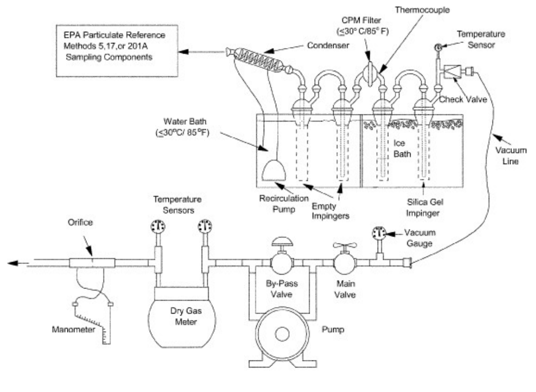


Figure 1. Schematic of Condensable Particulate Sampling Train

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

- 8.5.4.2 CPM Container #1, Aqueous liquid impinger contents. Quantitatively transfer liquid from the dropout and the backup impingers prior to the CPM filter into a clean, leak-proof container Rinse all sampling train components twice with water.

FRM 202
CPM Sampling Program

- 8.5.4.3 CPM Container #2, Organic rinses. Follow the water rinses of the back half with an acetone rinse. " Then repeat the entire rinse procedure with two rinses of hexane and save the hexane rinses in the same container as the acetone rinse.

FRM 202
CPM Sampling Program

- 8.5.4.4 CPM Container #3, CPM filter sample. Use tweezers and/or clean disposable surgical gloves to remove the filter from the CPM filter holder. Place the filter in the Petri dish labeled with test identification and "CPM Container #3, Filter Sample."

FRM 202
CPM Sampling Program

- 8.5.4.5 CPM Container #4, Cold impinger water. You must weigh or measure the volume of the contents of CPM Container #4 either in the field or during sample analysis (see Section 11.2.4). If the water from the cold impinger has been weighed in the field, it can be discarded.

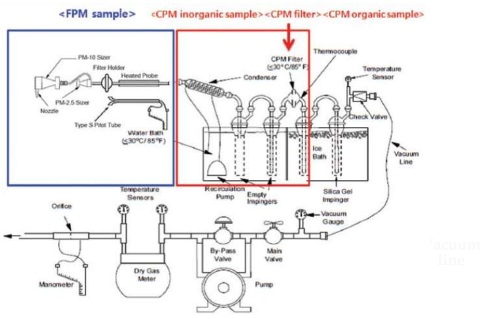
EPA FRM 202

- Requires post sample separation in field
- Requires post sample adjustments in lab
- Limited speciation

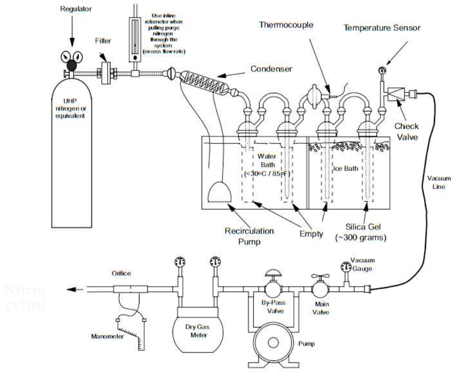
FRM 202

- FRM 202 is subject to false positive bias because of conversion of non-particulate species into CPM in the method’s sampling train

FRM 202 Sampling Train



FRM 202 Post Nitrogen Purge



FRM 202 Biases

- Normally non-condensable gases may react with other gases or condensables to form condensable 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

% Condensable 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 Condensable PM

- Coal-burning Boilers: condensable PM were ~76 % of the total PM_{10} stack emissions
- Oil/Natural Gas/Kerosene Combustion Turbines: condensable PM were ~ 68 % of the total PM_{10} stack emissions
- Oil/Natural Gas Boilers: condensable PM were ~ 49 % of the total PM_{10} stack emissions

FRM 202 Testing Conclusion

- Condensable 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)
- Based on review of FRM 202 stack tests, the condensable PM emissions can make a significant contribution PM constitutes a portion of the total PM_{10} emissions from Fossil Fuel-Fired Steam Generators (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

EPA Activities to Resolve PM_{cond} Test Methods Issues

- Recommending use of Method 202 with purge and use of condensable $PM_{2.5}$
  (USEPA EMC Website for RM 202)
  https://www.epa.gov/sites/production/files/2016-06/documents/m-202.pdf
- Assessing "improvements" to Method 202
  - Apply technologies tested in Canada and US
  - Reduce artifacts from ~10 mg to >2 mg

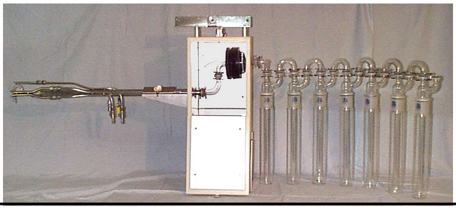
EPA Activities to Resolve PM_{cond} Test Methods Issues

- Revise M202 in Appendix M
    - More precise (no options)
    - More accurate (reduce artifacts)
    - Post on EPA/EMC web site in July 2007
    - Propose in 2007/2008
    - Promulgate 2008/2009

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
- 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 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

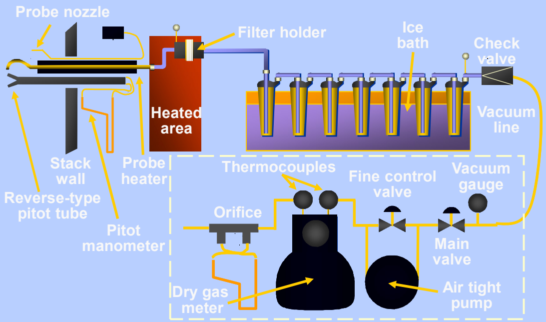
FRM 29/Method 0060 Design Requirements

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

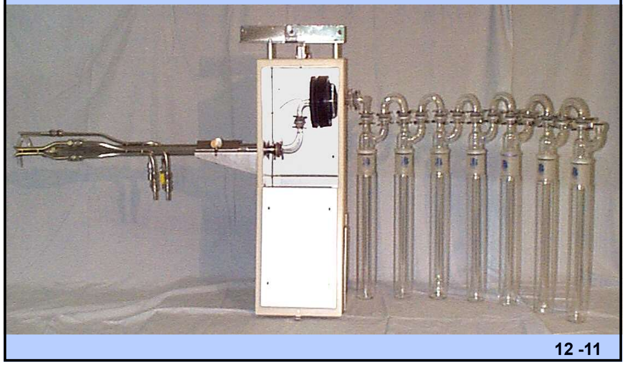
FRM 29/Method 0060 Sampling Train

- 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 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 Inductively Coupled Argon Plasma (ICAP) for all metals (except mercury)
- Aliquots taken of recovery reagents for mercury analyzed by Cold Vapor Atomic Absorption Spectroscopy (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(µg/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

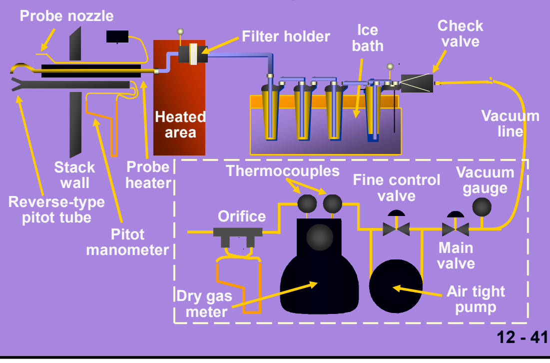
FRM 29/Method 0060
Key Points

- 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)

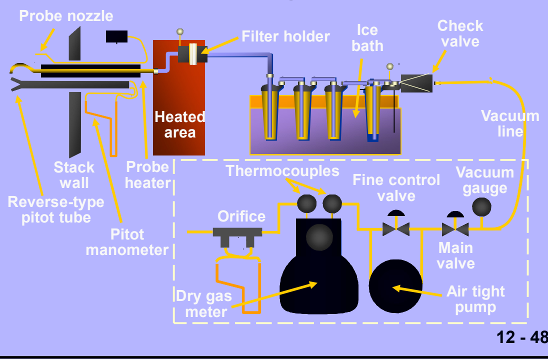
FRM 12
Design Requirements

- 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 $NaHCO_3$

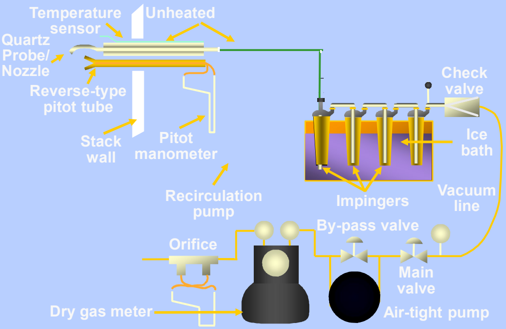
FRM 306 Summary

- 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 (ISDL)

- 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

ISDL

- The specified standard for Cr+6 is 0.03 mg/dscm. The ISDL is predetermined to be one tenth of the standard, 0.003 mg/DSCM (3.0E-6 mg/L). The sample will be prepared in a 250 ml (0.25 L) flask and the ion chromatograph used in the sample analysis has a detection limit of 40 ng/ml (0.04 mg/L). What sample volume is required to obtain an ISDL of 0.003 mg/L?

ISDL (cont.)

$$\text{Required Sample Volume} = \frac{0.04g\ \frac{mg}{L} \times 0.250L}{3.0 \times 10^{-6}\ \frac{mg}{L}} = 3333.3\ L = 3.33\ dscm$$

In order for the specified ISDL to be obtained, at least 3.33 dscm of stack gas must be collected in the sampling train

AU 144: Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography (thermofisher.com)

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 <u>isokinetic methods</u> 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

- A typical analytical detection limit for HCl is 0.2 µg/ml (sec. 13.3)
- 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 Hypochlorous acid (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

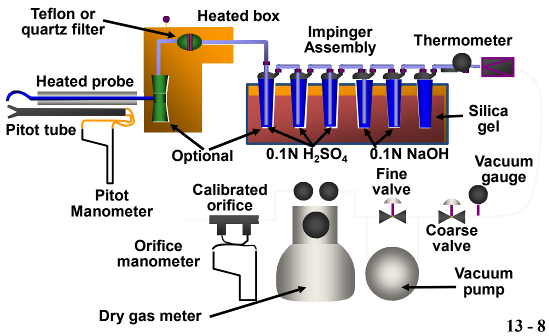
FRM 26A/Method 0050 Sampling Train

- 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 (0050 section 7.2.4)
- 1-hr sample at an anticipated rate of 2 l/m (FAQ #2)
- Probe/cyclone/filter between 120 and 134°C (248 and 273°F)

FRM 26A/Method 0050 Operational Requirements

- Post-sampling purge: If there is any possibility that liquid has collected in the glass cyclone and/or on the filter (30 minutes) to remove trapped HCl/Cl_2 from filter to impingers (Method 0050) (sec. 7.5.13)

FRM 26A/Method 0050 Operational Requirements

- 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
  - $Cl_2 + 0.1N\ NaOH \rightarrow H^+ + Cl^- + HClO$
    - 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

  (should be 2-hr sample run - Method 0050)

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 or continuously during the run to prevent loss of Cl_2.

FRM 26A/Method 0050 Operation

- If solution PH drops, resolve by:
  - 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 per Method 0050)
- Post-leak check in accordance with FRM 5
  - Leak rate must be <0.02 cfm

Sample Train Recovery Containers

1- Petri dish (filter) – Optional; for PM

2- Acetone rinse from probe nozzle/liner and front half of filter holder - Optional; for PM

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 $Na_2S_2O_3$ (Sodium Thiosulfate))

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, Optional; 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, total sampling time should be two hours (0050 sec. 7.2.4)
- Methodology quantitates HCl from Cl_2 emissions

FRM 26A/Method 0050 Key Points

- Complete Performance Evaluation (PE) sample prior to test
- The in-stack limit for HCl for the method is approximately 0.02 mg/dscm of stack gas. The method has a negative bias below 20 ppm HCl

FRM 26A/Method 0050 Key Points

- Post-sampling purge to move HCl from the cyclone/filter to impingers for 30 minutes at average ΔH (Method 0050)

FRM 26A/Method 0050 Key Points

Must maintain a basic solution in the 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 26A/Method 0050 Key Differences

- Method 0050
  - allows a filter temperature of 248 ± 25 °F
  - Ambient conditioning is required
  - High post leak rate – void sampling run
- FRM 26A
  - requires a filter temperature between 120 and 134°C (248 and 273°F) Ambient conditioning is optional
  - High Leak Rate – allows one to follow FRM 5, Section 12.3 (allows for correction)

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

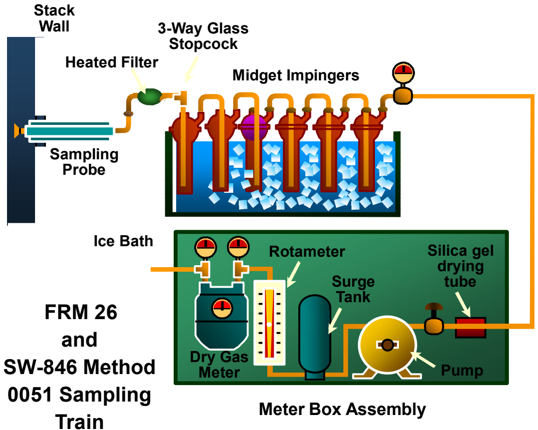
- Modified Method 6 sampling train
- Addition of 3-way stopcock and two more impingers to Method 6 sampling train
- 3-way stopcock used to purge probe

FRM 26/Method 0051 Sampling Train

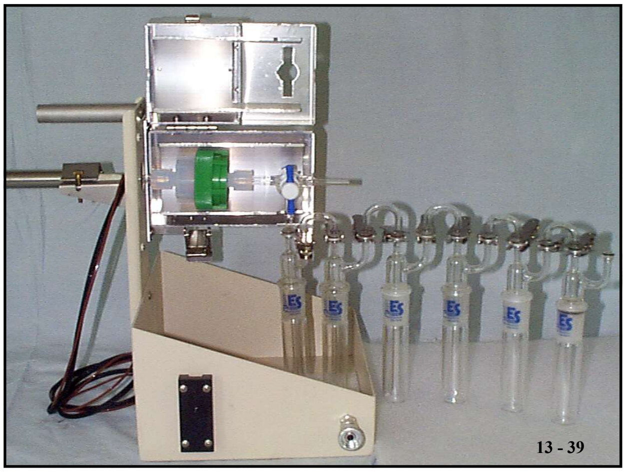
- Glass lined probe and Teflon elbow inlet
  - nozzle points downstream
- Heated Teflon mat Pallflex filter and three-way stopcock valve
  - can't use glass wool as particle control due to bias effects

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

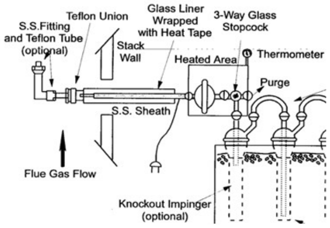
- Probe/filter temperature must be maintained between 120 and 134 °C (248 and 273 °F).
- Sampling at 2 L/min for 60 minutes
  - 120 liters total sample volume

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 5

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

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 Freon's
- 1990's: Clean Air Act Amendments of 1990 definition of hazardous air pollutants (HAPs), including VOCs

40 CFR Part 51.100

- "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.

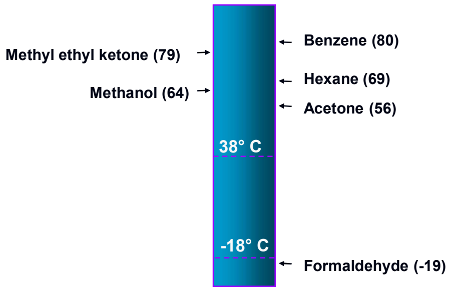
Historical Definition of VOCs

- 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

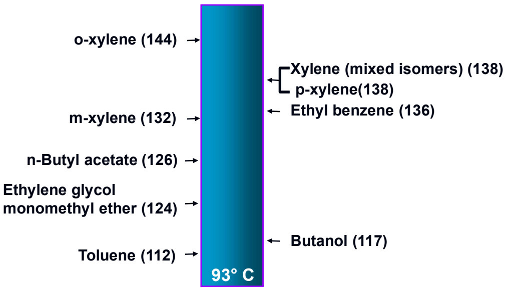
Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	$> 10^{-1}$	< 200°C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	200 - 500°C
Particles (NV)	$< 10^{-7}$	> 500°C

Boiling Points of Volatile Organic Compounds



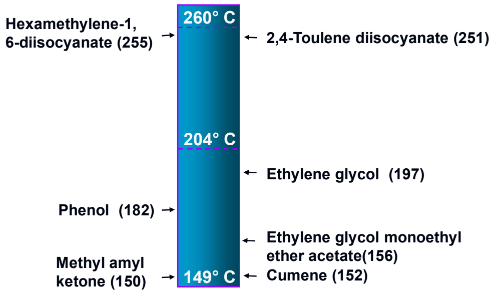
Methyl ethyl ketone (79) →
Methanol (64) →
← Benzene (80)
← Hexane (69)
← Acetone (56)
38° C
-18° C
← Formaldehyde (-19)

Boiling Points of Volatile Organic Compounds



o-xylene (144) →
m-xylene (132) →
n-Butyl acetate (126) →
Ethylene glycol monomethyl ether (124) →
Toluene (112) →
← Xylene (mixed isomers) (138)
p-xylene(138)
← Ethyl benzene (136)
← Butanol (117)
93° C

Boiling Points of Semi-volatile Organic Compounds



Hexamethylene-1, 6-diisocyanate (255) →
Phenol (182) →
Methyl amyl ketone (150) →
260° C
204° C
149° C
← 2,4-Toulene diisocyanate (251)
← Ethylene glycol (197)
← Ethylene glycol monoethyl ether acetate(156)
← Cumene (152)

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 Non-methane Organic Emissions
- FRM 25A: Total Gaseous Organic Concentration by Flame Ionization Analyzer

Methods Associated with Monitoring VOCs

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

Methods Associated with Monitoring VOCs

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

Definitions

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

Definitions

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

Definitions

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

Definitions

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

Definitions

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

Definitions

- Hazardous Air Pollutants (HAPs): Those compounds identified in the Clean Air Act Amendments of 1990, Title III list of 185 HAPs

As of 2022

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	1 ppm – 1 %
Method 25C	< 1 ppm
(CTM 035) SCAQMD	< 50 ppm(C) or 25 ppm(C) in trap

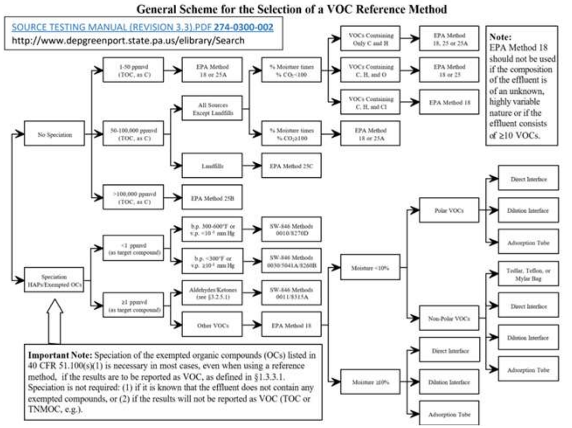
Applicability of Methods

	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

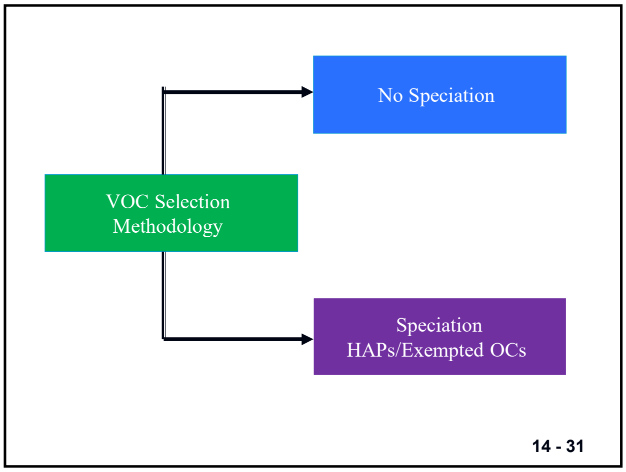
Nature of Emission	Report Emission As	Affected Facility
VOCs unknown/variable	Propane	Asphalt Plants Cement Plants Resource Recovery
Single VOC > 75 %	That single VOC	Bakeries SOCMI
Single VOC < 75 %	Surrogate	Surface Coat Graphite Art

General Scheme for the Selection of a VOC Reference Method



Note: EPA Method 18 should not be used if the composition of the effluent is of an unknown, highly variable nature or if the effluent consists of ≥10 VOCs.

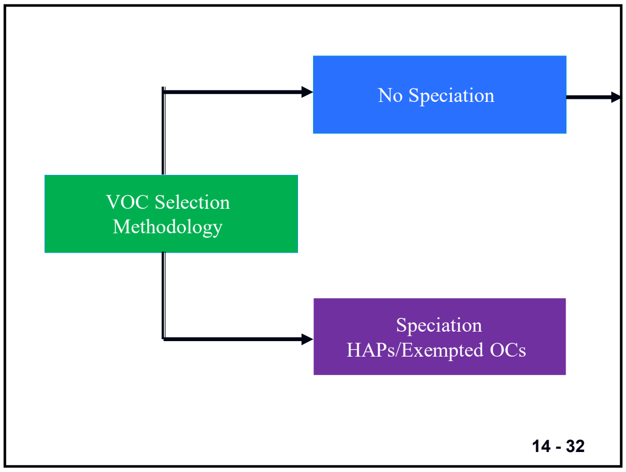
Important Note: Speciation of the exempted organic compounds (OCs) listed in 40 CFR 51.100(s)(1) is necessary in most cases, even when using a reference method, if the results are to be reported as VOC, as defined in §1.3.3.1. Speciation is not required: (1) if it is known that the effluent does not contain any exempted compounds, or (2) if the results will not be reported as VOC (TOC or TNMOC, e.g.).



VOC Selection Methodology

No Speciation

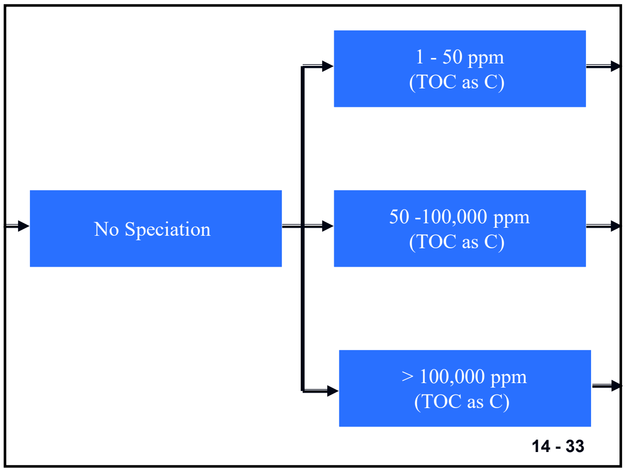
Speciation HAPs/Exempted OCs



VOC Selection Methodology

No Speciation

Speciation HAPs/Exempted OCs

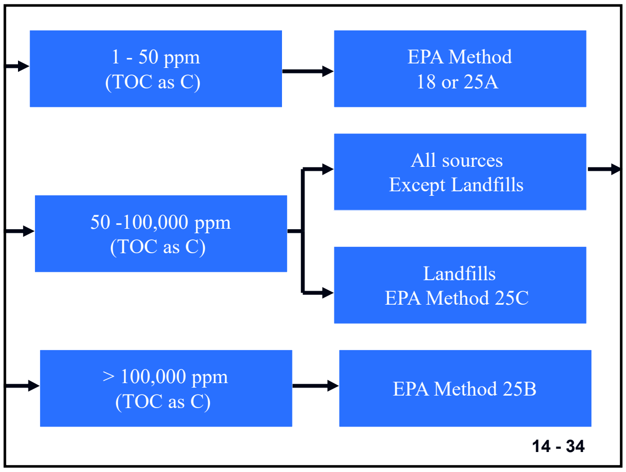


No Speciation

1 - 50 ppm (TOC as C)

50 -100,000 ppm (TOC as C)

> 100,000 ppm (TOC as C)



1 - 50 ppm (TOC as C)

EPA Method 18 or 25A

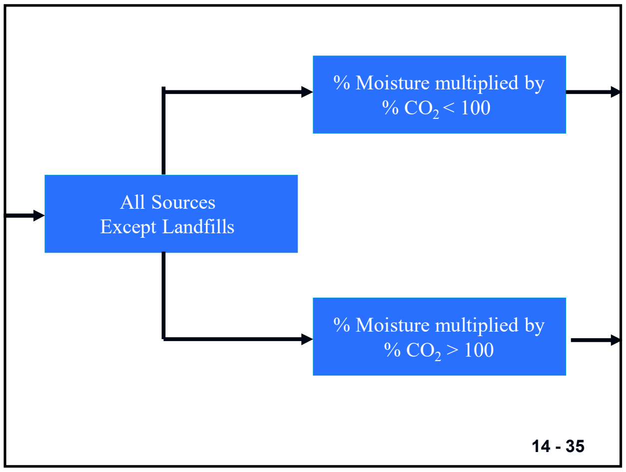
50 -100,000 ppm (TOC as C)

All sources Except Landfills

Landfills EPA Method 25C

> 100,000 ppm (TOC as C)

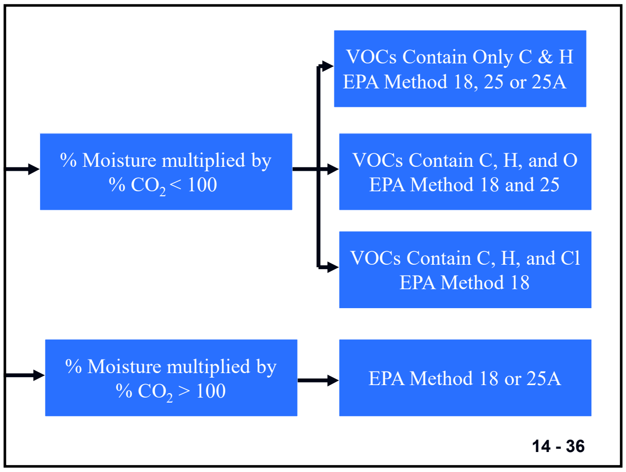
EPA Method 25B



All Sources Except Landfills

% Moisture multiplied by % $CO_2 < 100$

% Moisture multiplied by % $CO_2 > 100$



% Moisture multiplied by % $CO_2 < 100$

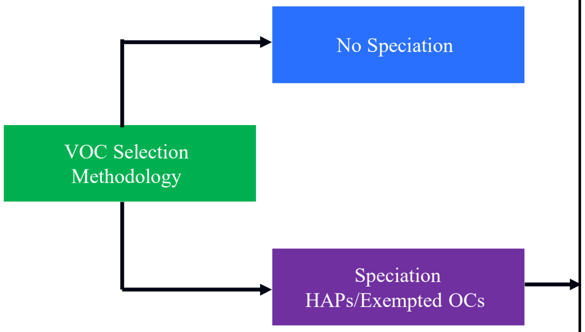
VOCs Contain Only C & H EPA Method 18, 25 or 25A

VOCs Contain C, H, and O EPA Method 18 and 25

VOCs Contain C, H, and Cl EPA Method 18

% Moisture multiplied by % $CO_2 > 100$

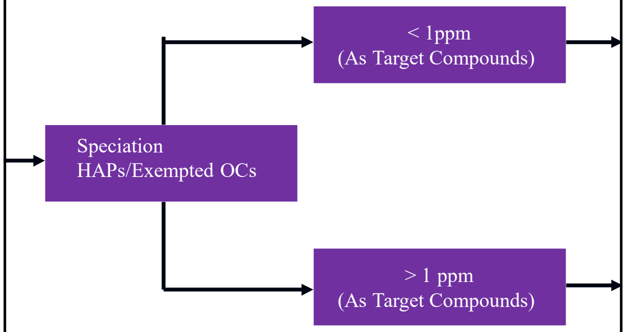
EPA Method 18 or 25A



VOC Selection Methodology

No Speciation

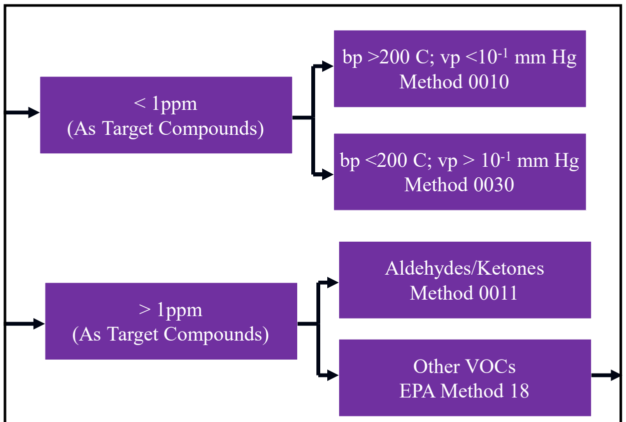
Speciation HAPs/Exempted OCs



Speciation HAPs/Exempted OCs

< 1ppm (As Target Compounds)

> 1 ppm (As Target Compounds)



< 1ppm (As Target Compounds)

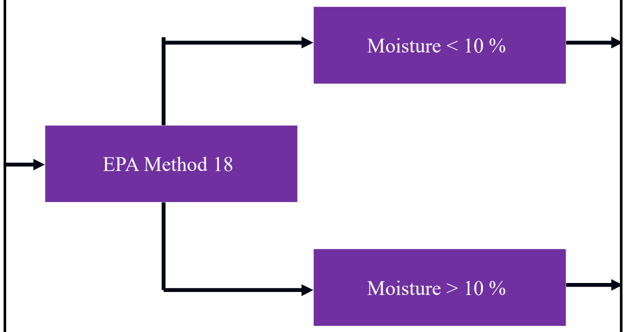
bp >200 C; vp <10^{-1} mm Hg Method 0010

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

> 1ppm (As Target Compounds)

Aldehydes/Ketones Method 0011

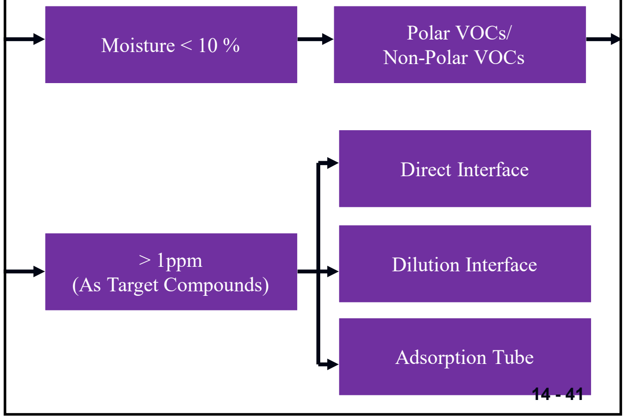
Other VOCs EPA Method 18



EPA Method 18

Moisture < 10 %

Moisture > 10 %



Moisture < 10 %

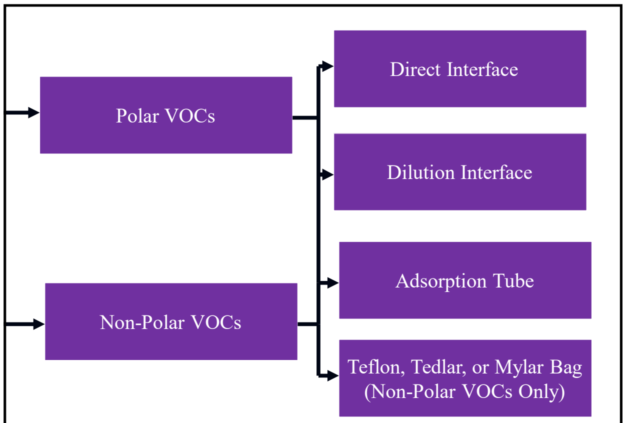
Polar VOCs/ Non-Polar VOCs

> 1ppm (As Target Compounds)

Direct Interface

Dilution Interface

Adsorption Tube



Polar VOCs

Non-Polar VOCs

Direct Interface

Dilution Interface

Adsorption Tube

Teflon, Tedlar, or Mylar Bag (Non-Polar VOCs Only)

Reporting of Emissions?

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

Reporting of Emissions

- FRM 18, because of the GC/MS analysis, reports results in terms of the concentration of specific organics
- FRM 25 is a method for measuring total gaseous 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.

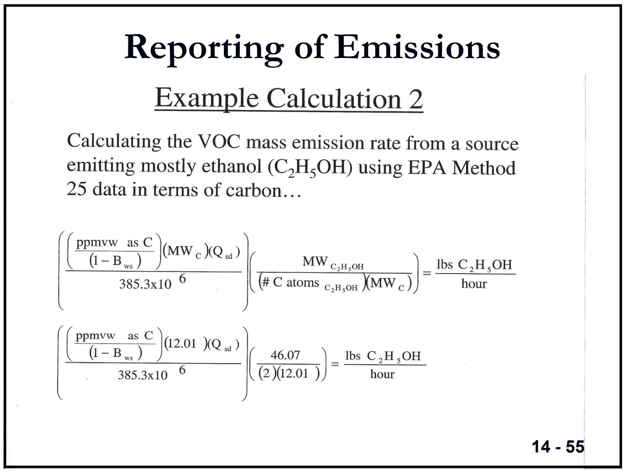
Reporting of Emissions

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…

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

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



Reporting of Emissions

Example Calculation 2

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

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

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

U.S. EPA APTI
Compliance Test and Source Test Observation
Overview and Comparison FRMs 18, 25, 25A and CTS 035

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
- VOC’s for control devices

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)

EPA's Conditional Test Method (CTM) 035

◆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

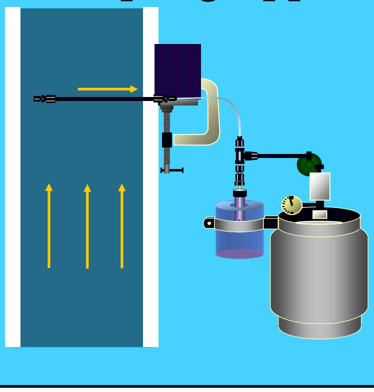
Applicability

- EPA's CTM-035 for combustion exhausts < 50 ppm C
- 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

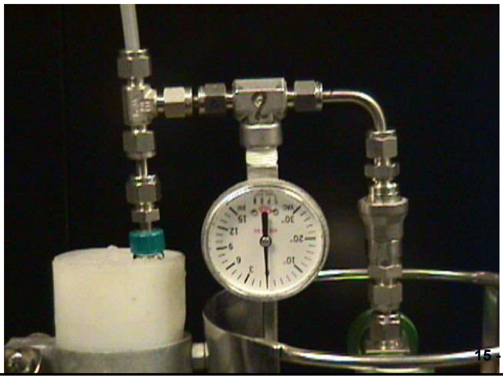
- Simple self contained sampler
  - No power, no heaters, no adjustments
  - Analysis is completed off-site
- Duplicate sampling
  - Probes are placed flush with port entrance

◆Sampling Apparatus



Duplicate Samplers

Trap Assembly

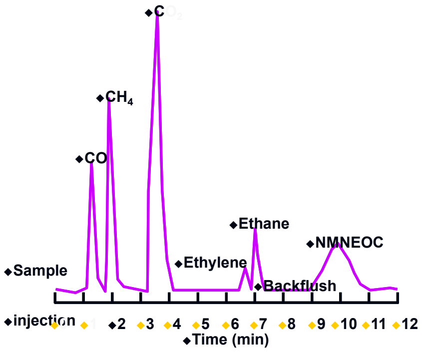


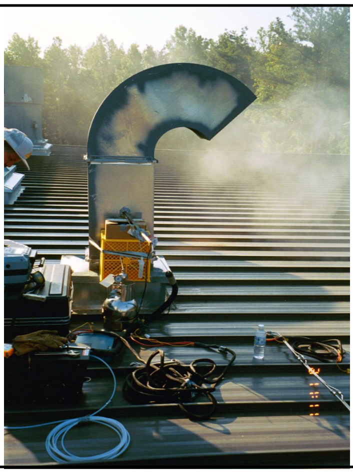
Condensate Trap

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

◆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 ppm C

NCASI Impinger and Canister Method

- National Council for Air and Stream Improvement (NCASI)
  - IM/CAN/WP-99.02
  - "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

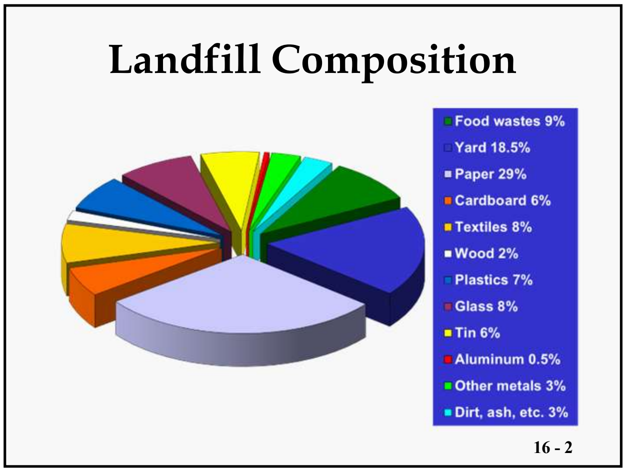
NCASI Impinger and Canister Method

- Total Hydrocarbons-Canister: Direct Injection GC/FID
- Bacharach Gas Analyzer For $CO/O_2/CO_2$-Canister: Direct Analysis By Bacharach Gas Analyzer

Method IM/CAN/WP-99.02 Impinger/Canister Source Sampling Method for Selected HAPs at Wood Products Facilities (ncasi.org)

Compliance Test and Source Test Observation

Landfill FRM Sampling Methods



Landfill Composition

What is Landfill Gas(LFG)?

- Landfill gas generated by the decomposition of organic municipal solid waste such as garbage, garden waste, and paper products

At Near Steady-state Conditions LFG Is Typically Composed Of:

- 45 - 58% methane (CH_4)
- 35 - 45% carbon dioxide (CO_2)
- <1 - 5% oxygen (O_2)
- <1 - 20% nitrogen (N_2)

At Near Steady-state Conditions LFG Is Typically Composed Of:

- <1 - 5% hydrogen (H_2)
- 1 - 5% water vapor
- <1 - 3% trace constituents

LFG is typically composed of:

- Small amounts of nonmethane organic compounds (NMOCs)
  - Benzene
  - Vinyl chloride
  - Chloroform
  - 1,1-dichlrorethene
  - Carbon tetrachloride

LFG is typically composed of:

- Nonorganic species
  - Hydrogen sulfide
  - Mercury
  - Particulate matter

Landfill Gases

- Methane
  - By-product of anaerobic decomposition
  - Colorless, odorless, tasteless gas
  - Lighter than air, relatively insoluble in water
  - Highly explosive in concentrations of 5 to 15% in air

Landfill Gases

- Carbon Dioxide (CO_2)
  - By-product of both aerobic and anaerobic decomposition
  - Colorless, odorless gas
  - Heavier than air, noncombustible
  - Soluble in water and decreases water pH

Landfill Gases

- Oxygen (O_2) and Nitrogen (N_2)
  - Not common constituents of LFG
  - Present as result of air intrusion (i.e., through cover, through recovery/control system
  - Typically combined volumes of oxygen and nitrogen < 10% with same ratios in air

Landfill Gases

- Hydrogen (H_2)
  - Typically produced during aerobic decomposition and early stages of anaerobic decomposition
  - Should have only trace concentrations in a mature landfill

Landfill Gases

- Water Vapor (H_2O)
  - LFG typically saturated with water vapor
  - Water in landfill entrained in the gas

Landfill Gases

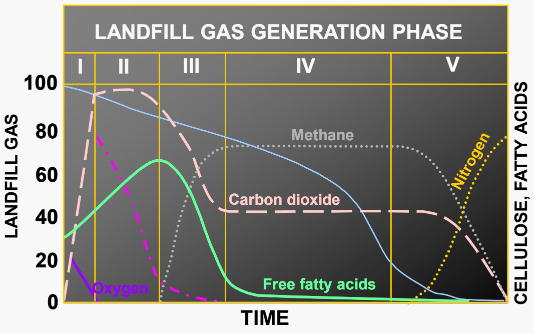
- Trace Constituents
  - Usually originate from waste within the landfill, but some may be present as a result of natural decomposition processes (H_2S)
  - Nonmethane organic compounds (NMOCs) usually < 1%

Landfill Gases

- Over 150 different organic gases have been identified
- Contaminants of potential concern (COPCs) in LFG

Landfill Gas Generation Stages

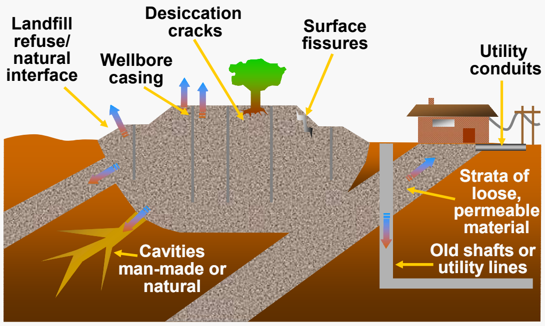
- Mainly methane and carbon dioxide produced by microorganisms within the landfill under anaerobic conditions



Four Characteristic Phases of Gas Generation at Landfills

- Phase I: Aerobic
- Phase II: Anaerobic/ Acid Generation
- Phase III: Transition to Anaerobic
- Phase IV: Anaerobic
- Phase V: Transition to Stability

Path of Least Resistance

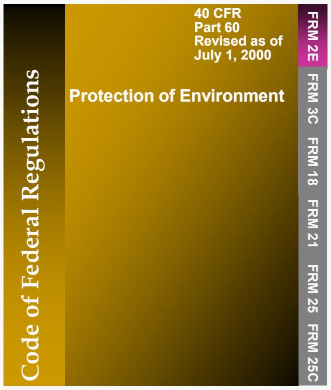


Depends Upon the Path of Least Resistance

- To the atmosphere through the landfill surface
- Migrate laterally into surrounding soils
- Enter groundwater and follow water path
- Through LFG extraction systems

Federal Reference Method 2E

Determination of Landfill Gas Production Flow Rate



Applicability

- Applies to measurement of landfill gas (LFG) production flow rate from municipal solid waste (MSW) landfills
- Used to calculate the flow rate of nonmethane organic compounds (NMOC) from landfills
- Also applies to calculating a site-specific “k” value

Principle

- Extraction wells are installed in a cluster of three, or at five locations dispersed throughout the landfill
- A blower is used to extract LFG from the landfill

Principle

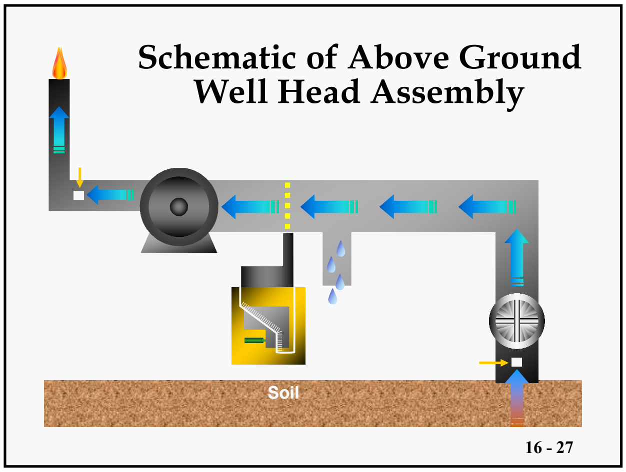
- LFG composition, landfill pressures near the extraction well, and volumetric flow rate are measured and landfill gas production flow rate determined

Apparatus

- Well drilling rig
- Material
    - Gravel
    - Bentonite
    - Backfill material

Apparatus

- Wellhead assembly
    - Control valve
    - Orifice meter/manometer
    - Blower
    - Sampling ports (Well head/outlet)



Schematic of Above Ground Well Head Assembly

Placement of Extraction Wells

- Single cluster of three (3) extraction wells in a test area (Waste known)
    - Near perimeter of site
    - Depth equal to or greater than the average depth of the landfill
    - Waste 2-10 years old

Placement of Extraction Wells

- Five (5) wells spaced over the landfill (waste unknown)
    - Divide landfill into five (5) equal areas and place extraction well at centroid of each area

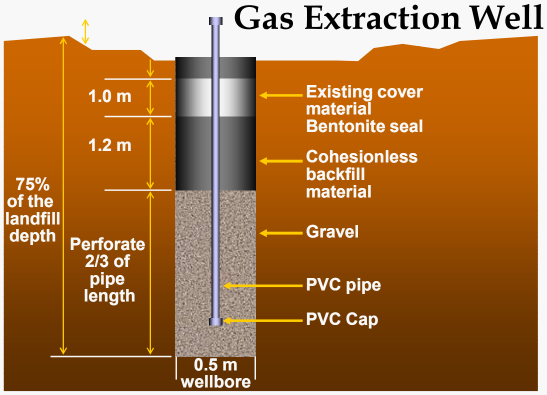
Extraction Well Pipe Configuration

- PVC, HDPE, fiberglass, stainless steel or other materials of construction
- Minimum diameter of 0.075 meters

Extraction Well Pipe Configuration

- Bottom two-thirds of the pipe perforated
    - Holes/slots 1.0 centimeter diameter
    - Spaced 90 degrees apart every 0.1 to 0.2 meters

Gas Extraction Well



Extraction Well Pipe Placement

- Place in center of hole
- Backfill with gravel to 0.3 meters above perforation
- Add backfill material 1.2 meters thick
- Add layer of bentonite 1.0 meters thick
- Remainder cover material

Pressure Probe

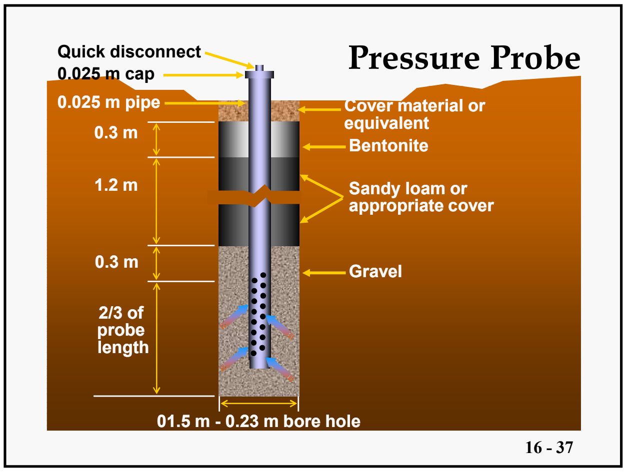
- Pressure probes are used in the check for infiltration of air into the landfill and radius of influence
    - Shallow pressure probes used for determination of infiltration of air into landfill
    - Deep pressure probes used to determine the radius of influence

Pressure Probe Configuration

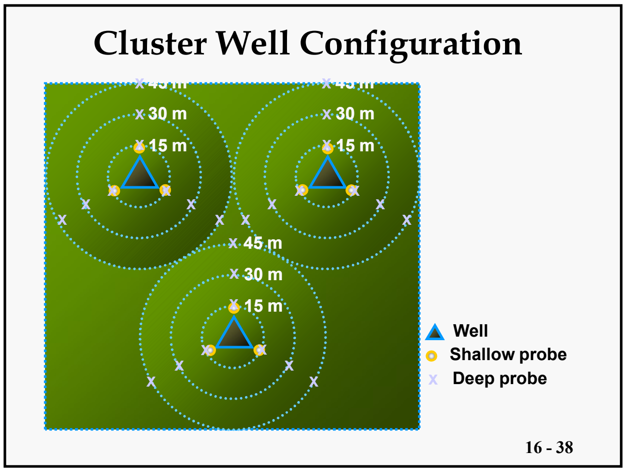
- PVC or stainless steel, 0.025 meter
- Bottom two-thirds of pipe perforated
    - Four 6-mm diameter holes
    - Placed 90 degrees apart
    - Every 0.15 meters

Pressure Probe Placement

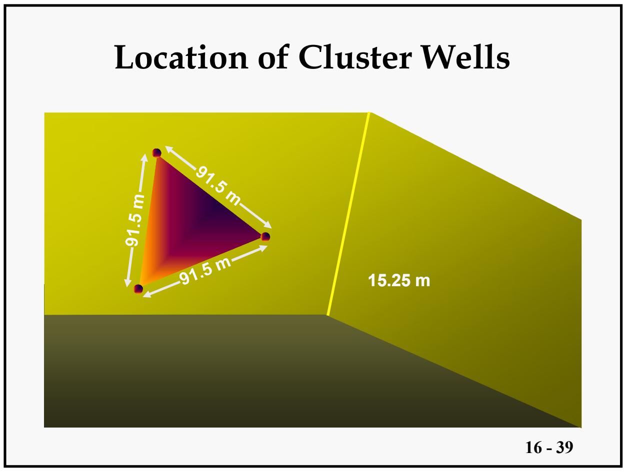
- Shallow pressure probes placed in close proximity to cluster well
- Deep pressure probes
    - Along three radial arms from the extraction wells
    - Approximately 120 degrees apart
    - Distances of 3, 15, 30, and 45 meters from extraction wells



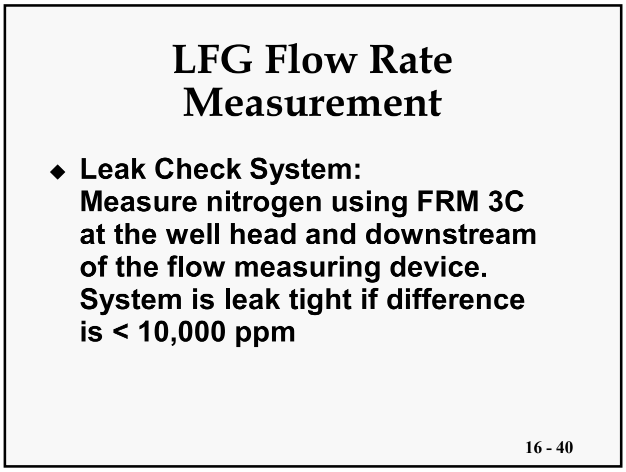
Pressure Probe



Cluster Well Configuration

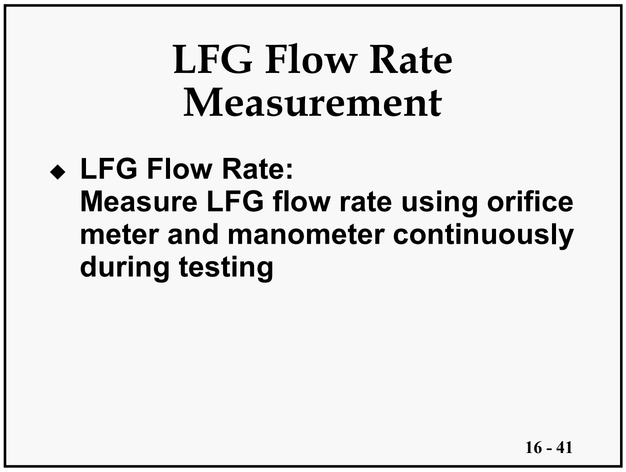


Location of Cluster Wells



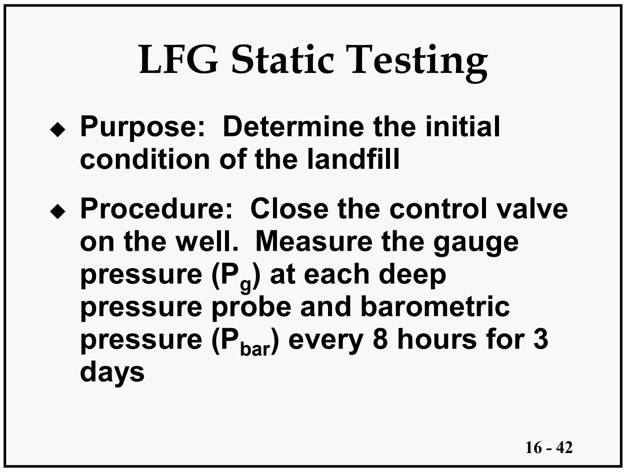
LFG Flow Rate Measurement

- Leak Check System:
  Measure nitrogen using FRM 3C at the well head and downstream of the flow measuring device. System is leak tight if difference is < 10,000 ppm



LFG Flow Rate Measurement

- LFG Flow Rate:
  Measure LFG flow rate using orifice meter and manometer continuously during testing



LFG Static Testing

- Purpose: Determine the initial condition of the landfill
- Procedure: Close the control valve on the well. Measure the gauge pressure (P_g) at each deep pressure probe and barometric pressure (P_{bar}) every 8 hours for 3 days

LFG Static Testing

- Calculate: $P_i = P_{bar} + P_g$
- Average all 8 hours reading for each well to record P_{ia}

Well Temperature and Static Flow Rate

- Measure the LFG temperature at each well head
- Measure static flow rate using Type S pitot tube at each well head

Short Term Testing

- The purpose of short term testing is to determine the maximum vacuum that can be applied to the wells without infiltration of air into the landfill
  - Use blower to extract LFG from single well (others capped) at a rate at least twice the static flow rate

Short Term Testing

  - Check for infiltration of air into the landfill by measuring the temperature of the LFG at the wellhead, the gauge pressures of the shallow pressure probes, and LFG nitrogen using FRM 3C
- LFG concentration of nitrogen is > 20 %
- Any shallow probes have a negative gauge pressure

Short Term Testing

- LFG temperature > 55°C
- Increase the blower vacuum by 4 mm Hg, wait 24 hours, and repeat infiltration test
- Continue increasing blower vacuum by 4 mm Hg until infiltration occurs

Short Term Testing

- Then reduce blower vacuum until nitrogen < 20%, shallow probes are positive, or LFG temperature < 55°C
- This is the maximum vacuum at which infiltration does not occur
- At this maximum vacuum, measure P_{bar} every 8 hours for 24 hours
- Record LFG flow rate: Q_s

Short Term Testing

- Deep probe gauge pressures for all probes every 8 - hours: P_f
- Average 8 hour readings of deep probes: P
- Compare initial average pressure (P_{ia}) to final average pressure (P_{fa})

Short Term Testing

- Determine furthermost point from the wellhead along each radial arm where $P_{fa} < P_{ia}$

Short Term Testing

- This is the distance of maximum radius of influence (ROI)
- Average ROIs to determine the average maximum radius of influence (R_{ma})
- Calculate depth (D_{st}) affected by the extraction well:
  - $D_{st} = WD + R_{ma}^2$

Short Term Testing

- Calculate void volume (V)
  - $V = (0.40)(R_{ma}^2)(D_{st})$
- Calculate total void volumes (V_v)
  - Sum of all V

Long Term Testing

- The purpose of long term testing is to determine the methane generation rate constant, k
  - Set blower vacuum to previously determined highest vacuum rate acceptable without infiltration
  - Every 8 hours, sample LFG, measure gauge pressure at shallow pressure probes, the blower vacuum, the LFG flow rate, and check for infiltration

Long Term Testing

- Calculate Vt, the total volume of landfill gas extracted:

$$V_t = \sum_{i\ 1}^{n}(60)(Q_i)(T_{vi})$$

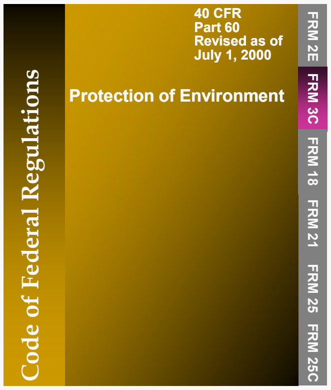
Calculating NMOC mass emission rate

$$Q_t = 2kL'_o C_{NMOC}(3.595x10^{-9})\sum_{i=1}^{n} M_i e^{-[(k)(t_i)]}$$

Eq. 2E-14

Federal Reference Method 3C

Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources (40 CFR 60, Appendix A)



Applicability

- This method applies to the analysis of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart

Principle

- A portion of the sample is injected into a gas chromatograph (GC) and the CO_2, CH_4, N_2, and O_2 concentrations are determined by using a thermal conductivity detector (TCD) and integrator

Apparatus

- Gas Chromatography equipped with separation column, sample loop, conditioning system, and thermal conductivity detector
- Recorder, tubing, regulators and adsorption tubes to remove any oxygen in the carrier gas

GC System and Analytical Apparatus

Calibration and Linearity Gases

- Standard cylinder gas mixtures for each compound of interest with at least three (3) concentration levels spanning the range of sample concentration

Sample Collection

- Direct Injection
- Tedlar® Bag
- Whole Air Flask/Canister

Whole Air Flask/canister at Extraction Well

Analytical System Standardization

- Optimize GC system according to manufacturer's specifications
- Linearity Check and Calibration
  - Three calibration gases over the range of suspected sample concentration (This initial check may also serve as the initial instrument calibration)

Analytical System Standardization

- Plot linear regression of concentration vs. area values to obtain relative response to each compound

Analytical System Standardization

- Single Point Calibration Check
  - Use standard calibration gas which is within 20% of the sample component concentration

Sample Analysis

- Purge sample loop with sample
- Analyze each sample in duplicate
  - Peak areas should agree within 5% of their average

Method 3C Calculations

- Moisture content in the sample
  - $B_w = P_w/P_{bar}$
- Compound concentration
  - $C = A/R(1-B_w)$

Concentration of Sample Components

$$C = [P_{tf}/T_{tf}]/[(P_t/T_t) - (P_{ti}/T_{ti})][(A)/R(1-B_w)]$$

Federal Reference Method 25C

40 CFR
Part 60
Revised as of
July 1, 2000

Protection of Environment

Code of Federal Regulations

Applicability

- This method is applicable to the sampling and measurement of nonmethane organic compounds (NMOC) as carbon in MSW landfill gases

Principle

- In operation, a sample probe that has been perforated at one end is driven or augured to a depth of 1.0 meter below the bottom of the landfill cover
- A sample of the landfill gas is extracted with an evacuated cylinder

Principle

- The NMOC content of the gas is determined by injecting a portion of the gas from the evacuated cylinder into a gas chromatographic column to separate the NMOC from CO, CO_2, and CH_4

Principle

- The NMOC from the separation is oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID)

FRM 25C Sampling System

- Probe: Stainless steel with the bottom third perforated. Must be long enough to go a minimum of 1 meter below landfill cover
- Rotameter: With flow control valve (< 500 mL/min)
- Sampling valve: Stainless steel

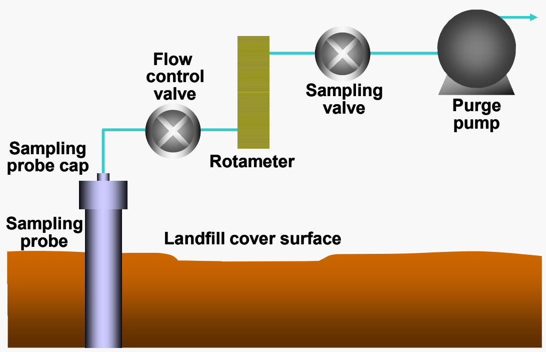
FRM 25C Sampling System

- Pressure gauge: U-tube mercury manometer
- Purge pump: Capable of purging probe
- Vacuum pump: Capable of evacuating to an absolute pressure of 10 mm Hg

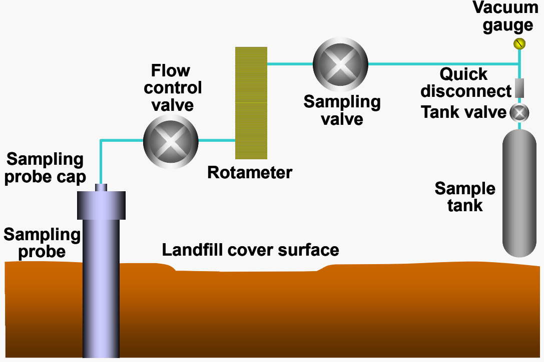
FRM 25C Sampling System

- Sampling tank: Stainless steel or aluminum cylinder with a minimum volume of 4 liters and equipped with a stainless steel sample tank valve

Sampling Probe Purging System



Sampling Train



Canister Sampling at MSW Landfill

Syringe Sampling at MSW Landfill

Tank Sampling Procedure

- Sample Tank Evacuation: Evacuate to 10 mm Hg absolute (field/laboratory), set aside for 60 minutes, check vacuum, no change; acceptable

Tank Sampling Procedure

- Sampling
  - Evacuate/pressurize sampling tank three time with final vacuum of 325 mm Hg; set aside
  - Assemble sample probe, flow control valve, rotameter and purge pump

Pilot Probe Sampling Procedure

- Sample Probe Installation
  - Pilot Probe Procedure:
    - Use post driver to 1 meter below landfill cover
    - Insert sample probe
    - Seal with bentonite
    - Cap

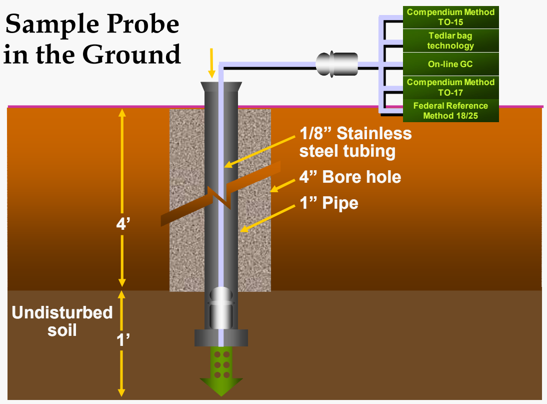
Pitot Probe Sampling Procedure

- Purge at least 2 probe volumes at flow rate of 500 mL/min
- Replace purge pump with sample tank

Pilot Probe Sampling Procedure

- Auger Procedure:
  - Drill hole to 1 meter below landfill cover
  - Place sample probe in hole
  - Backfill with pea gravel to level of 0.6 meters from the surface
  - Seal around probe with bentonite
  - Equilibrate for 24 hours before sampling

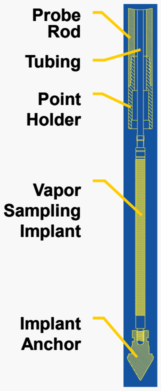
Sample Probe in the Ground



Geoprobe Bore-hole Sampling Technique

Geoprobe on Truck

Soil Gas Sampling



Sampling Procedure

- Sampling
  - Open the sampling valve and tank valve
  - Sample at a flow rate of 500 mL/min until sample tank gauge is zero
  - Disconnect from sampling system
  - Pressurize to 1,060 mm Hg with helium

Sampling Procedure

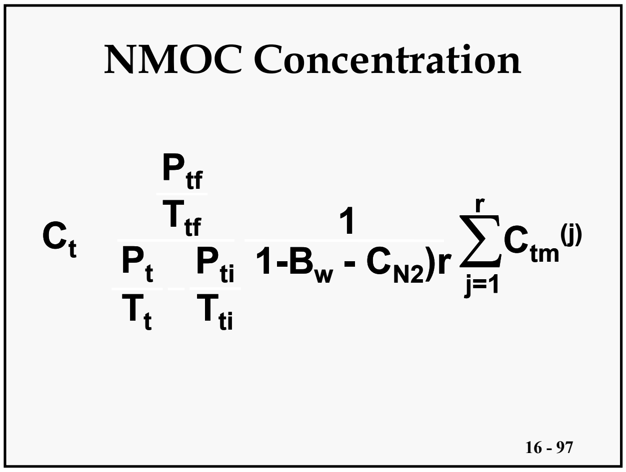
- Record final pressure (may also be pressurized in the laboratory)
- Landfill gas sample is acceptable if N_2 is < 20%

Federal Reference Method 25C Analysis

- FRM 25C: Oxidation, reduction and measurement of NMOC
- Initial NMOC analyzer performance test:
  - Oxidation catalyst efficiency check
  - Reduction catalyst efficiency check
  - Analyzer linearity check (not CO_2)

Federal Reference Method 25C Analysis

- NMO Analyzer daily calibration
- NMO response factor



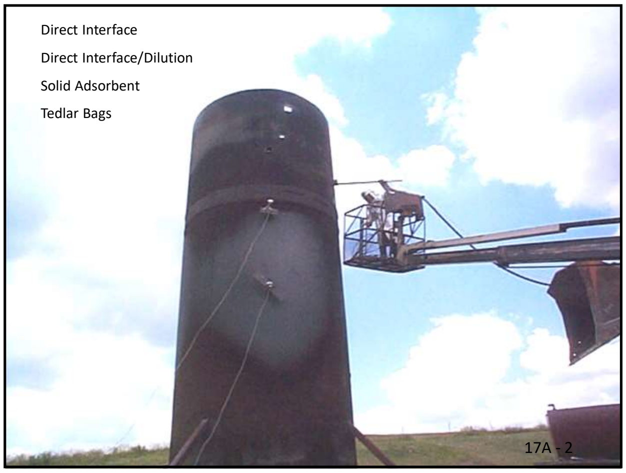
NMOC Concentration

$$C_t \quad \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \; \frac{1}{1-B_w - C_{N2})r} \sum_{j=1}^{r} C_{tm}^{(j)}$$

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

Federal Reference Method 18

General GC Methodology
(Work Horse for VOCs Speciation Detection)



Direct Interface
Direct Interface/Dilution
Solid Adsorbent
Tedlar Bags

Survey Canister Sampling

Applicability

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

Applicability

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

Applicability

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

Principle

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

Overview Items

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

Overview Items

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

Overview Items

- FRM 18 identifies only those analytes for which sampling and analysis is specifically conducted
- FRM 18 can’t be used if emissions are unknown
  - FRM 18 (CH_3OH,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
  - Commercial cylinders
  - Gas cylinder dilution (FRM 205)
  - Flash vaporization
- FRM 18 requires determination of response factor 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 an upper limit of GC detector (saturation of detector limiting factor; upper limit can be extended by dilution)
- A lower range may be achievable by concentrating the sample, thus lowering the limit of detection below the 1
- Sensitivity: minimum detection limit or signal-to-noise ratio 3:1

Method Criteria

- Precision: 5 to 10% relative standard deviation(RSD) of mean value (usually 5% with experience GC operator)
- Accuracy: Within 10% audit sample value
- Must conduct recovery study
  - 70-130 % recovery criteria

Method Criteria

- Audit Samples are required

- As of July 2021, the requirement to obtain these audit samples is no longer in effect until such time as another independent accredited audit sample providers (AASP) has audit samples available for purchase.

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 can be used (Wide open method)
  - Source decides combination provide the 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

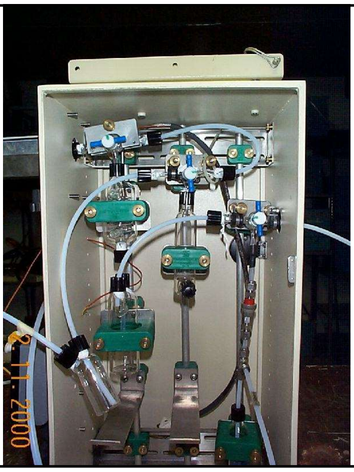
- Pre-survey samples collected in Tedlar® or aluminized Mylar flexible bags
- Flexible bag certification
  - Use new bag
  - Leak check all bags

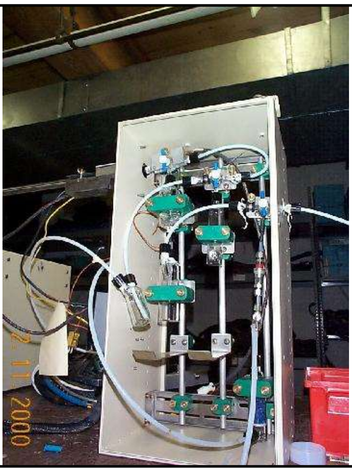
Flexible Bag Sampling Procedure

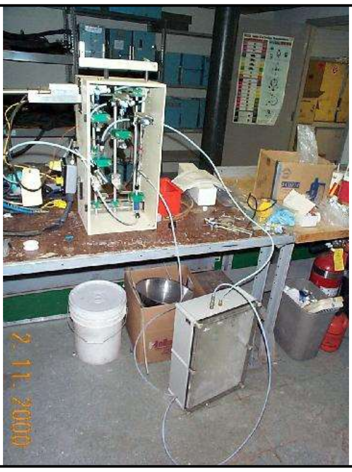
- Check for contamination by filling with nitrogen
- Analyze 24 hours later with GC

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 (> C12)
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

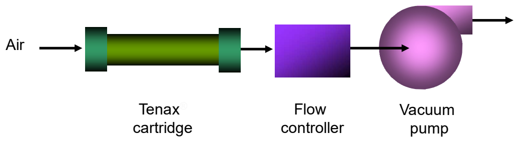
Adsorbent Recovery Solvent Extraction

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

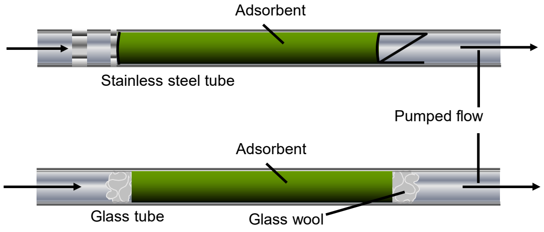
Adsorbent Tube Sampling Train

- 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

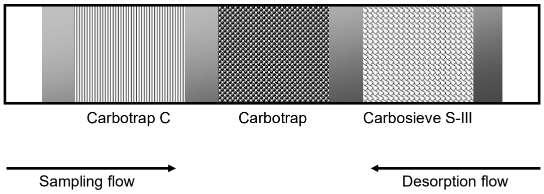
Active Sampling System Utilizing Solid Adsorbents

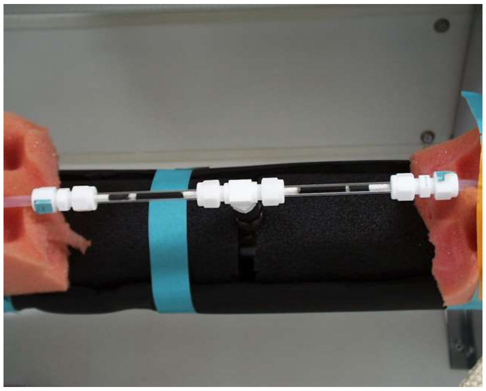


Single Tube Design-Glass/Stainless Steel



Multi-bed Adsorbent Trap





Adsorbent Tube Sampling

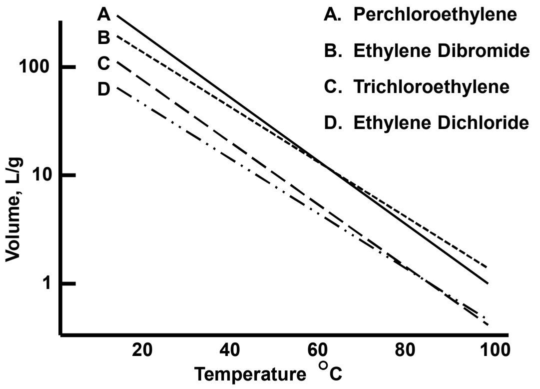
- Strengths
  - Sample compact and easy to use
  - Sample returned to laboratory for analysis
  - Good sample storage time

Adsorbent Tube Sampling

- Weaknesses
  - Quantitative recovery poor
  - Breakthrough possible of interested analytes
  - Moisture may affect 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 principal solvents are chlorinated hydrocarbons
  - Generally, for any situation where a 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 is 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
- No real time data (sample must be returned to laboratory for analysis)
- High moisture and CO_2 together can cause interference
    - $(\%CO_2)x(\%H_2O)>100$ gives potential high bias (EPA Guidelines)

Method 25 Summary

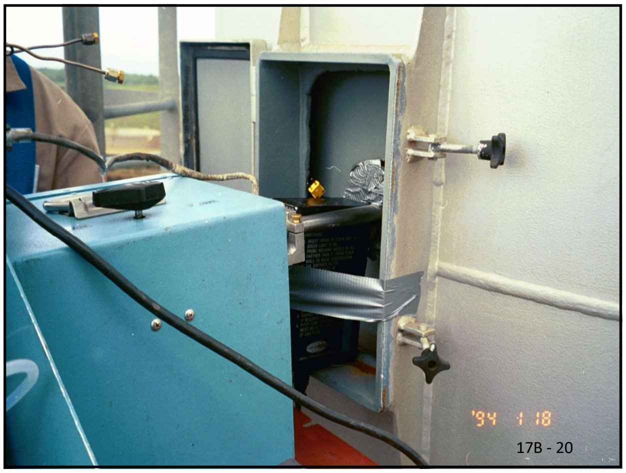
Withdraw	Analyze	Oxidize	Reduce
Withdraw emission sample from stack through chilled condensate trap (dry ice) into evacuated cylinder	Analyze contents of trap and cylinder separately	Oxidize organic content of trap to CO2	Reduce to methane, measure with FID

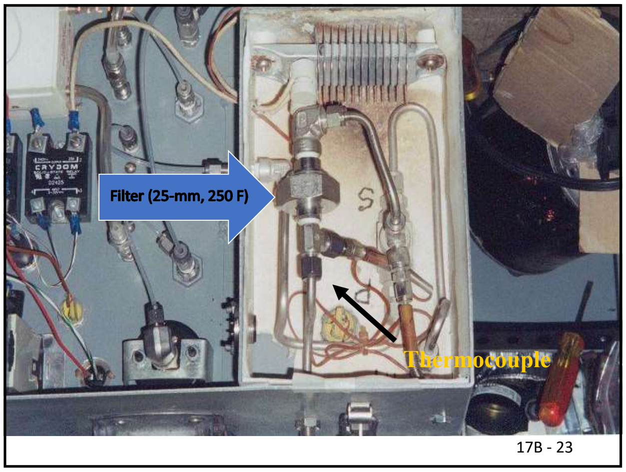
Method 25 Summary

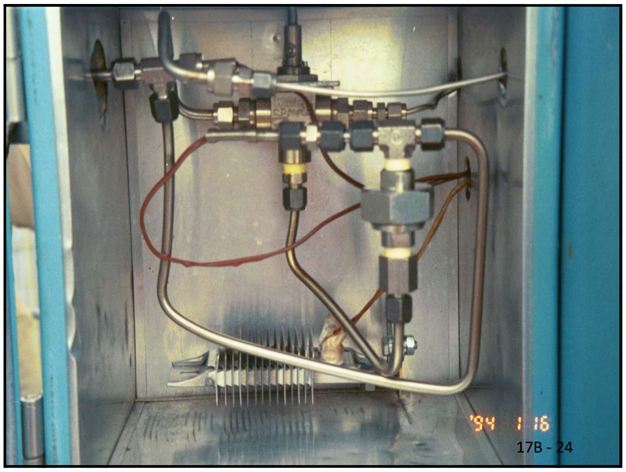
- Inject portion of cylinder sample into GC to separate non-methane organics, oxidize NMO to CO_2, reduce to methane, and measure with FID
- Combine results (condensable and non-condensable) and report as total gaseous nonmethane organics (TGNMO)

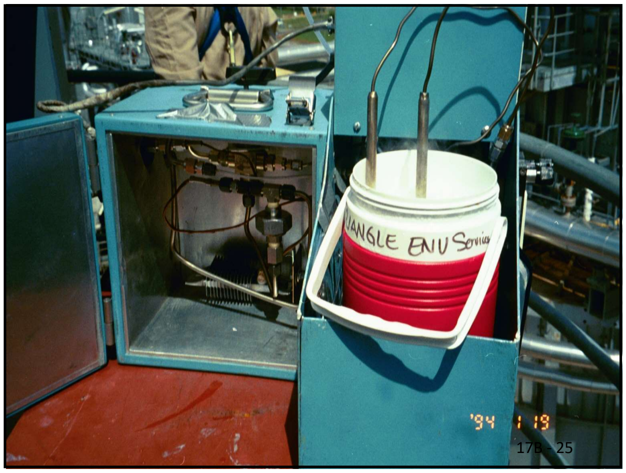
Method 25 Apparatus

- 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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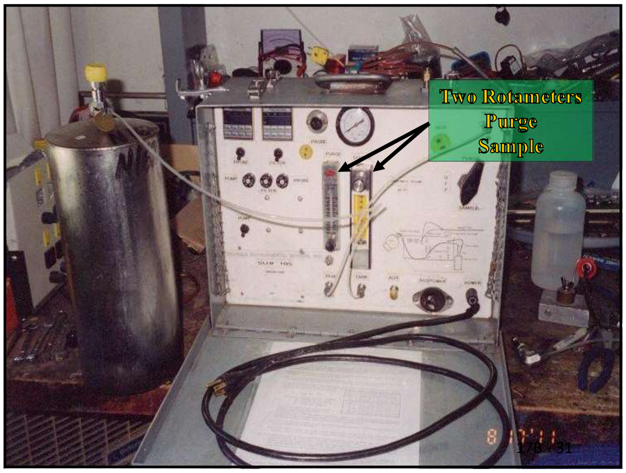


Calibration of
Sampling System

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

Calibration of Sampling System

- Sample tank: to the nearest 5 g (if using deionized water) or to the nearest 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 ΔP. 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 ΔP
- Record findings on FTDS

Method 25 Sampling

- Mark probe for point of average stack gas velocity (probe $\leq$ 36 in. as specified 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

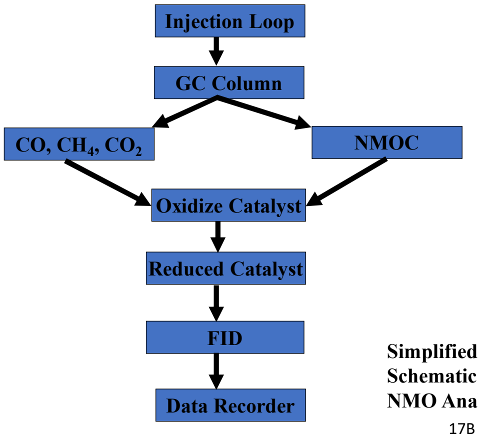
- Attach trap to sampling train
- Position probe tip perpendicular to stack gas flow (Take plug off end)
- Purge sampling train, then adjust flow rate

Method 25 Sampling

- Record sample tank vacuum, flow meter settings, and temperatures at 5 - minute intervals on FTDS
- Adjust the flow rate as necessary to maintain a constant rate, ±10% over duration
- 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

- Condensable organics 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

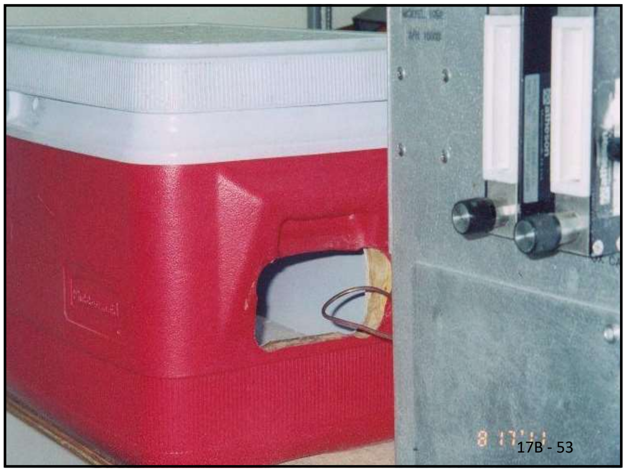
- Non-Condensable Organics
  - The non-condensable sample in the original field sample tank (#1) is injected into the analyzer
  - Methane, CO, CO_2, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO_2, reduced to methane and detected with an FID

Method 25 Apparatus

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

Method 25 Apparatus

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



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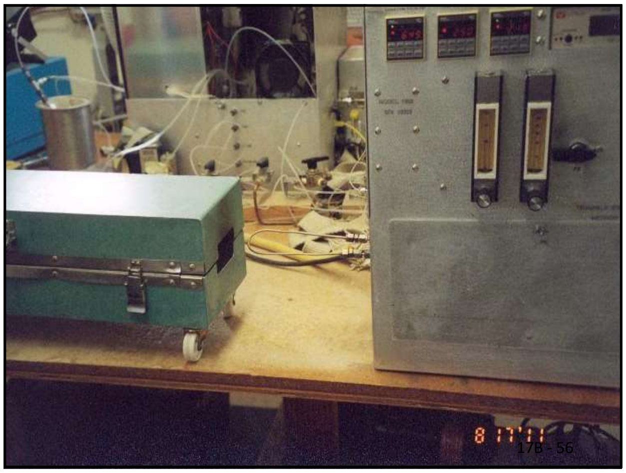

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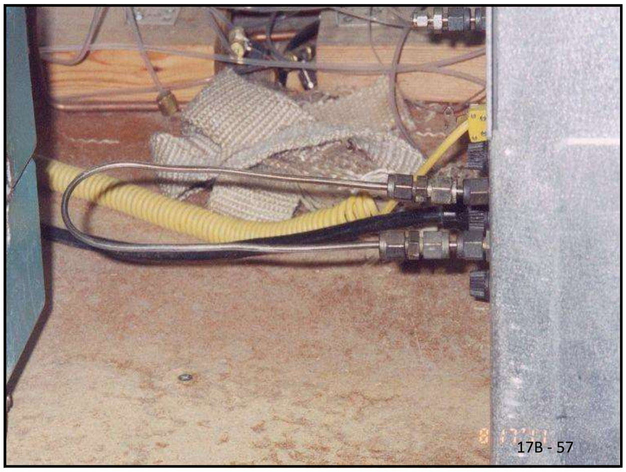

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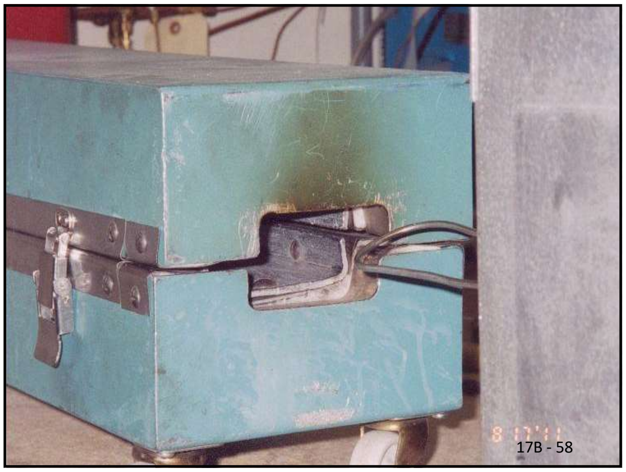

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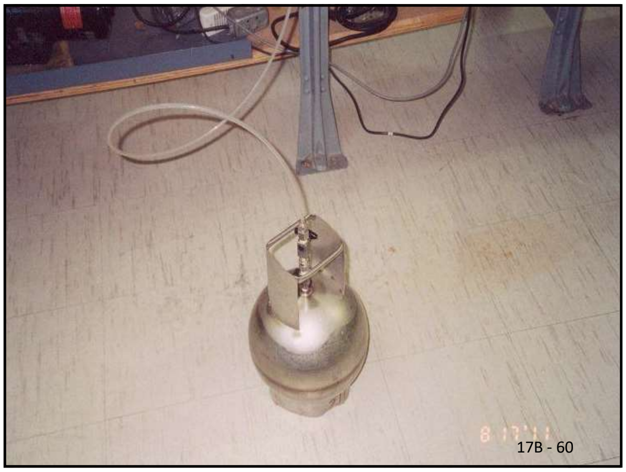

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Initial Performance Check of Condensate Recovery and Conditioning Apparatus

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

Daily Performance Tests

1

Condensable organic recovery system

- Leak test
- System background test
- Oxidation catalyst efficiency test

2

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

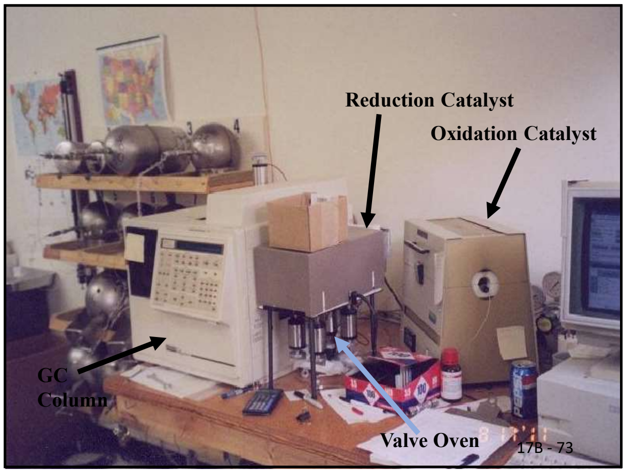
- Remove condensate trap from dry ice and allow to warm to room temperature
- Heat trap by placing it in a furnace at 200 ˚C

Condensable Organic Fraction Recovery

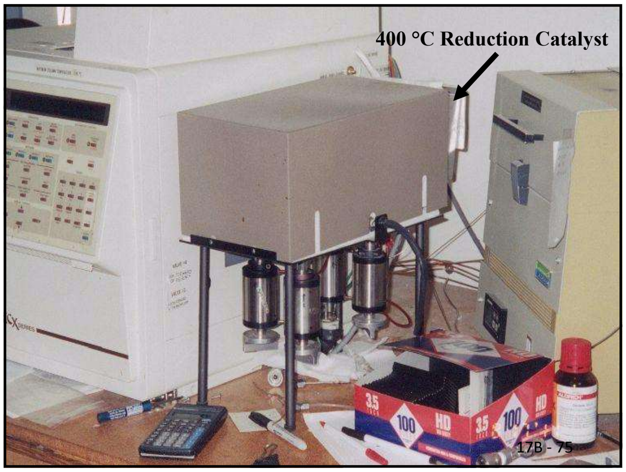
- Recovery of condensable organics
  - After NDIR analyzer indicates a CO_2 concentration of < 10,000 ppm, begin heating the tubing that connects the condensate trap to the oxidation catalyst with a heat gun

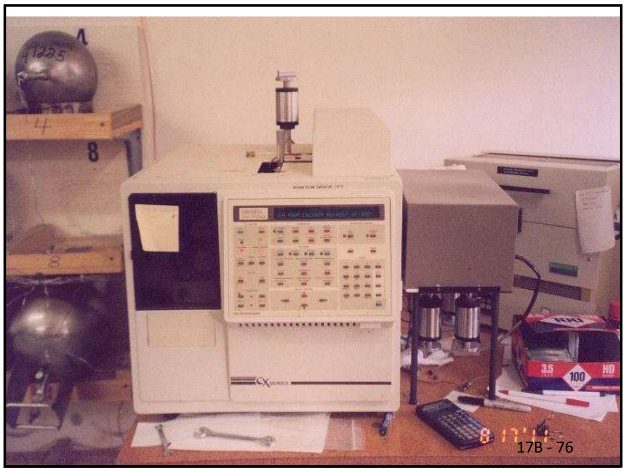
Condensable Organic Fraction Recovery

- 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
GC Column
Valve Oven
17B - 73


17B - 74


400 °C Reduction Catalyst
17B - 75


17B - 76


17B - 77

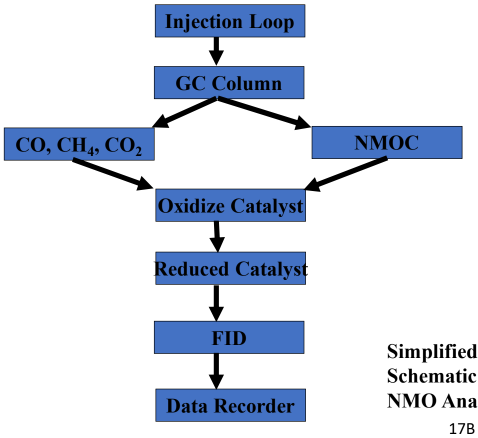

17B - 78

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

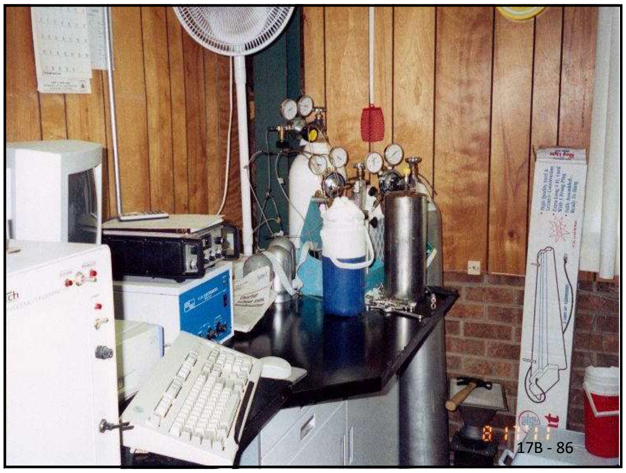
- After detection of any NMOC, return column oven temperature to 85˚C
- Record the CO_2 peak area and NMO peak area
- Repeat analysis two additional times

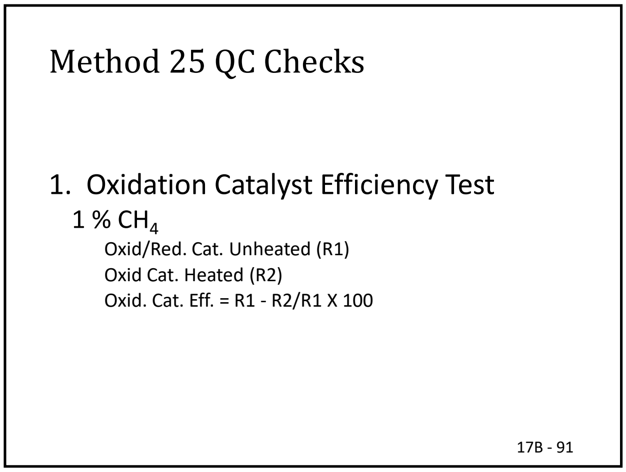
Method 25 Analysis

- 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

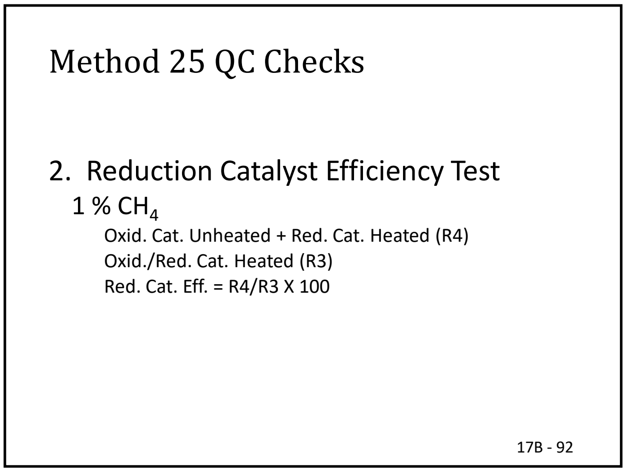
- Sample volume
- Noncondensable organics
- Condensable organics
- Total gaseous nonmethane organics
- Percent recovery
- Relative standard deviation
- EPA provides audit sample





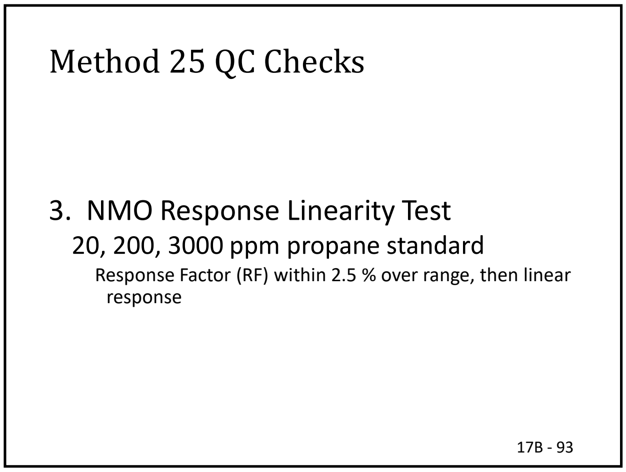
Method 25 QC Checks

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



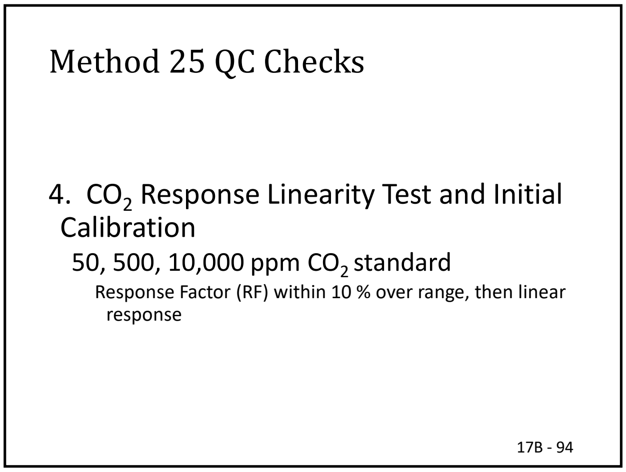
Method 25 QC Checks

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



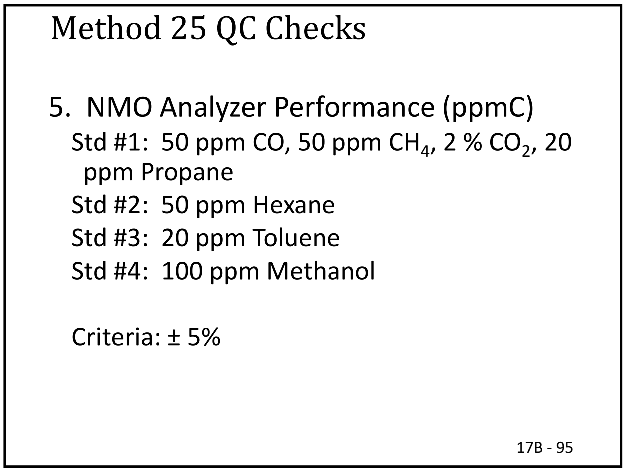
Method 25 QC Checks

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

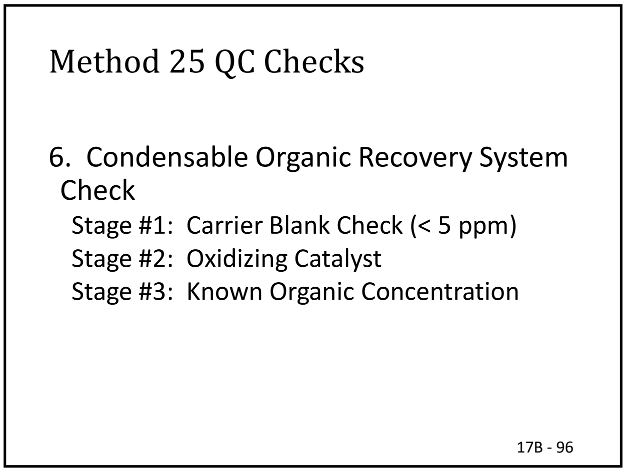
4. CO_2 Response Linearity Test and Initial Calibration
   - 50, 500, 10,000 ppm CO_2 standard
     - Response Factor (RF) within 10 % over range, then linear response



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. Condensable 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. 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

Federal Reference Method 25A

Determination of Total Gaseous Organic Concentration Using A Flame Ionization Detector (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

Applicability

- 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 sample line should be heated (≥ 110°C) to prevent any condensation. 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

FRM 25A Items

- 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 %
- 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:
  - $C_{s(dry)} = \frac{C_{s(wet)}}{(1-Bws)}$
  - $C_{s(dry,\ STP)} = \frac{C_{s(wet)}}{(1-Bws)} \times \frac{(T_s)(P_{std})}{(T_{std})(P_s)}$

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 sampling components leading to the analyzer shall be heated ≥ 110°C (220°F)
- The flame ionization detector block shall be heated >120°C (250°F).

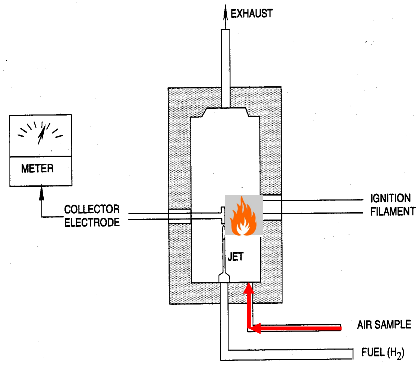
Principle

- 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

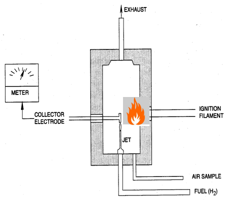
FID Theory

- 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

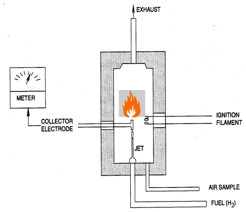


Flame Ionization Detection



- 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 and water 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 affect 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^{o}F) stainless steel or Teflon® tubing
- All components must be heated > 250^{o}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^{o}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^{o}F) glass fiber filter assembly
- Pump: A heated (> 250^{o}F) leak-free diaphragm type

Sampling System

- Organic Concentration Analyzer:
  A heated (> 250^{o}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.)

- Method 1

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

- 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)x(Coating Usage)x(1-DE)x(CE)} + {(Coating Usage)x(VOC Content)x(1-CE)}

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

Weakness/Strengths FRMs 18, 25, & 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

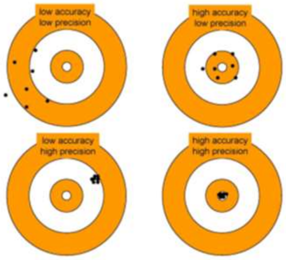
- Where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed
- Where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example)

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

USEPA Guidance Document 033
(www3.epa.gov/ttn/emc/guidlnd/gd-033.pdf)

- 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

FRM 204
PTE/TTE Enclosures,
Capture Efficiency
/Calculations

USEPA Method 204

- Procedure used to determine whether a permanent or temporary enclosure meets the criteria for a total enclosure.
- An enclosure is evaluated against a set of criteria. If the criteria are met and if all the exhaust gases from the enclosure are ducted to a control device, then the volatile organic compounds (VOC) capture efficiency (CE) is assumed to be 100 percent, and CE need not be measured.

Natural Draft Opening (NDO)

- Natural Draft Opening (NDO). Any permanent opening in the enclosure that remains open during operation of the facility and is not connected to a duct in which a fan is installed.

Equivalent diameter

$$ED = \sqrt{\frac{4*A}{\pi}} \quad \textit{(Circle or square/rectangle)}$$

or

$$ED = \frac{2LW}{(L+W)} \quad \textit{(square/rectangle)}$$

Permanent Total Enclosure (PTE)

- Permanently installed enclosure that completely surrounds a source of emissions such that all VOC emissions are captured and contained for discharge to a control device.

Criteria for Permanent Total Enclosure

1. Any NDO shall be at least four equivalent opening diameters from each VOC emitting point unless otherwise specified by the Administrator.
2. The total area of all NDO's shall not exceed 5 percent of the surface area of the enclosure's four walls, floor, and ceiling.
3. The average facial velocity (F_V) of air through all NDO's shall be at least 3,600 m/hr (200 fpm). The direction of air flow through all NDO's shall be into the enclosure.
4. All access doors and windows whose areas are not included in section 5.3 and are not included in the calculation in section
5. shall be closed during routine operation of the process
6. All VOC emissions must be captured and contained for discharge through a control device

Permanent Total Enclosure

Temporary Total Enclosure (TTE)

- Temporarily installed enclosure that completely surrounds a source of emissions such that all VOC emissions that are not directed through the control device (*i.e.*, uncaptured) are captured by the enclosure and contained for discharge through ducts that allow for the accurate measurement of the uncaptured VOC emissions.

Criteria for Temporary Total Enclosure

1. Any NDO shall be at least four equivalent opening diameters from each VOC emitting point unless otherwise specified by the Administrator.
2. Any exhaust point from the enclosure shall be at least four equivalent duct or hood diameters from each NDO.
3. The total area of all NDO's shall not exceed 5 percent of the surface area of the enclosure's four walls, floor, and ceiling.
4. The average facial velocity (FV) of air through all NDO's shall be at least 3,600 m/hr (200 fpm). The direction of air flow through all NDO's shall be into the enclosure.
5. All access doors and windows whose areas are not included in section 5.3 and are not included in the calculation in section
6. shall be closed during routine operation of the process

Temporary Total Enclosure

Building Enclosure (BE)

- Building Enclosure (BE). An existing building that is used as a TTE.

Alternative Capture Efficiency

- Guidance Document 035
- Must be included in SIP
- Liquid to gas mass balance without an enclosure
- Statistical analysis is required for alternatives
  - DQO or LCL

Data Quality Objective (DQO)

- The purpose of the DQO is to allow sources to use alternative CE test procedures while ensuring reasonable precision consistent with pertinent requirements of the Clean Air Act. The DQO requires that the width of the 2-sided 95 percent confidence interval of the mean measured value be less than or equal to 10 percent of the mean measured value (see Figure 1). This ensures that 95 percent of the time, when the DQO is met, the actual CE value will be +5 percent of the mean measured value (assuming that the test protocol is unbiased).

Lower Confidence Limit (LCL)

- The LCL approach compares the 80 percent (2-sided) LCL for the mean measured CE value to the applicable CE regulatory requirement. The LCL approach requires that either the LCL be greater than or equal to the applicable CE regulatory requirement or that the DQO is met. A

Lower Confidence Limit (LCL)

- The purpose of the LCL approach is to provide sources, who may be performing much better than their applicable regulatory requirement, a screening option by which they can demonstrate compliance. The approach uses less precise methods and avoids additional test runs which might otherwise be needed to meet the DQO while still being assured of correctly demonstrating compliance.

Lower Confidence Limit (LCL) (cont.)

- It is designed to reduce "false positive" or so called "Type II errors" which may erroneously indicate compliance where more variable test methods are employed. Because it encourages CE performance greater than that required in exchange for reduced compliance demonstration burden, the sources that successfully use the LCL approach could produce emission reductions beyond allowable emissions. Thus, it could provide additional benefits to the environment as well.

Method 204
Criteria for and Verification of a PTE or TTE

- Method 204

(https://www.epa.gov/sites/production/files/2019-06/documents/method_204_0.pdf)

Quality Control - TTE

- The success of this method lies in designing the TTE to simulate the conditions that exist without the TTE (i.e., the effect of the TTE on the normal flow patterns around the affected facility or the amount of uncaptured VOC emissions should be minimal).
- The TTE must enclose the application stations, coating reservoirs, and all areas from the application station to the oven. The oven does not have to be enclosed if it is under negative pressure. The NDO's of the temporary enclosure and an exhaust fan must be properly sized and placed.

TTE - Baseline VOC Measurement

- Monitor the VOC concentration of the captured gas steam in the duct before the capture device without the TTE. To minimize the effect of temporal variation on the captured emissions, the baseline measurement should be made over as long a time period as practical. However, the process conditions must be the same for the measurement in section 7.5 as they are for this baseline measurement. This may require short measuring times for this quality control check before and after the construction of the TTE.

Measure VOC inside TTE

- After the TTE is constructed, monitor the VOC concentration inside the TTE. This concentration should not continue to increase and must not exceed the safe level according to Occupational Safety and Health Administration requirements for permissible exposure limits. An increase in VOC concentration indicates poor TTE design.

TTE VOC Measurement

- Monitor the VOC concentration of the captured gas stream in the duct before the capture device with the TTE. To limit the effect of the TTE on the process, the VOC concentration with and without the TTE must be within 10 percent. If the measurements do not agree, adjust the ventilation rate from the TTE until they agree within 10 percent.

Enclosure Criteria Determination

1. Determine the equivalent diameters of the NDO's and determine the distances from each VOC emitting point to all NDO's. Determine the equivalent diameter of each exhaust duct or hood and its distance to all NDO's. Calculate the distances in terms of equivalent diameters. The number of equivalent diameters shall be at least four.

Enclosure Criteria Determination

2. Measure the total surface area (A_T) of the enclosure and the total area (A_N) of all NDO's in the enclosure. Calculate the NDO to enclosure area ratio (NEAR) as follows:

$$NEAR = \frac{A_N}{A_T}$$

- The NEAR must be ≤0.05.

Enclosure Criteria Determination

3. Measure the volumetric flow rate, corrected to standard conditions, of each gas stream exiting the enclosure through an exhaust duct or hood using EPA Method 2.

- The FV shall be at least 3,600 m/hr (200 fpm). Alternatively, measure the pressure differential across the enclosure. A pressure drop of 0.013 mm Hg (0.007 in. H2O) corresponds to an FV of 3,600 m/hr (200 fpm).

Volumetric Flow Rate

- Measure the volumetric flow rate, corrected to standard conditions, of each gas stream exiting the enclosure through an exhaust duct or hood using EPA Method 2.

$$\boldsymbol{Fv = \frac{Q_O - QI}{A_N}}$$

Volumetric Flow Rate (cont.)

- Q_O= the sum of the volumetric flow from all gas streams exiting the enclosure through an exhaust duct or hood
- Q_I= the sum of the volumetric flow from all gas streams into the enclosure through a forced makeup air duct; zero, if there is no forced makeup air into the enclosure

Enclosure Criteria Determination

4. Verify that the direction of air flow through all NDO's is inward. If FV is less than 9,000 m/hr (500 fpm), the continuous inward flow of air shall be verified using streamers, smoke tubes, or tracer gases. Monitor the direction of air flow for at least 1 hour, with checks made no more than 10 minutes apart.

Capture Efficiency

Protocol	Enclosure Verification	Liquid Input (L)	Captured emissions (G)	Fugitive Emissions (F or F_B)	Capture Efficiency Formula
PTE	RM 204	N/A	N/A	N/A	Assumed 100%
TTE Gas/Gas	RM 204	N/A	RM 204B or C	RM 204D	G/(G+F)
TTE Liquid/Gas	RM 204	RM 204A or F	N/A	RM 204D	(L-F)/L
BE Gas/Gas	RM 204	N/A	RM 204B or C	RM 204E	G/(G-F_B)
BE Liquid/Gas	RM 204	RM 204 A or F	N/A	RM 204E	(L-F_B)/L

Method 204A – Volatile Organic Compounds Content in Liquid Input Stream

- Method 204A

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204a.pdf)

Method 204B – Volatile Organic Compounds in Captured Stream

- Method 204B

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204b.pdf)

Method 204C – Volatile Organic Compounds Emissions in Capture Stream (Dilution Technique)

- Method 204C

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204c.pdf)

Method 204D – Volatile Organic Compounds Emissions in Uncaptured Stream from TTE

- Method 204D

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204d.pdf)

Method 204E – Volatile Organic Compounds Emissions in Uncaptured Stream from BE

- Method 204E

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204e.pdf)

Method 204F – Volatile Organic Compounds Content in Liquid Input Stream (Distillation Approach)

- Method 204F

(https://www.epa.gov/sites/production/files/2017-08/documents/method_204f.pdf)

Compliance Test and Source Test Observation

Stack Testing Special Topics:

Compliance Test and Source Test Observation

Stack Testing Special Topics:

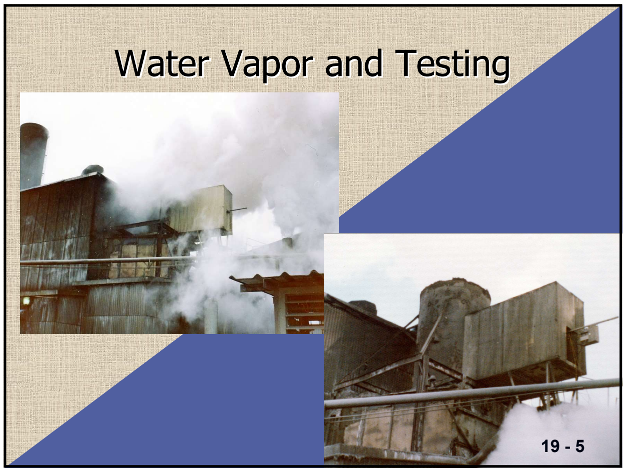
- High Moisture
- High Pressure Stacks
- High Temperature Stacks
- Low Flow Rate

Typical Sources With High Moisture Content In Stack

- Lime Hydrators
- Evaporators
- Coke Oven Quench Towers
- Ammonia Nitrate Prilling Facilities
- Steam Generators
- Processes with wet scrubbers
- Other

The Problem

- High moisture in stack gas causes pitot tube to plug, thus poor Δp readings (i.e., velocity measurements)
- Problems with maintaining isokinetic sampling rate (i.e., $\Delta H = k\Delta p$)
- Water droplets on filter increasing pressure drop and effecting isokinetics
- Dilution of impinger solutions thus effecting collection efficiency of analytes
- Condensation in pitot tube sample lines



Water Vapor and Testing

High Moisture Potato Chip Fryer

The Problem: FRM 5 Isokinetic Rate Equation

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

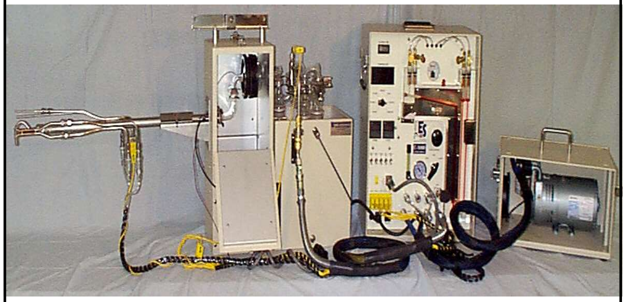
High Moisture Error

- 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

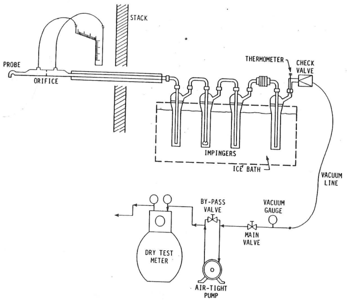
What Approaches Can Be Taken To Sample Under High Moisture Situations?



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

EPA HIGH MOISTURE SAMPLING TRAIN



24-12

FIGURE 5-2.

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

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

JACA HIGH MOISTURE SAMPLING TRAIN

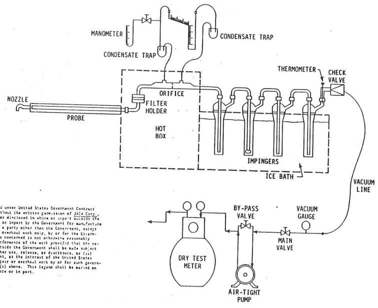


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FIGURE 5-1.

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

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

EPA HIGH MOISTURE SAMPLING TRAIN

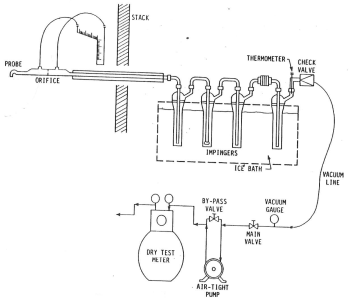


FIGURE 5-2.

24-12

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

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

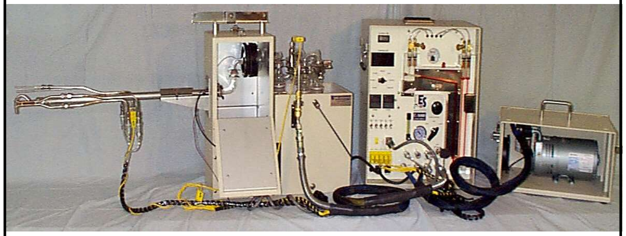
Preventing Sample Losses

- 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

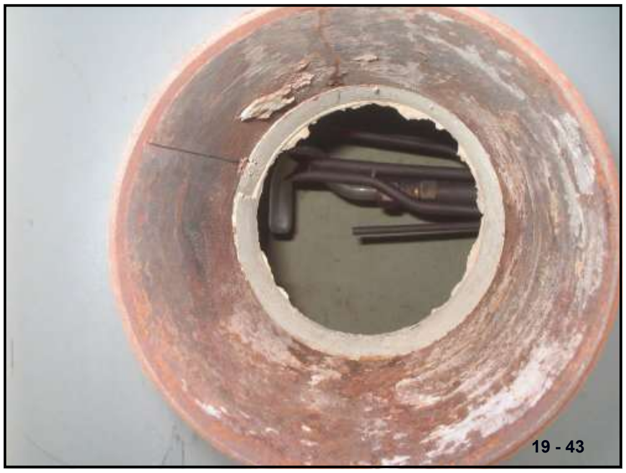
Stack Testing Special Topics:

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



Typical Sources With High Temperature In Stack

- Gas Turbines
- Municipal Incinerators
- Glass Furnaces
- Flares
- Kilns
- Other Sources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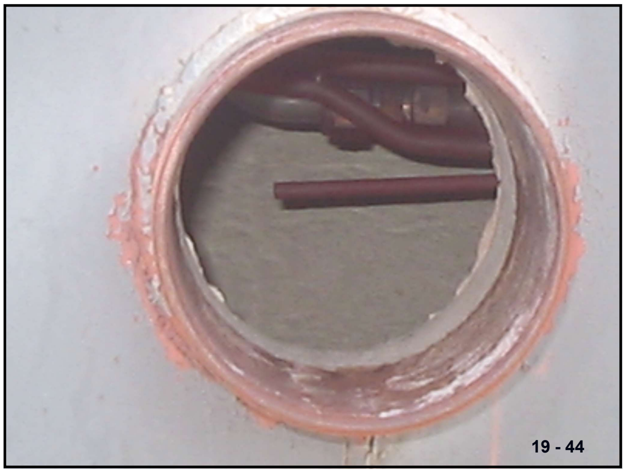
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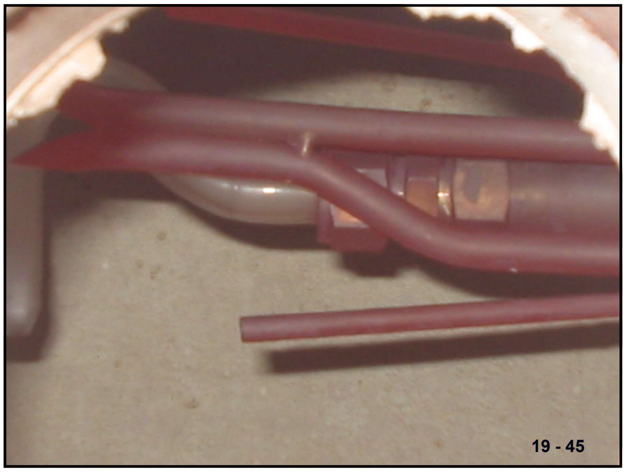
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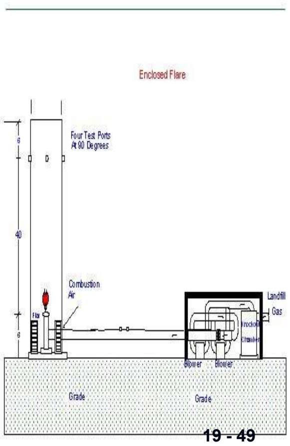
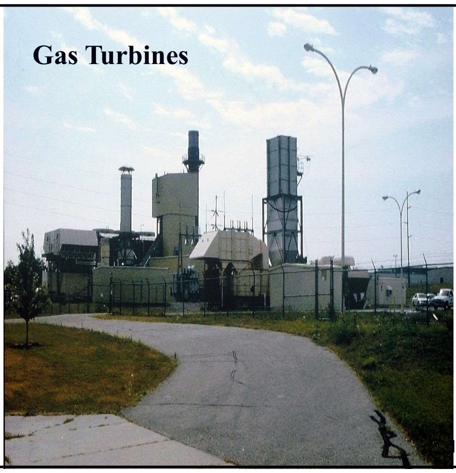
Landfill Flare



Gas Turbines



Rotary Kiln Incinerators

Other Sources

The Problem

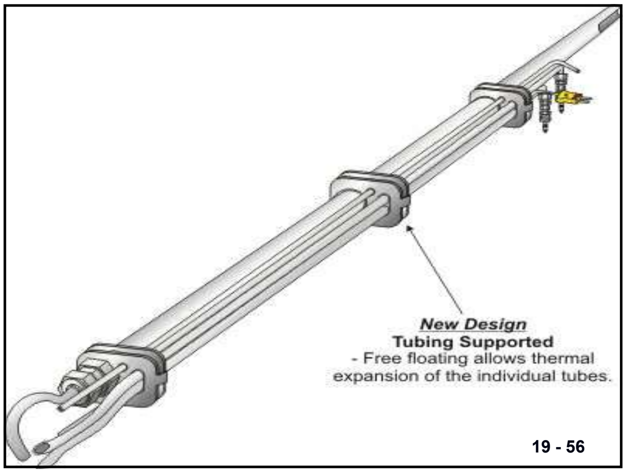
- High stack temperatures causes problems with obtaining proper leak check of sampling system and safety problems
- Problems with achieving airtight seal between nozzle and probe liner
- Breakage of glass probe liner due to different coefficients of thermal expansion between probe liner and stainless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

Stack Temperatures

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

Maximum Temperature of Various Materials

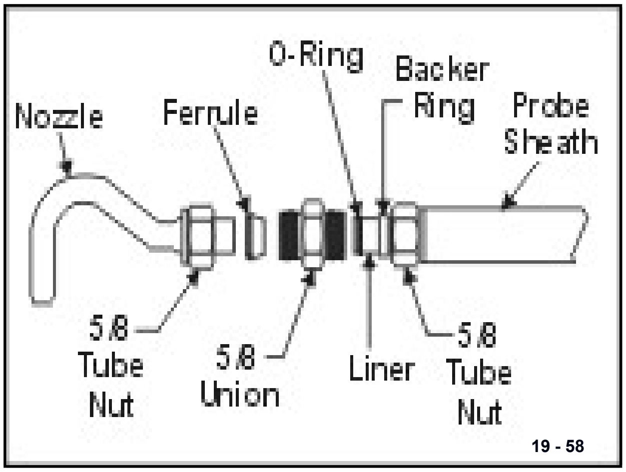
- Teflon: < 350 °F
- Glass: < 900 °F
- Stainless Steel: < 1210 °F
- Quartz: < 1650 °F
- Inconel: < 1800 °F



New Design
Tubing Supported
- Free floating allows thermal expansion of the individual tubes.

Sampling Problems

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



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

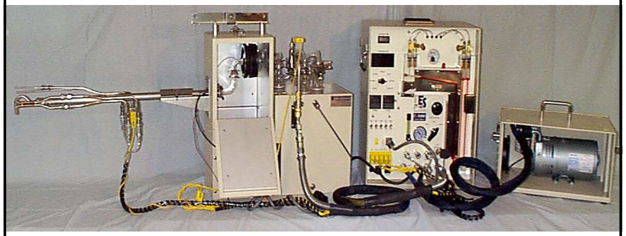
Miscellaneous Sampling Problems

- 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

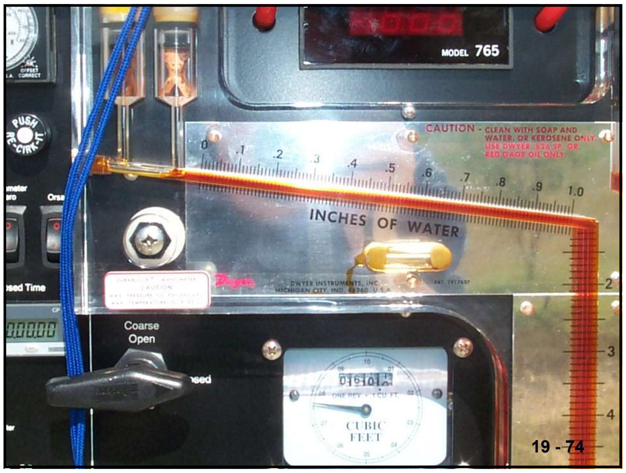
$$Q_{std} = 3600 \left(1 - B_{ws(avg)}\right) v_{s(avg)} A \frac{T_{std}}{T_{s(avg)}} \frac{P_s}{P_{std}}$$

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

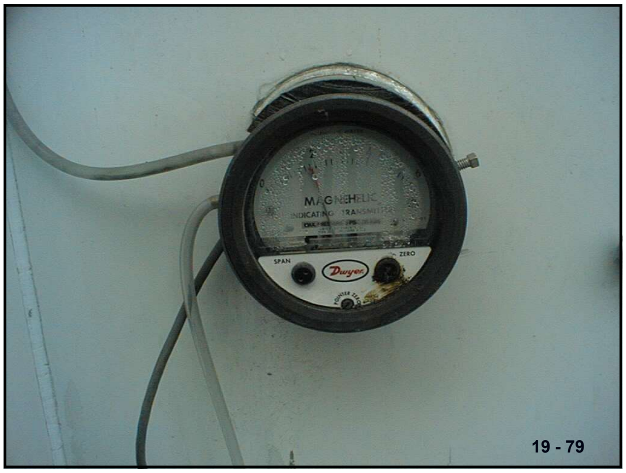
- As an alternative to criteria (1) through (3) above, the following equation may be used to determine the necessity of using a more sensitive differential pressure gauge. If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

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

Compliance Test and Source Test Observation

Reciprocating Internal Combustion Engines (RICE) Sampling and Overview of CEMS for Engines and Gas Turbine Testing

Stationary Engines - Video

Compliance Test and Source Test Observation

FRMs 6C, 7E, 3A and 20 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

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

Eight Major Points (cont.)

4. Interference Check (SO_2 Analyzer): Use Modified Method 6 (3 Runs 1 L/min) vs. Analyzer at Vent (7%)
5. Converter Check (NO_X Analyzer): Introduce CO @ 500 ppm, SO_2@200 ppm, CO_2@10% and O_2@20.9%; < 2% of span response, pass

Eight Major Points (cont.)

6. Calibration Error (Both Analyzer): Zero, mid, high (2%)
7. Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span or Reject
8. 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 SO_2/N_2, SO_2/Air, SO_2/CO_2, or $SO_2/CO_2/O_2$
- Emission data corrected with determined bias number
- No EPA Method 6 audit vial required due to “Interference Check”

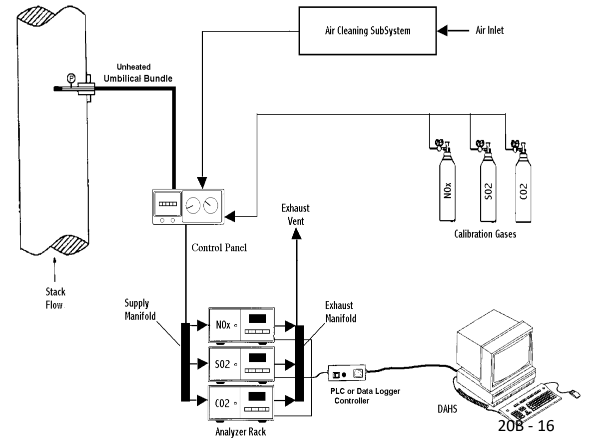
Interesting Points

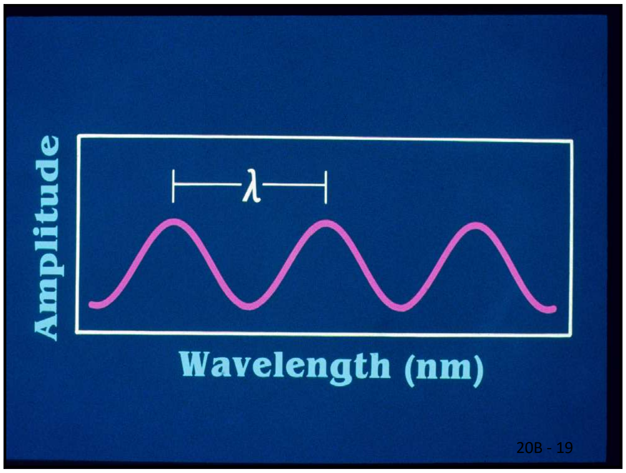
- Sampling system bias test done before and after test, then average, and apply value to emission data to correct
- Zero/Calibration Drift (Both Analyzer): Proceeding/Following Each Run): < 3% of span; May not reject if pass bias check!

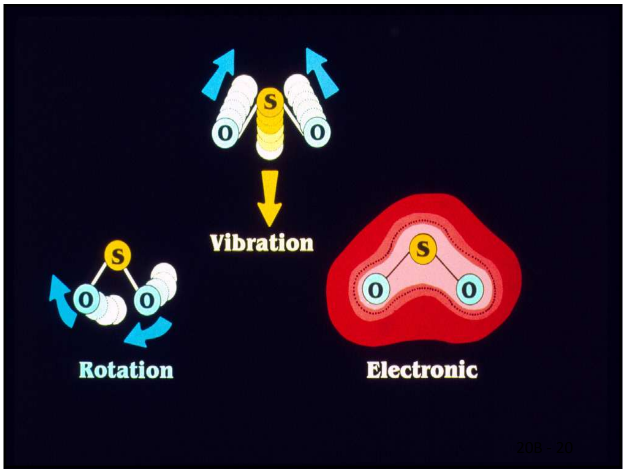
Method 6C
Typical Analytical Methods

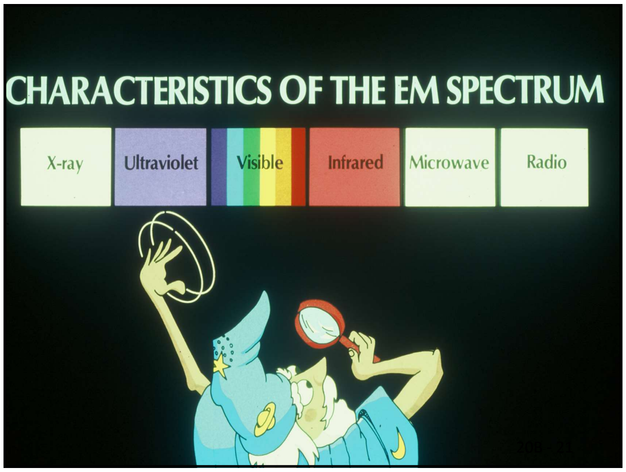
- Ultraviolet Absorption (UV)
- Nondispersive Infrared (NDIR)
- Fluorescence
- FTIR

- Analyzer must meet the performance requirements of this method.

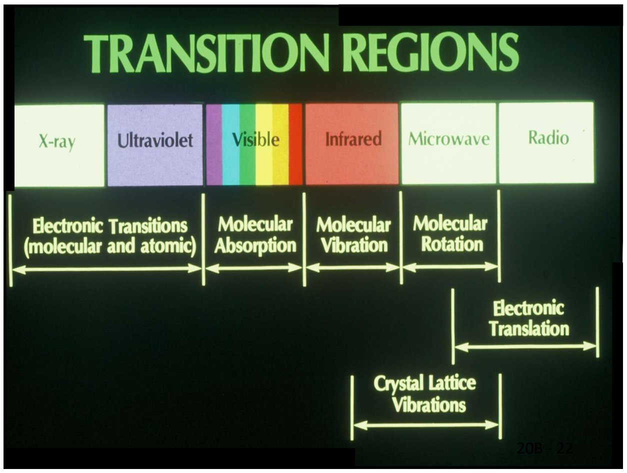








CHARACTERISTICS OF THE EM SPECTRUM



TRANSITION REGIONS

Electronic Transitions (molecular and atomic)

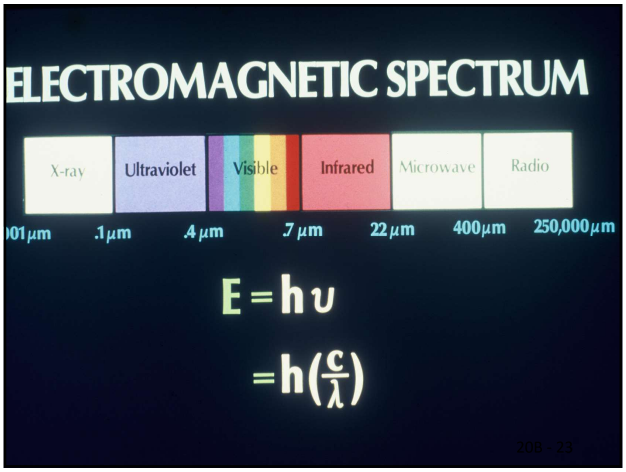
Molecular Absorption

Molecular Vibration

Molecular Rotation

Electronic Translation

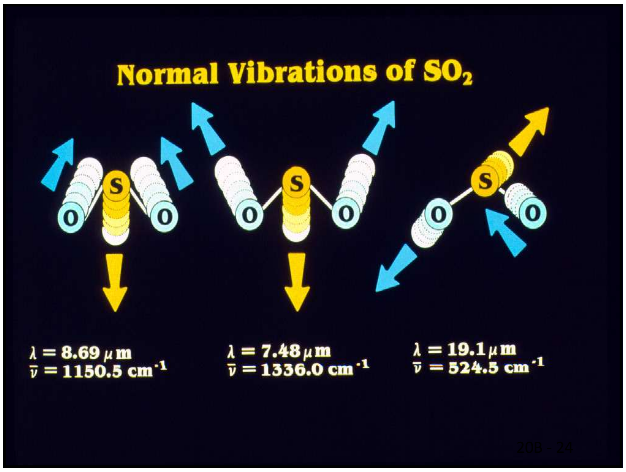
Crystal Lattice Vibrations



ELECTROMAGNETIC SPECTRUM

$$E = h\upsilon$$

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

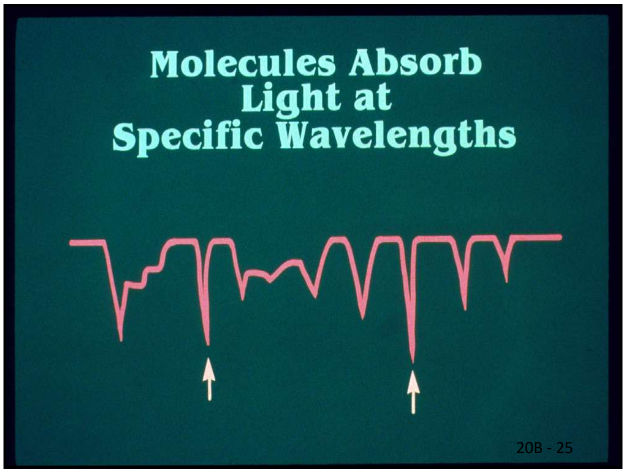


Normal Vibrations of SO_2

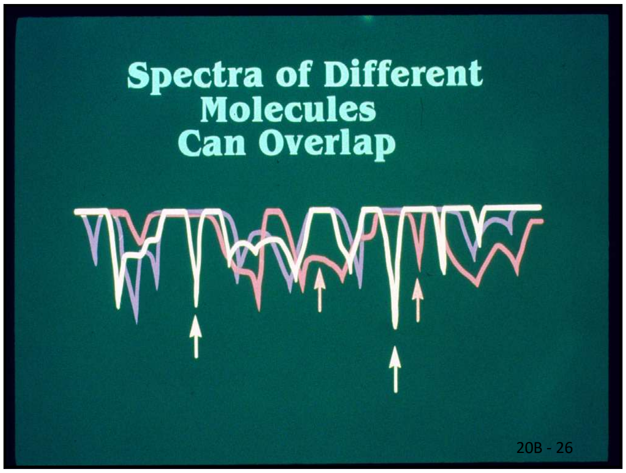
$\lambda = 8.69\,\mu m$
$\bar{\nu} = 1150.5\ cm^{-1}$

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

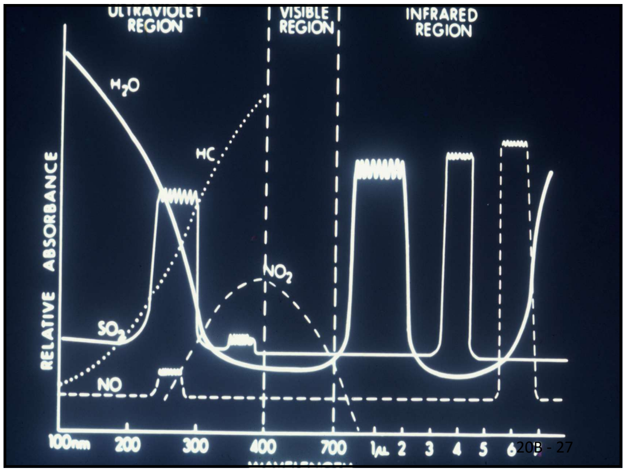
$\lambda = 19.1\,\mu m$
$\bar{\nu} = 524.5\ cm^{-1}$

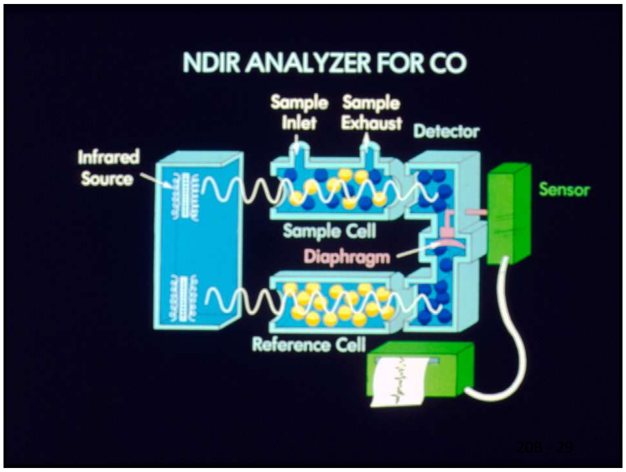


Molecules Absorb Light at Specific Wavelengths

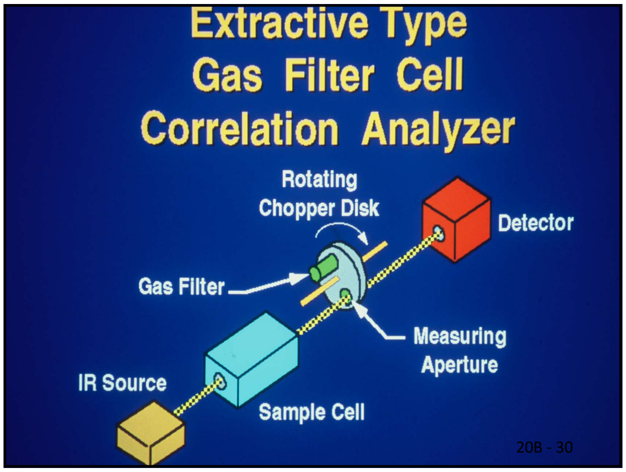


Spectra of Different Molecules Can Overlap

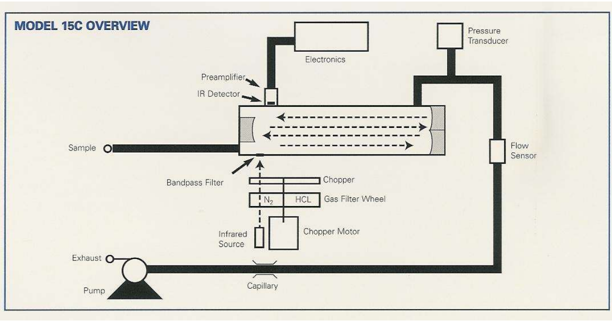


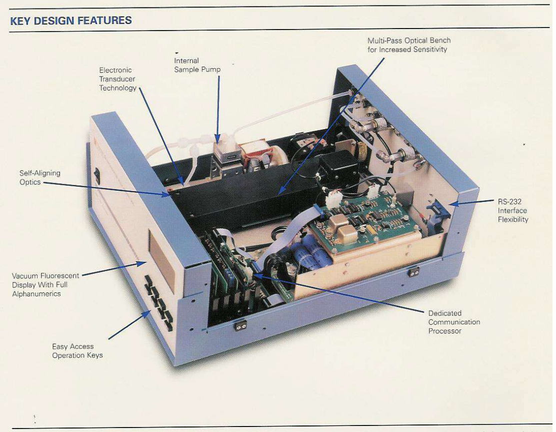


NDIR ANALYZER FOR CO

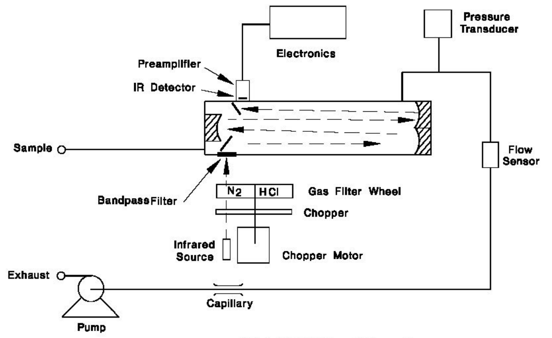


Extractive Type Gas Filter Cell Correlation Analyzer

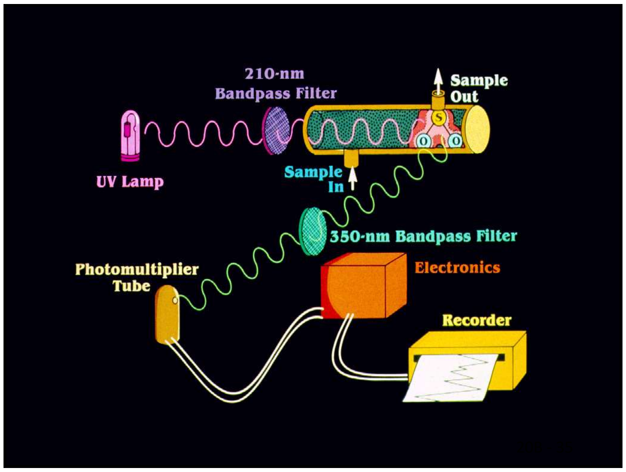




ADVANCED TECHNOLOGY **Model 15 Gas Filter Correlation HCl Analyzer**



Model 15C Flow Schematic



MODEL 43C- SO_2 ANALYZER

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

MODEL 43C-SO2 Analyzer

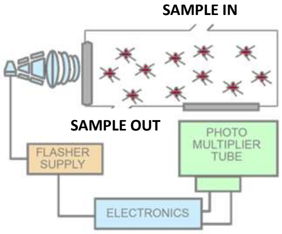
$$SO_2 + h\upsilon_1 \xrightarrow{I_a} SO_2^*$$

$$SO_2^* \xrightarrow{K_f} SO_2 + h\upsilon_2$$

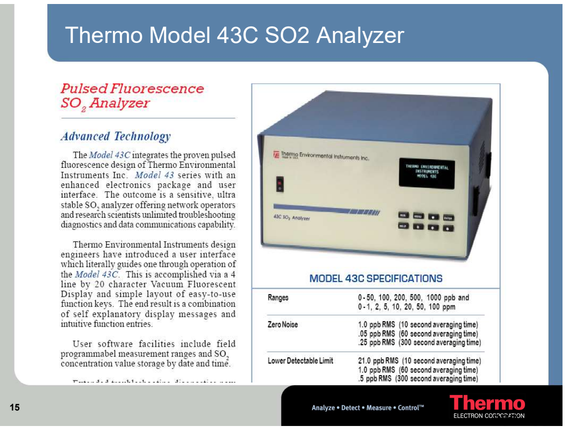
$$I_a = I_o[I-e^{-\{ax(SO_2)\}}]$$

$$I_f = I_o ax(SO_2) \text{ or}$$

$$K\,(SO_2)$$



Thermo Model 43C SO2 Analyzer



Pulsed Fluorescence SO_2 Analyzer

Advanced Technology

The *Model 43C* integrates the proven pulsed fluorescence design of Thermo Environmental Instruments Inc. *Model 43* series with an enhanced electronics package and user interface. The outcome is a sensitive, ultra stable SO_2 analyzer offering network operators and research scientists unlimited troubleshooting diagnostics and data communications capability.

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

User software facilities include field programmabel measurement ranges and SO_2 concentration value storage by date and time.

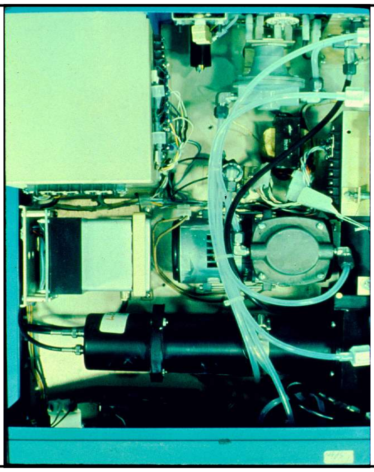
MODEL 43C SPECIFICATIONS

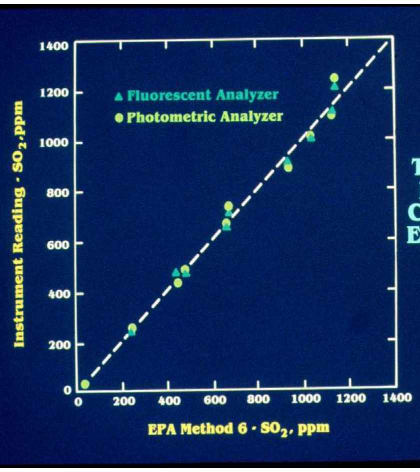
Ranges	0 - 50, 100, 200, 500, 1000 ppb and 0 - 1, 2, 5, 10, 20, 50, 100 ppm
Zero Noise	1.0 ppb RMS (10 second averaging time) .05 ppb RMS (60 second averaging time) .25 ppb RMS (300 second averaging time)
Lower Detectable Limit	21.0 ppb RMS (10 second averaging time) 1.0 ppb RMS (60 second averaging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

15

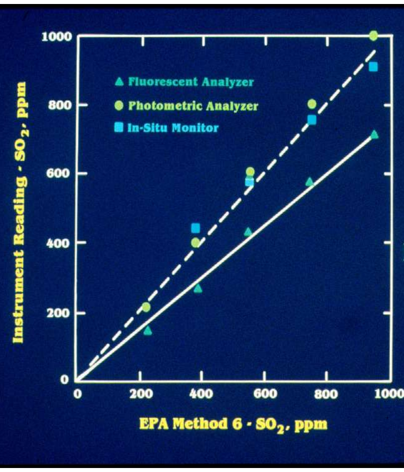
Analyze • Detect • Measure • Control™

Thermo
ELECTRON CORPORATION





Twenty-one Percent O_2 Calibration Experiment



SO_2 in Nitrogen Span Gas Experiment

(371 ppm SO_2 in N_2) Span Gas

HOW IS NO MEASURED?

Chemiluminescence Technique

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

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

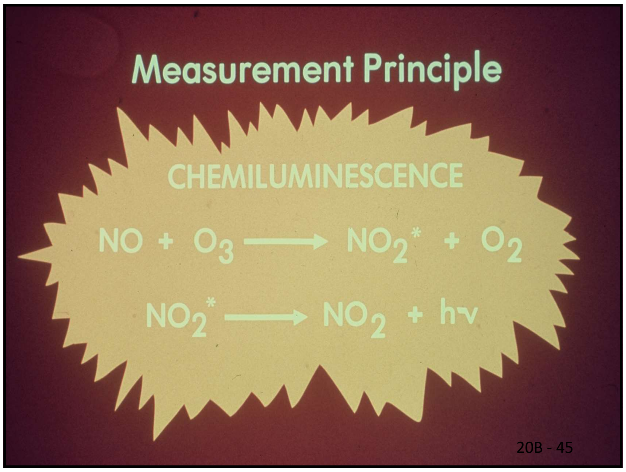
Intensity of emitted light is proportional to NO concentration

Chemiluminescent

Reduction of NO_2 to NO

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

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

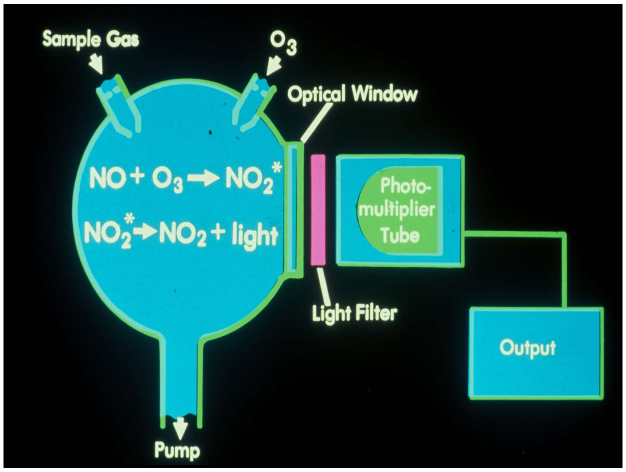


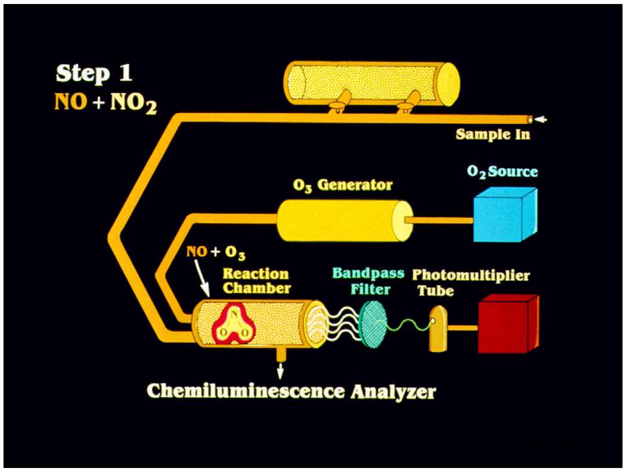
Measurement Principle

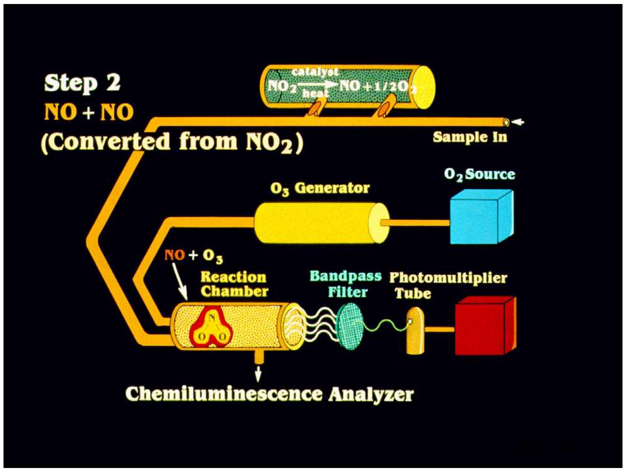
CHEMILUMINESCENCE

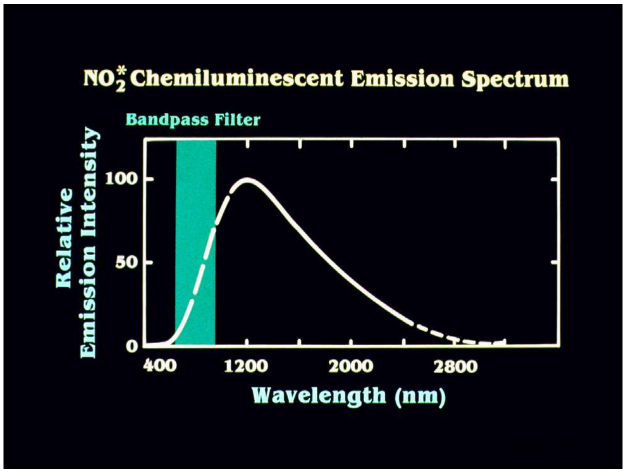
$NO + O_3 \longrightarrow NO_2^* + O_2$

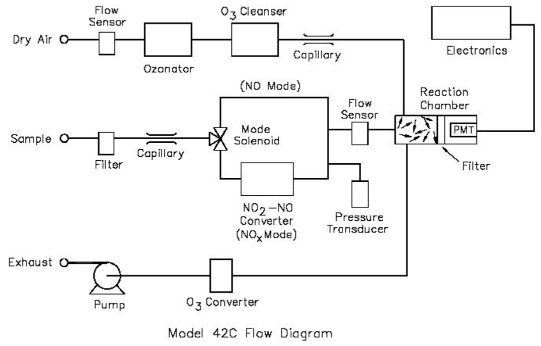
$NO_2^* \longrightarrow NO_2 + h\nu$











Analytical Range

- "…To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. …"
- "No valid run average concentration may exceed the calibration span."

Performance Specifications

- *Analyzer Calibration Error*, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.
- Analyzer calibration error
  - Less than ± 2% of span for zero, mid, and high-range gases

Performance Specifications

- *System Bias* means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

Performance Specifications

- *System Calibration Error* applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

Performance Specifications

- Sampling system bias
  - Less than ± 5% of span for zero and mid or high-range gases
- *Drift* means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).
- Zero drift and calibration drift
  - Less than ± 3% of span over the period of the run

Calibration Gases

- High-range = Equal to the calibration span
- Mid-range = 40-60% of span
- Zero gas = < 0.25% of span

Calibration Gases

- Protocol 1
- Traceability protocol (G1, G2)
- Valid certificate required Uncertainty ≤2.0% of tag value

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

- Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in method 7E, section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

Emission Testing

- Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement.

Sampling Procedures

- Conduct sampling system bias checks before and after each run
- Make no calibration adjustments prior to recording bias results after a run
- Sample run duration plus twice the sampling system response time

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

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

- *Interference Check* means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

Interference Check

- The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

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

Dilution Probes for Method 6C/7E/3A

- *Dilution-Type Systems—Special Considerations.* When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures.

Dilution Probes for Method 6C/7E/3A

- Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

Calibration Gas - Dilution Systems

- USEPA Method 205
- Not approved for acid rain (40 CFR 75) testing

Method 7E - NO_x

- ? 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

Method 20

- **Determination of Nitrogen Oxides, Sulfur Dioxide, and Diluent Emissions From Stationary Gas Turbines**

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines.

Method 20

- The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

Method 20

- In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:
- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).
- (c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

Method 20

- (d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).
- (e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

Method 20

- You must follow the procedures of Section 8.4 of the appropriate methods listed in Section 2.0.
- A test run must have a duration of at least 21 minutes.

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

RATA / CGA

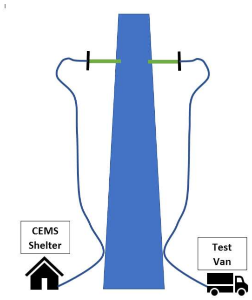
Quality Assurance Activities

- Relative Accuracy Test Audit Procedures
- Cylinder Gas Audit and Linearity Check
- Opacity Calibration Error Assessment

Relative Accuracy Test Audit (RATA)

- Requirements found in:
  - Part 60
    - New Source Performance Standards
    - Industry/Process Specific
  - Part 75
    - Acid Rain Program
    - Electric Generating Units

Relative Accuracy Test Audit (RATA)



Verification of CEMS performance by a third-Party testing company using USEPA Methods

Types of RATAs

- Gaseous
  - NO$_X$
  - CO
  - SO$_2$
  - Diluent (O_2 or CO_2)
  - Other
- Flow Rate
- Particulate
- Mercury

RATA General Concepts

- Compare CEMS to Reference Method
- Reference Method is the "Correct" data
  - Can be wet or instrumental version of the method
  - Typically, instrumental is preferred (real time data)
- Typical RATA is 12 runs, must use 9 to determine accuracy
- RATA Frequency – Varies on Rule

RATA General Concepts (cont.)

- RM tests should be on same basis as CEM system
  - Wet to wet, or dry to dry
- For gaseous pollutants: 21-minute runs
- For flow rate: as long as it takes to do a traverse
- Match up RM and CEM times (critical)

Required Reference Method QC

- Stratification test
- NOx converter efficiency
- Protocol calibration gases
- Linearity checks of analyzers
- Bias/drift checks
- Leak checks

Part 60 RATA

“Out of Control”

- NOx/SO_2: > 20% RM mean, or >10% standard (whichever is less restrictive)
- O_2/CO_2: >20% RM mean, or 1% O_2/CO_2
- CO: >10% RM mean, or >5% standard
- “Out of Control” lasts until pass next RATA

Part 75 RATA

“Out of Control”

RATA	Semiannual	Annual
SO_2 or NO_X	7.5% < RM ≤ 10% or ±15 ppm	RM ≤ 7.5% or ±12 ppm
SO_2/diluent	7.5% < RM ≤ 10% or ±0.030 lb/mmBtu	RM ≤ 7.5% or ±0.025 lb/mmBtu
NO_X/diluent	7.5% < RM ≤ 10% or ±0.020 lb/mmBtu	RM ≤ 7.5% or ±0.015 lb/mmBtu
CO_2/O_2	7.5% < RM ≤ 10% or ±1.0% CO_2/O_2	RM ≤ 7.5% or ±0.7% CO_2/O_2
Moisture	7.5% < RM ≤ 10% or ±1.5% H_2O	RM ≤ 7.5% or ±0.10% H_20
Flow	7.5% < RM ≤ 10% or ±2.0% fps	RM ≤ 7.5% or ±1.5 fps

Part 60 Requirements

- Unit load
  - 50% of capacity, or
  - Normal” load
- Repeat every four calendar quarters
  - i.e.: annually

Part 75 Requirements

- Unit load
  - Test at “normal” load
  - Defined at Part 75, Appendix A, 6.5.2.1
- Frequency
  - Every 2 operating quarters (semi-annual), except:
  - Can go to annual if RA ≤ 7.5%
  - Fall back into semi-annual if RA > 7.5%

Cylinder Gas Audit (CGA)

- Challenge the CEMS three times at each audit point using a protocol gas, and use the average of the three responses in determining accuracy
- Each CEMS must be audited at least once each calendar quarter. Successive quarterly audits shall occur no closer than 2 months.

CGA (cont.)

CGA - may be conducted in three of four calendar quarters, but in no more than three quarters in succession

1. Challenge the CEMS (both pollutant and diluent portions of the CEMS, if applicable) with an audit gas of known concentration at two points

CGA (cont.)

2. Operate each monitor in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling, and as much of the sampling probe as is practical.

CGA (cont.)

3. Use Certified Reference Materials (CRM's) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used.

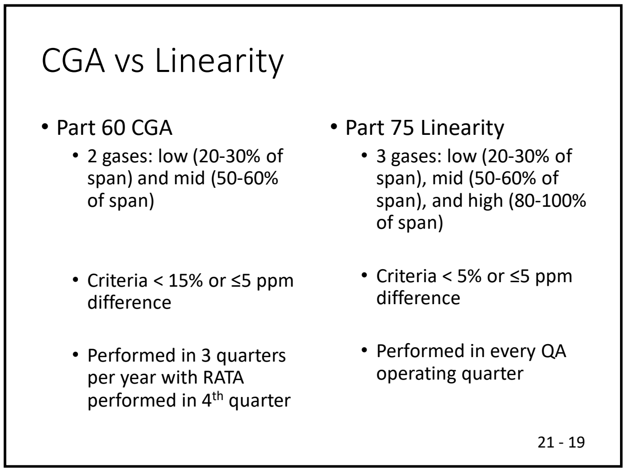
CGA (cont.)

- The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS

Cylinder Gas Audit (CGA)
Part 60

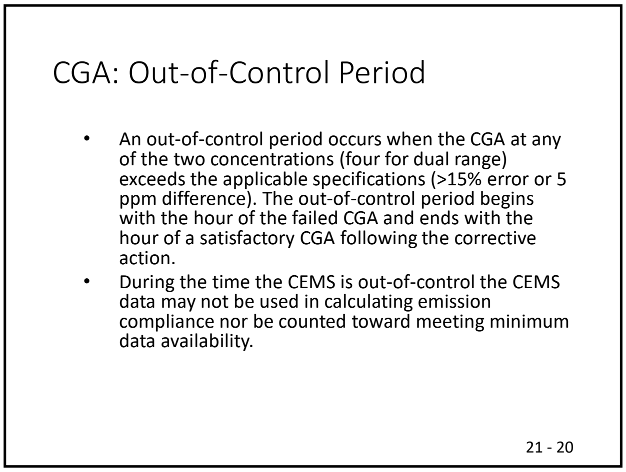
CGA Calibration Gas Requirements

Audit Point	Pollutant Analyzers % of Span	CO_2 % by volume (actual conc.)	O_2 % by volume (actual conc.)
1	20 to 30	5 to 8	4 to 6
2	50 to 60	10 to 14	8 to 12



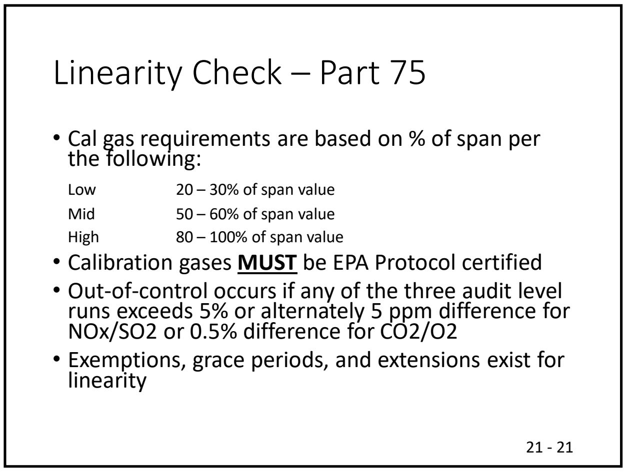
CGA vs Linearity

- Part 60 CGA
  - 2 gases: low (20-30% of span) and mid (50-60% of span)
  - Criteria < 15% or ≤5 ppm difference
  - Performed in 3 quarters per year with RATA performed in 4th quarter
- Part 75 Linearity
  - 3 gases: low (20-30% of span), mid (50-60% of span), and high (80-100% of span)
  - Criteria < 5% or ≤5 ppm difference
  - Performed in every QA operating quarter



CGA: Out-of-Control Period

- An out-of-control period occurs when the CGA at any of the two concentrations (four for dual range) exceeds the applicable specifications (>15% error or 5 ppm difference). The out-of-control period begins with the hour of the failed CGA and ends with the hour of a satisfactory CGA following the corrective action.
- During the time the CEMS is out-of-control the CEMS data may not be used in calculating emission compliance nor be counted toward meeting minimum data availability.



Linearity Check – Part 75

- Cal gas requirements are based on % of span per the following:

Low	20 – 30% of span value
Mid	50 – 60% of span value
High	80 – 100% of span value

- Calibration gases **<u>MUST</u>** be EPA Protocol certified
- Out-of-control occurs if any of the three audit level runs exceeds 5% or alternately 5 ppm difference for NOx/SO2 or 0.5% difference for CO2/O2
- Exemptions, grace periods, and extensions exist for linearity

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

Method 205
Gas Dilution System

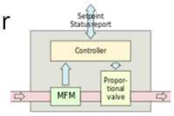
Background

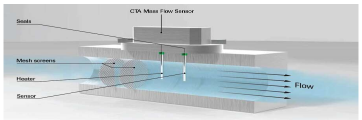
- Originated as Conditional Test Method 007 (CTM-007)
  - Assures Regional, State, and Local Authorities the gas dilution systems in use were producing accurate calibration gas at a fixed site.
  - Allow testers the advantage of avoiding costs and burden associated with purchasing transporting multiple gas cylinders over long distances.
- Promulgated as a Reference Method on May 30, 1994, as Method 205
  - Allows dilution system for most instrumental test method that requires multi-level cylinder gases.
  - Allows use of dilution systems when conducting performance specifications according to 40 CFR Part 60, Appendix F (CGAs), with Administrator Approval.
    - Administrative Approval for this has been delegated to Regions and in many instances down to the state level.

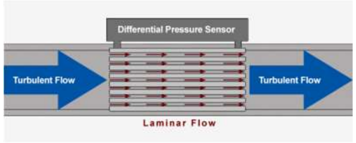
Equipment Criteria

- Gas Dilution System
  - Multiple vendors, however, the market appears to be dominated by a single provider
    - Internal mass flow controllers (MFC) used to set dilution ratio
    - Dilution Ratio can be set by other equipment (e.g., critical orifice, capillary tubes, etc…)
  - Must produce a calibration gas within ± 2 percent of the predicted value
  - Must be recalibrated once per calendar year using a NIST-traceable primary flow standards with an uncertainty ≤0.25 percent.
    - Must be labeled with the calibration date and expiration date
    - **NO** set requirement to report the calibration documentation…
- High and Mid-Level Calibration Gas
  - Protocol Gas is recommended
  - Mid Level gas **SHALL** be within 10% of one of the dilution levels.

Mass Flow Controller and Meters







Gas Dilution System Calibration

- No set calibration procedure for the systems
  - Critical Orifices/Capillary Tubes are fixed
  - Mass Flow Meters and Controllers should be calibrated at multiple flow rates
- Requirement to use a primary standard with an uncertainty of 0.25 % should restrict most testers from performing this measurement in-house.
  - Primary Standards of the quality are Cost Prohibitive (20-50K initial cost)
  - A number of metrology labs/vendors capable of maintaining these calibrations.
  - Appropriate alternative to using a primary standard that has proven uncertainty below ≤0.25 % is a Laminar Flow Element (i.e., Molbloc). Not currently included in the method, but any future revisions would include transfer standards.

Method 205 (Requirements)

- Field Evaluation (Mandatory)
  - Must be performed at the **Test Site**, prior to testing.
  - Prepare two different dilutions within the range of each dilution device.
    - Calculate a predicted value based on the dilution set-point(s) and high-level concentration
    - Challenge the Dilution System
      - At each set-point three times, by introducing gas to the analyzer through the dilution system
        - Precision Check – <2% of the average response
        - Accuracy Check – <2% of the predicted value
      - Introduce a mid-level gas (protocol gas and within 10% of a dilution level) directly to the analyzer
        - Accuracy Check – <2% of the certified concentration

Method 205 (Requirements)

- Lab Evaluation (Optional)
  - Applies to reactive compounds (i.e., non-propane THCs , TRS compounds)
  - Must be conducted on an annual basis for each reactive compound
  - Same Procedures as the Field Evaluation

Example – NOx/O_2 rata

Field Calibration - Oxygen Analyzer

- Instrument (Span for Testing) – O_2 - 21.0% ***NOx – 12.2 ppmv***
- High Calibration Gas – O_2 @ 21.0%, ***NO @ 99.2 ppmv*** – Protocol Gas
- Mid-Level Calibration Gas – 20.9%, ***NO @ N/A*** – Protocol Gas
- Predicted Dilution Levels @ 2.1% and 21.0%
- Average Dilution Response of 2.2% and 20.6%
- Mid-Level Calibration Response – 20.9%

Acceptable

Example A – NOx/O_2 RATA

Field Calibration - Oxygen Analyzer

- ✓ Instrument (Span for Testing) – O_2 - 21.0% ***NOx – 12.2 ppmv***
- ✓ High Calibration Gas – O_2 @ 21.0%, ***NO @ 99.2 ppmv*** –Protocol Gas
- ✓ Mid-Level Calibration Gas – 20.9%, ***NO @ N/A*** – Protocol Gas
- ✓ Predicted Dilution Levels @ 2.1% and 21.0%
- ✓ Average Dilution Response of 2.2% and 20.6%
- ✓ Mid-Level Calibration Response – 20.9%

Good - Incorporated the dilution range for all analyzers
Bad – Mid level Verification check performed at the "0" dilution point.
Hmmm…. Was there a leak in the calibration system?

Example B – THC, CO, AND O_2 Compliance Test

Field Calibration – Carbon Monoxide Analyzer

- Instrument (Span for Testing)
  CO – 100 ppmv, THC – 10 ppmv ,O2 - 15.0%
- High Calibration Gas – Certified ± 5 %
  CO @ 10,000 ppmv, Propane @ 500 ppmv, O2 @ 20.9
- Mid-Level Calibration Gas – Protocol Gas
  CO @990 ppmv, THC @ N/A, O2 @ N/A, –
- Predicted Dilution Levels @ 1,000 ppmv and 5,000 ppmv
- Average Dilution Response of 1000 ppmv and 5000 ppmv
- Mid-Level Calibration Response – 1000 ppmv

Acceptable?

Example B – THC, CO, AND O_2 Compliance Test

Field Calibration – Carbon Monoxide Analyzer

- ✓ Instrument (Span for Testing) – CO – 100 ppmv, ***THC 10 ppmv ,O_2 - 15.0%***
- ✓ High Calibration Gas – CO @ 10,000 ppmv, ***Propane @ 500 ppmv, O_2 @ 20.9***
  – Certified ± 5 %
- ✓ Mid-Level Calibration Gas – CO @990 ppmv, ***THC @ N/A, O_2 @ N/A,*** – Protocol Gas
- ✓ Predicted Dilution Levels @ 1,000 ppmv and 5,000 ppmv
- ✓ Average Dilution Response of 1000 ppmv and 5000 ppmv
- ✓ Mid-Level Calibration Response – 1000 ppmv

Good – Met The Method Criteria
Bad – Did Not Bracket the Dilution Range (10:1 vs 200:1)
Should of – Used a more appropriate high-level calibration gas
Could of – Additional mid-level verification for high dilution ratio
Hmmm…. That data looks really good

Cylinder Gas Audits (CGAs)

- Can I use a Dilution System for Cylinder Gas Audit ?
  - Section 1.1 permits the use for CGA under Part 60
  - Broadly Applicable Alternative 25 (ALT-025) permitted the use under Part 63 as well. (September 3, 1999)
- You still must conduct the field evaluation at each site.
  - Multiple Gases Requirement (High and Mid) still required
  - Field evaluation takes a significant amount time.
- Diminishing Returns
  - Field Evaluation test should take twice as long as a normal CGA
  - Protocol Gas for Criteria Pollutants are widely available and relatively inexpensive with a long shelf life
    - 10 Year Certificate
    - Gas Cost – less than $250/ Demurrage (2 cents/day) = 10 year cost $323
- Compelling Applications
  - When cylinder gases are very expensive
    - Reactive Compounds
    - Low-Level Standards
  - When cylinder gases are not widely available
  - For some reason, if the tester cannot predict the exact concentration needed.

Method 205 Concerns

- Indeterminate Method Criteria
  - Calibration of the Dilution System
  - No record keeping
  - Maximum/Minimum Dilution Ration Undefined, manufacture suggestion
- Technology
  - Open to any device that meets criteria
  - Multiple (Blended) Gas Calibration is undefined
  - Data Reporting/Recording/Logging

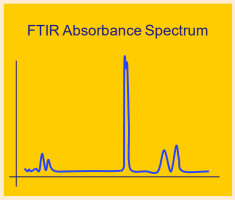
Acid Rain Program (Part 75) Applications

- Method 205 is only permitted with Administrator Approval
- Part 75 is a “Cap and Trade” System
  - Tighter Protocol Gas Requirements (PGVP)
  - Quarterly Audits have a tighter criteria than CGAs
  - Quality Protocol Gases are widely available.

Future Revisions to Method 205

- No immediate plans for major revisions to Method 205
  - Minor revision to incorporate the use of NIST transfer standards to calibrate the dilution devices.
- Future Revisions
  - Report/Record Requirements
  - Limit CGAs of criteria pollutants
  - Requirement to bracket dilution ranges
  - Defined System Calibration Requirements
  - PS 12 or 18 Applicability
  - Formatting Change – EMMC Format

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



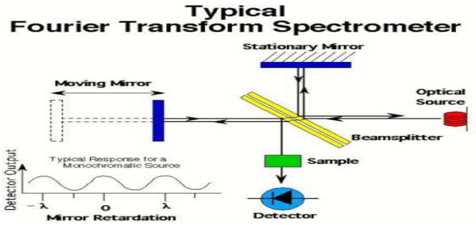
Introduction to FTIR Operation

- Absorption peaks in an infrared absorption spectrum arise from molecular vibrations
- Absorbed energy causes molecular motions which create a net change in the dipole moment

Introduction to FTIR Operation

- Fourier-transform infrared spectroscopy is a vibrational spectroscopic technique, meaning it takes advantage of asymmetric molecular stretching, vibration, and rotation of chemical bonds as they are exposed to designated wavelengths of light.
- Fourier transform is to transform the signal from the time domain to its representation in the frequency domain

FTIR Theory and Instrumentation



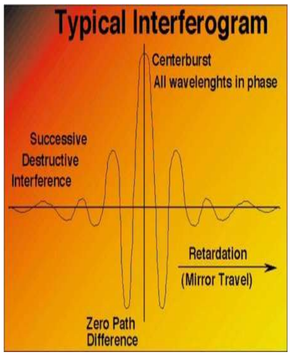
- Light enters the spectrometer and is split by the beam splitter. The figure above shows what is referred to as the Michelson interferometer

FTIR Theory and Instrumentation

- Light originates from a He-Ne laser
- Half of the light is reflected 90 degrees, while the other half passes through the beam splitter and hits the moving mirror
- The split beams are recombined, after having traveled different distances, they exhibit an interference pattern with each other
- As they pass through the sample, the detector collects the interfering signals and returns a plot of response v. mirror displacement known as an interferogram

FTIR Theory and Instrumentation

- The heart of the system is the interferometer in which the light from the source is divided into two beams.
- Beams pass through the sample cell and then recombine resulting in a signal.
- All information required to identify and quantify the gases in the sample is present in the interferogram.
- Interferogram signal is converted to a frequency spectrum by a mathematical technique called Fourier Transformation.



FRM 320

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 (cont'd)

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

FRM 320 Sampling Types

- Screening
- Emission Test
- Validation

FRM 320 (cont'd)

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

FRM 320

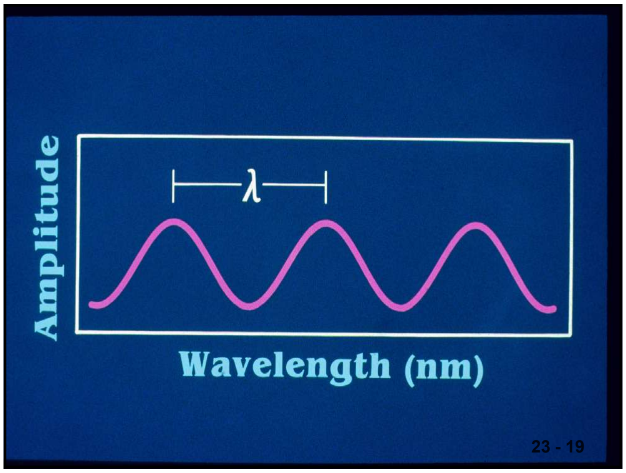
- *"…This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm^{-1} (25 to 2.5 um). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is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

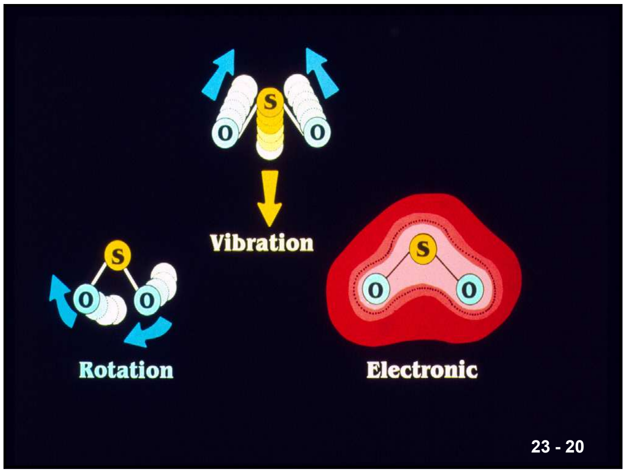
Infrared Spectroscopy

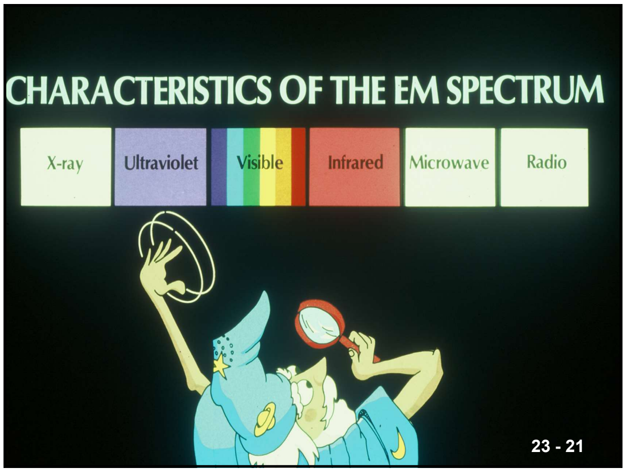
- Infrared light (IR) waves at discreet frequencies to molecular bond motions
- Vibrational and pure rotational motions
- When the frequencies match, energy is absorbed by that bond and resulting excitation increases molecular bond energy state (non-ionizing)

Infrared Spectroscopy

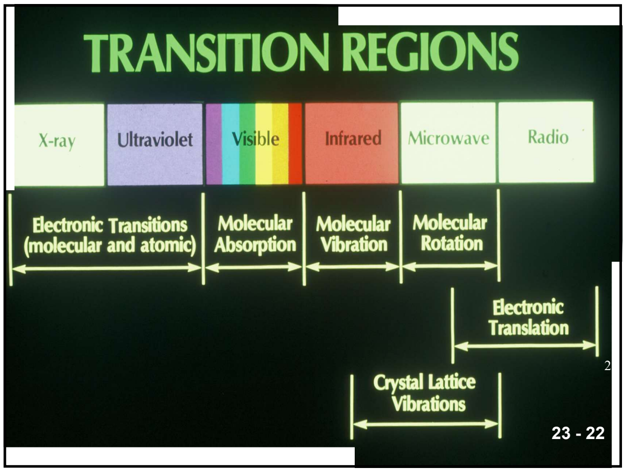
- The energy absorbed by the bond at discreet frequencies is proportional to the number of molecules
- FTIR spectrum is a plot of decreased energy at discreet frequencies corresponding to the absorption bands of the compounds in the sample. High resolution 0.5 cm-



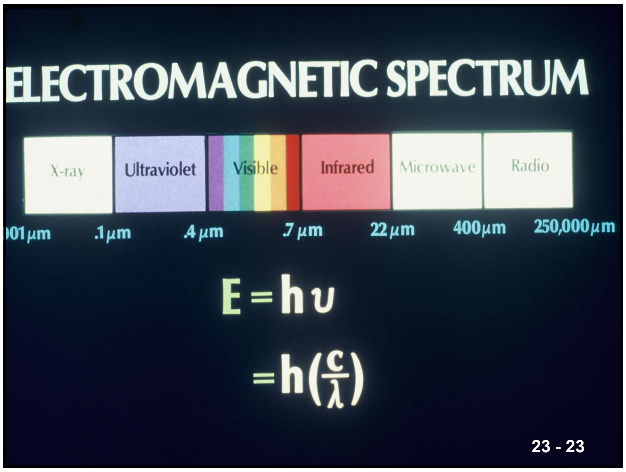




CHARACTERISTICS OF THE EM SPECTRUM

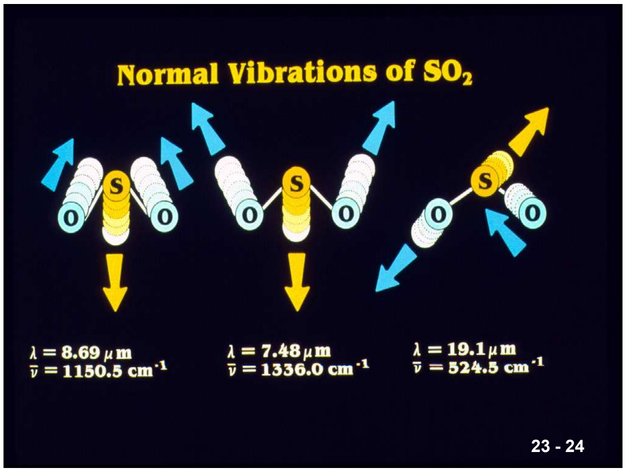


TRANSITION REGIONS



ELECTROMAGNETIC SPECTRUM

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

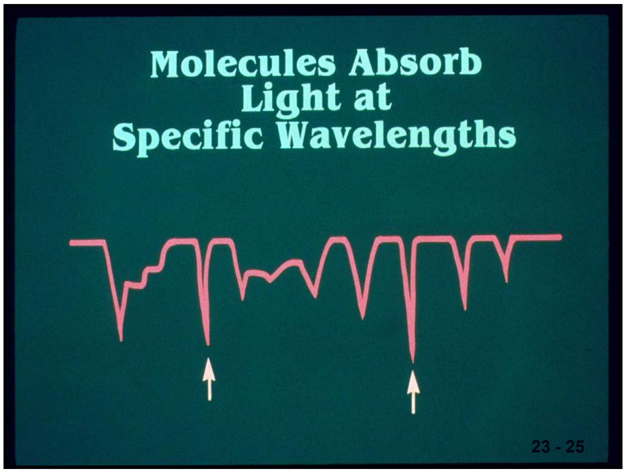


Normal Vibrations of SO_2

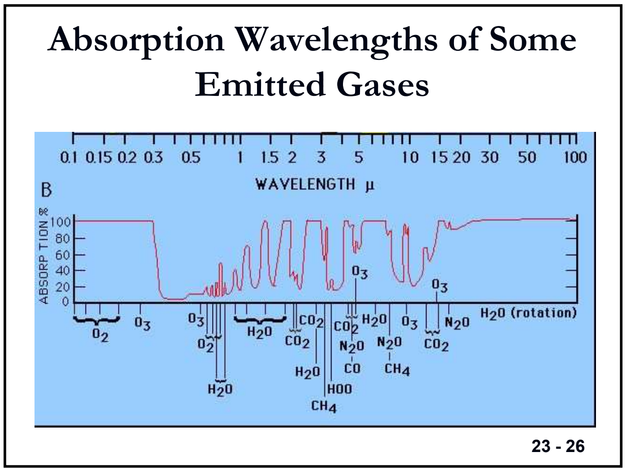
$\lambda = 8.69\ \mu m$
$\bar{\nu} = 1150.5\ cm^{-1}$

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

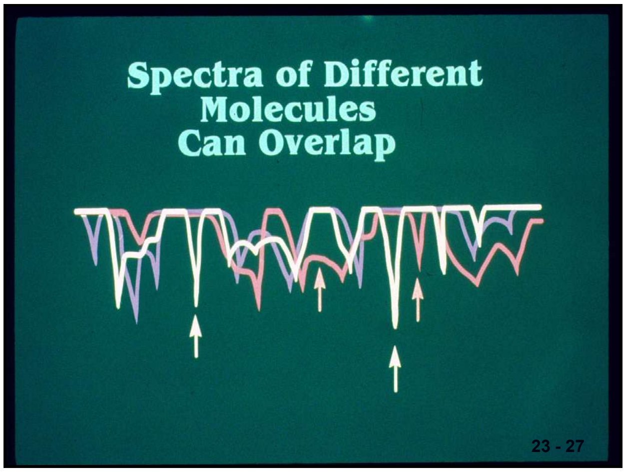
$\lambda = 19.1\ \mu m$
$\bar{\nu} = 524.5\ cm^{-1}$



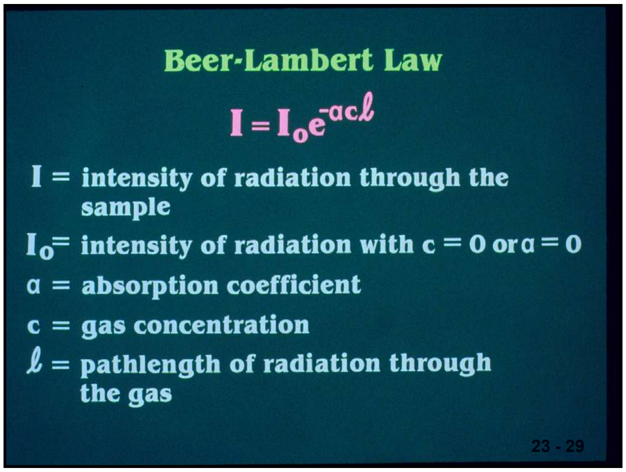
Molecules Absorb Light at Specific Wavelengths



Absorption Wavelengths of Some Emitted Gases



Spectra of Different Molecules Can Overlap



Beer-Lambert Law

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

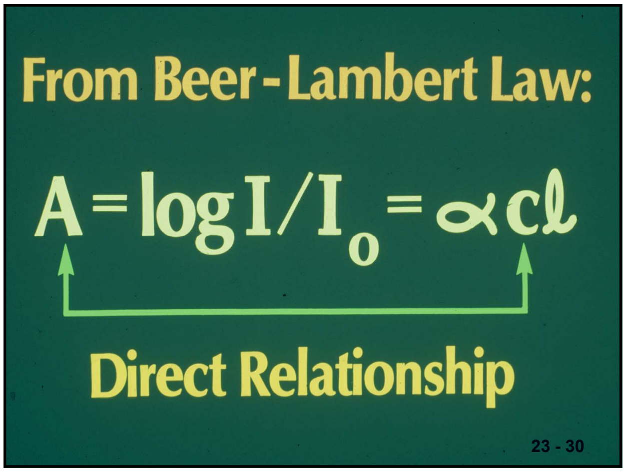
I = intensity of radiation through the sample

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

α = absorption coefficient

c = gas concentration

ℓ = pathlength of radiation through the gas

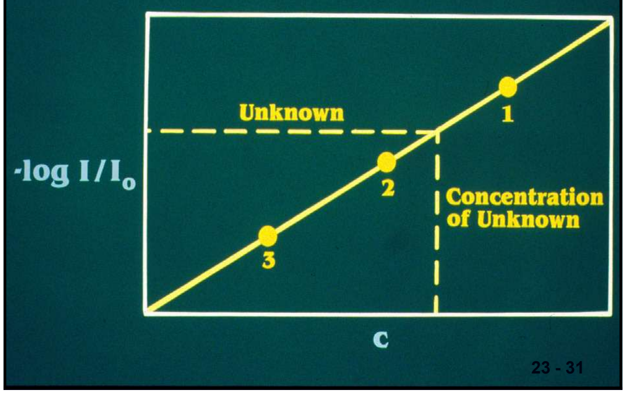


From Beer-Lambert Law:

$$\underset{\uparrow}{A} = \log I/I_o = \alpha c \underset{\uparrow}{\ell}$$

Direct Relationship

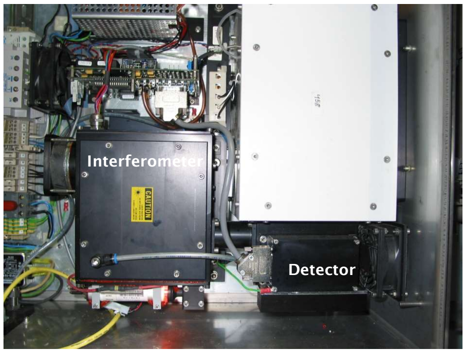
Calibrating a Spectrometer



Infrared Band Centers Of Some Common Gases

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

FTIR Interferometer Cell



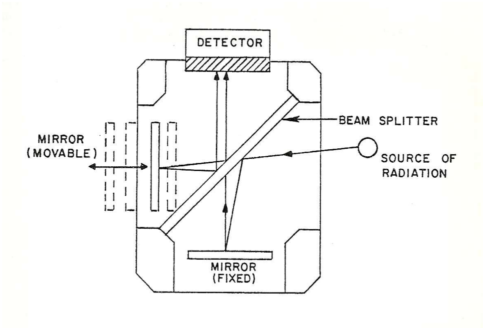
Operation of the FTIR Spectrometer

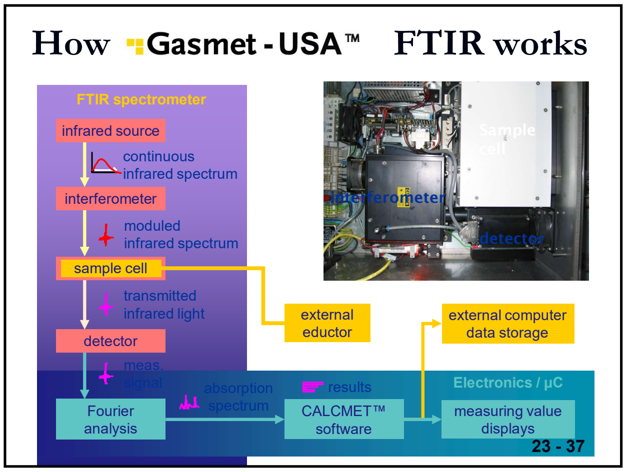
- IR energy enters the spectrometer
- A beam splitter reflects back 50 percent and transmits 50 percent of the incoming infared radiation
- The two beams are then reflected back to the beam splitter by a moving mirror and a stationary mirror
- Depending on the position of the moving mirror, these two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

Operation of the FTIR Spectrometer

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

Operation of the FTIR Mirror





How Gasmet - USA™ FTIR works

FTIR spectrometer

infrared source

continuous infrared spectrum

interferometer

moduled infrared spectrum

sample cell

transmitted infrared light

detector

meas. signal

Fourier analysis

absorption spectrum

results

CALCMET™ software

Electronics / µC

measuring value displays

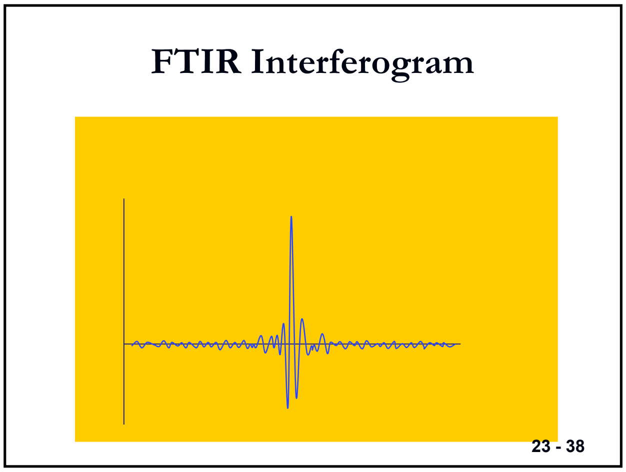
external eductor

external computer data storage

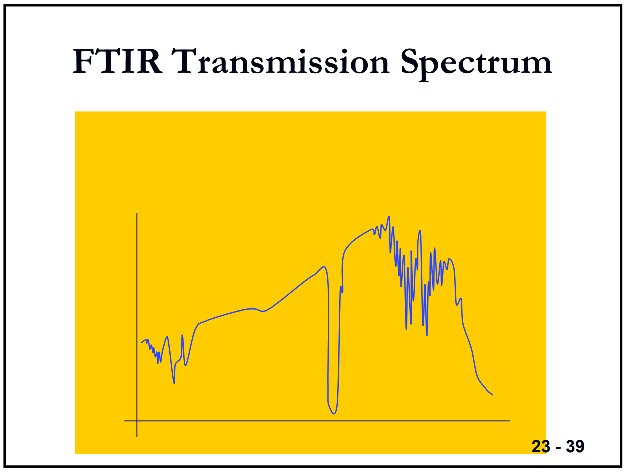
Sample cell

interferometer

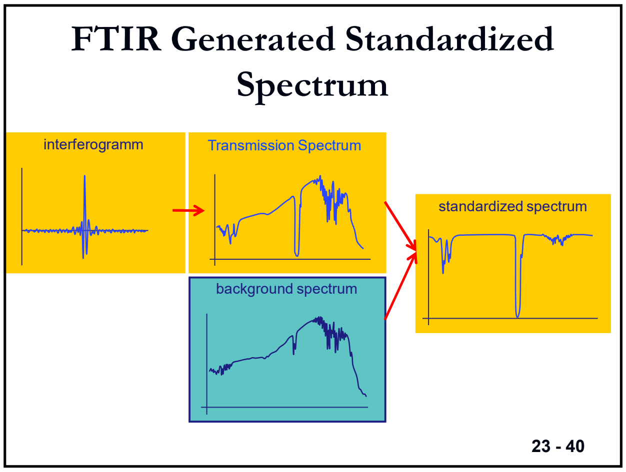
detector



FTIR Interferogram



FTIR Transmission Spectrum



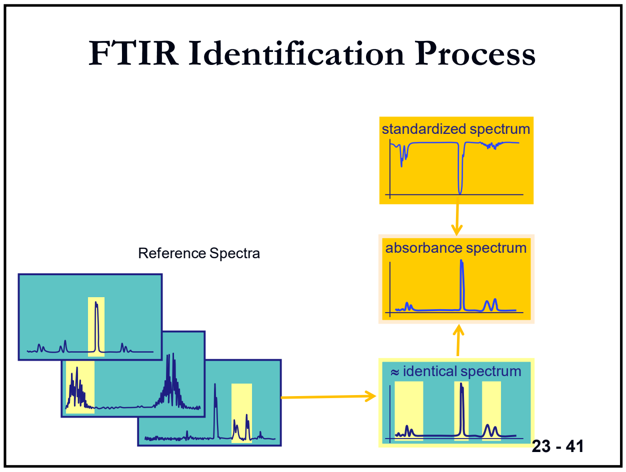
FTIR Generated Standardized Spectrum

interferogramm

Transmission Spectrum

background spectrum

standardized spectrum



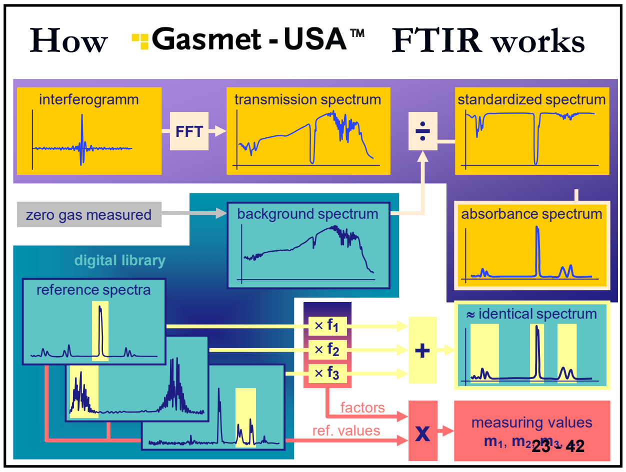
FTIR Identification Process

Reference Spectra

standardized spectrum

absorbance spectrum

≈ identical spectrum



How Gasmet - USA™ FTIR works

interferogramm

FFT

transmission spectrum

÷

standardized spectrum

zero gas measured

background spectrum

absorbance spectrum

digital library

reference spectra

$\times f_1$

$\times f_2$

$\times f_3$

\+

≈ identical spectrum

factors

ref. values

x

measuring values

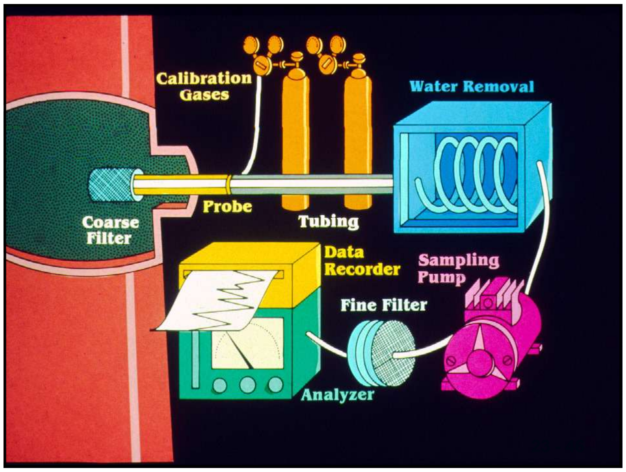
$m_1, m_2, m_3, \ldots$

Components of FRM 320

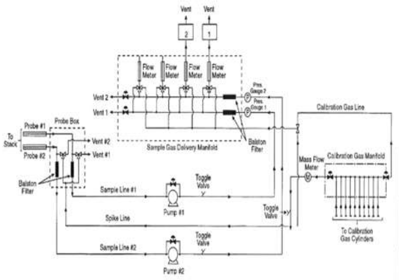
- Sample probe: Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating.
- Particulate filter: A glass wool plug inserted at the probe tip and a filter to remove particulate matter.
- Heat trace sample line: Heated sufficiently to prevent condensation.

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)

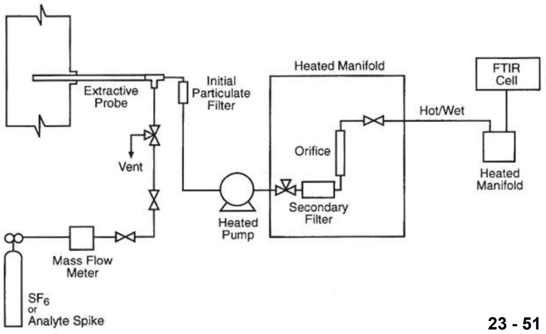
Sampling and Analysis Procedures

- 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:

$$B = S_m - CS$$

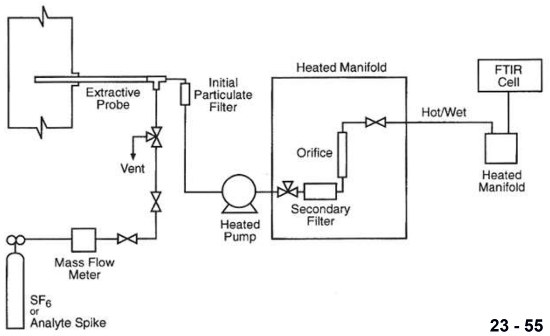
Where:

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

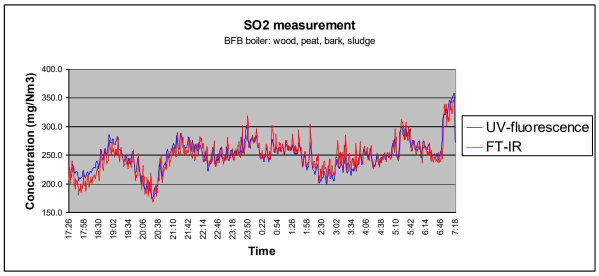
- Method Validation Procedure (Section 13)-
  - Use Method 301 to evaluate statistical significance of the bias.
  - If bias is significant (0.7 ≤ CF ≤ 1.3), then develop a correction factor (CF) is calculated and emission results are multiplied by the CF for final analyte concentration.
  - If CF ≥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

FRM 320 Interferences

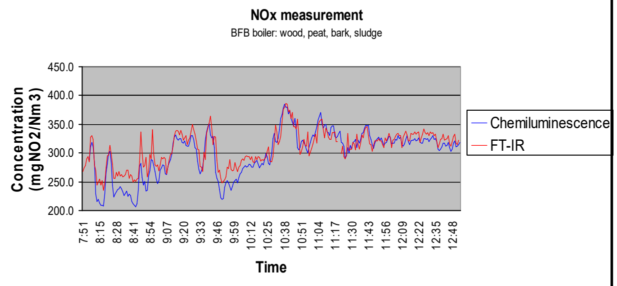
- Analytical Interferences (Background and Sampling)
  - Background interference occurs when unexpected change in background spectra from dirt on lenses, changes in detector sensitivity, changes in infrared source etc. This requires a new background to be generated.
  - Spectral interferences from mostly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

GASMET CEMS APPLICATIONS

Gasmet CEMS and reference measurements:

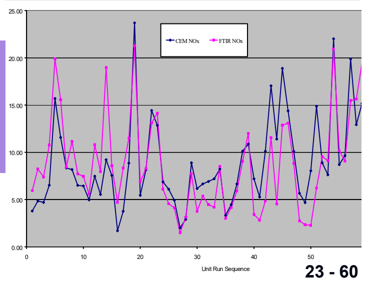


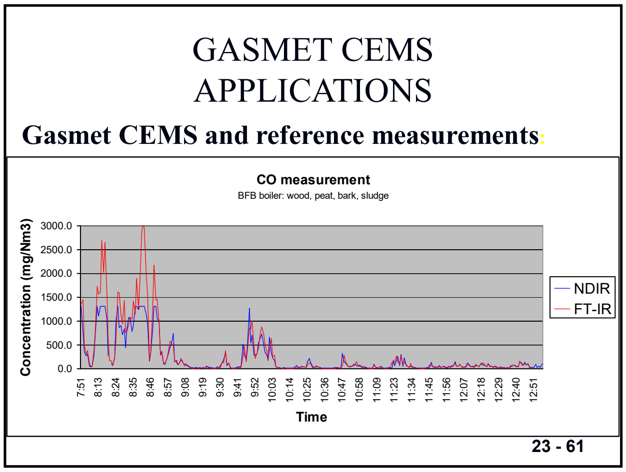
Gasmet CEM'S Applications



Austin Energy Sandhill Unit #1 Demonstration Results

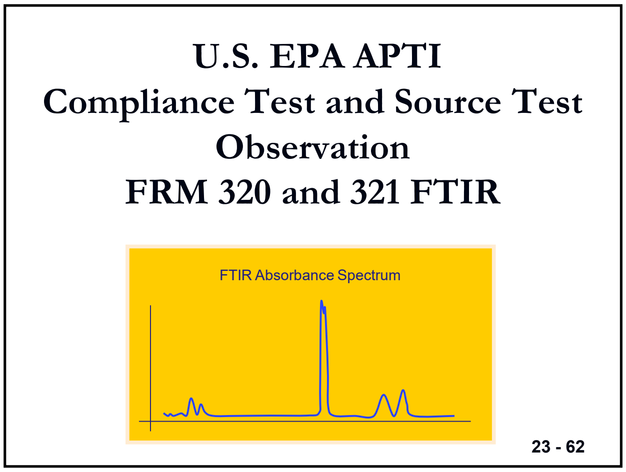
	CEM NOx	FTIR NOx	FTIR Dev
Average	9.38	9.25	**-0.29**
Min	1.70	1.19	**-9.45**
Max	24.87	35.65	**10.78**
Std Dev	5.21	5.89	**3.61**
CI			**0.82**





GASMET CEMS APPLICATIONS

Gasmet CEMS and reference measurements:

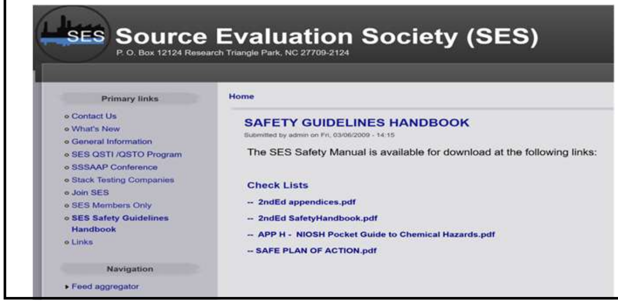


U.S. EPA APTI
Compliance Test and Source Test Observation
FRM 320 and 321 FTIR

Source Sampling Observation Safety

SES Safety Guidelines Handbok

SAFETY GUIDELINES HANDBOOK | Source Evaluation Society (SES) (sesnews.org)



Source Evaluation Society (SES)
P. O. Box 12124 Research Triangle Park, NC 27709-2124

Primary links

- Contact Us
- What's New
- General Information
- SES QSTI /QSTO Program
- SSSAAP Conference
- Stack Testing Companies
- Join SES
- SES Members Only
- SES Safety Guidelines Handbook
- Links

Navigation

- Feed aggregator

Home

SAFETY GUIDELINES HANDBOOK

Submitted by admin on Fri, 03/06/2009 - 14:15

The SES Safety Manual is available for download at the following links:

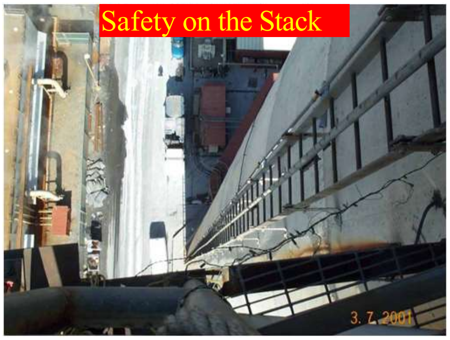
Check Lists

-- 2ndEd appendices.pdf

-- 2ndEd SafetyHandbook.pdf

-- APP H - NIOSH Pocket Guide to Chemical Hazards.pdf

-- SAFE PLAN OF ACTION.pdf


Safety on the Stack
3. 7. 2001

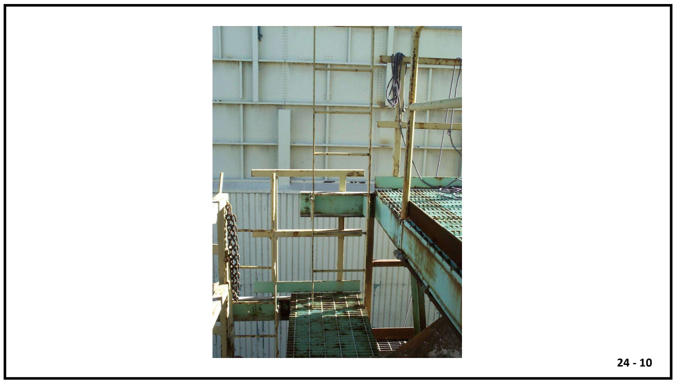

3. 6. 2001

2

24 - 7

24 - 8

24 - 9



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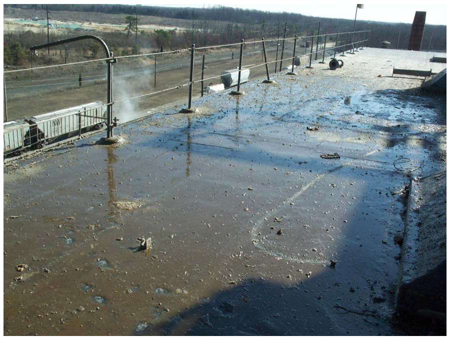
24 - 11

24 - 12



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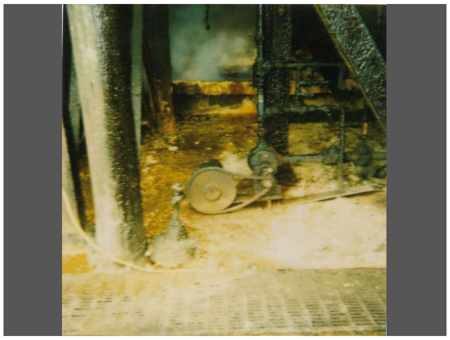


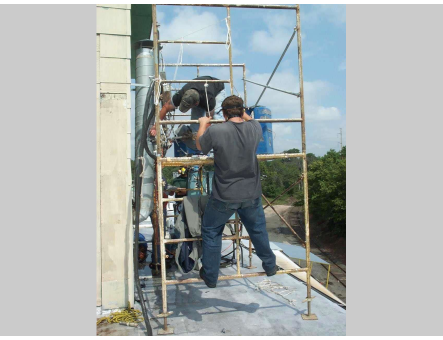

24 12:20PM


20 7:45


20 9:31

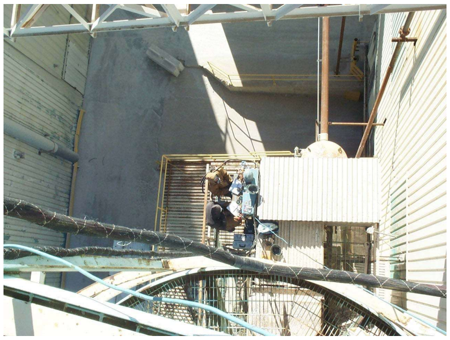

7M-550
LAB

24 - 31



24 - 32

24 - 33



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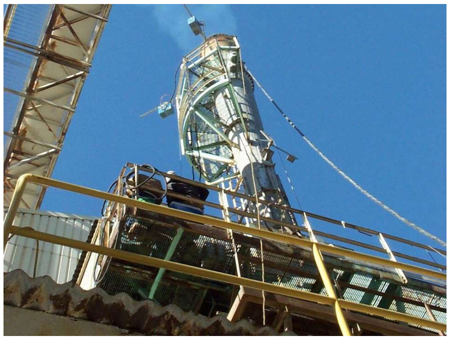
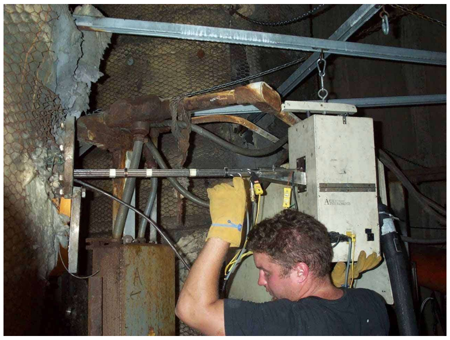


24 - 35



24 - 36

4. 5. 1999

Platform Location Where Grating Collapsed
(130 Feet Above Ground Level)

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

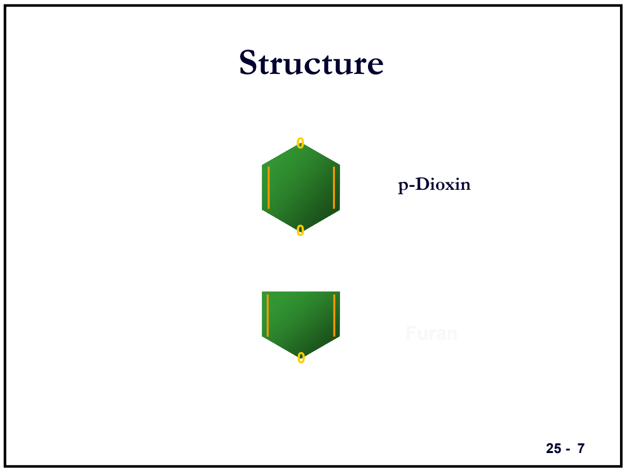
- Simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), semi-volatile organic compounds (SVOCs), and polybrominated diphenyl ethers (PBDE) can also be performed along with PCDDs and PCDFs

Applicability

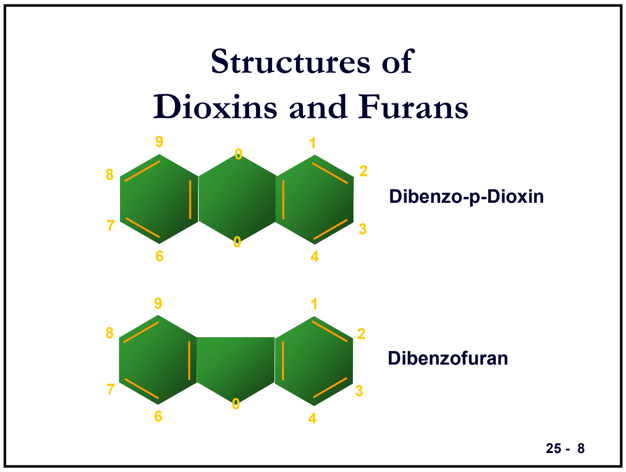
- SW-846, Method 0023A is used to determine destruction removal efficiency (DRE) of PCDDs and PCDFs at 99.9999% (six 9's) from incinerators
- General detection limits are 0.010 pg/m^3
- FRM 23 is used to quantify PCDD's and PCDF's from stationary sources

What Are Dioxins?

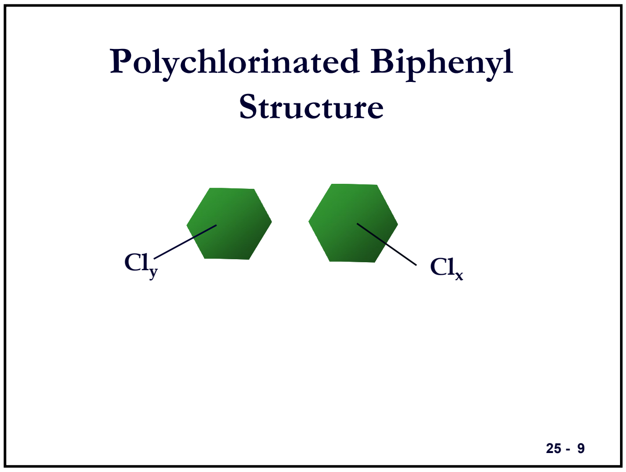
- Dioxins are a family of 210 different molecules with one or two basic structures
  - The dioxin structure with two oxygen atoms
  - The furan structure with one oxygen atom



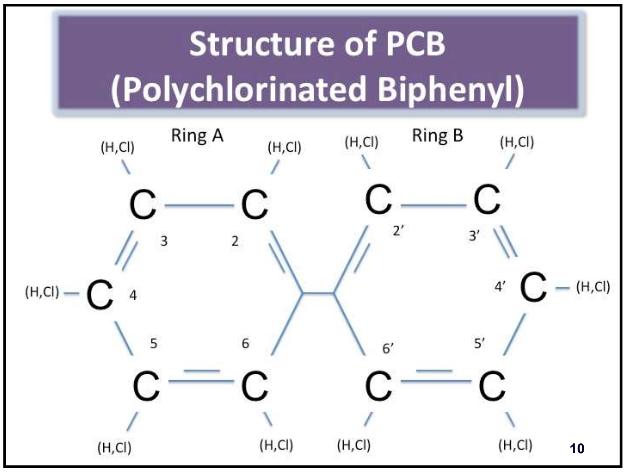
Structure



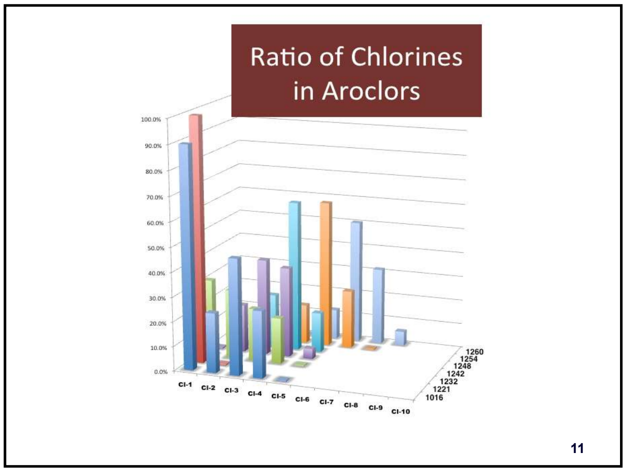
Structures of Dioxins and Furans



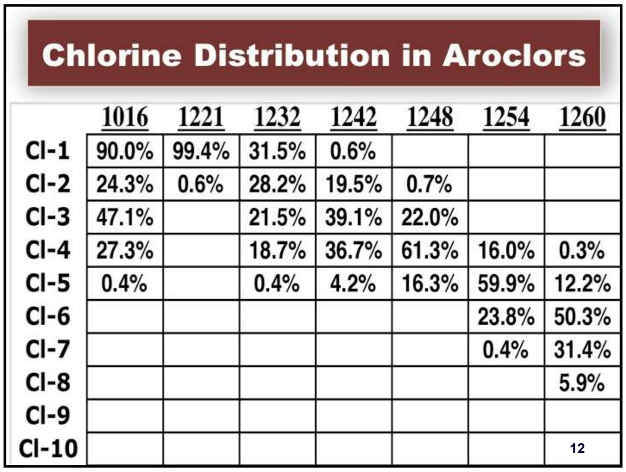
Polychlorinated Biphenyl Structure



Structure of PCB (Polychlorinated Biphenyl)



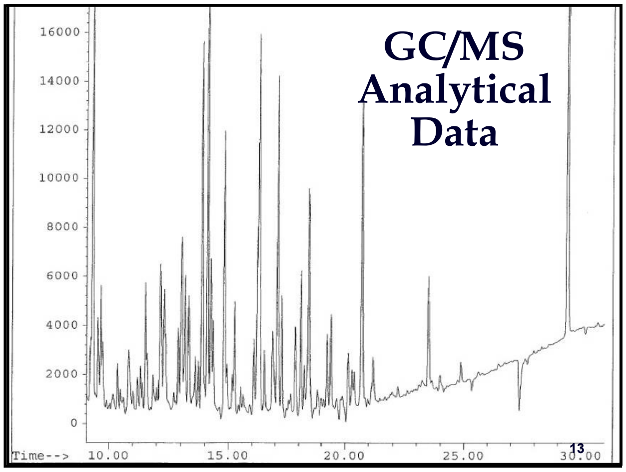
Ratio of Chlorines in Aroclors



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							

GC/MS Analytical Data



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)

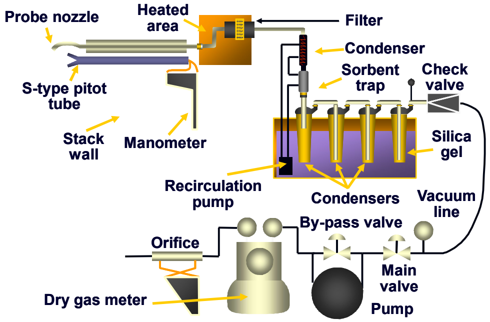
FRM 23 and SW-846 Method 0023A Sampling Train

- 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

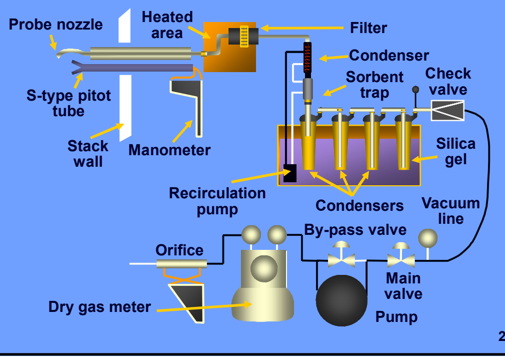
- XAD-2 is a cross-linked styrene-divinylbenzene - Organic Polymeric Adsorbent
- Amberlite XAD-2 physical characteristics

  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

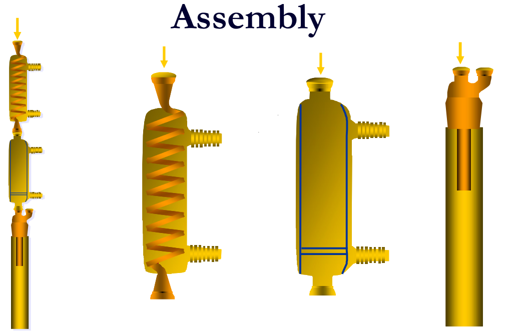
FRM 23/Method 0023A Sampling Train

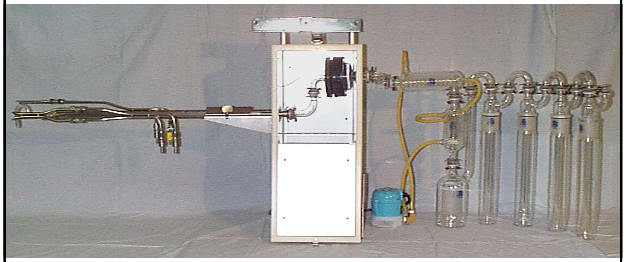


Percent Phase Distribution of Dioxins in Sampling Train

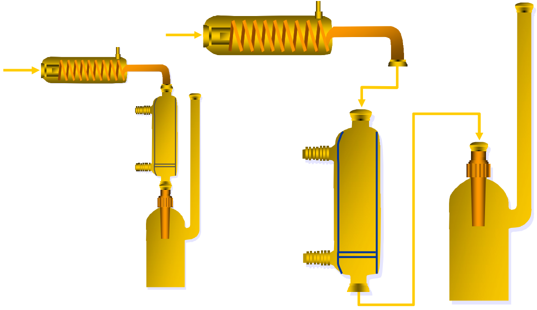
Phase	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Vapor	55	26	4	2	1
Particle	45	74	96	98	99

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 = $0.5\ \text{ng}/[(0.85\ \text{m}^3/\text{hr}) \times (0.1\ \text{ng}/\text{m}^3)]$ = 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

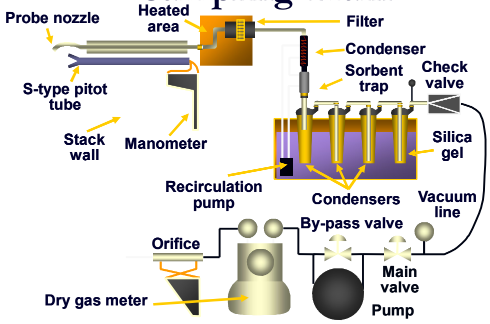
Preparation of Sample Train

- 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

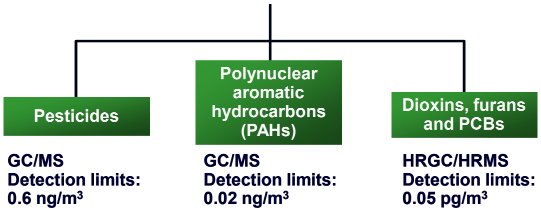
Criteria for On-site Invalidation

- 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



Pesticides	Polynuclear aromatic hydrocarbons (PAHs)	Dioxins, furans and PCBs
GC/MS Detection limits: 0.6 ng/m³	GC/MS Detection limits: 0.02 ng/m³	HRGC/HRMS Detection limits: 0.05 pg/m³

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

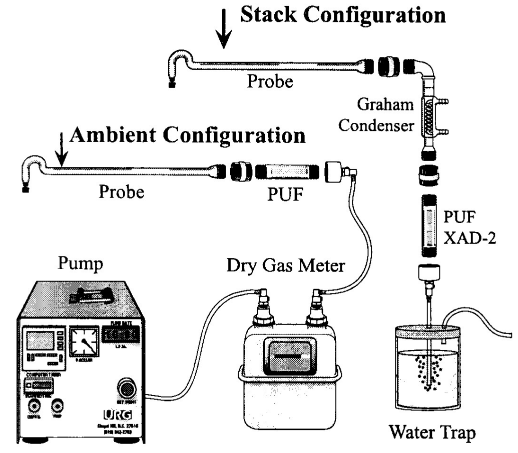
- Allows for Long-Term D/F Measurements – up to 4 weeks
- Annual D/F Method 23 Estimates for Plants Have Increased 15 to 25% When Measured by AMESA & DMS
  - Increases attributed to: 1) daily plant operation variations and 2) that very few of the D/F are “non detects” as seen in Method 23 analyses.

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

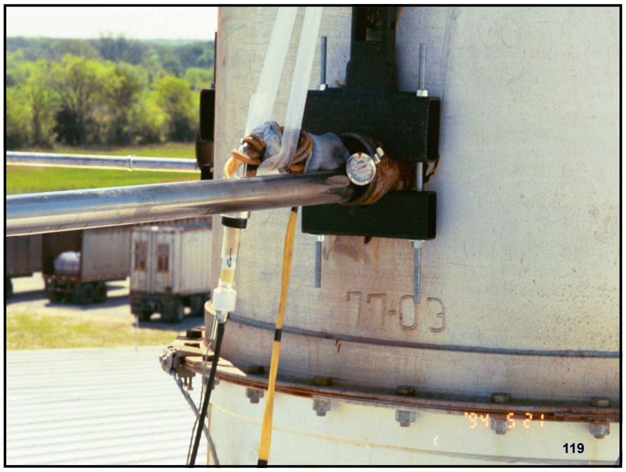


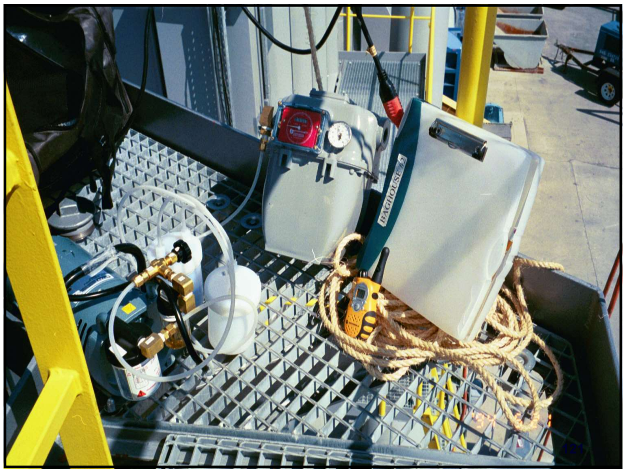
AmbStack Dioxin Sampling

- 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

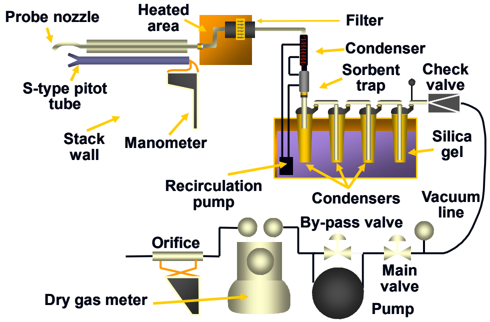
AmbStack Dioxin Sampling

- 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



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

FRM 30 Mercury

Acceptable Reference Methods

- Originally, the Ontario Hydro method (ASTM D6784-02) and EPA Method 29 were the only acceptable reference methods.
- August 22, 2007, EPA released a direct and final rule that allowed two other reference methods.
  - EPA Method 30A – Instrumental reference method (IRM)
  - EPA Method 30B – Sorbent trap method
- Both methods were promulgated November 2007.

Federal Register / Vol. 81, No. 168 / Tuesday, August 30, 2016 / Rules and Regulations

- *Z. Method 30A of Appendix A–8 of Part 60*

  In Method 30A, the heading of section 8.1 is changed from ‘‘Sample Point Selection’’ to ‘‘Selection of Sampling Sites and Sampling Points.’’
- *AA. Method 30B of Appendix A–8 of Part 60*

  In Method 30B, the heading of section 8.1 is changed from ‘‘Sample Point Selection’’ to ‘‘Selection of Sampling Sites and Sampling Points.’’ In section 8.3.3.8, the reference to ASTM WK223 is changed to ASTM D6911–15, and the last two sentences in this section (inadvertently omitted in the proposed rule) are re-inserted.

EPA Method 30A

- ***Determination of Total Vapor-Phase Mercury Emissions from stationary Sources Using an instrumental analyzer***
  - Sample point selection
  - Analytical procedures
  - Sampling procedures
  - QA/QC

EPA Method 30A - Sample point selection

- Use twelve sampling points located according Table 1-1 or Table 1-2 of Method 1 in appendix A-1
- Alternatively, conduct a stratification test as described in section 8.1.3 to determine the number and location of the sampling points

EPA Method 30A - Analytical procedures

- Real-time
- Performance-based
- Consistent w/ SO_2 & NO_X instrumental methods
- Key elements
  - ➢Calibration error/linearity
  - ➢System integrity/conversion efficiency
  - ➢System response time
  - ➢Interference test
  - ➢Dynamic spiking (gaseous method of standard additions)

EPA Method 30A - Hg Gas Standards

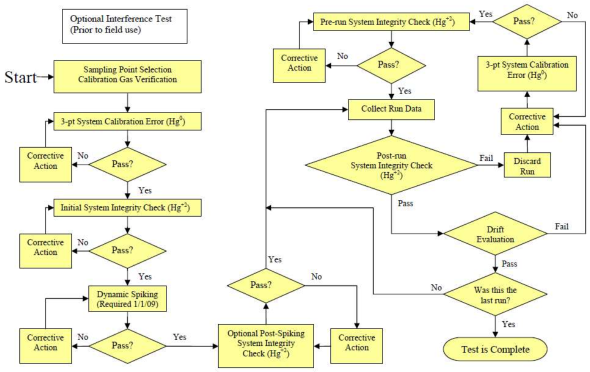
EPA Method 30A - Hg Gas Standard Traceability

Method Requires “NIST Traceable” Hg gas standards

- NIST Traceability is defined by EPA
  Documented in EPA-600/R-97/121 “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards”
- Traceable to a measured concentration, not theoretical

EPA Method 30A - Sampling procedures

- Two-point system integrity test
- Drift Check
- System equilibrates Two times system response prior to testing
- Traverse points
- Moisture correction



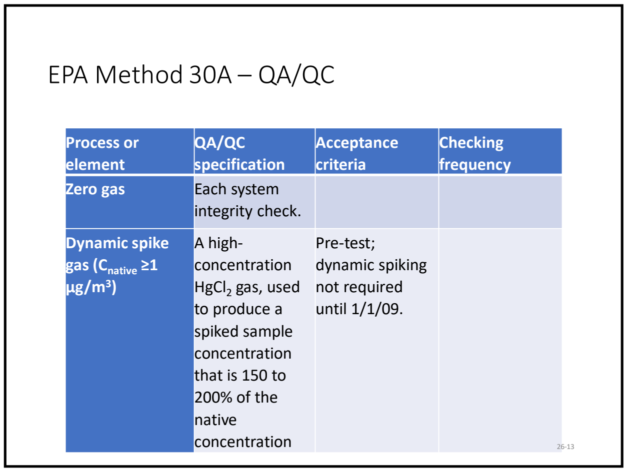
Mercury Testing Flow Chart

EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Calibration Gases	Traceability protocol	Validation of concentration required	
High-level Hg^0 gas	Equal to the calibration span	Each calibration error test.	
Mid-level Hg^0 gas	40 to 60% of calibration span	Each calibration error test.	
Low-level Hg^0 gas	10 to 30% of calibration span	Each calibration error test.	

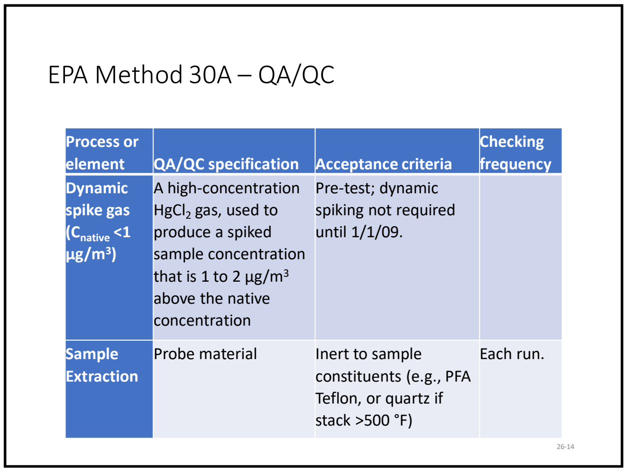
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
High-level $HgCl_2$ gas	Equal to the calibration span	Each system integrity check (if it better represents C_{native} than the mid level gas).	
Mid-level $HgCl_2$	40 to 60% of calibration span	Each system gas integrity check (if it better represents C_{native} than the high level gas).	



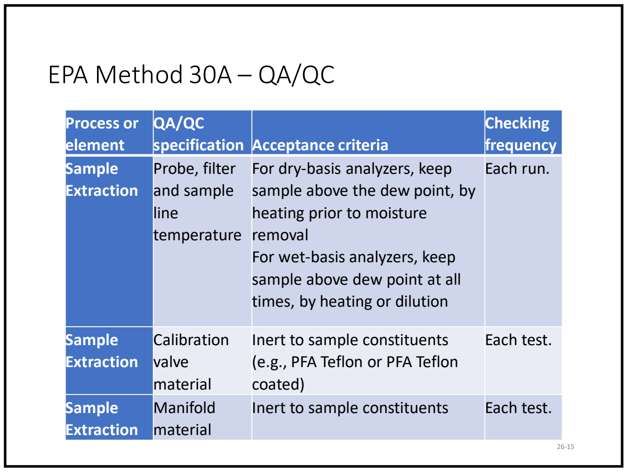
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Zero gas	Each system integrity check.		
Dynamic spike gas (C_{native} ≥1 $\mu g/m^3$)	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 150 to 200% of the native concentration	Pre-test; dynamic spiking not required until 1/1/09.	



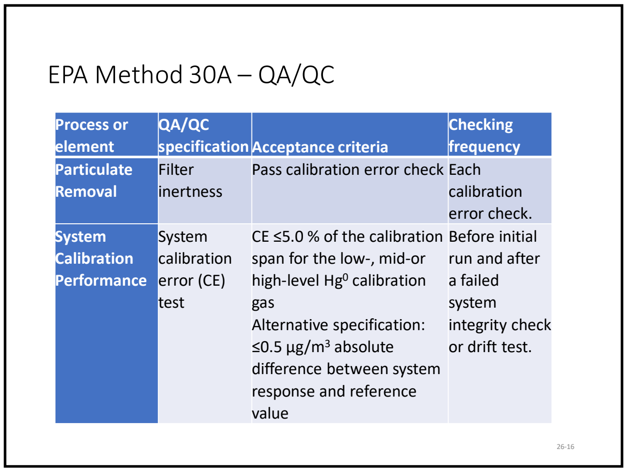
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Dynamic spike gas (C_{native} <1 $\mu g/m^3$)	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 1 to 2 $\mu g/m^3$ above the native concentration	Pre-test; dynamic spiking not required until 1/1/09.	
Sample Extraction	Probe material	Inert to sample constituents (e.g., PFA Teflon, or quartz if stack >500 °F)	Each run.



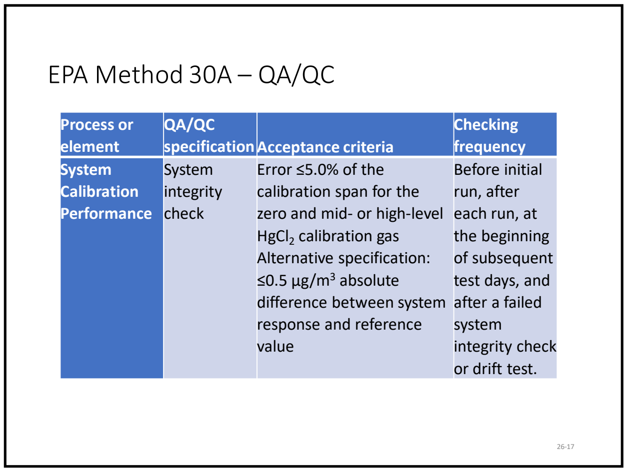
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Sample Extraction	Probe, filter and sample line temperature	For dry-basis analyzers, keep sample above the dew point, by heating prior to moisture removal For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution	Each run.
Sample Extraction	Calibration valve material	Inert to sample constituents (e.g., PFA Teflon or PFA Teflon coated)	Each test.
Sample Extraction	Manifold material	Inert to sample constituents	Each test.



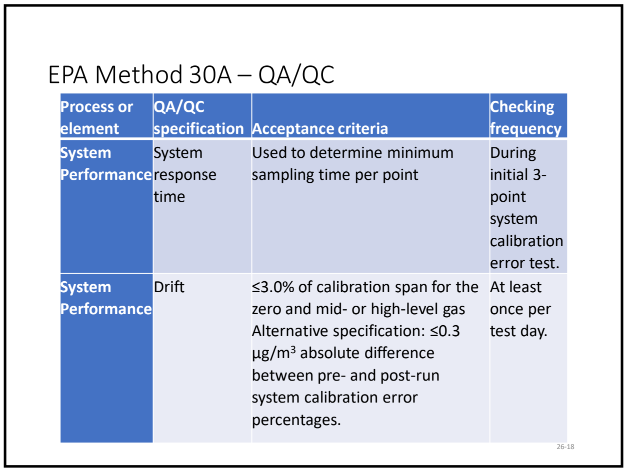
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Particulate Removal	Filter inertness	Pass calibration error check	Each calibration error check.
System Calibration Performance	System calibration error (CE) test	CE ≤5.0 % of the calibration span for the low-, mid-or high-level Hg^0 calibration gas Alternative specification: ≤0.5 $\mu g/m^3$ absolute difference between system response and reference value	Before initial run and after a failed system integrity check or drift test.



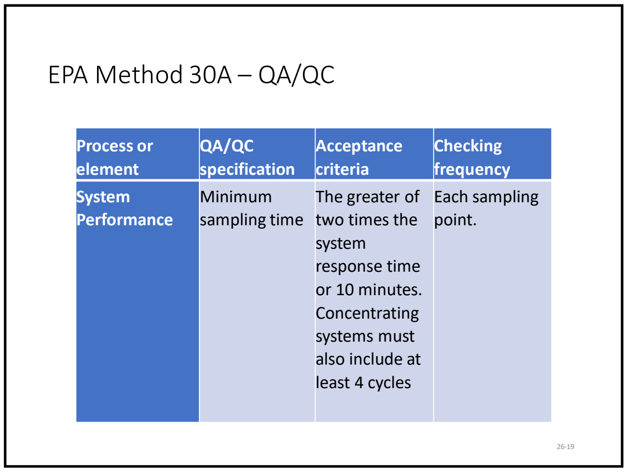
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
System Calibration Performance	System integrity check	Error ≤5.0% of the calibration span for the zero and mid- or high-level $HgCl_2$ calibration gas Alternative specification: ≤0.5 $\mu g/m^3$ absolute difference between system response and reference value	Before initial run, after each run, at the beginning of subsequent test days, and after a failed system integrity check or drift test.



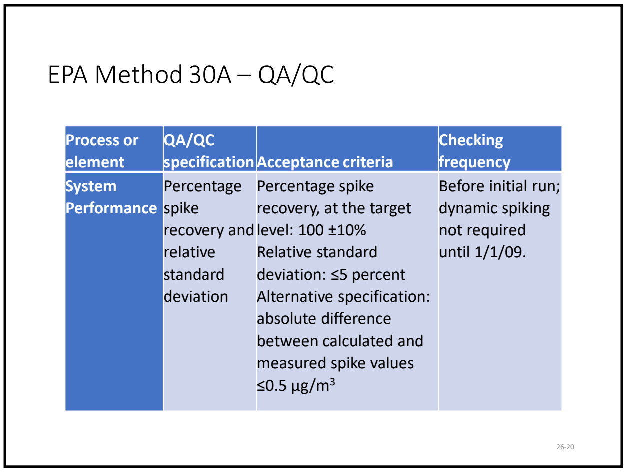
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
System Performance	System response time	Used to determine minimum sampling time per point	During initial 3-point system calibration error test.
System Performance	Drift	≤3.0% of calibration span for the zero and mid- or high-level gas Alternative specification: ≤0.3 $\mu g/m^3$ absolute difference between pre- and post-run system calibration error percentages.	At least once per test day.



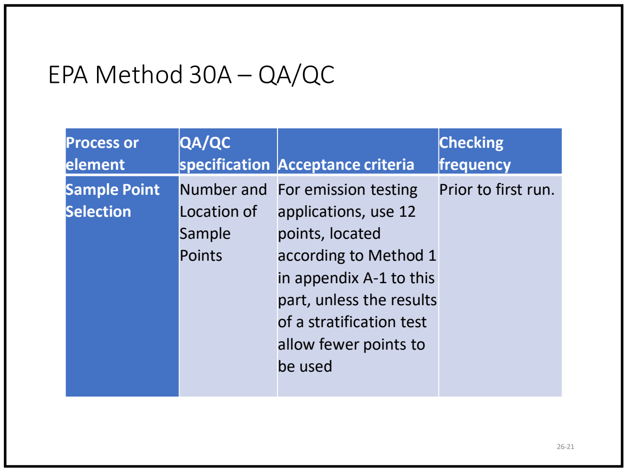
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
System Performance	Minimum sampling time	The greater of two times the system response time or 10 minutes. Concentrating systems must also include at least 4 cycles	Each sampling point.



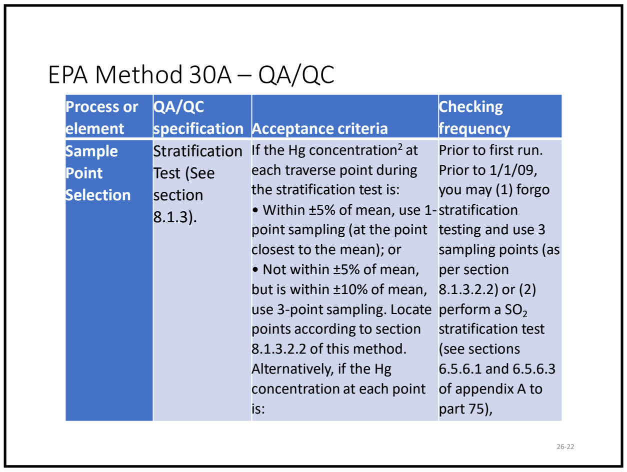
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
System Performance	Percentage spike recovery and relative standard deviation	Percentage spike recovery, at the target level: 100 ±10% Relative standard deviation: ≤5 percent Alternative specification: absolute difference between calculated and measured spike values ≤0.5 $\mu g/m^3$	Before initial run; dynamic spiking not required until 1/1/09.



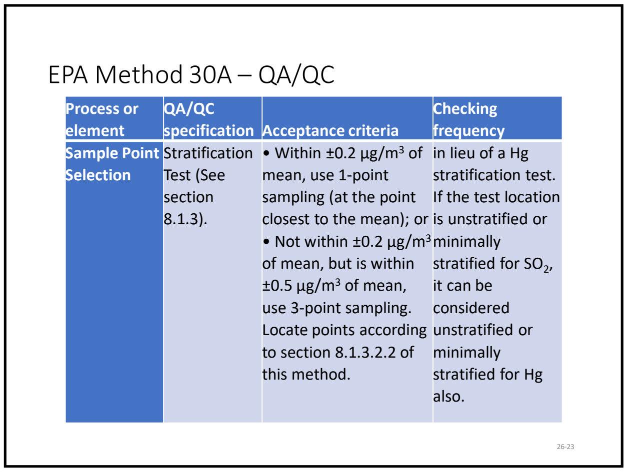
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Sample Point Selection	Number and Location of Sample Points	For emission testing applications, use 12 points, located according to Method 1 in appendix A-1 to this part, unless the results of a stratification test allow fewer points to be used	Prior to first run.



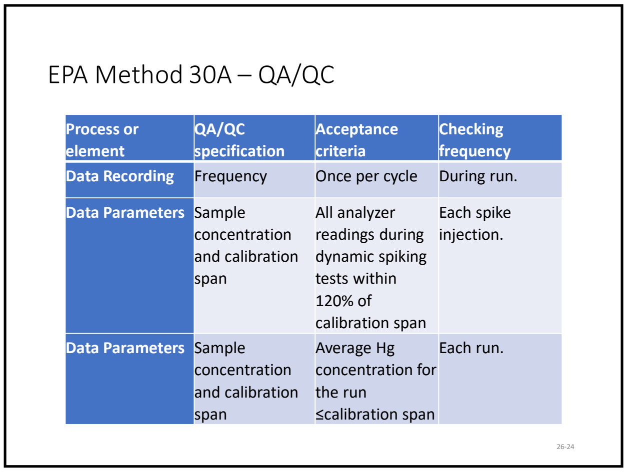
EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Sample Point Selection	Stratification Test (See section 8.1.3).	If the Hg concentration[2] at each traverse point during the stratification test is: • Within ±5% of mean, use 1-point sampling (at the point closest to the mean); or • Not within ±5% of mean, but is within ±10% of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method. Alternatively, if the Hg concentration at each point is:	Prior to first run. Prior to 1/1/09, you may (1) forgo stratification testing and use 3 sampling points (as per section 8.1.3.2.2) or (2) perform a SO_2 stratification test (see sections 6.5.6.1 and 6.5.6.3 of appendix A to part 75),



EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Sample Point Selection	Stratification Test (See section 8.1.3).	• Within ±0.2 $\mu g/m^3$ of mean, use 1-point sampling (at the point closest to the mean); or • Not within ±0.2 $\mu g/m^3$ of mean, but is within ±0.5 $\mu g/m^3$ of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method.	in lieu of a Hg stratification test. If the test location is unstratified or minimally stratified for SO_2, it can be considered unstratified or minimally stratified for Hg also.



EPA Method 30A – QA/QC

Process or element	QA/QC specification	Acceptance criteria	Checking frequency
Data Recording	Frequency	Once per cycle	During run.
Data Parameters	Sample concentration and calibration span	All analyzer readings during dynamic spiking tests within 120% of calibration span	Each spike injection.
Data Parameters	Sample concentration and calibration span	Average Hg concentration for the run ≤calibration span	Each run.

EPA Method 30B

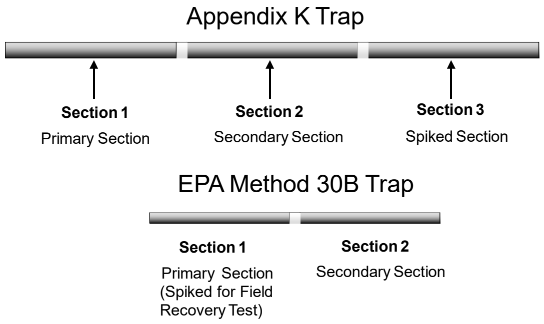
Determination of Total Vapor-Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps

- Sample point selection
- Analytical procedures
- Measurement system performance tests
- Sampling procedures
- Sampling handling
- QA/QC

Sorbent Traps as a Reference Method and for Appendix K

- Both are sorbent trap methods
- Both are procedural not proscribed methods
- **But:**
- A reference method is designed to certify or prove another method is working properly. In this case, a continuous Hg monitor (CMM).
- Appendix K is a CMM.

Differences Between Method 30B and Appendix K Carbon Traps



Appendix K Trap

Section 1
Primary Section

Section 2
Secondary Section

Section 3
Spiked Section

EPA Method 30B Trap

Section 1
Primary Section
(Spiked for Field Recovery Test)

Section 2
Secondary Section

Sample Point Selection

- Do a Long-line traverse for the RATA or,
- Conduct a 12-point mercury stratification test prior to the RATA.

Analytical Procedures

- Modified EPA Method 1631 Digestion Procedures followed by analysis using cold- vapor atomic fluorescence (CVAF)
- Thermal desorption – Ohio Lumex RA-915+ Hg analyzer with RP-324 attachment
- Thermal combustion – Leeman, Leco, Milestone

Measurement System Performance Tests

- Determination of minimum mass of Hg to be collected
- Analytical matrix test (wet analysis method)
- Hg^0 and $HgCl_2$ analytical bias test (instrumental analysis method)
- Field recovery test

Determination of Minimum Mass of Hg to Be Collected

- Perform a multipoint calibration of the analyzer at a minimum of three points (the linear coefficient r^2 must be ≥0.99).
- All field samples analyzed must fall within the range of the calibration curve.
- Lowest point in your calibration curve must be ≥10, the minimum detection limit of your instrument (MDL).
- Select a calibration check standard that is >2 times the lowest concentration in your calibration curve.
- Minimum sample time is 30 minutes.

Hg^0 and $HgCl_2$ Analytical Bias Test

- This test defines the bounds within which the field samples must be to be valid.
- Only done once for each sorbent type or instrument.
- Analyze the front section of three sorbent traps spiked with Hg^0 at the lower and upper concentrations (must be spiked with vapor-phase Hg^0).
- Analyze the front section of three sorbent traps spiked with $HgCl_2$ at the lower and upper concentrations (liquid standards may be used).
- To be valid, the average recovery of each set of three samples must be between 90% and 110% of the known value.

Field Recovery Test

- Done once for each unit tested.
- Requires three sets of dual-train tests using one Hg^0-spiked trap (first section) paired with a nonspiked trap.
- Based on the Hg mass to be collected on the first section of the trap, the spike must be within 50% to 150% of this mass.
- Sample the stack gas and analyze traps using the same sampling procedures and analytical methods as for the standard field samples

Field Recovery Test

- The average of the percentage of the spike recovered must be between 85% and 115% to begin the RATA.
- It is acceptable to perform the field recovery test concurrent with the actual test run using a quad probe.
- It is also acceptable to use field recovery test data as part of the RATA if the difference between the spiked and unspiked samples after subtracting out the spike has a RD of ≤10%.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration (At 3 settings or points)	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y)	Prior to initial use and when post-test check is not within ±5% of Y	Recalibrate at 3 points until the acceptance criteria are met.
Gas flow meter post-test calibration check (Single-point)	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration	After each field test. For mass flow meters, must be done on-site, using stack gas	Recalibrate gas flow meter at 3 points to determine a new value of Y. For mass flow meters, must be done on-site, using stack gas. Apply the new Y value to the field test data.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor	Prior to initial use and before each test thereafter	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer	Prior to initial use and before each test thereafter	Recalibrate; instrument may not be used until specification is met.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Pre-test leak check	≤4% of target sampling rate	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	Sample invalidated.*
Analytical matrix interference test (wet chemical analysis, only)	Establish minimum dilution (if any) needed to eliminate sorbent matrix interferences	Prior to analyzing any field samples; repeat for each type of sorbent used	Field sample results not validated.

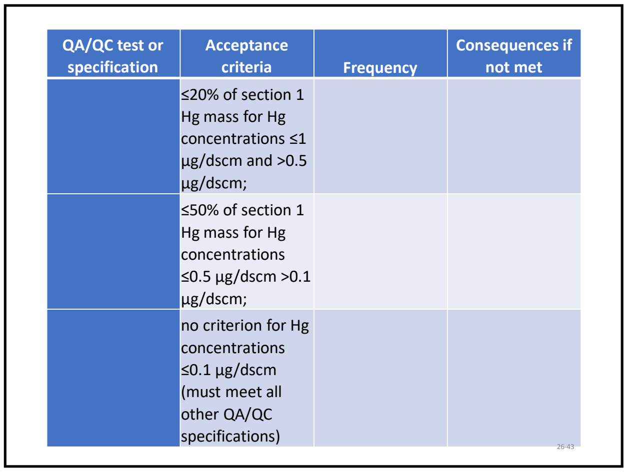
QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analytical bias test	Average recovery between 90% and 110% for Hg^0 and $HgCl_2$ at each of the 2 spike concentration levels	Prior to analyzing field samples and prior to use of new sorbent media	Field samples shall not be analyzed until the percent recovery criteria has been met.
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value and $r^2 \geq 0.99$	On the day of analysis, before analyzing any samples	Recalibrate until successful.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analysis of independent calibration standard	Within ±10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful.
Analysis of continuing calibration verification standard (CCVS)	Within ±10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible; for destructive techniques, samples invalidated.

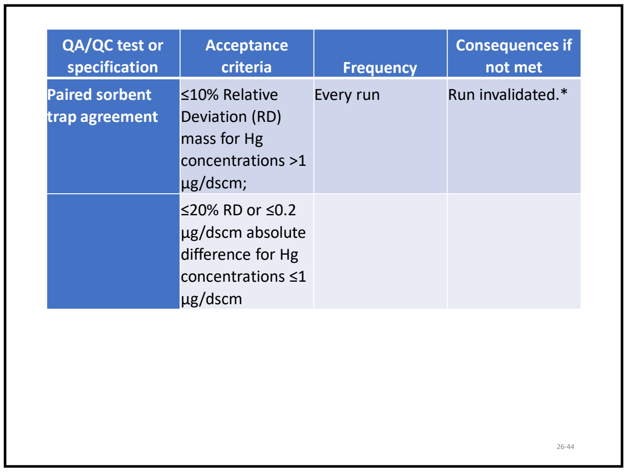
QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Test run total sample volume	Within ±20% of total volume sampled during field recovery test	Each individual sample	Sample invalidated.
Sorbent trap section 2 breakthrough	For compliance/emissions testing:	Every sample	Sample invalidated.*
	≤10% of section 1 Hg mass for Hg concentrations >1 µg/dscm;		
	≤20% of section 1 Hg mass for Hg concentrations ≤1 µg/dscm		

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
	≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit		
Sorbent trap section 2 breakthrough	For relative accuracy testing:		
	≤10% of section 1 Hg mass for Hg concentrations >1 µg/dscm;		

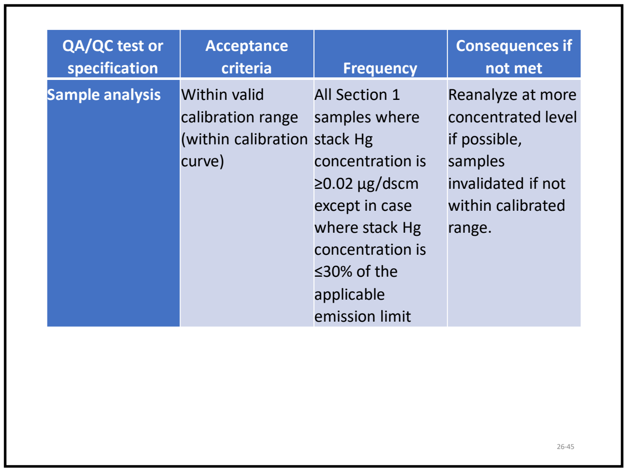
QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
	≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit		
Sorbent trap section 2 breakthrough	For relative accuracy testing:		
	≤10% of section 1 Hg mass for Hg concentrations >1 µg/dscm;		



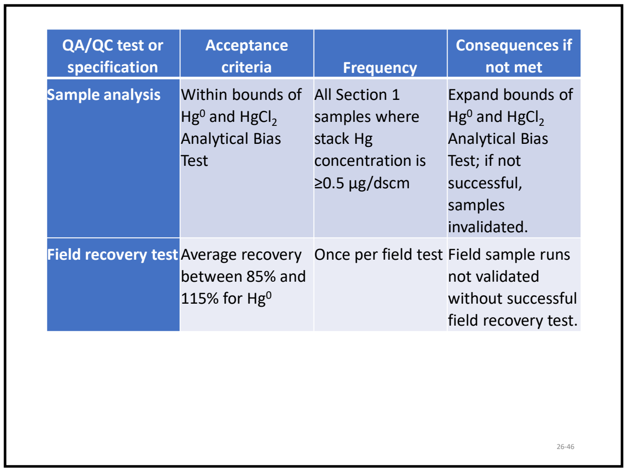
QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
	≤20% of section 1 Hg mass for Hg concentrations ≤1 µg/dscm and >0.5 µg/dscm;		
	≤50% of section 1 Hg mass for Hg concentrations ≤0.5 µg/dscm >0.1 µg/dscm;		
	no criterion for Hg concentrations ≤0.1 µg/dscm (must meet all other QA/QC specifications)		



QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Paired sorbent trap agreement	≤10% Relative Deviation (RD) mass for Hg concentrations >1 µg/dscm;	Every run	Run invalidated.*
	≤20% RD or ≤0.2 µg/dscm absolute difference for Hg concentrations ≤1 µg/dscm		



QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Sample analysis	Within valid calibration range (within calibration curve)	All Section 1 samples where stack Hg concentration is ≥0.02 µg/dscm except in case where stack Hg concentration is ≤30% of the applicable emission limit	Reanalyze at more concentrated level if possible, samples invalidated if not within calibrated range.



QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Sample analysis	Within bounds of Hg^0 and $HgCl_2$ Analytical Bias Test	All Section 1 samples where stack Hg concentration is ≥0.5 µg/dscm	Expand bounds of Hg^0 and $HgCl_2$ Analytical Bias Test; if not successful, samples invalidated.
Field recovery test	Average recovery between 85% and 115% for Hg^0	Once per field test	Field sample runs not validated without successful field recovery test.