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**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, [jwinberry@mindspring.com](mailto:jwinberry@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 products 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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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 has taken the initiative to update EPA's APT! Course #450/#468.

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<sub>2</sub> (FRMs 6, 6A, and 8), NO<sub>x</sub> (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>.



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

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



1 - 1

### Compliance Testing and Source Test Observation



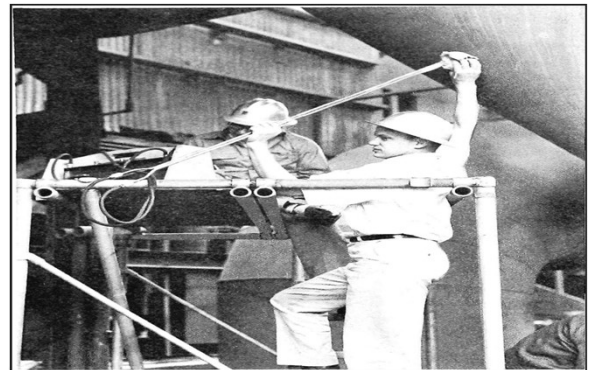
1 - 2



Stack Measurement in Donora (Circa 1948)

1 - 3

### LA APCD Source Testing Personnel 1960's



1 - 4

### Source Sampling At a Scrap Metal Dryer Circa 1970's



1 - 5

### Source Sampling At a Scrap Metal Dryer Circa 1970's

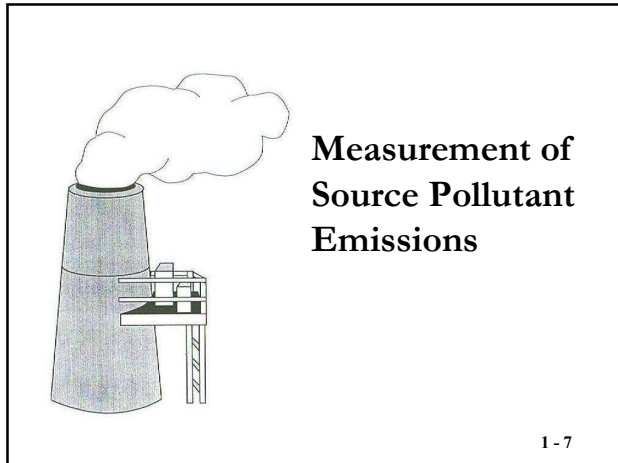


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# APTI #450/468 Compliance Test and Source Test Observation

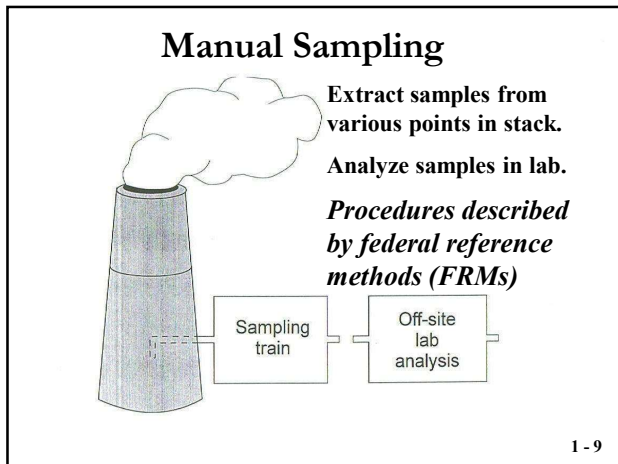
## Lesson 1: Introduction Driving Force for HAP's Monitoring



### Measurement Methods of Source Pollutant Emissions

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

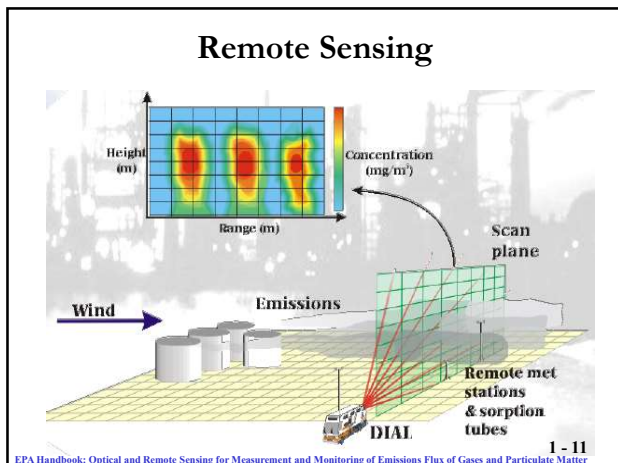
1 - 8



### Manual vs. Instrumental

Manual	Instrumental
Anything related to PM and some gases	Anything related to gases
<ul style="list-style-type: none"><li>• PM</li><li>• PM<sub>10</sub></li><li>• Metals</li><li>• Semi-volatile</li><li>• Organisms</li><li>• HCL &amp; H2SO4</li></ul>	<ul style="list-style-type: none"><li>• NO<sub>x</sub></li><li>• SO<sub>2</sub></li><li>• CO</li><li>• Opacity</li><li>• O<sub>2</sub></li><li>• CO<sub>2</sub></li><li>• VOC</li><li>• H<sub>2</sub>S</li><li>• Volatile Organics</li></ul>

1 - 10



### EPA Manual Federal Reference Methods (FRMs)

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

1 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### Agency's Purpose for Stack Testing

Compliance Evaluation  
Regulatory Support  
Emission Inventory  
Method Development  
Certify CEM's

1 - 13

### Industry's Purpose for Stack Testing

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

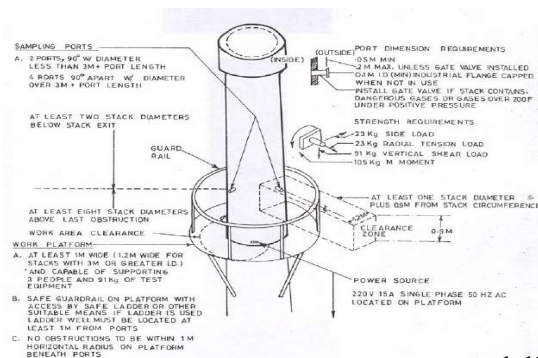
1-14

### Types of Emission Points Tested

Stacks  
Process vents  
Building exhausts  
Tank emissions  
Fugitive emissions

1 - 15

### Typical Sampling Point Provisions



1 - 16

### Four H's of Source Testing

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

1 - 17



1 - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### Source Testing a Wet Mill Corn Dryer



1 - 19

### Something Source Testers use a lot of?



1 - 20

### Types of Emissions Tested

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

Inorganic gases

Organic gases and vapors

Combinations of solids and gases

1 - 21

### Where Methods are Found

U.S. EPA test methods (CFR)

State Implementation Plans (SIPs)  
and regulations

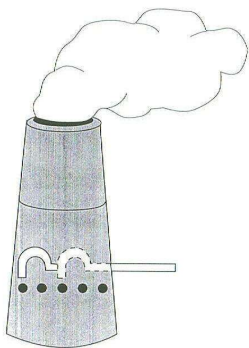
Industrial and trade associations,  
Publications

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

1 - 22

### Method 1

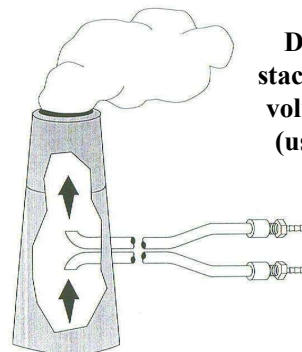
Selection of  
sampling traverse  
points



1 - 23

### Method 2

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

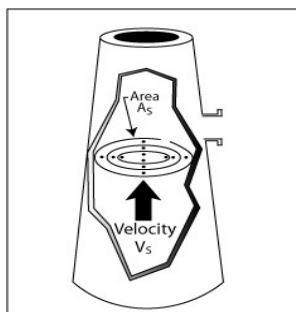


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# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

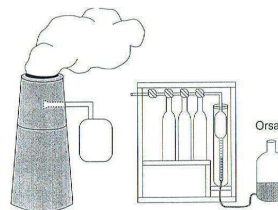
### Distributed Sampling Points



1 - 25

### Method 3

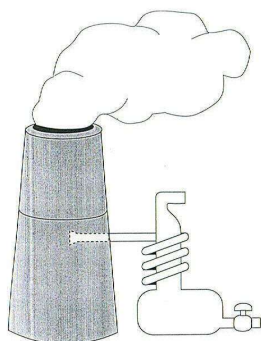
Determination of the dry molecular weight of flue gas (using Orsat apparatus measuring %O<sub>2</sub>, %CO<sub>2</sub>, and %CO)



1 - 26

### Method 4

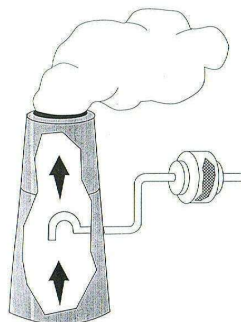
Determination of moisture content of stack gas (by condensation method)



1 - 27

### Method 5

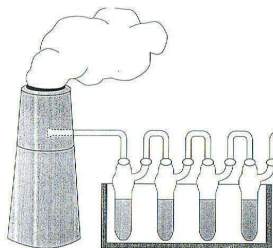
Sampling method for particulate matter (isokinetic collection of particles on a filter)



1 - 28

### Method 6

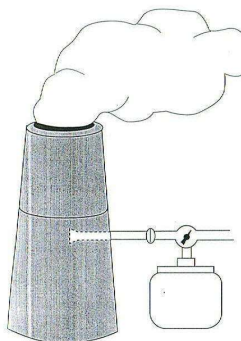
Sampling and analytic method for determining SO<sub>2</sub> emissions (barium-thorin titration)



1 - 29

### Method 7

Determination of NO<sub>x</sub> emissions (colorimetric phenoldisulfonic acid method)



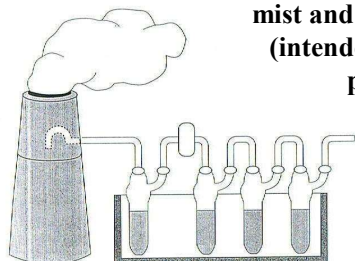
1 - 30

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### Method 8

**Determination of H<sub>2</sub>SO<sub>4</sub> mist and SO<sub>2</sub> emissions (intended for H<sub>2</sub>SO<sub>4</sub> plants)**



1 - 31

FRM 10	Determination of CO
FRM 11	Determination of flourides
FRM 12	Determination of inorganic lead emissions
FRM 13, 14	Determination of H <sub>2</sub> S
FRM 15	Determination of H <sub>2</sub> O, COS, CS <sub>2</sub>
FRM 16	Determination of total reduced sulfur
FRM 17	Determination of particulates (in-stack filtration method)

1 - 32

FRM 26	Determination of HCl/Cl <sub>2</sub>
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.

1 - 33

### 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**

1 - 34

### Objectives

**Focus on groups of compounds**

**Volatile Organic Compounds (VOCs)**

**Hydrogen Halides and Halogens**

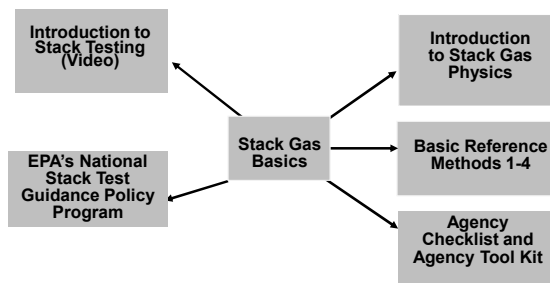
**Particulate Matter (Total and Speciated) and Condensibles**

**Inorganic-base Compounds (Lead and Metals)**

**Update changes associated with FRMs 1-5**

1 - 35

### What We Will Cover



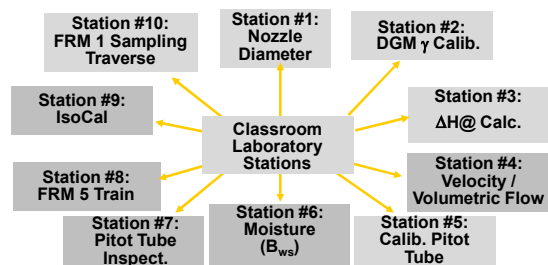
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# APTI #450/468 Compliance Test and Source Test Observation

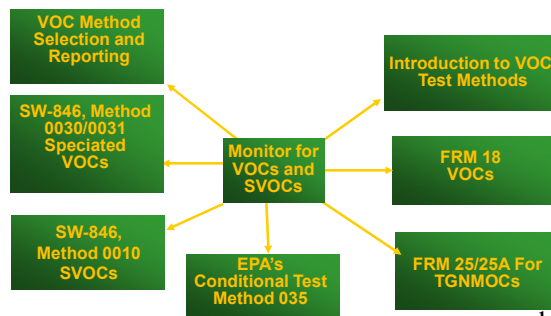
## Lesson 1: Introduction Driving Force for HAP's Monitoring

### What We Will Cover



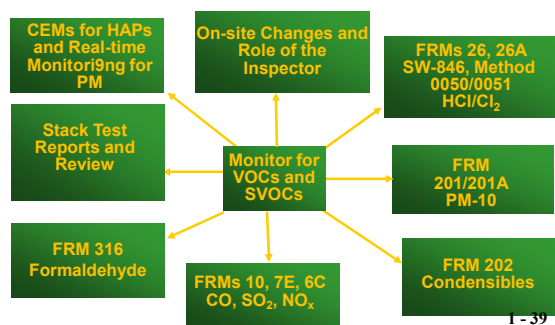
1 - 37

### What We Will Cover



1 - 38

### What We Will Cover



1 - 39

### 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

1 - 40

### 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

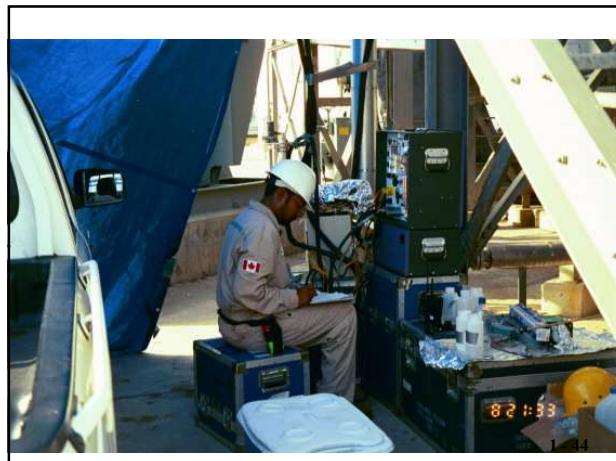
1 - 41



1 - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring



### 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)?

1 - 45

### Historical Questions?

How do we define “condensable 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?”

1 - 46

### Historical Questions?

How do we report VOC emissions? As “C,” as “propane,” as “VOCs?”

What requirements must be met in order 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)?

1 - 47

### 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 determine 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](https://www.epa.gov/sites/production/files/2016-02/documents/flexible_approaches_to_environmental_measurement_-_reaffirmed_112015.pdf)

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# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

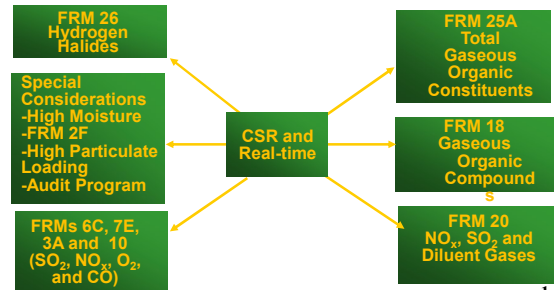
### Historical Questions?

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?

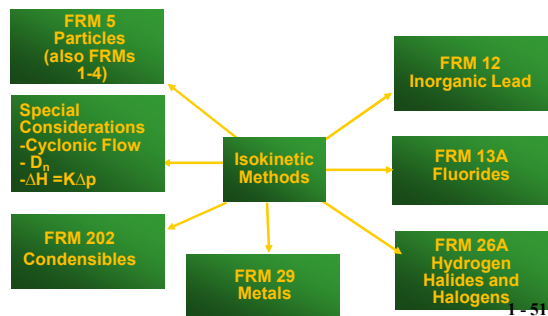
1 - 49

### Constant Sampling Rate (CSR) and Real-time Methods



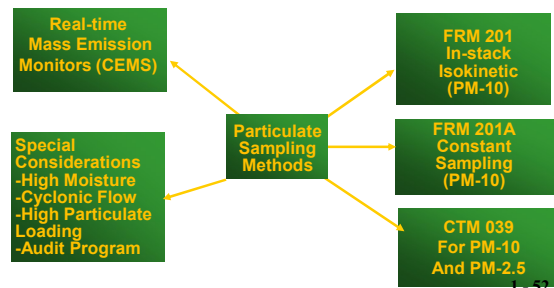
1 - 50

### Isokinetic Sampling Rate Methods



1 - 51

### Particulate Sampling Methods



1 - 52

### Stack Test Methods

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

1 - 53

### 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

1 - 54



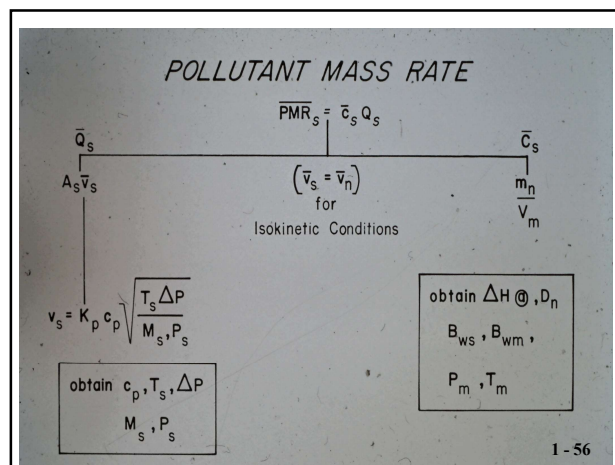
# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### 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 <sup>6</sup> Btu)
Process weight rate	E (lb/lbs product produced)

1 - 55



1 - 56

### 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)

1 - 57

### 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

1 - 58

### 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

1 - 59

### Why Have Title III Hazardous Air Pollutants?

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

1 - 60

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

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### 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)

1 - 61

### 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

1 - 62

### 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

1 - 63

### 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

1 - 64

### 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 SOCM

370 Facilities

111 of the 188 Title III HAPs

1 - 65

### 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

1 - 66

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### Where Do We Find the Test Methods?

<https://www.epa.gov/emc/emc-test-methods>

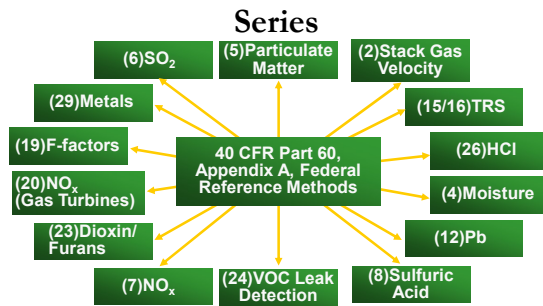
1 - 67

### Regulations

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

1 - 68

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



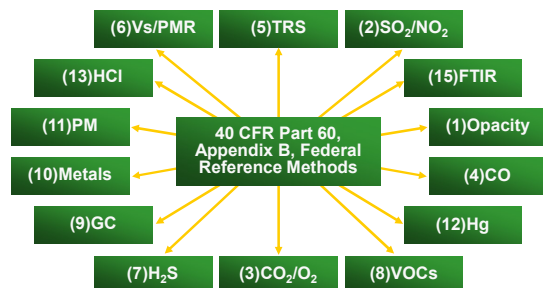
1 - 69

### 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)

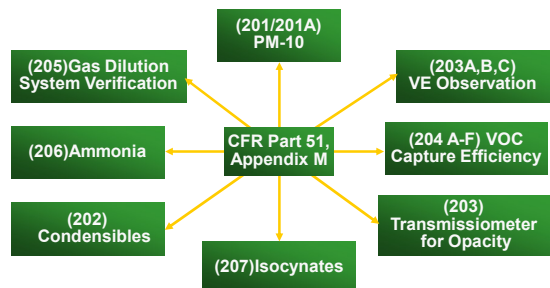
1 - 70

### Performance Specification Test (PSTs)-00 Series



1 - 71

### State Implementation Plan (SIP)-200 Series



1 - 72

# APTI #450/468 Compliance Test and Source Test Observation

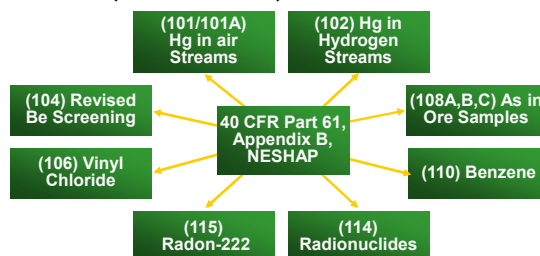
## Lesson 1: Introduction Driving Force for HAP's Monitoring

### 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)

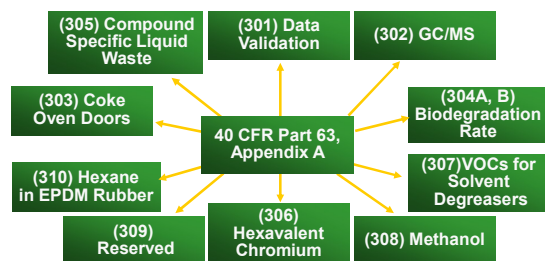
1 - 73

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



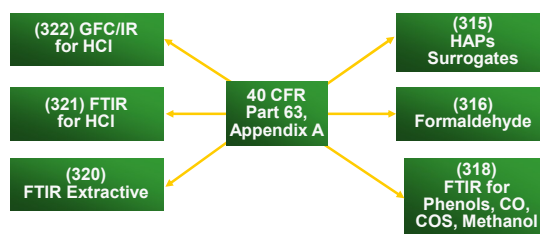
1 - 74

### Maximum Achievable Control Technology (MACT)-300 Series



1 - 75

### Maximum Achievable Control Technology (MACT)-300 Series



1 - 76

### 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

1 - 77

### 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

1 - 78

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

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### Categories

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

1 - 79

### Categories

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

These methods generally have had no EPA review or analysis

1 - 80

### 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)

1 - 81

### Example Category Stack Test Methods

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

1 - 82

### Example Category Stack Test Methods

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

1 - 83

### Example Category Stack Test Methods

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

All categories of methods found on

<https://www.epa.gov/emc/emc-test-methods>

1 - 84

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

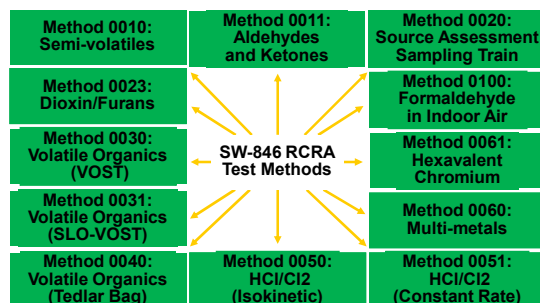
### Resource Conservation And Recovery Act (RCRA)

SW-846 is the compendium of analytical and test methods used in determining regulatory compliance under RCRA

<https://www.epa.gov/hw-sw846/sw-846-compendium>

1 - 85

### SW-846 Stack Test Methods



1 - 86

### 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)

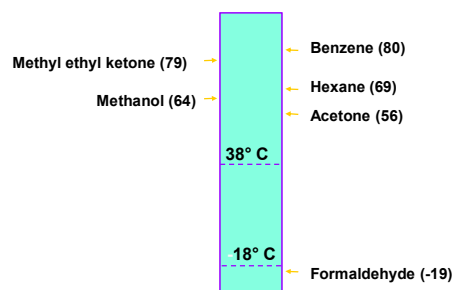
1 - 87

### General Classification of VOCs

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

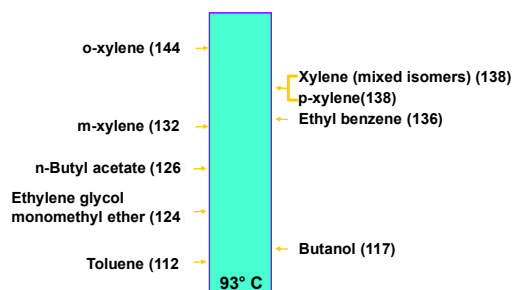
1 - 88

### Boiling Points of Volatile Organic Compounds



1 - 89

### Boiling Points of Volatile Organic Compounds

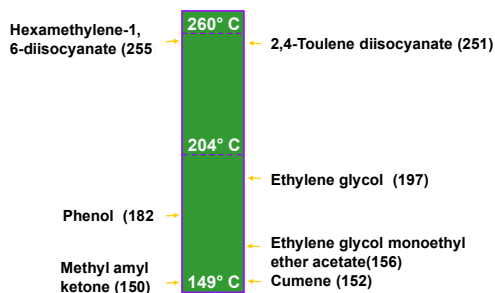


1 - 90

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 1: Introduction Driving Force for HAP's Monitoring

### Boiling Points of Semi-volatile Organic Compounds



1 - 91

### General Classification of HAPs

Volatility Class	Number of HAPs in Class
Volatiles (VV/V)	106
Semi-volatiles (SV)	65
Non-Volatile (NV) Particles	17
<b>Total HAPs</b>	<b>188</b>

1 - 92

### 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

1 - 93

### Example of HAPs in Each Volatility Class

**VP (10<sup>-7</sup> to 10<sup>-1</sup> mm Hg)  
BP (200 to 500°C)**

#### SEMI-VOLATILE (65 HAPs)

Benzidine	10 <sup>-5</sup> mm Hg	402°C
Captan	10 <sup>-6</sup> mm Hg	479°C
Phosphorus	10 <sup>-2</sup> mm Hg	280°C
Mercury Compounds	10 <sup>-3</sup> mm Hg	356°C

1 - 94

### Example of HAPs in Each Volatility Class

**VP (< 10<sup>-7</sup> mm Hg)  
BP (>500°C)**

#### NON-VOLATILE [Particles] (17 HAPs)

3,3'-Dimethoxybenzidine	10 <sup>-13</sup> mm Hg	458°C
Antimony	Very Low	656°C
Coronene	10 <sup>-13</sup> mm Hg	525°C

1 - 95

### General Classification of VOCs

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

1 - 96



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 2: EPA's EPA's National Stack Testing Guidance**

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**Compliance Test and Source Test Observation**  
**EPA's National Stack Testing Guidance**



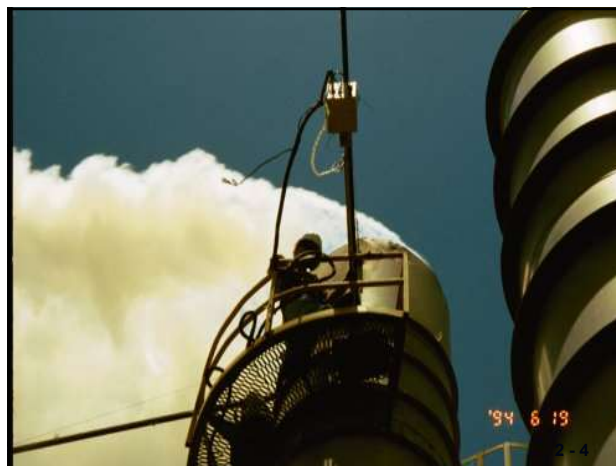
2 - 1



2 - 2



2 - 3



2 - 4

**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

2 - 5

**Major Issues Addressed By Guidance**

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

2 - 6



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 2: EPA's EPA's National Stack Testing Guidance

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### 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

2 - 7

### Definition

- Definition and "Scope of Guidance" sections clarify guidance applies only to tests conducted for compliance purposes under NSPS, NESHAP, and MACT programs:  
*Any Performance Testing Conducted for the Purposes of Determining and Demonstrating Compliance with the Applicable Standards of 40 CFR Parts 60, 61, and 63 Using Promulgated Test Methods, Other Test Methods or Procedures Cited in the Applicable Subpart(s), or Alternative Test Methods Approved by the Administrator Under §§60.8, 61.13, or 63.7. It Does Not Include Visible Emission Observation Testing.*

2 - 8

### 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)

2 - 9

### 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

2 - 10

### 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

2 - 11

### 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

2 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 2: EPA's EPA's National Stack Testing Guidance

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### 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

2 - 13

### 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<sup>2</sup>

2 - 14

### 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

2 - 15

### 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

2 - 16

### 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

2 - 17

### 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

2 - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 2: EPA's EPA's National Stack Testing Guidance

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### 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

2 - 19

### 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

2 - 20

### 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

2 - 21

### 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

2 - 22

### 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

2 - 23

### 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

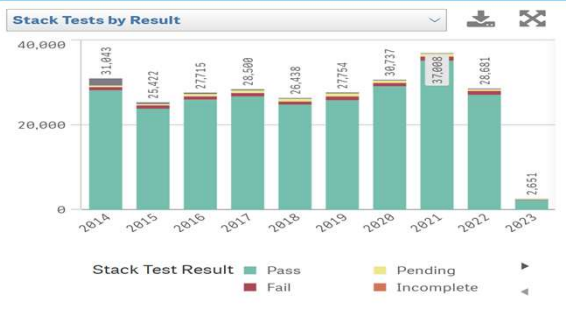
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\*States/EPA have until 12/1 to report FY '08 data 2 - 24

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 2: EPA's EPA's National Stack Testing Guidance

### Analyze Trends: State Air Dashboard

#### Compliance Monitoring Strategy Activities

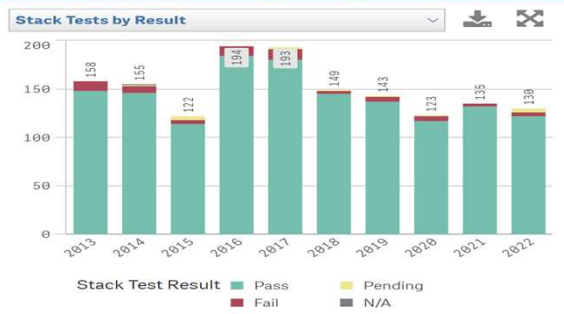


<https://echo.epa.gov/trends/comparative-maps-dashboards/state-air-dashboard>

2 - 25

### Illinois CMS Stack Tests

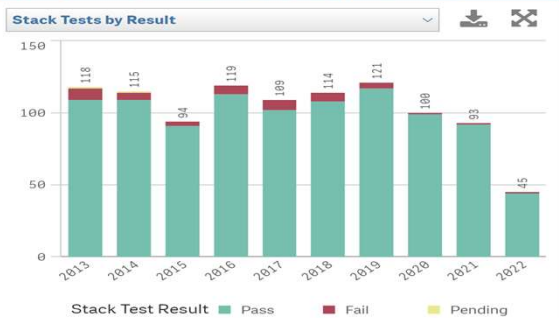
#### Compliance Monitoring Strategy Activities



2 - 26

### New York CMS Stack Tests

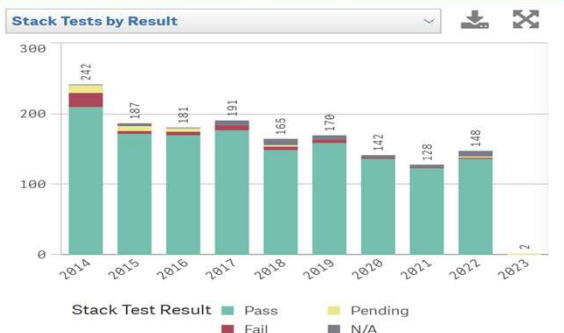
#### Compliance Monitoring Strategy Activities



2 - 27

### Alaska CMS Stack Tests

#### Compliance Monitoring Strategy Activities



2 - 28

### Additional Information

#### ■ Robert Lischinsky

[lischinsky.robert@epa.gov](mailto:lischinsky.robert@epa.gov)

202-564-2628

#### ■ Internet Address:

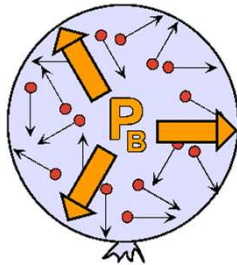
<https://echo.epa.gov/trends/comparative-maps-dashboards/state-air-dashboard?state=IL&view=activity>

2 - 29

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

### Compliance Test and Source Test Observation Properties of Gases



3 - 1

### Properties of Gases

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

3 - 2

### Temperature

- Degrees Fahrenheit: °F
- Degrees Centigrade: °C
- $^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32)$
- $^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32$

3 - 3

### Absolute Temperature

- Degrees Rankine: R
- Degrees Kelvin: K
- $\text{R} = ^{\circ}\text{F} + 459.49$
- $\text{K} = ^{\circ}\text{C} + 273.16$

3 - 4

### Absolute Pressure, P

- $P = P_b + p_g$
- $P_b$  = Barometric pressure
- $P_g$  = Gauge pressure



3 - 5

### Units of Pressure

- in. Hg
- mmHg
- in. H<sub>2</sub>O
- Atmospheres
- Torr
- pascals

3 - 6

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

---

### 1 Atmosphere =

- 29.92 in. Hg
- 39.90 ft H<sub>2</sub>O
- 14.70 lbs/in.<sup>2</sup>
- 760 mmHg
- 1 torr

3 - 7

### EPA Standard Pressure and Temperature

- P<sub>std</sub> = 29.92 in. Hg
- T<sub>std</sub> = 20° C or 68° F

**for source testing**

3 - 8

### 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)

3 - 9

### Molecular Weight, M

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

MW of CO

$$12 + 16 = 28$$

3 - 10

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

3 - 11

1 gram-mole =

$6.023 \times 10^{23}$  molecules  
(Avogadro's Number)

3 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

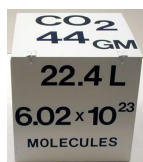
1 mole = Avogadro's Number  
worth of molecules

$(6.023 \times 10^{23})$

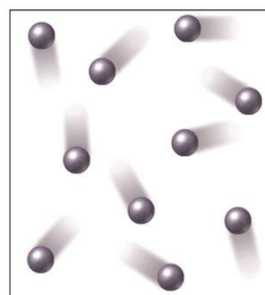
Occupies

22.4 L

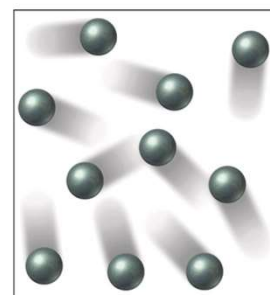
At 0° C and 1 atmosphere



3 - 13



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

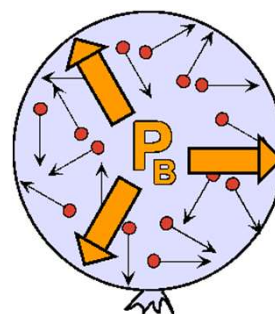
3 - 14

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

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

3 - 15

### The Ideal Gas Law



3 - 16

### The Ideal Gas Law

$$PV = nRT$$

Absolute Pressure points to P  
Volume points to V  
# moles points to n  
Absolute Temperature points to T  
Ideal Gas Law constant points to R

3 - 17

### R

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

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

3 - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

Correcting Volume to Standard Conditions

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

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

3 - 19

Dividing top by bottom gives

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

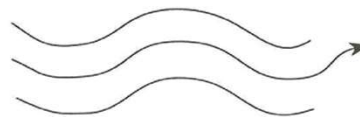
3 - 20

Properties of Moving Gases

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

3 - 21

Velocity



$$V_s = \text{ft/sec or ft/hr}$$

3 - 22

Velocity,  $V_s$ ,  $\frac{\text{ft}}{\text{sec}}$ ,  $\frac{\text{ft}}{\text{hr}}$

Determined by Method 2 using the  
Type S pitot tube

3 - 23

The Pitot Tube Equation

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

USEPA Method 2, Eq. 2-7

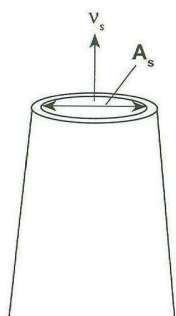
3 - 24



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

### Volumetric Flow Rate



$$Q_s = V_s A_s$$

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

or

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

3 - 25

### Isokinetic Sampling

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

3 - 26

### FRM 5 Isokinetic Rate Equation

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

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

3 - 27

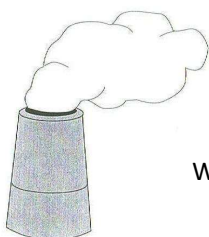
### FRM 5 Isokinetic Rate Equation (Simplified)

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

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

3 - 28

### Pollutant Mass Rate (pmr)



$$pmr = c_s Q_s$$

Where:  $c_s$  = the pollutant concentration

3 - 29

### Concentration, $c_s$

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

Units: g/m<sup>3</sup>, lbs/ft<sup>3</sup>, gr/ft<sup>3</sup>, ppm

Note : 7000 grains (gr) = 1 lb

3 - 30

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 3: Introduction to Stack Testing and Gas Physics

$$pmrS = c_s Q_s$$

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

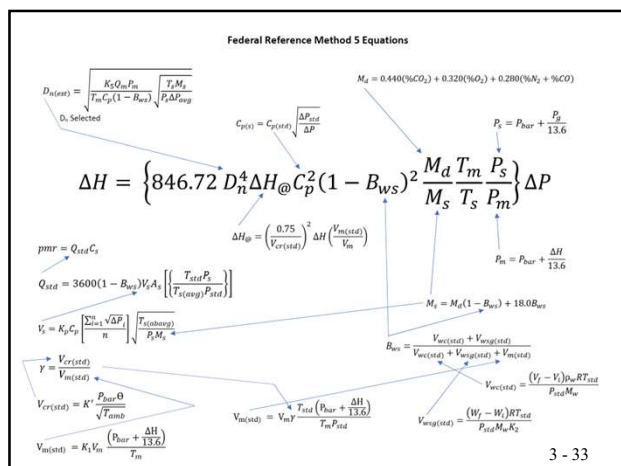
3 - 31

Emission Rate  
(Combustion Sources)

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

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

3 - 32

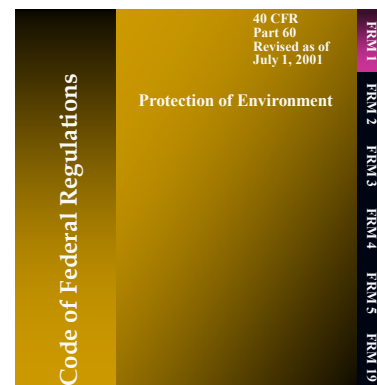


# APTI #450/468 Compliance Test and Source Test Observation

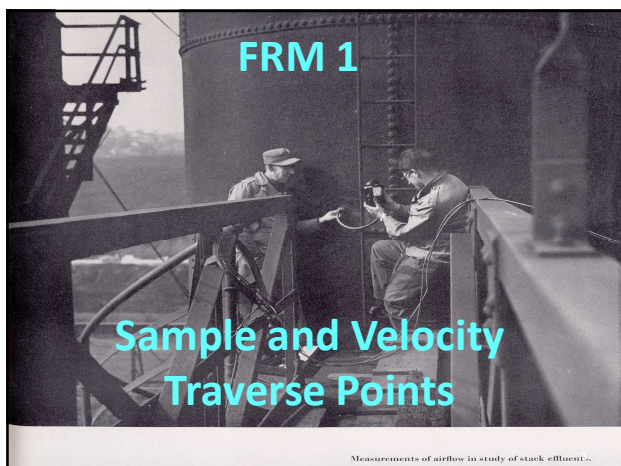
## Lesson #4A: *FRM 1*: Sampling/Velocity Traverse Points

### Compliance Test and Source Test Observation

#### *FRM 1: Sampling/Velocity Traverse Points*



4A - 2



### 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

4A - 5

### 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

4A - 6

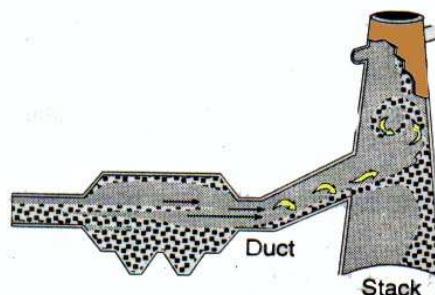
# APTI #450/468 Compliance Test and Source Test Observation Lesson #4A: *FRM 1*: Sampling/Velocity Traverse Points

## FRM 1 Basic Principle

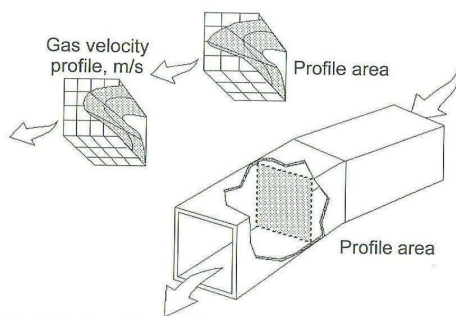
- "...the more convoluted the ductwork, the more points will need to be tested."
- Representative measurement
- Modifications to FRM 1
  - Rectangular stacks
  - Only measuring velocity
  - Stacks smaller than 12 inches

4A - 7

## FRM 1 Sampling Site Locations



## Particle mass concentration profile, $\text{mg}/\text{m}^3$



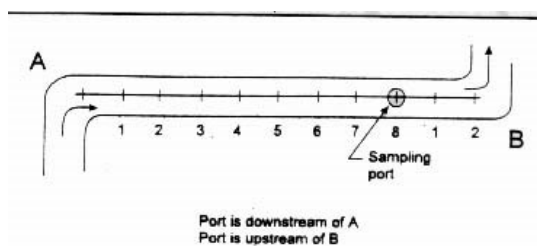
Source: Adapted from Buhne, 1977

4A - 9

## FRM 1 Siting Criteria



## Ideal Siting Criteria



## FRM 1 Applicability

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

4A - 12

### **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<sup>2</sup> (113 in<sup>2</sup>), Use Method 1A

4A - 13

### **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)

4A - 14

### **FRM 1 Flow Disturbance**

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

4A - 15

### **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

4A - 16

### **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

4A - 17



# APTI #450/468 Compliance Test and Source Test Observation Lesson #4A: *FRM 1*: Sampling/Velocity Traverse Points



## 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

4A - 19

## FRM 1 Siting Criteria

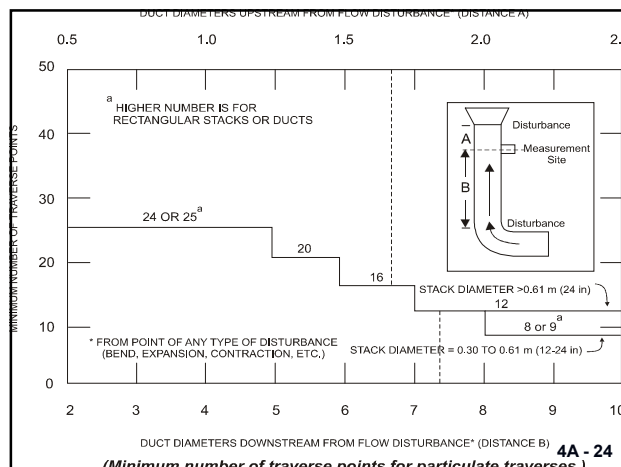
- The minimum number of sampling points can be used
  - 8 or 9 for 12-24 in. stacks
  - 12 for > 24 in. stacks

4A - 22

## 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)

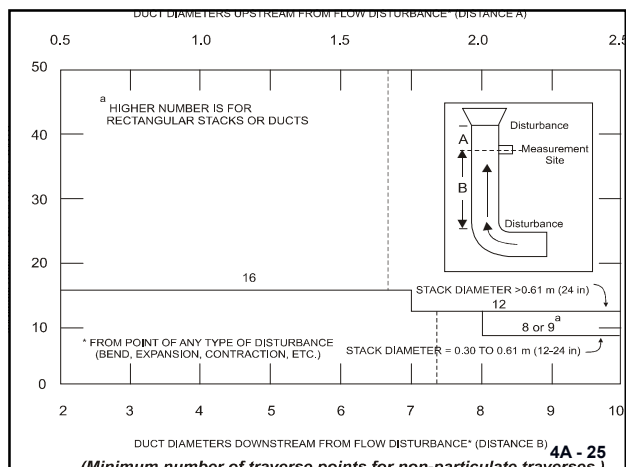
4A - 23





# APTI #450/468 Compliance Test and Source Test Observation

## Lesson #4A: FRM 1: Sampling/Velocity Traverse Points



### 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.”

4A - 26

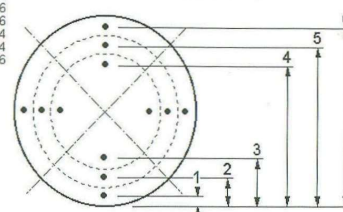
Table 1 - 2 Location of Traverse Points in Circular Stacks (Percent of stack diameter from inside wall to traverse point)		Number of traverse points on a diameter											
Traverse point on a diameter		2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1	
2	85.4	25.0	14.6	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		83.3	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	36.8	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

4A - 27

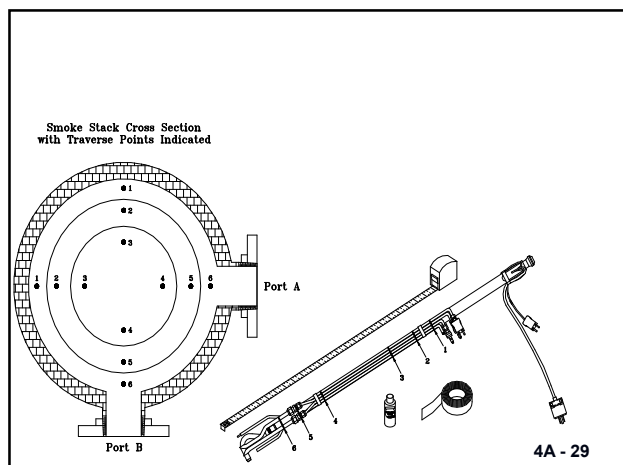
Pt. 60, App. Meth. 1

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

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



4A - 28





### 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

4A - 31



4A - 32

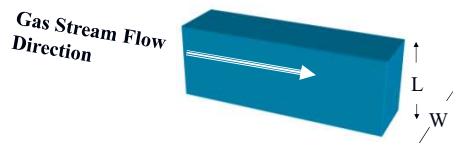
### FRM 1 Rectangular Ducts

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

4A - 33

### FRM 1 Diameter Equivalent Formula for Rectangular Ducts

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

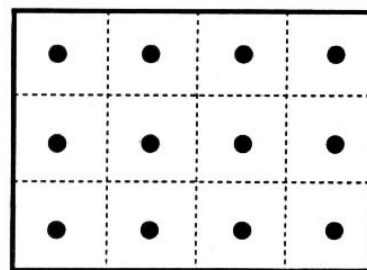


**Table 1–1 Cross-section Layout For  
Rectangular Stacks 40CFR Part 60 Appendix A**

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

4A - 35

### Rectangular Duct (3 X 4)



4A - 36

### **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.

4A - 37

### **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

4A - 38

### **Cyclonic Flow Determination (Ducts >4in.)**

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

4A - 39

### **FRM 1 Alternative Measurement Site Selection Procedure**

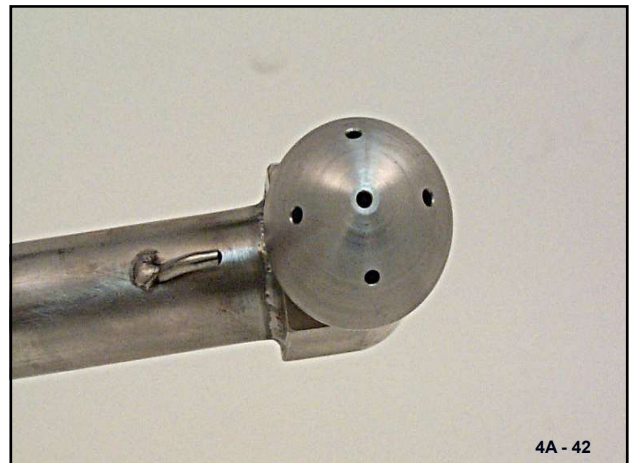
- Applies at sites  $< 2/0.5$  siting
  - Must use "directional probe" to measure "yaw" and "pitch" angles at more than 40 traverse points
  - Calculate Resultant Angle ( $R_i$ )
    - $R_i = \text{Arccos}[(\cos Y_i)(\cos P_i)]$
    - If  $R_i < 20$  degrees, then can use sample location

4A - 40

### **Method 2F Equipment**

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

4A - 41



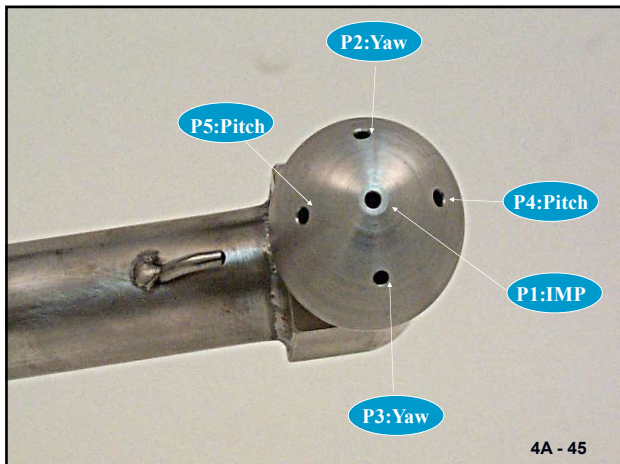
4A - 42



### 3-D Probe Measurements

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

4A - 44



### 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

4A - 46

### 3-D Probe Measurement

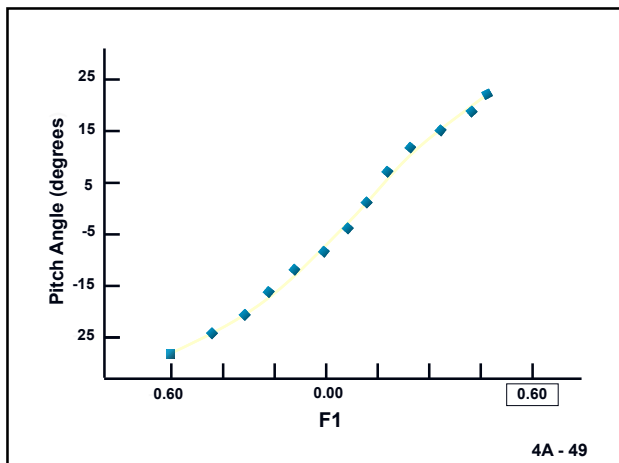
- Yaw to "null"; Record gauge reading yaw angle ( $Y_i$ ) at traverse point.
- Record gauge reading pitch angle and determine pitch angle ( $P_i$ ) from calibration curve.
- Complete for each traverse point.
- Calculate Resultant Angle ( $R_i$ )
  - $R_i = \text{Arccos}[(\cos Y_i)(\cos P_i)]$

4A - 47

### 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)

4A - 48



### 3-D Probe Measurement For Acceptance Criteria

- Calculate Resultant Angle ( $R_i$ )
  - $R_i = \text{Arccos}[(\cos Y_i)(\cos P_i)]$
- Measurement location is acceptable if
  - $R_{i\text{avg}} \leq 20$  degrees
  - $S_d = 10$  degrees

4A - 50

### 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)

4A - 51

### 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

4A - 52

### 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)

4A - 53

### 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)

4A - 54

### **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)

4A - 55

### **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)

4A - 56

### **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

4A - 57

### **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

4A - 58

### **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

4A - 59

### **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

4A - 60

**Dismiss Stack Test FRM 1**

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

4A - 61

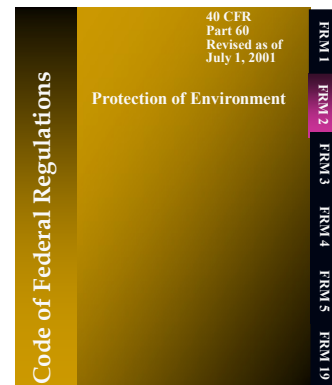
# APTI #450/468 Compliance Test and Source Test Observation Lesson 4B: FRM 2: Stack Gas Velocity

## Compliance Test and Source Test Observation

### FRM 2: Stack Gas Velocity



4B - 1



4B - 2

## POLLUTANT MASS RATE

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

$$\overline{Q}_s = A_s \overline{v}_s$$

$$\overline{c}_s = \frac{m_n}{V_m}$$

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

$$\overline{v}_s = \overline{v}_n$$

Isokinetic Conditions

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

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

4B - 3

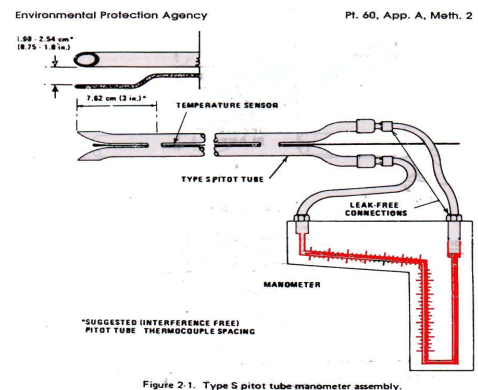


Figure 2-1. Type S pitot tube manometer assembly.

4B - 4



4B - 5

## 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

4B - 6



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 4B: FRM 2: Stack Gas Velocity

### FRM 2 History

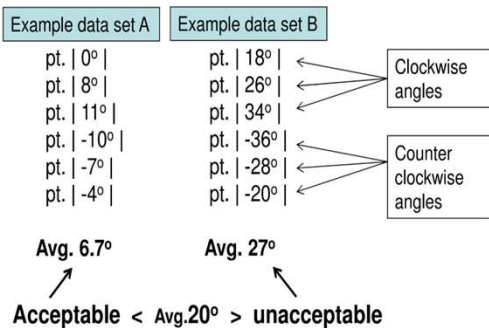
- 1970 Promulgation of FRM 2
- 1983 FRM 2A in Small Ducts
- 1983 FRM 2B Stoichiometry Flow
- 1989 FRM 2C Std Pitot Small Ducts
- 1989 FRM 2D Rate Meter
- 1996 FRM 2E Landfills
- 1999 FRM 2F 3-D Yaw/Pitch Angle
- 1999 FRM 2G Type S/3-D
- 1999 FRM 2H Wall Effects

4B - 7

### 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

4B - 8



4B - 9

### 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:
  - $\Delta p > 0.05$  " water, then 0-10 " manometer adequate
  - $\Delta p < 0.05$  " water, then use manometer with 0.005 /division (i.e., micro-manometer)
  - $\Delta p < 0.01$  "water, then use high sensitivity transducer such as Hasting Thermo Probe<sup>11</sup>

### Interference-Free Component Arrangement

- Pitot tube distance to nozzle: >3/4 inches for 1/2 nozzles
- Center of nozzle and pitot tube opening aligned
- Thermocouple location to pitot tube > 3/4 inch for 3 inches
- Back-recess thermo. > 2 inches
- Gas sampling assembly > 3 inches from pitot tube

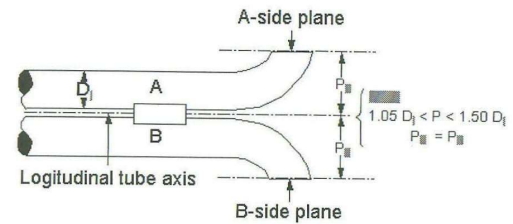
4B - 12

## Type S Pitot Tube

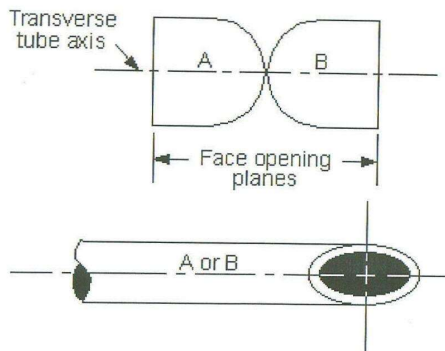
Design criteria for assigning

$$C_p = 0.84$$

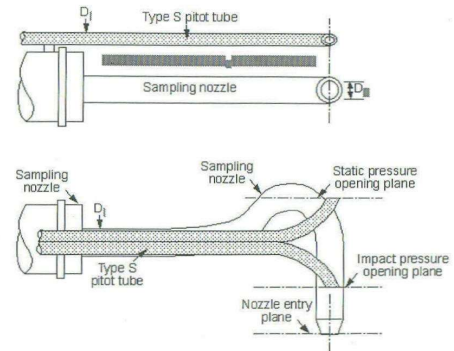
4B - 13



4B - 14

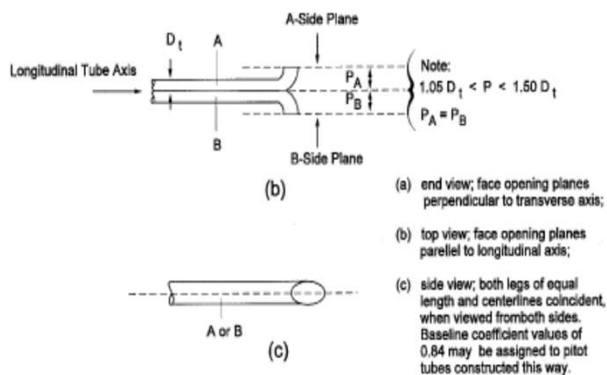


4B - 15



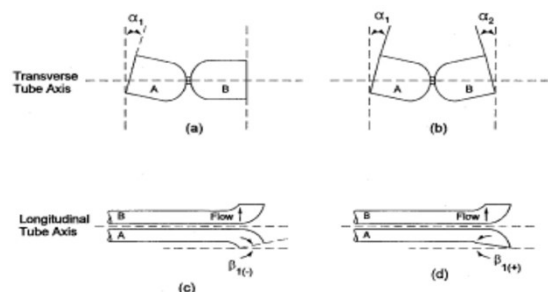
4B - 16

### ■ Properly Constructed S-type Pitot Tube



4B - 17

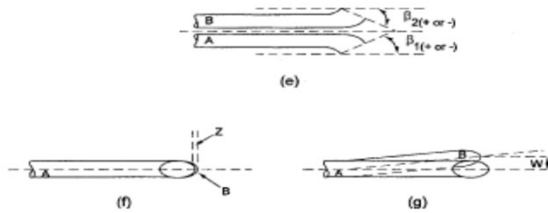
### ■ Types of face opening mis-alignments that can result from field use or improper construction of type S pitot tubes



4B - 18

# APTI #450/468 Compliance Test and Source Test Observation Lesson 4B: FRM 2: Stack Gas Velocity

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



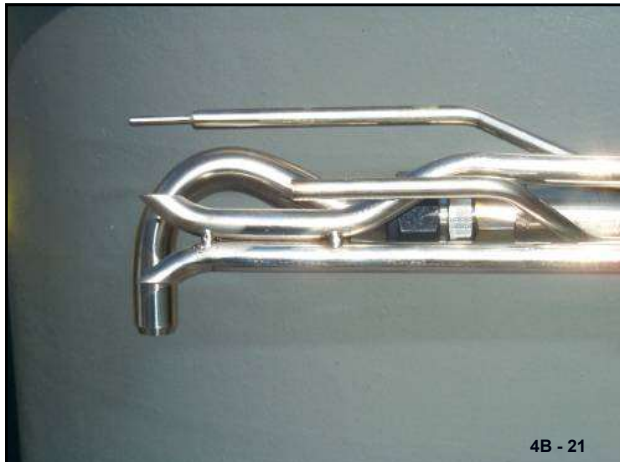
The types of face-opening misalignment shown above will not affect the baseline value of  $C_{p_{avg}}$  so long as  $\alpha_1$  and  $\alpha_2 \leq 10^\circ$ ,  $\beta_1$  and  $\beta_2 \leq 5^\circ$ ,  $z \leq 0.32$  cm (1/8 in.), and  $w \leq 0.08$  cm (1/32 in.) (Reference 11.0 in Section 16.0)

4B - 19

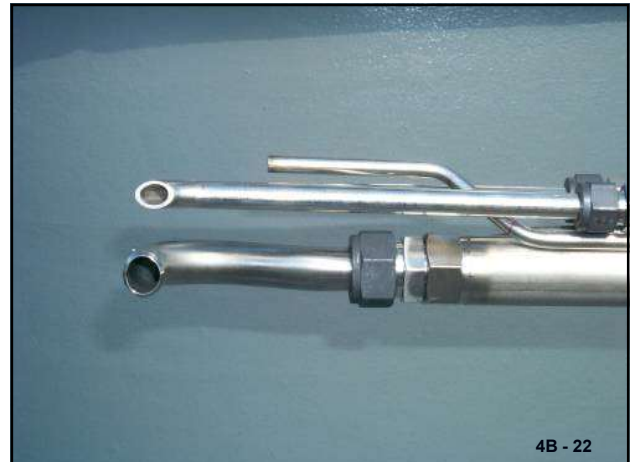
## Verification of Geometry of Type S Pitot Tube To Assign 0.84

- $\alpha$  1 and 2 (+/- 10 degrees)
- $\beta$  1 and 2 (+/- 5 degrees)
- $Z = \leq 0.125$  inches
- $W = \leq 0.031$  inches
- $P_a$  and  $P_b$  0.263 to 0.375
- $D_t = 0.188$  to 0.375

4B - 20



4B - 21



4B - 22

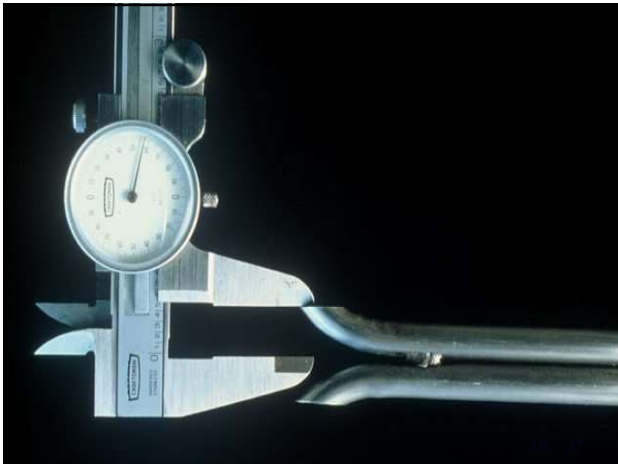
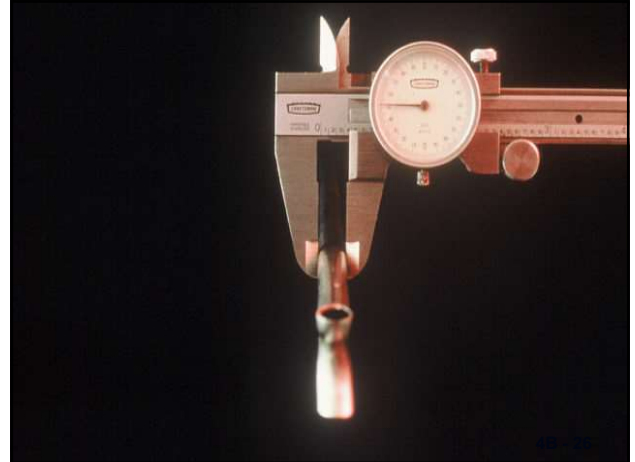
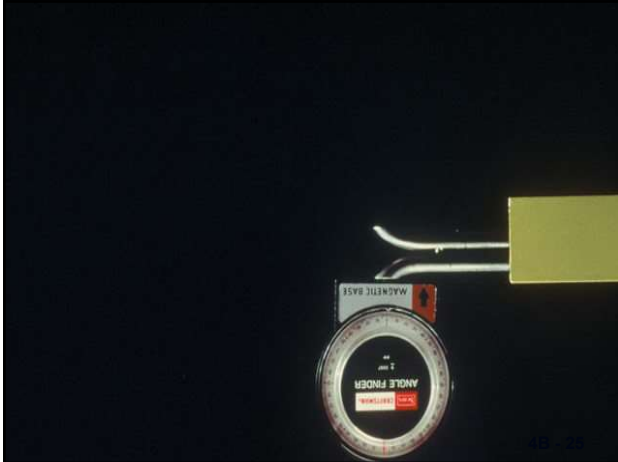


4B - 23



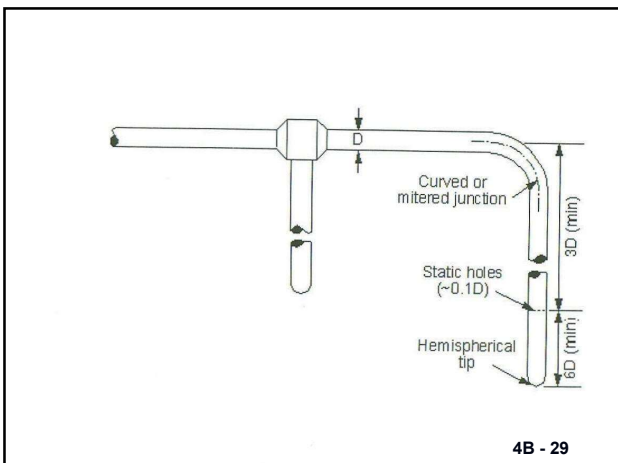
**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 4B: FRM 2: Stack Gas Velocity**

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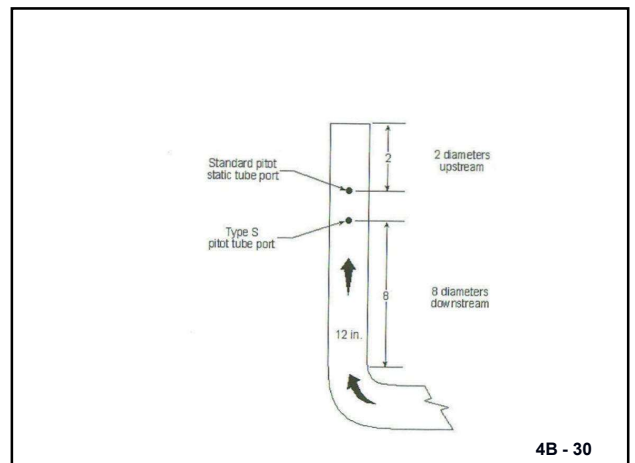


**Type S Pitot Tube  
Calibrate Using a  
Standard Pitot Tube  
and  
Wind Tunnel**

4B - 28



4B - 29



4B - 30

### Pitot Tube Calibration Equation

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

4B - 31

### Pitot Tube Calibration Data Sheet

4B - 32

### 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.

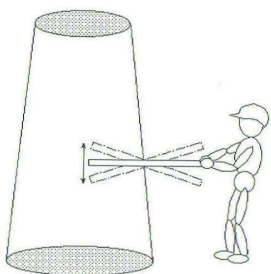
4B - 33

### 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.

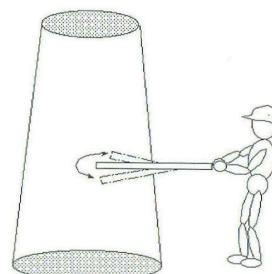
4B - 34

### Pitch Angle



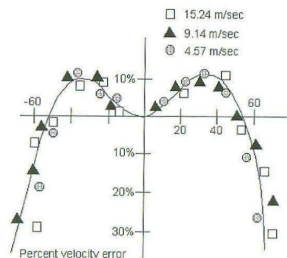
4B - 35

### Yaw Angle



4B - 36

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



4B - 37

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

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

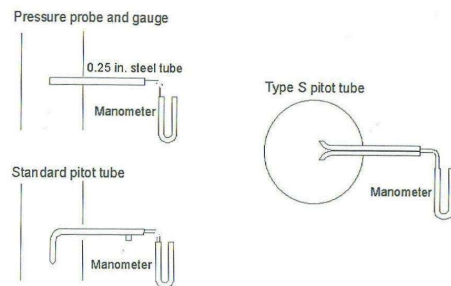
4B - 38

### Average Stack Gas Dry Volumetric Flow Rate

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

4B - 39

### Static Pressure Measurements



4B - 40

### Stack Pressure ( $P_s$ )

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

4B - 41

### 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.

4B - 42

### Pressure Probe and Gauge

Static pressure measurement must be accurate to within 1 in. Hg (13.6 in. H<sub>2</sub>O).

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

4B - 43

### Applicability

Method 2 is applicable only at sites that:

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

4B - 44

### 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.

4B - 45

### 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

4B - 46

### FRM 2 Velocity Equation

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

4B - 47

### FRM 2 Inspector Tools

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

4B - 48



### **FRM 2 Inspector Tools**

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

4B - 49

### **Major Points in FRM 2**

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

4B - 50

### **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)

4B - 51

### **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)

4B - 52

### **Major Points in FRM 2**

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

4B - 53

### **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)

4B - 54

### **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)

4B - 55

### **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)

4B - 56

### **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)

4B - 57

### **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)

4B - 58

### **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

4B - 59

# APTI #450/468 Compliance Test and Source Test Observation Lesson 5A Stack Test Basics – FRM 3

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 %CO<sub>2</sub>, %O<sub>2</sub>, and %CO)



5A - 1

## POLLUTANT MASS RATE

$$\begin{aligned} \overline{PMR}_s &= \overline{c}_s Q_s \\ &= \overline{c}_s v_s \\ &= \overline{c}_s v_n \quad \text{for} \\ &\quad \text{Isokinetic Conditions} \\ v_s &= K_p C_p \sqrt{\frac{T_s \Delta p}{M_s P_s}} \end{aligned}$$

Obtain  $C_p, T_s, \Delta p$   
 $M_s, P_s$

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

5A - 2

## Federal Reference Method 3 History

- 1970FRM 3      Promulgated
- 1986FRM 3A    Instrumental
- 1990FRM 3B    Orsat for Correction Factor and Excess Air (F<sub>o</sub>- Factor)
- 1996FRM 3C    Landfill Gas

5A - 3

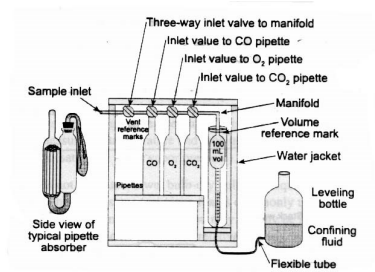
## Federal Reference Method 3

- Gas analysis: measuring percent of CO<sub>2</sub>, percent of O<sub>2</sub> and percent of CO to determine the dry molecular weight of the flue gas (using Orsat Apparatus)

5A - 4

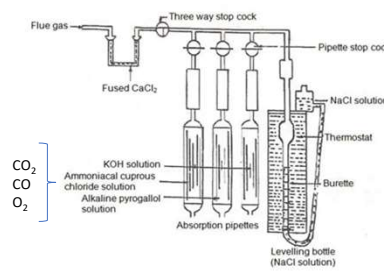
## Orsat Analyzer

**Oxidation  
Reduction  
Selective  
Absorption  
Technique**



5A - 5

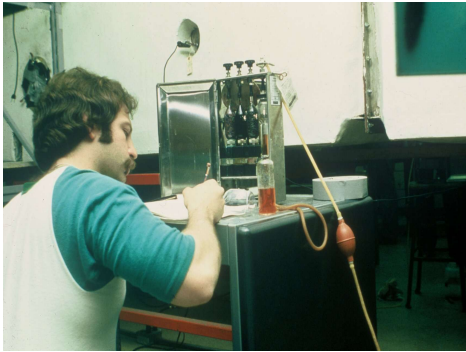
## Orsat Analyzer



5A - 6

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 5A Stack Test Basics – FRM 3



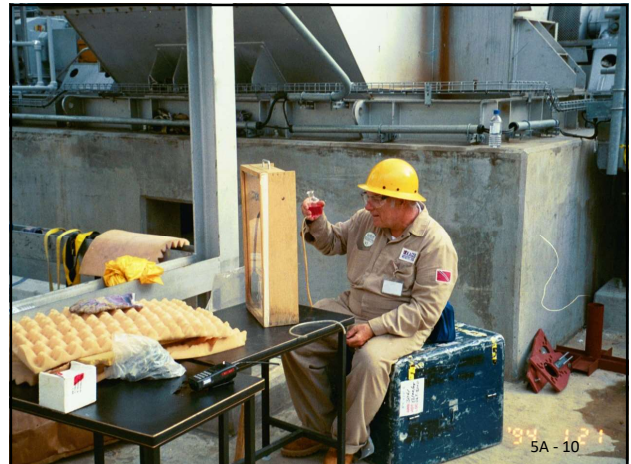
5A - 7



5A - 8



5A - 9



5A - 10

### Fyrite Gas Analyzer



5A - 11



5A - 12

# APTI #450/468 Compliance Test and Source Test Observation Lesson 5A Stack Test Basics – FRM 3

## FRM 3 Sampling Techniques

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

5A - 13

## Single-Point Grab Sampling Train

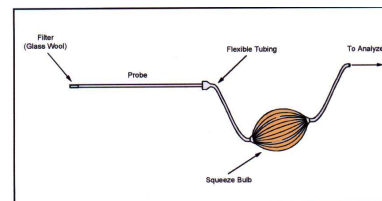


Figure 3-1. Grab-Sampling Train.

5A - 14

## Single-Point Integrated Sampling Train

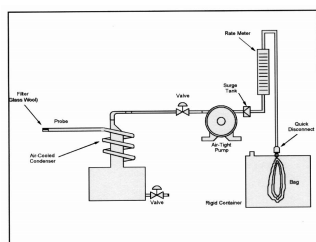
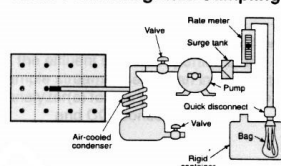


Figure 3-2. Integrated Gas-Sampling Train.

5A - 15

## Multi-point Integrated Sampling Train

### Multi-Point Integrated Sampling



5A - 16

## 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<sub>2</sub>, 6 % O<sub>2</sub>)
- For emission rate calculations (F-factor)
- For molecular weight determination

5A - 17

## 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<sub>2</sub> = present CO<sub>2</sub> by volume (dry basis)

%O<sub>2</sub> = present O<sub>2</sub> by volume (dry basis)

%CO = present CO by volume (dry basis)

%N<sub>2</sub> = present N<sub>2</sub> by volume (dry basis)

0.44 = molecular weight of CO<sub>2</sub> divided by 100

0.32 = molecular weight of O<sub>2</sub> divided by 100

0.28 = molecular weight of N<sub>2</sub> divided by 100

5A - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 5A Stack Test Basics – FRM 3

### 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<sub>2</sub> or % CO<sub>2</sub>

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

5A - 19

### Method 3 Data Uses

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

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

5A - 20

### Problems with FRM 3

- Leak in pump or bag
- Process gives off CO<sub>2</sub> or O<sub>2</sub>
  - Cement plant- Cannot validate F<sub>o</sub>
  - FGD scrubber- Cannot validate F<sub>o</sub>
- Incomplete combustion cannot validate F<sub>o</sub>- Too low for fuel
- Processes removing CO<sub>2</sub> or O<sub>2</sub>

5A - 21

### FRM 3B Equations

#### *Fuel Factor*

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

#### *Excess Air*

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

5A - 22

### FRM 3B F<sub>o</sub> 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

5A - 23

### FRM 3 Major Points

- Applicability (Sec. 1.2)
- Method modifications (Sec. 1.2)
  - A multi-point sampling method/ Orsat at each point
  - Using CO<sub>2</sub> or O<sub>2</sub> and stoichiometric calculations
  - Assigning value of 30.0

5A - 24

### 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

5A - 25

### 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 Fryite (Method 3B)
- Triplicate trials

5A - 26

### FRM 3 Inspector Tools

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

5A - 27

### 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 ( $P_g$ ):  $P_g/13.6$

5A - 28

### 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.)

5A - 29

### FRM 3 Tips

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

5A - 30



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 5A Stack Test Basics – FRM 3

---

#### 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
  - $\pm 0.3\%$  if  $\text{CO}_2 > 4\%$
  - $\text{O}_2 < 15\%$
  - then  $\pm 0.2\%$

5A - 31

#### Dismiss FRM 3 Stack Test

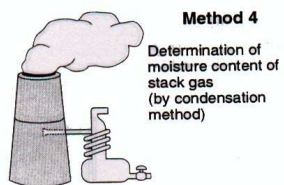
- Failed to calibrate Orsat analyzer
- Tedlar bag found to be leaking
- $F_o$  outside of  $\pm 5\%$  of calculated value
- $\text{O}_2/\text{CO}_2$  outside of typical range

5A - 32

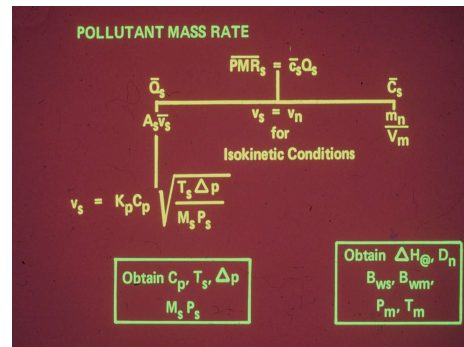
# APTI #450/468 Compliance Test and Source Test Observation Lesson 5B Stack Test Basics - FRM 4

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

### Stack Test Basic Continued



5B - 1

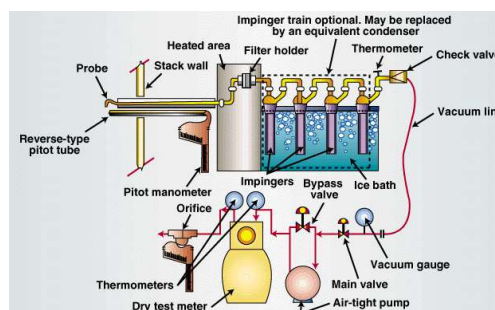


5B - 2

## Two Methods in FRM 4

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

5B - 3



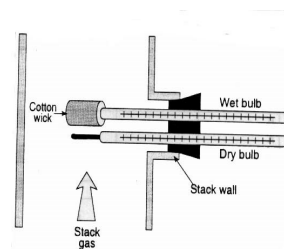
5B - 4

## Federal Reference Method 4



5B - 5

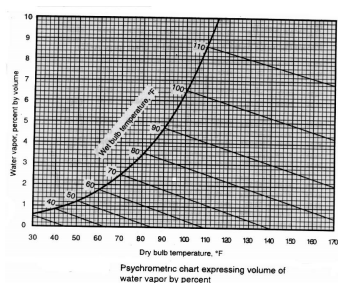
## Wet Bulb/Dry Bulb



5B - 6

# APTI #450/468 Compliance Test and Source Test Observation Lesson 5B Stack Test Basics - FRM 4

## Psychrometric Chart



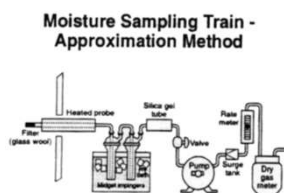
5B - 7

## Calculating % Moisture Under Saturated Gas Stream

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

5B - 8

## FRM 4 Approximate Method Sampling Train



5B - 9

Bws = Proportion of water vapor in the gas stream.  
(by volume)

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

5B - 10

## 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)

5B - 11

## 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)

5B - 12

#### 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)

5B - 13

#### 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

5B - 14

#### FRM 4 Inspector Tools

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

5B - 15

#### 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
- Condensables other than water leads to positive bias in results (i.e., acid aerosols and condensable organics)
- Stack gases that are supersaturated or no demisting

5B - 16

#### 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

5B - 17

APTI #450/468 Compliance Test and Source Test Observation  
Lesson 6: FRM 5: Particulate Emissions Sampling

Compliance Test and Source Test  
Observation  
*FRM 5: Particulate Emissions*



6 - 1



6 - 2

Federal Reference Method 5  
Sampling Train



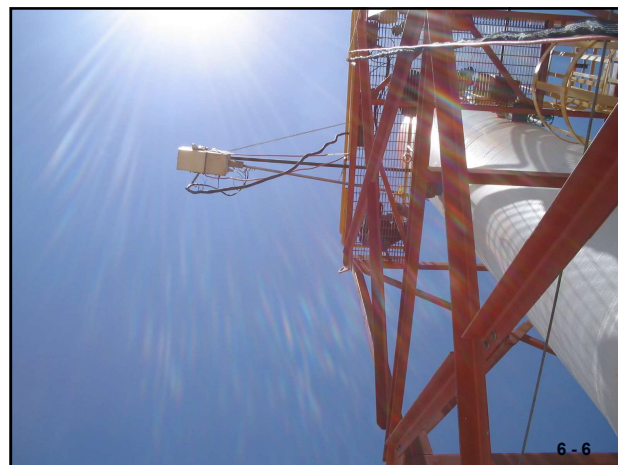
6 - 3



6 - 4



6 - 5



6 - 6



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 6: FRM 5: Particulate Emissions Sampling



6 - 7

### FRM 5 Sampling Train

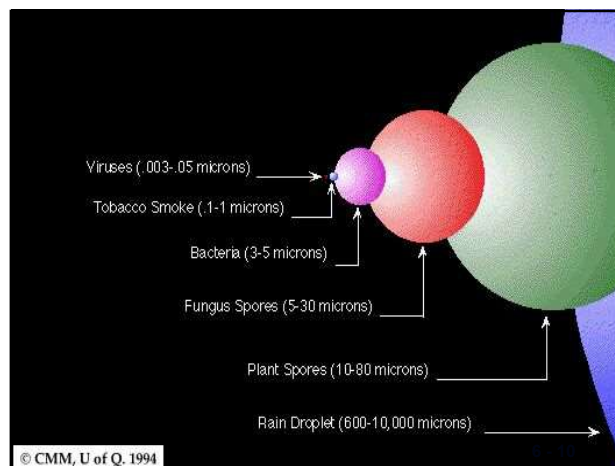


6 - 8

### Particles

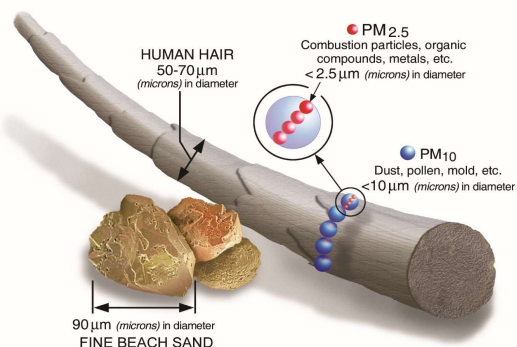
PM stands for particulate matter (also called particle pollution): the term for a mixture of solid particles and liquid droplets found in the air. Some particles, such as dust, dirt, soot, or smoke, are large or dark enough to be seen with the naked eye. Others are so small they can only be detected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

6 - 9



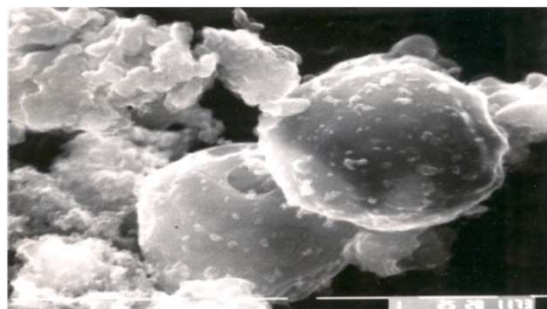
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### Size comparisons for PM particles



6 - 11

### 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.)

6 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 6: FRM 5: Particulate Emissions Sampling

**Air Contaminants**

Figure 1 Characteristics of Particles and Particle Dispersoids

Particle Diameter, micrometers (μm)

Particle Diameter (μm)	Source	Health Effects	Measurement Method
0.1 - 0.5	Resuspension of road dust, construction activities	Respiratory irritation, exacerbation of asthma	Gravimetric, optical
0.5 - 2.5	Combustion of fossil fuels, industrial processes	Respiratory irritation, exacerbation of asthma	Gravimetric, optical
2.5 - 10	Combustion of fossil fuels, industrial processes	Respiratory irritation, exacerbation of asthma	Gravimetric, optical
10 - 100	Combustion of fossil fuels, industrial processes	Respiratory irritation, exacerbation of asthma	Gravimetric, optical
100 - 1000	Combustion of fossil fuels, industrial processes	Respiratory irritation, exacerbation of asthma	Gravimetric, optical

6 - 13

### 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 PM<sub>2.5</sub> continue to the lungs.
3. PM<sub>2.5</sub> can penetrate deep into the lungs, having serious health consequences for the lungs and heart.

6 - 14

### Health Effects - Nontoxic Particles

Concentration of Particles in μg/m <sup>3</sup>	Effect
2000 μg/m <sup>3</sup> with 0.4 ppm SO <sub>2</sub> (24-hr avg) episodes of several days duration	Increase in deaths due to bronchitis
1000 μg/m <sup>3</sup> with 0.25 ppm SO <sub>2</sub> (24-hr avg) during episodes	Increase in mortality from all causes including respiratory and cardiac disease
300 μg/m <sup>3</sup> with 0.21 ppm SO <sub>2</sub> (annual avg)	Significant increase in bronchitis symptoms
130 μg/m <sup>3</sup> with SO <sub>2</sub> (annual avg)	Increase in frequency and severity of lower respiratory illness
100-200 μg/m <sup>3</sup> with 0.05 to 0.08 ppm SO <sub>2</sub> (avg seasonal levels)	Increase in incidences of bronchitis reported above this level

6 - 15

### How Do We Define Particulate Matter for Source Emissions?

- TPM?
- FPM?
- FPM-I?
- TPM-PM<sub>10</sub>?
- FPM-I-PM<sub>10</sub>?
- CPM?
- MCEM?

6 - 16

### 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)

6 - 17

### 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

6 - 18



### 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

6 - 19

### 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.

6 - 20

### 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)

6 - 21

### 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 Volatilization of Filter @ 320 °F
- Reserved FRM 5C: Small Ducts (Reserved)
- 1984 FRM 5D: PM @ 248 °F from Positive Fabric Filters

6 - 22

### History of FRM 5

- 1985 FRM 5E: PM @ 248 °F from Mineral Wool Plus Captured Condensable 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 subtraction

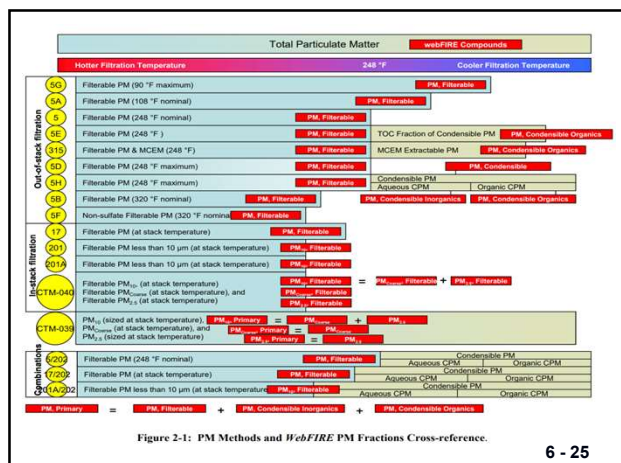
6 - 23

### 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 1<sup>st</sup> filter @ 248 °F, then impingers followed by 2<sup>nd</sup> 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%)

6 - 24

# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling



6 - 25

## Emission Generation Categories

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

6 - 26

## 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.

6 - 27

## 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.

6 - 28

## Solid Waste Disposal

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

6 - 29

## FRM 5 Sampling Train



6 - 30

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

6 - 31

## Simplified Isokinetic Rate Equation

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

6 - 32

## Isokinetic Sampling and Bias

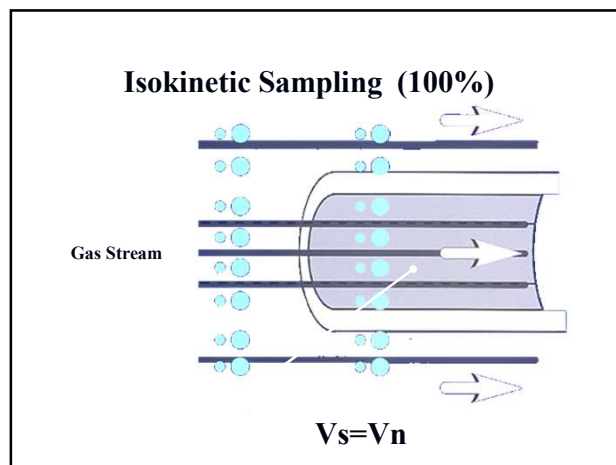
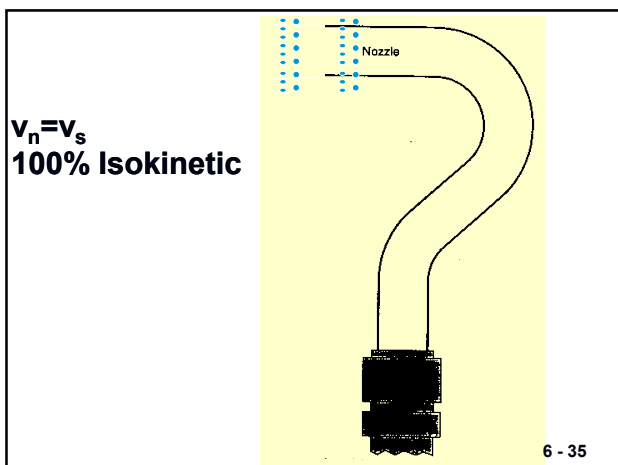
- To obtain average pollutant concentration, need parameters:
  - Quantity of mass emitted from stack
  - Total quantity of volume from stack

6 - 33

## Isokinetic Sampling and Bias

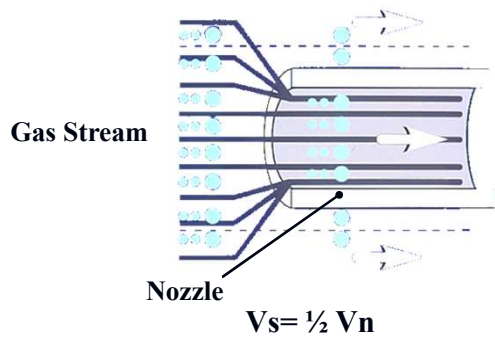
- Isokinetic sampling provides best approach for accurate data
- Pollutant mass rate (pmr)
  - $\text{pmr}_a$  (Ratio-of-areas:  $A_n$  ratio  $A_s$ )
  - $\text{pmr}_c$  (Ratio-of-conc.:  $m_n$  ratio  $A_n$ )

6 - 34

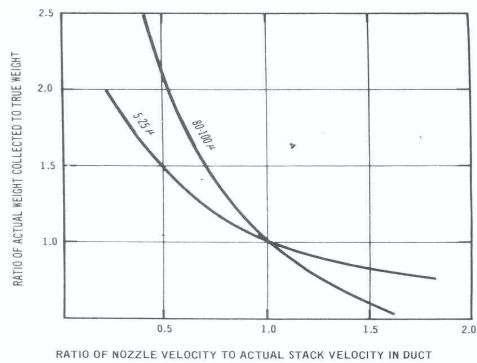
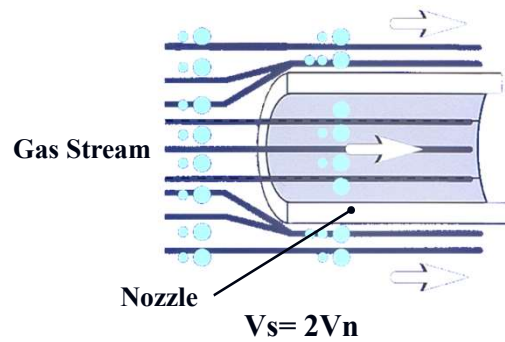


APTI #450/468 Compliance Test and Source Test Observation  
Lesson 6: FRM 5: Particulate Emissions Sampling

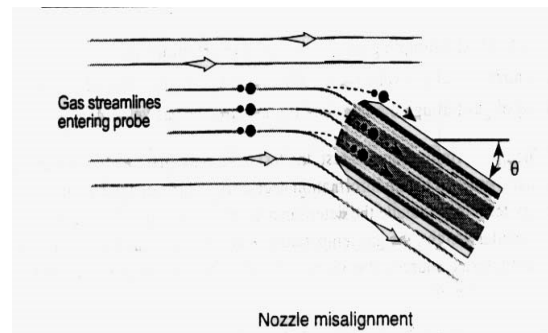
Over Isokinetic Sampling (200%)



Under Isokinetic Sampling (50%)

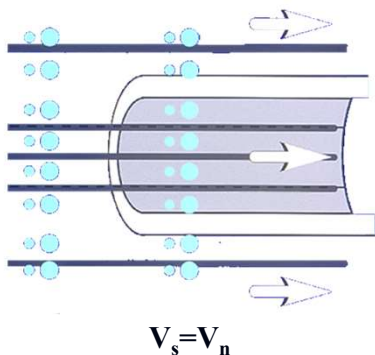


Nozzle Misalignment



6 - 40

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



6 - 41

Isokinetic Sampling

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

6 - 42

### 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

6 - 43

### FRM 5 Isokinetic Rate Equation

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

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

6 - 44

### FRM 5 Isokinetic Rate Equation (Simplified)

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

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

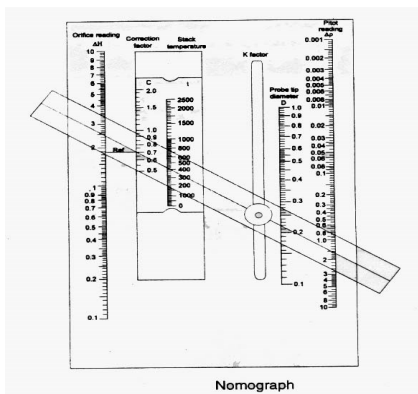
6 - 45

### 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 “ $\Delta p$ ” from the pitot tube and setting the proper “ $\Delta H$ ” on the meter box allows one to sample isokinetically

6 - 46

### FRM 5 Nomograph



6 - 47

### FRM 5 Isokinetic Rate Equation

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

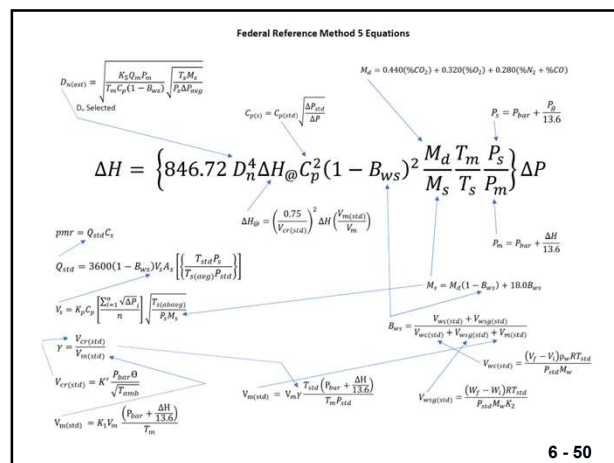
6 - 48

## FRM 5 Operation

### Setting $\Delta H$ Based Upon $\Delta p$ Observation and Calculated K Factor

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

6 - 49



### FRM 5 Causes for not Meeting 100% Isokinetics

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

6 - 51

### FRM 5 Causes for not Meeting 100% Isokinetics

- Moisture value wrong in setting preliminary isokinetic rate equation
- Inability to follow rapid fluctuations in  $\Delta p$  and corresponding calculating/setting  $\Delta H$

6 - 52

### 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

6 - 53

### Difficulty in Maintaining Isokinetics

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

6 - 54

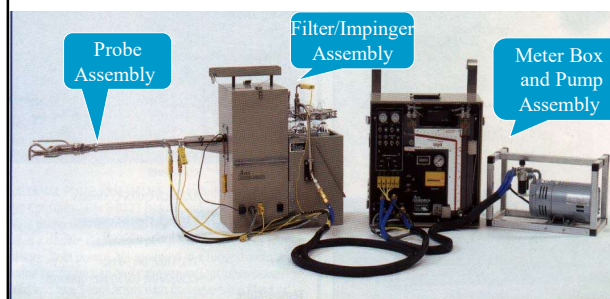


### Difficulty in Maintaining Isokinetics

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

6 - 55

### FRM 5 Sampling Train



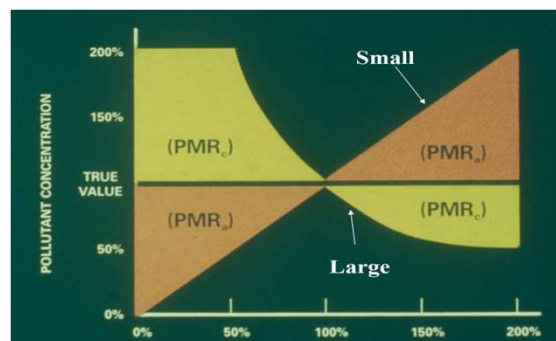
6 - 56

### 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  $A_n$ )

6 - 57

### Percent Isokinetic vs: Pollutant Concentration



6 - 58

### 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
- $\Delta H$ : 5.0 %
- $D_n$ : 1.0 %
- $\Delta H_{@}$ : 1.5 %

6 - 59

### 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.)?

6 - 60



# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling

## 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?

6 - 61

## 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)

6 - 62

ERROR ANALYSIS OF SAMPLING PARAMETERS

Parameter	True value	Error	Erroneous value	Concentration (%) <sup>a</sup>	O <sub>2</sub>	O <sub>2</sub> std	Pollutant mass rate (lb/d) <sup>b</sup>	Requirement
P <sub>bar</sub>	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 <sub>2</sub> O	30.97 in. Hg	+0.2	-	-	+0.2	none
tn	520°F	5°F	525°F	+0.9	-	-	+0.9	45-47°F
P <sub>s</sub>	30 in. Hg	2 in. H <sub>2</sub> O	30.16 in. Hg	+0.1	+0.2	+0.2	+0.3	21-36 in. H <sub>2</sub> O
ts	400°F	10°F	410°F	+0.4	+0.8	+0.8	+1.2	21-56
ΔP	1 in. H <sub>2</sub> O	0.1 in. H <sub>2</sub> O	1.1 in. H <sub>2</sub> O	+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	15 CO <sub>2</sub>	28.15	+0.1	+0.3	+0.3	+0.4	+0.15
Md	29	15 O <sub>2</sub>	29.03	+0.1	+0.1	+0.1	+0.2	+0.15
Md	29	15 CO	29	-	-	-	-	+0.15
Mo	100 mg	1 mg	101 mg	+1.0	-	-	+1.0	20-5 mg
Time	120 min	1 min	121 min	+0.4	-	-	+0.4	none
Y	1.00	0.01	1.01	+1.0	-	-	+1.0	42%
Cp	0.84	0.01	0.85	+1.2	+1.2	+1.2	+0.03	+0.03
Nozzle diameter	0.250 in.	0.005 in.	0.255 in.	+2.0	-	-	+2.0	20-002 in.
Isokinetic	100%	10%	110%	+5.0	-	-	+5.0	+10%
F factor	55 O <sub>2</sub>	15 O <sub>2</sub>	65 O <sub>2</sub>	+6.7%	N/A <sup>c</sup>	N/A <sup>c</sup>	N/A <sup>c</sup>	10-15 O <sub>2</sub>
F factor	105 O <sub>2</sub>	15 O <sub>2</sub>	115 O <sub>2</sub>	+10.1%	N/A <sup>c</sup>	N/A <sup>c</sup>	N/A <sup>c</sup>	10-15 O <sub>2</sub>
F factor	155 O <sub>2</sub>	15 O <sub>2</sub>	165 O <sub>2</sub>	+9.7%	N/A <sup>c</sup>	N/A <sup>c</sup>	N/A <sup>c</sup>	10-15 O <sub>2</sub>

Notes: 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.

<sup>a</sup>Error due to calculation and combined isokinetic bias.

<sup>b</sup>Error due to calculation and combined isokinetic bias.

<sup>c</sup>No effect on the measured value.

<sup>d</sup>lb/10<sup>6</sup> lbs is actually a concentration standard.

<sup>e</sup>N/A - not applicable.

6 - 63

## 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!

6 - 64

## 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!

6 - 65

## 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

6 - 66

# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling

## 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

6 - 67

## FRM 5

- “Front Half” is defined as particulate emissions
- Filter Temperature
  - 248°F
  - 320°F
- Isokinetic Sampling
  - $Velocity_{nozzle} = Velocity_{stack}$
  - 90% - 110%

6 - 68

## FRM Method 5 Limits

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

6 - 69

## 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

6 - 70

## Example

Given the following information use the isokinetic  $\Delta H$  equation to find a  $K$  factor for setting isokinetic rate through the sampling train:

$Q_m = 0.75 \text{ CFM}$   
 $\Delta H_{@} = 1.85$   
 $P_{\text{tote tube } C_p} = 0.85$   
 $t_m = 80^\circ\text{F}$   
 $P_m = 30.0 \text{ in. Hg}$   
 $P_s = 29.6 \text{ in. Hg}$   
 $B_{atm} = 0$   
 $B_{ws} = 0.12$   
 $t_s = 280^\circ\text{F}$   
 $M_d = 29 \text{ lb/lb-mole}$   
 $\text{Average } \Delta p = 0.80 \text{ in. H}_2\text{O}$

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

6 - 71

## Example Problem (cont.)

Ans:

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

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

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

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

$$= .241$$

6 - 72

### Example Problem (cont.)

choose .25" nozzle

then

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

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

$$= 2.59 \Delta p$$

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

.73

### Example Problem (cont.)

What do you do if  $\Delta p = 1.0$

.80  
.60

Say if moving probe from traverse point to traverse point  
— get new  $\Delta p$ 's at each point, calculate and set new  $\Delta H$ 's  
at each point.

How do you set the  $\Delta H$ ?

6 - 74

### FRM 5 Isokinetic Rate Equation

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

6 - 75

### Sampling Train Components

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

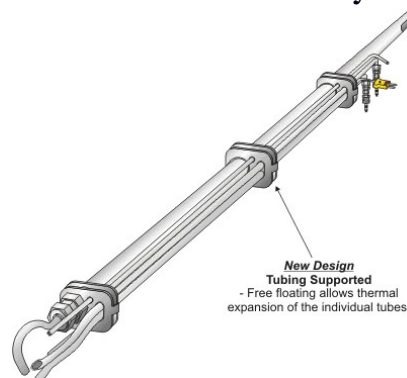
6 - 76

### The Probe Assembly

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

6 - 77

### The Probe Assembly



6 - 78

### **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

6 - 79

### **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

6 - 80

### **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

6 - 81

### **FRM 5 Sampling Probe**

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

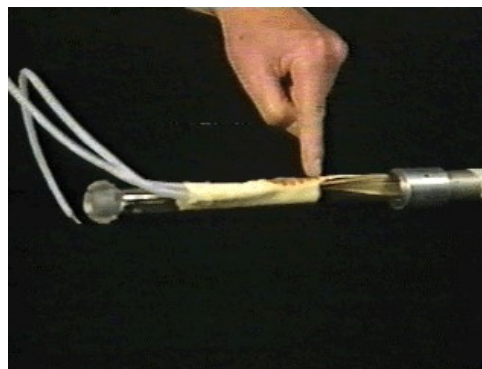
6 - 82

### **Probe Sheath**

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

6 - 83

### **Probe liner and sheath**



6 - 84

### FRM 5 Ceramic Probe Heater



6 - 85



6 - 86



6 - 87



6 - 88

### 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

6 - 89

### 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

6 - 90



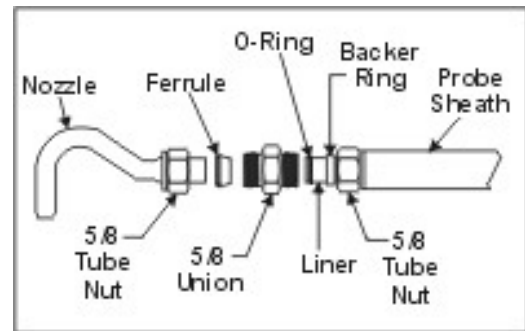
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Lesson 6: FRM 5: Particulate Emissions Sampling

FRM 5 Sampling Nozzle



6 - 91

Sampling Nozzle



6 - 92



6 - 93



6 - 94



6 - 95



6 - 96



6 - 97

### FRM 5 Sample Nozzle

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

6 - 98

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

6 - 99

### FRM 5 Isokinetic Rate Equation (Simplified)

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

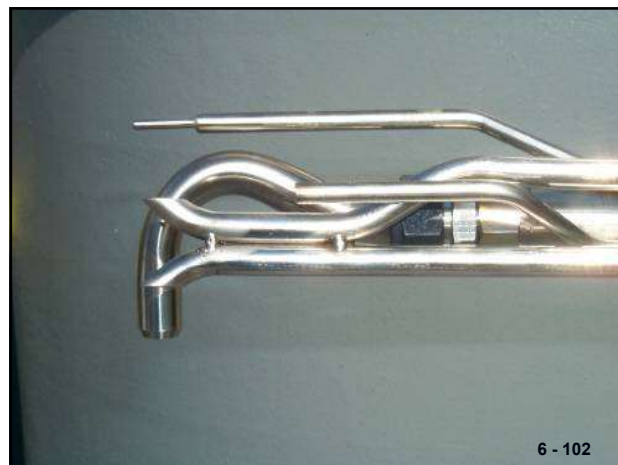
$$\Delta H = \left\{ 846.72 D_n^4 \Delta H_{@} C_p^2 (1 - B_{ws})^2 \frac{M_d}{M_s} \frac{T_m P_s}{T_s P_m} \right\} \Delta P$$

6 - 100

### FRM 5 Nozzle/Pitot Tube/Thermocouple Orientation

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

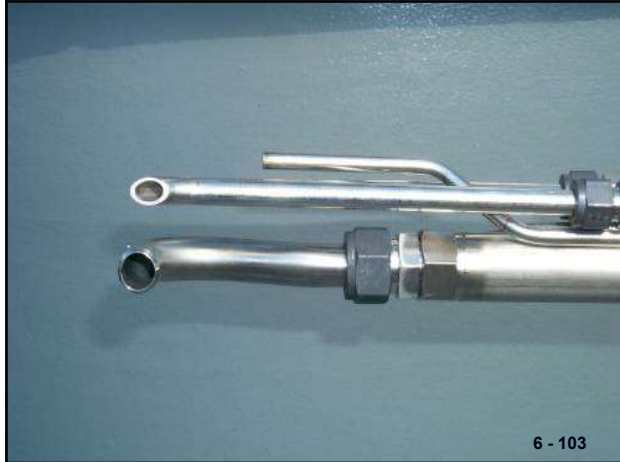
6 - 101



6 - 102



APTI #450/468 Compliance Test and Source Test Observation  
 Lesson 6: FRM 5: Particulate Emissions Sampling

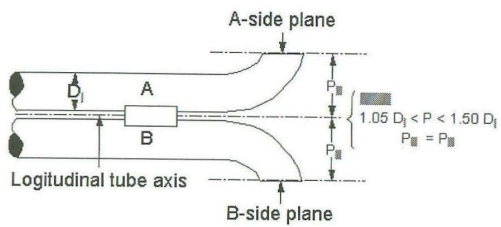


6 - 103

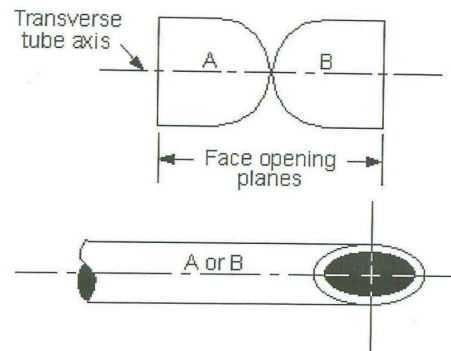
## Type S Pitot Tube

Design criteria for assigning

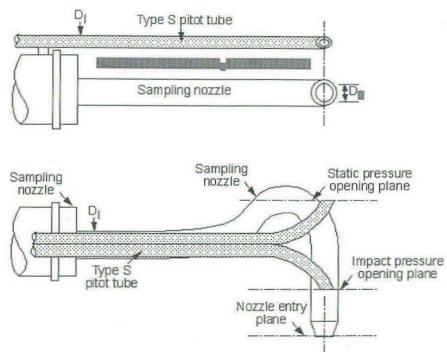
6 - 104



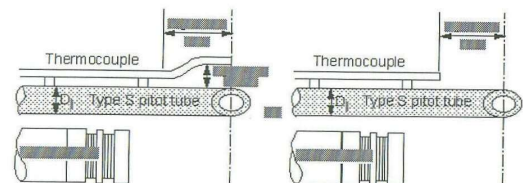
6 - 105



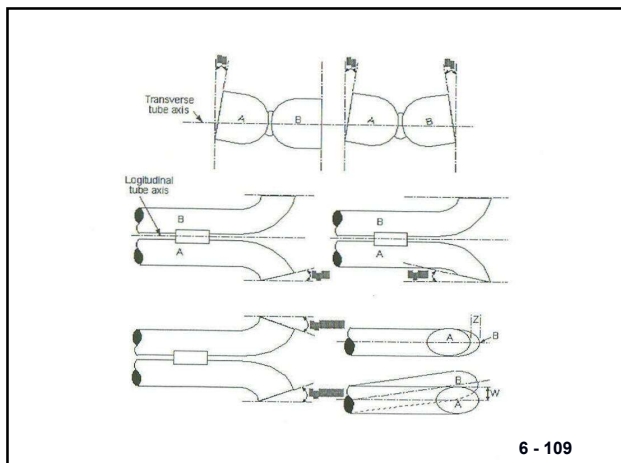
6 - 106



6 - 107



6 - 108



6 - 109

### Verification of Geometry of Type S Pitot Tube To Assign 0.84

- $\alpha$  1 and 2 (+/- 10 degrees)
- $\beta$  1 and 2 (+/- 5 degrees)
- $Z = \leq 0.125$  inches
- $W = \leq 0.031$  inches
- $P_a$  and  $P_b$  0.263 to 0.375
- $D_t = 0.188$  to 0.375

6 - 110

### 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

6 - 111

### FRM 2 Velocity Equation

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

6 - 112

### FRM 5 Sampling Train



6 - 113

### Sampling Train Components

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

6 - 114

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 6: FRM 5: Particulate Emissions Sampling

### 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

6 - 115

### 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

6 - 116



### 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

6 - 121

### 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

6 - 122

### FRM 5 Impinger Assembly



6 - 123



6 - 124



6 - 126



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6: FRM 5: Particulate Emissions Sampling**

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**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)

6 - 133

### 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

6 - 134

### FRM 5 Train Components/pmr Error

- $P_{bar}$ : + 5.9%
- $\Delta p$ : + 2.4%
- Moisture: + 1.4%
- Nozzle diameter: - 2.0%
- Isokinetic rate: - 5.0%

6 - 135

### Sampling Train Components

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

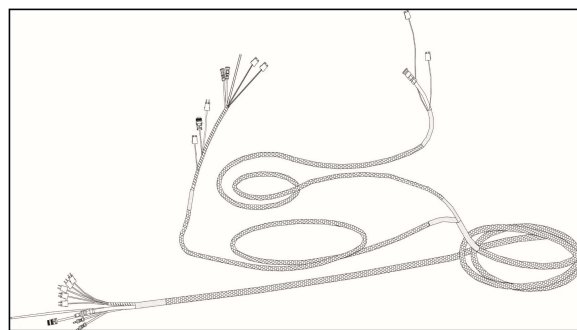
6 - 136

### The Umbilical Line

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

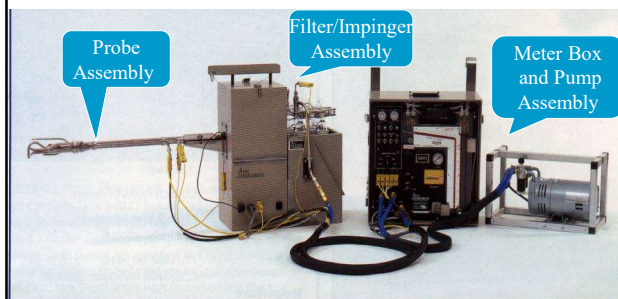
6 - 137

### FRM 5 Transfer Line



6 - 138

### FRM 5 Sampling Train



6 - 139

### Sampling Train Components

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

6 - 140

### The Meter Box

- Pump
- Dry gas meter
- Inclined manometer for  $\Delta p$  and  $\Delta H$  readings
- Flow control valves
- Ports for integrated gas sampling

6 - 141

### FRM 5 Meter Console Desirable Features

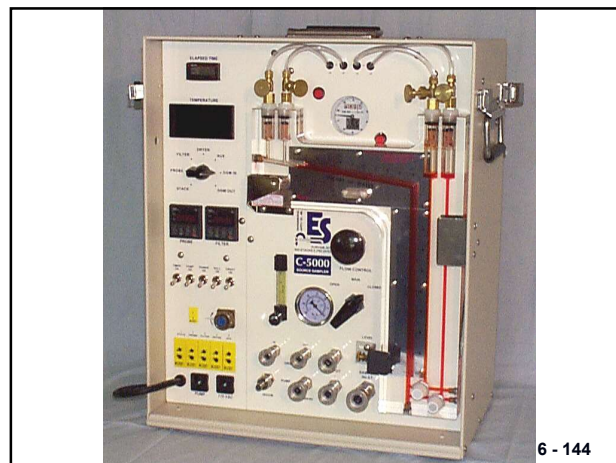
- Light weight
- Reliable leak free pump
- Good temperature controls
- Rugged construction/  
good carrying handles

6 - 142

### FRM 5 Meter Console Desirable Features

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

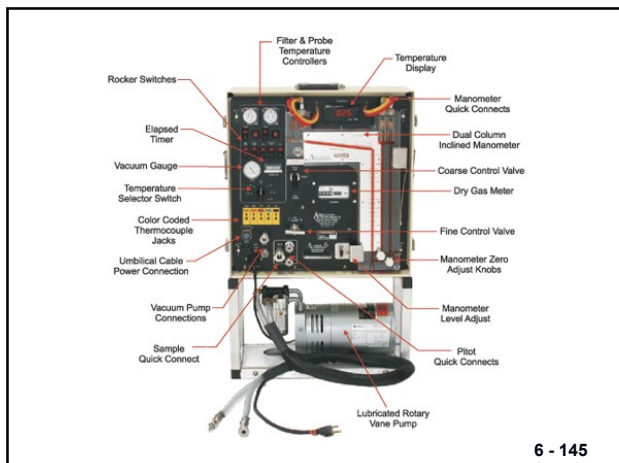
6 - 143



6 - 144



# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling



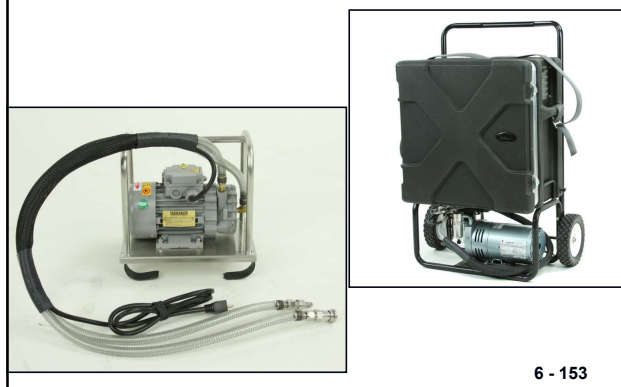
APTI #450/468 Compliance Test and Source Test Observation  
Lesson 6: FRM 5: Particulate Emissions Sampling



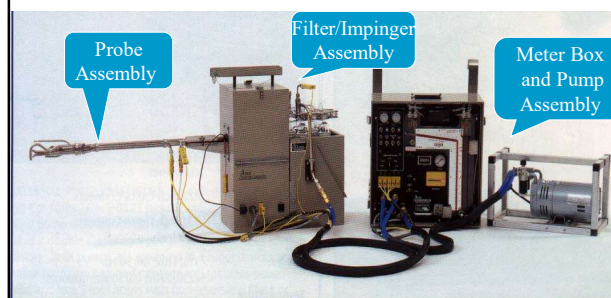
FRM 5 Digital Meter Box



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
- $\Delta H$ : 5.0 %
- $D_n$ : 1.0 %
- $\Delta H_{@}$ : 1.5 %

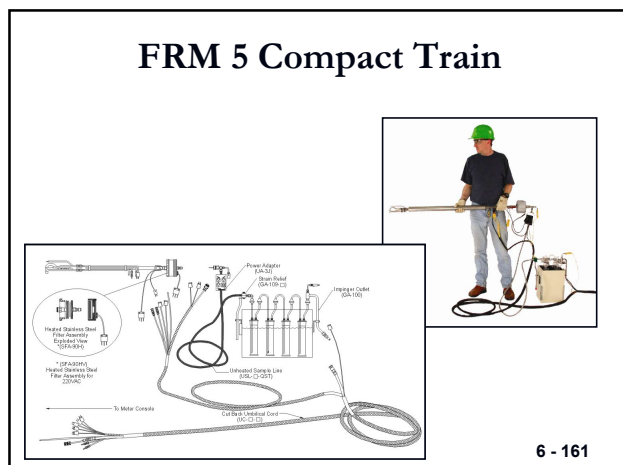
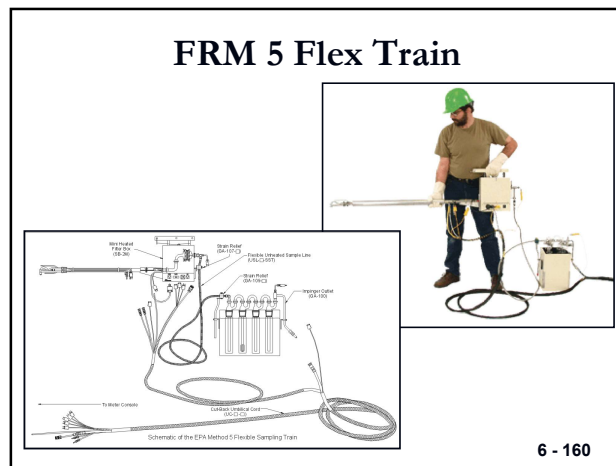
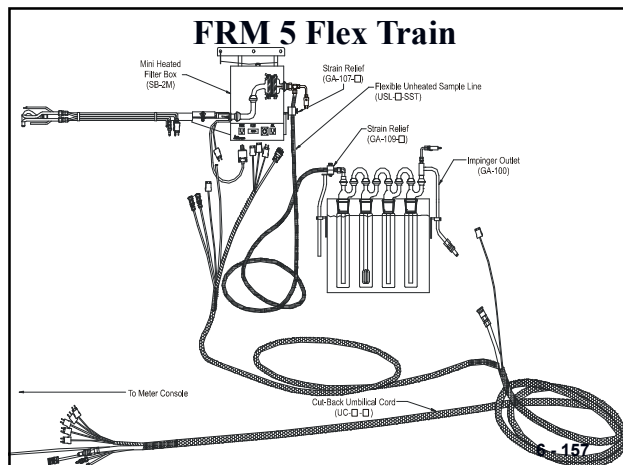
6 - 155

Calibration Laboratory for DGM “ $\gamma$ ”  
and Orifice Meter “ $\Delta H_{@}$ ”  
Determinations





# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling



## 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

6 - 162

### 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

6 - 163

### 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

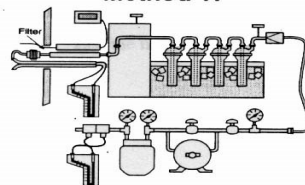
6 - 164

### FRM 5 Sample Recovery Items

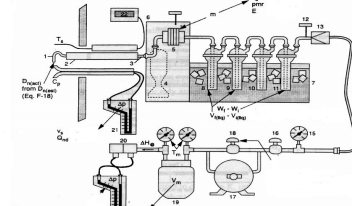


6 - 165

### Method 17



### Method 5



6 - 166

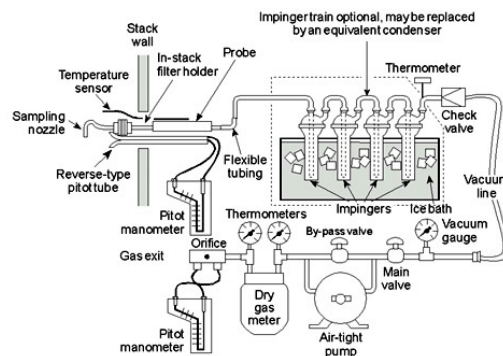
## Method 17

### In-stack Filter Applicability

In sources where particulate matter concentration is independent of temperature

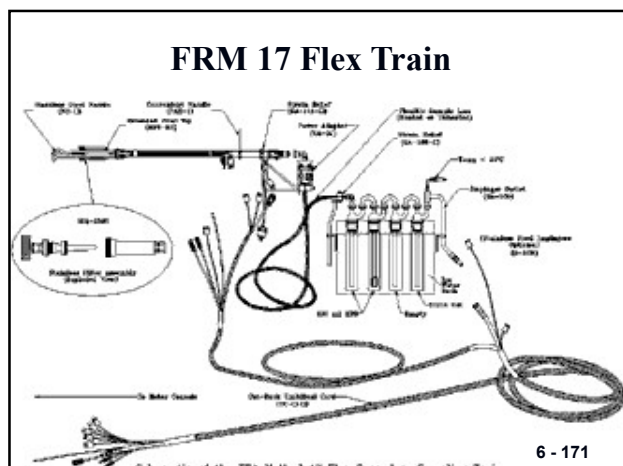
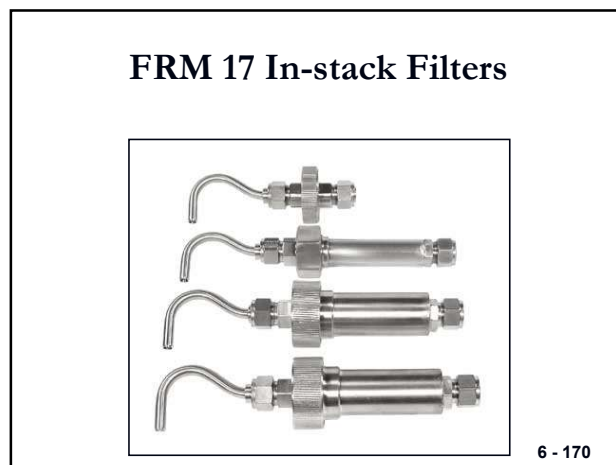
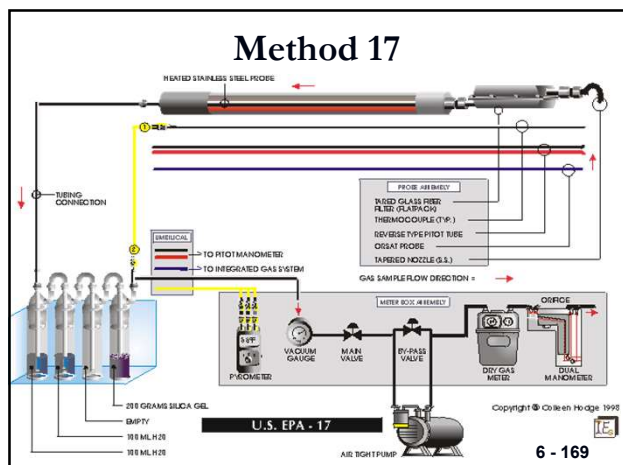
6 - 167

## FRM 17



6 - 168

# APTI #450/468 Compliance Test and Source Test Observation Lesson 6: FRM 5: Particulate Emissions Sampling



- ## 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
- 6 - 172

- ## 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
- 6 - 173

- ## 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)
- 6 - 174

### **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

6 - 175

### **Method 5I Low PM Concentrations**

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

6 - 176

### **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

6 - 177

### **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
  - $RSD = 100\% \mid (C_a - C_b) \mid / (C_a + C_b)$
  - Acceptable limits of < 10%

6 - 178

### **FRM 5 Sampling Train**



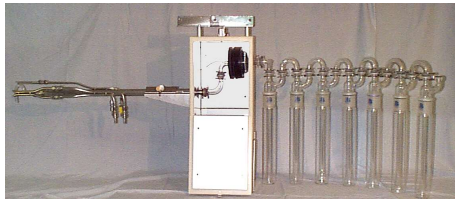
6 - 179



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

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**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**



6B - 1



6B - 2

**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

6B - 3

**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)

6B - 4

**Metals Detected**

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

6B - 5

**Interferences**

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

6B - 6

### Interferences

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

6B - 7

### FRM 29/Method 0060 Design Requirements

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

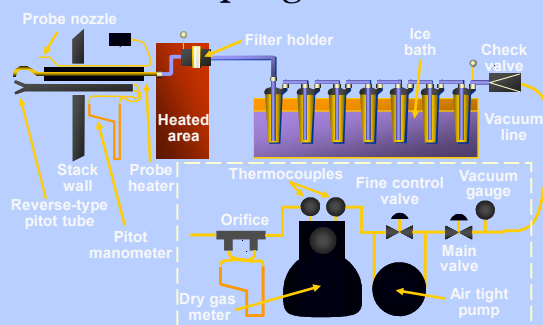
6B - 8

### FRM 29/Method 0060 Sampling Train

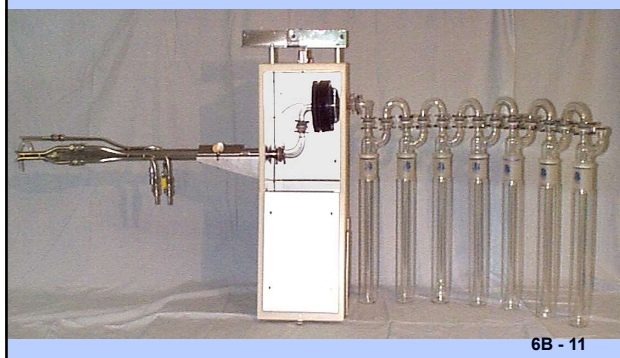
- Probe with quartz nozzle and liner
- Pitot tube/temperature sensor array
- Heated filter assembly
- Seven impingers
- Pump/dry gas meter/orifice assembly

6B - 9

### 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

6B - 12

**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

6B - 13

**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

6B - 14

**FRM 29/Method 0060  
Impinger Arrangement**

- 1st Impinger- empty (Optional)
- 2nd & 3rd Impinger- 5% HNO<sub>3</sub>/10% H<sub>2</sub>O<sub>2</sub> (vapor multi-metals)
- 4th Impinger- empty

6B - 15

**FRM 29/Method 0060  
Impinger Arrangement**

- 5th & 6th Impinger- 4% KMnO<sub>3</sub>/10% H<sub>2</sub>SO<sub>4</sub> (For mercury vapor)
- 7th Impinger- Silica gel

6B - 16

**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<sub>3</sub> for 4 hours

6B - 17

**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

6B - 18

**FRM 29/Method 0060  
Sample Train Requirements**

- Glass or Teflon<sup>®</sup> nozzle
- Nonmetallic probe line
- Nonmetallic brushes

6B - 19

**FRM 29/Method 0060  
Sample Train Requirements**

- Daily preparation of  $\text{KMnO}_4$  solution
- Polypropylene tweezers
- Storage bottles of glass with Teflon lined caps

6B - 20

**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

6B - 21

**FRM 29/Method 0060 Operation**

- Prevent  $\text{KMnO}_4$  from contacting other glassware and prevent  $\text{H}_2\text{O}_2$  from mixing with  $\text{KMnO}_4$
- Leak check in accordance with FRM 5
- Sample collection in general accordance with FRM 5

6B - 22

**FRM 29/Method 0060 Operation**

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

6B - 23

**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-  $\text{HNO}_3$  rinse of probe nozzle/liner, and front half of filter holder (exactly 100 mL)

6B - 24

**Sample Train  
Recovery Containers**

- 4- Combined impingers 1, 2 and 3 (measured) and  $\text{HNO}_3$  acid rinse of impingers and back half of filter holder (exactly 100 mL)

6B - 25

**Sample Train  
Recovery Containers**

- 5A- Impinger 4 (measured) and  $\text{HNO}_3$  rinse of impinger 4 (100 mL)  
5B-  $\text{KMnO}_4$  impingers contents (measured) and  $\text{KMnO}_4$  (100 mL) + water (100 mL)

6B - 26

**Sample Train  
Recovery Containers**

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

6B - 27

**Sample Train  
Recovery Containers**

- 6- Silica gel contents (note color, weigh)  
7- Acetone blank (100 mL)  
8A-  $\text{HNO}_3$  reagent blank (300 mL)  
8B- Water reagent blank (100 mL)

6B - 28

**Sample Train  
Recovery Containers**

- 9- 5 %  $\text{HNO}_3$ /10%  $\text{H}_2\text{O}_2$  reagent blank (200 mL)  
10-  $\text{KMnO}_4$  reagent blank (100 mL)  
11- 8 M  $\text{HCl}$  reagent blank (200 mL of water + 25 mL of 8 M  $\text{HCl}$ )  
12- Filter blank

6B - 29

**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)

6B - 30

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

---

**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

6B - 31

**Calculation**

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

6B - 32

**Calculation**

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

- 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

6B - 33

**Calculation**

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

6B - 34

**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

6B - 35

**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

6B - 36



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

---

**FRM 29/Method 0060**

**Key Points**

- Storage containers must be made of glass with Teflon<sup>®</sup>-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

6B - 37

**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

6B - 38

**FRM 29/Method 0060**

**Key Points**

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

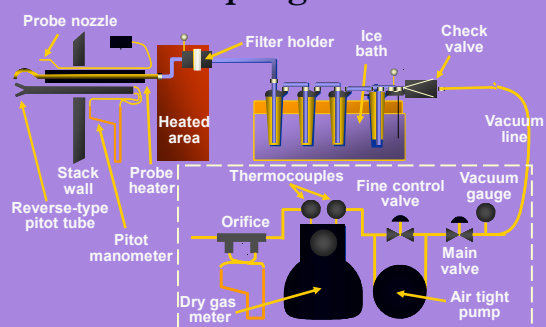
6B - 39

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

**FRM 12, Inorganic Lead**

6B - 40

**FRM 12**  
**Sampling Train**



6B - 41

**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

6B - 42

## 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

**6B - 43**

## 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

**6B - 44**

## 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)

6B - 45

## FRM 12

### Design Requirements

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

**6B - 46**

## FRM 12

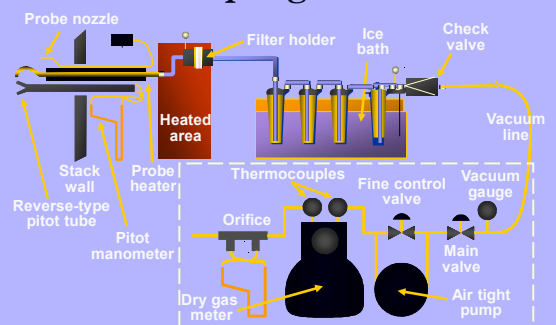
### Sampling Train

- 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<sub>3</sub>
- Pump/dry gas meter/orifice assembly

6B - 47

## FRM 12

### Sampling Train



6B - 48

### **Sample Recovery**

- **FRM 12 Recovery**
  - Container #1: Recover filter for lead PM same as FRM 5
  - Container #2: Front-half 0.1 N HNO<sub>3</sub> 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

6B - 49

### **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<sub>3</sub> each impinger and collect in container #4
  - Container #5: Reagent blank of 200 mL of 0.1 N HNO<sub>3</sub>

6B - 50

### **Sample Analysis**

- **Container #1:** Filter cut into strips and digested with 10 mL of 50% of HNO<sub>3</sub>, heat on hot plate, add 10 mL of 3 % H<sub>2</sub>O<sub>2</sub> 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

6B - 51

### **Sample Analysis**

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

6B - 52

### **Sample Analysis**

- **Container #3:** Weigh silica gel to nearest 0.5 grams (B<sub>ws</sub>)
- **Container #5:** Dry the 200 mL on a steam bath to dryness, add 15 mL of 50 % H<sub>2</sub>O<sub>2</sub> and 50 mL of hot DI water, dilute to a total volume of 100 mL

6B - 53

### **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 5<sup>th</sup> sample

6B - 54

**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

6B - 55

**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

6B - 56

**FRM 12**  
**Impinger Arrangement**

- 1<sup>st</sup> and 2<sup>nd</sup> Impinger- 100 mL 0.1 N HNO<sub>3</sub>
- 3rd Impinger- Dry
- 4th Impinger- 200-300 g silica gel

6B - 57

**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

6B - 58

**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<sub>3</sub>

6B - 59

**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

6B - 60

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

---

**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<sub>3</sub>
  - Use of glass fiber filter with low background lead concentration
  - Treat and analyzes the entire sample train contents, including the impingers, for lead

6B - 61

**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<sub>3</sub> 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

6B - 62

**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**

6B - 63

**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<sub>3</sub>

6B - 64

**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<sub>3</sub>
  - Don't have to brush probe for recovery

6B - 65

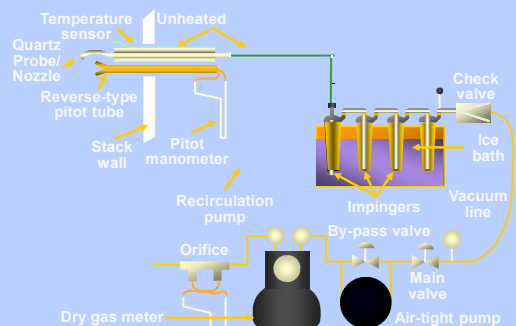
**FRM 316 Summary**

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

6B - 66

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

### FRM 306 Sampling Train



6B - 67

### 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<sup>+6</sup> by Ion Chromatography (IC)

6B - 68

### Discussion

- Cr<sup>+6</sup> Emissions?
  - If Cr<sup>+6</sup> emissions, then at end of sampling run, 1<sup>st</sup> 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)

6B - 69

### Discussion

- Total Chromium (TC) Emissions?
  - High Concentrations: Inductively coupled plasma emission spectrometer (ICP) @ 267.72 nm
  - Low concentrations: Digestion with HNO<sub>3</sub>, then graphite furnace atomic absorption spectroscopy (GFAAS) @ 357.9 nm

6B - 70

### Discussion

- Interferences: Stack and ICP Interferences
  - High SO<sub>2</sub> 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

6B - 71

### Discussion

- GFAA Interferences
  - Spectral: CN<sup>-</sup>
  - Chemical: Ca and PO<sub>4</sub><sup>-</sup>
- IC/PCR
  - Compounds which cause Cr<sup>+6</sup> to Cr<sup>+3</sup> etc.
  - Coeluting compounds

6B - 72



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 6B: FRM 29/SW-846, Method 0060, Multi-Metals Sampling**  
**FRM 12 for Inorganic Lead and FRM 306 for Chromium**

---

**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.)

6B - 73

**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 1<sup>st</sup> sampling point
- Block off opening around the probe to prevent in-leakage

6B - 74

**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

6B - 75

**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<sup>+6</sup> Sample Option

6B - 76

**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

6B - 77

**Recovery**

- Option #2: Cr<sup>+6</sup> Sample Option
  - Measure volume of liquid in first, second, and third impingers
  - Measure pH with indicator strip of 1<sup>st</sup> impinger. Must be > 8.5 for 0.1 N NaOH or > 8.0 for NaHCO<sub>3</sub>. If not, discard and redo test

6B - 78

### Recovery

- Option #2: Cr<sup>+6</sup> 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

6B - 79

### 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)

6B - 80

### In-stack Detection Limits (ISDL)

- 1.4 µg Cr/dscm for ICAP
- 0.15 µg Cr/dscm for GFAAS
- 0.015 µg Cr<sup>+6</sup>/dscm for IC/PCR with preconcentration

6B - 81

### 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?

6B - 82

### ISDL (cont.)

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

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

6B - 83

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

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 7: The Source Test

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



7 - 1



7 - 2



7 - 3

### 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?)

7 - 4

### Reviewing the Test Protocol

- Rules/Regulations
- Permits
- Previous Testing History

<http://www.dep.pa.gov/BUSINESS/AIR/BAQ/BUSINESSSTOPICS/SOURCETESTING/Pages/default.aspx>

[SOP-Test-Obs-03012019.pdf \(ohio.gov\)](#)

[Emission Monitoring Unit \(Testing Group\) | Ohio Environmental Protection Agency](#)

7 - 5

### Reviewing the Test Protocol

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

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

7 - 6

## Lesson 7: The Source Test

- **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

7-7

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

7-8

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

7-9

- 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

[illegible]

**7 - 10**

- Calibration and span gases used
- Manometers to scale
- Meter Box Values :  $\Delta H@$ ,  $\gamma$  and calibration dates
- Static and barometric pressures



7 - 11

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



7 - 12

### 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

7 - 13

### Types of Problems Found

- Unacceptable Sample Locations
- Port Locations
- Upstream & Downstream Diameters
- Equipment & Electrical Needs/Limitations
- Equipment Clearances
- Port Diameters
- Traversing needs (vertical)

7 - 14

### Types of Problems Found

#### • Equipment Errors

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

7 - 15



7 - 16

### Types of Problems Found

#### • Procedural Errors

- Cyclonic flow checks
- Leak checks
- Traverse points
- Isokinetics
- Temperatures and ice downs
- Recovery procedures

7 - 17



7 - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 7: The Source Test

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### 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 <sub>2</sub> and CO <sub>2</sub> Measurements
4	Use of Flexible Tubes Between Impingers	Tester	None
5	Nozzle Design Other Than Button-hook or Elbow	Administrator	None or Less

7 - 19



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector



Compliance  
Test and Source Test  
Observation

*Role of the Agency  
Inspector/Observer*

8 - 1


Why Compliance Stack Test and  
Observation Program ?

Identify Air  
Pollutants

Quantify

Evaluate Test  
Results

*by prescribed  
EPA Federal Reference  
Methods (FRMs)*



8 - 2

### Example of Typical Industries

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

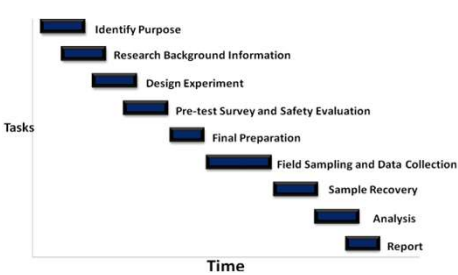
8 - 3

### 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)

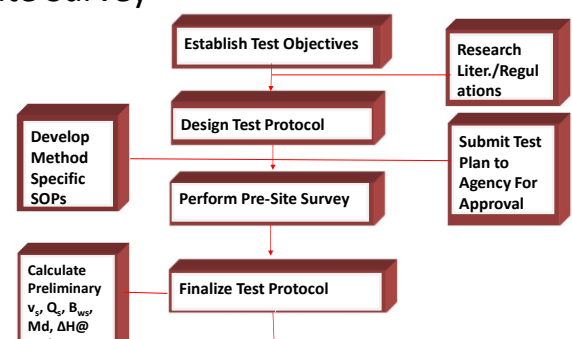
8 - 4

### Source Test Time-line



8 - 5

### Step 1: Objectives, Protocols and Pre-site Survey

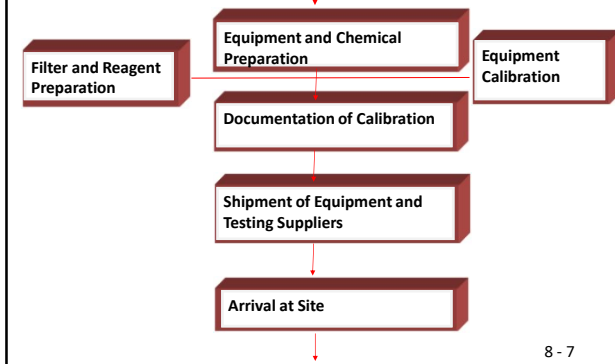


8 - 6

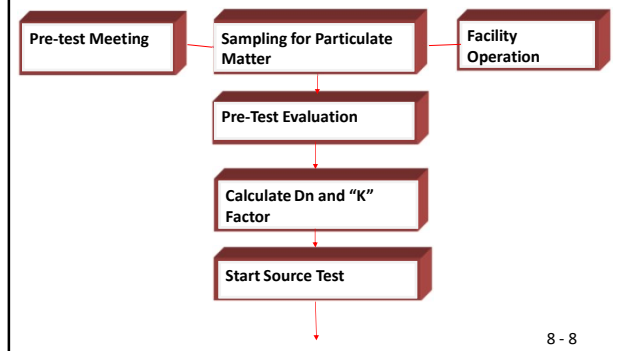
# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector

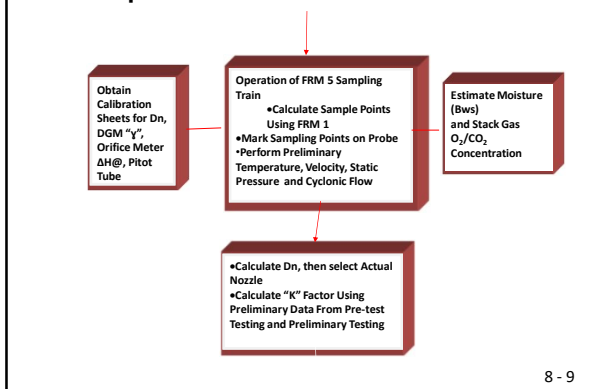
### Step 2: Equipment Preparation



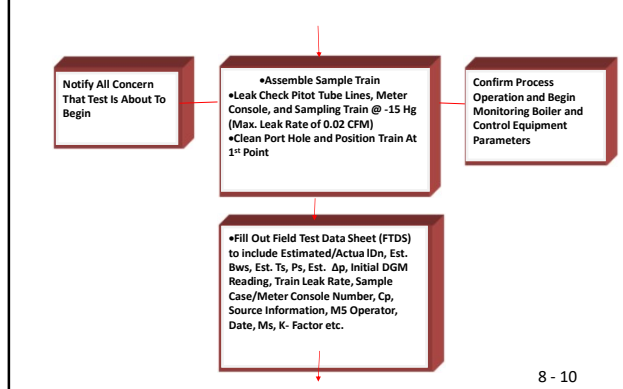
### Step 3: Pre-test Conference and Evaluation



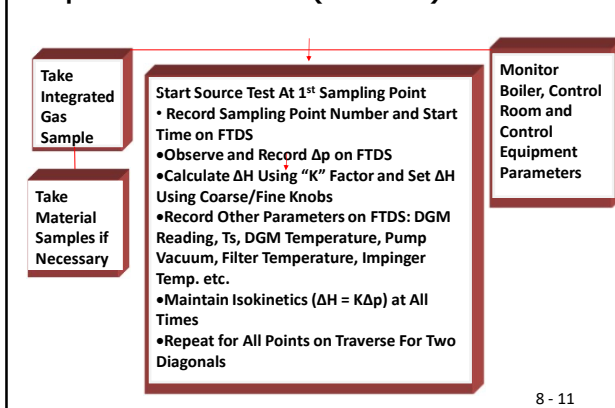
### Step 4: The Test



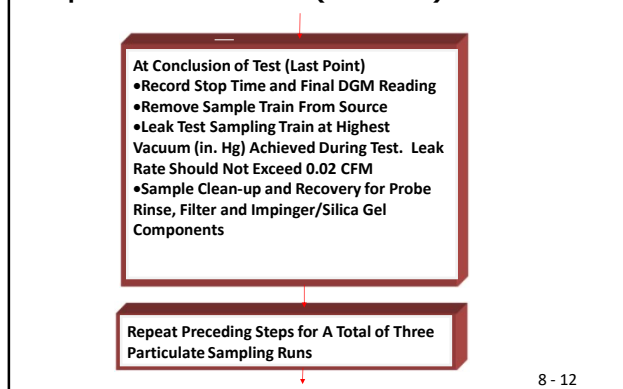
### Step 4: The Test



### Step 4: The Test (Cont'd)

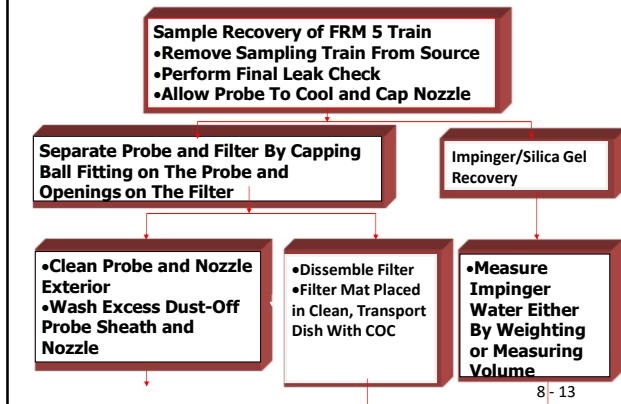


### Step 4: The Test (Cont'd)

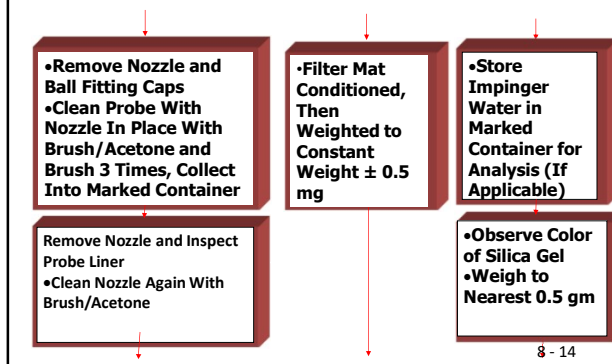


# APTI #450/468 Compliance Test and Source Test Observation Lesson 8: Role of the Agency Inspector

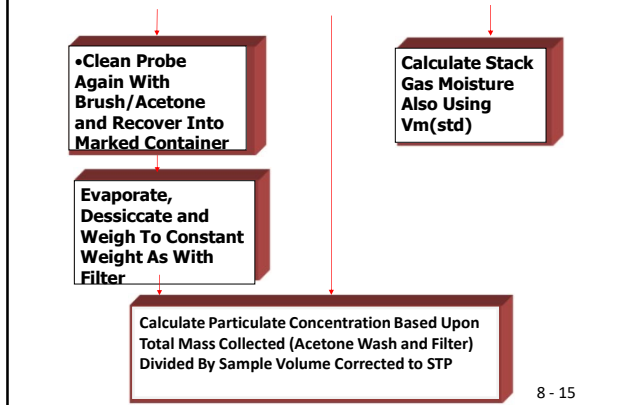
## Step 5: Sample Recovery



## Step 5: Sample Recovery (Cont'd)



## Step 5: Sample Recovery (Cont'd)



## 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.”*

8 - 16

## 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

8 - 17

## Inspectors Do's and Don'ts

- |   |  |
|---|--|
| <p><b>DO</b></p> <ul style="list-style-type: none"> <li>•Ask intelligent questions that add value</li> <li>•Become “familiar” with test methods rules and test plans</li> <li>•Show Up! Presence is critical</li> <li>•Be critical but reasonable</li> <li>•Reward “quality testing”</li> </ul> | <p><b>DON'T</b></p> <ul style="list-style-type: none"> <li>• “Umpire” a test</li> <li>•Challenge a test w/o good cause</li> <li>•Be unresponsive to requests</li> <li>•Hesitant to say “I don't have an answer”</li> <li>•Be Careless</li> </ul> |
|---|--|

8 - 18

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

---



#### 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

8 - 20

#### 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.

8 - 21

#### Seven Areas of Responsibility of Agency Personnel

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

8 - 22

#### 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

8 - 23

#### 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

8 - 24

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

---

#### 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

8 - 25

#### 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

8 - 26

#### 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

8 - 27

#### Role of The Observer

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

8 - 28

#### 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

8 - 29

#### Observer Techniques

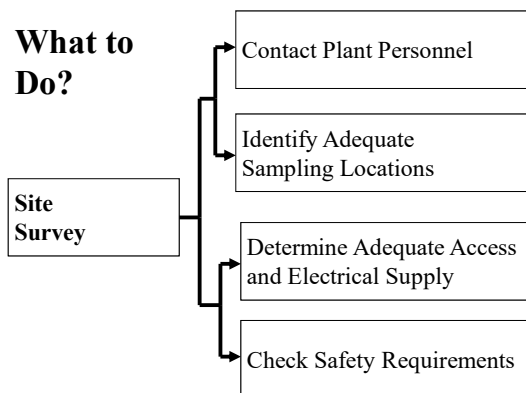
- Do not write on process charts and graphs
- Do not turn knobs and dials
- Do not collect unnecessary data
- Do not touch or adjust testing equipment
- Do not question tester or interfere during critical times of the test
- Do not conceal unacceptable acts or procedures

8 - 30

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

#### What to Do?



8 - 31

#### 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

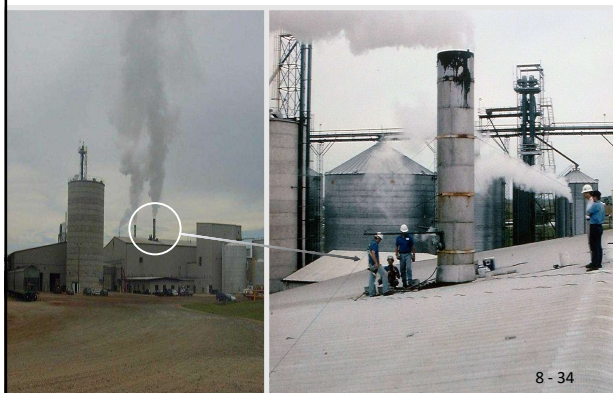
8 - 32

#### 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

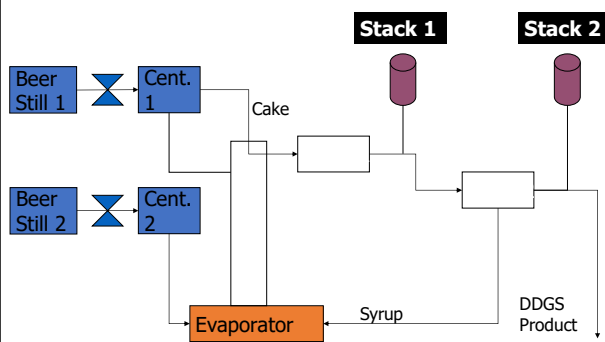
8 - 33

#### Ethanol Plant – Methods 5, 25A



8 - 34

#### Ethanol Flowchart



8 - 35

#### 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

8 - 36



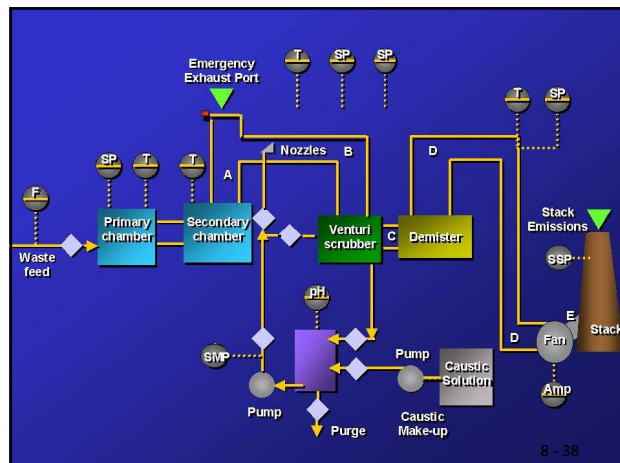
# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector

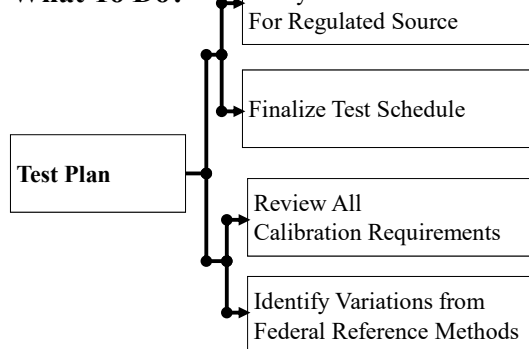
### Symbols Used in Block-Style Flowcharts

- 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

8 - 37



### What To Do?



8 - 39

### 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

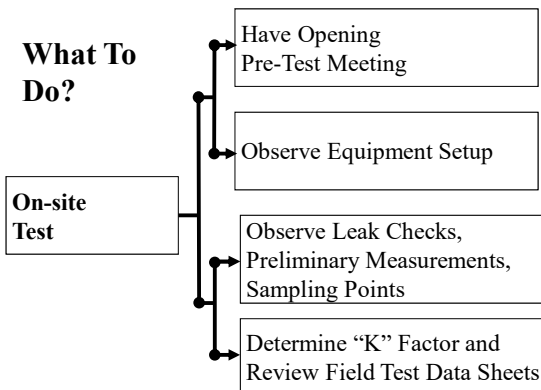
8 - 40

### 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

8 - 41

### What To Do?



8 - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector

### 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

8 - 43

### 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”

8 - 44

### What To Do?

#### The Test

Observe 1st Test

Observe 2nd Test

Observe 3rd Test

Observe Checking Stack Parameters/new “K-factors”

8 - 45

### 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

8 - 46



8 - 47

### What to Watch

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

8 - 48

### Examine Probe Nozzle, Pitot, And Thermocouple Design

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

8 - 49

### 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

8 - 50

### What to Watch

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

8 - 51

### What to Watch

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

8 - 52

### What to Watch

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

8 - 53

### Sample Train Leak Check

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

8 - 54

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

---

#### 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

8 - 55

#### 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

8 - 56

#### 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

8 - 57

#### What to Watch

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

8 - 58

#### What to Watch

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

8 - 59

#### 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

8 - 60

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

---

#### What to Watch

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

8 - 61

#### What to Watch

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

8 - 62

#### 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

8 - 63

#### 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 ( $\Delta p$ , bag failure logbook etc.)
      - Wet scrubbers (pH, flow rate etc.)

8 - 64

#### 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

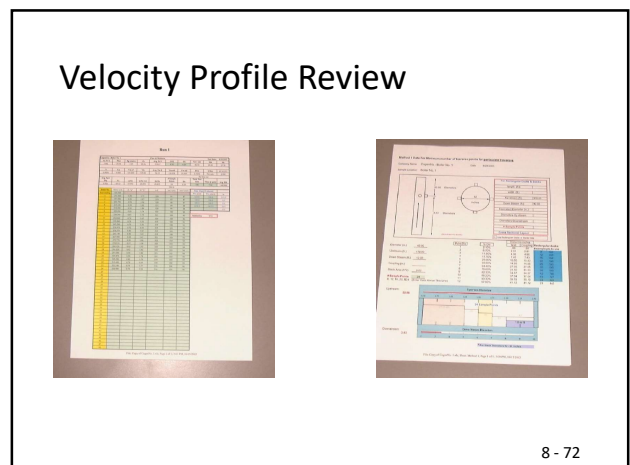
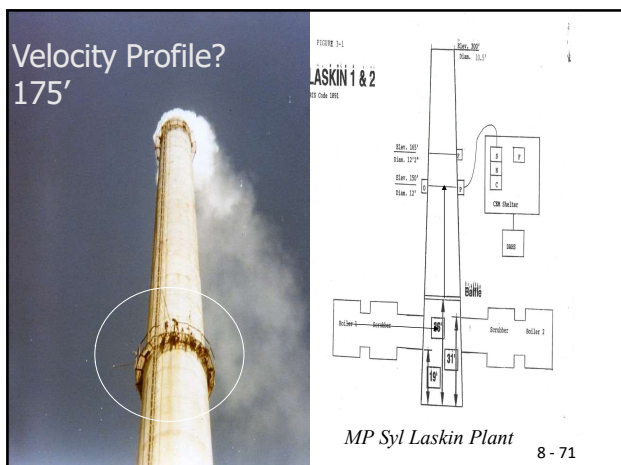
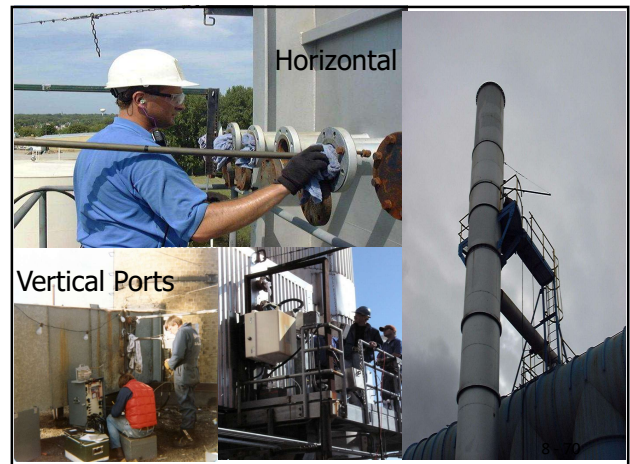
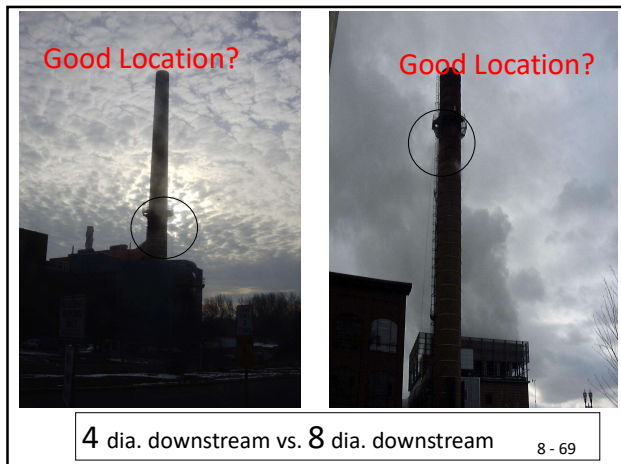
8 - 65

#### 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

8 - 66

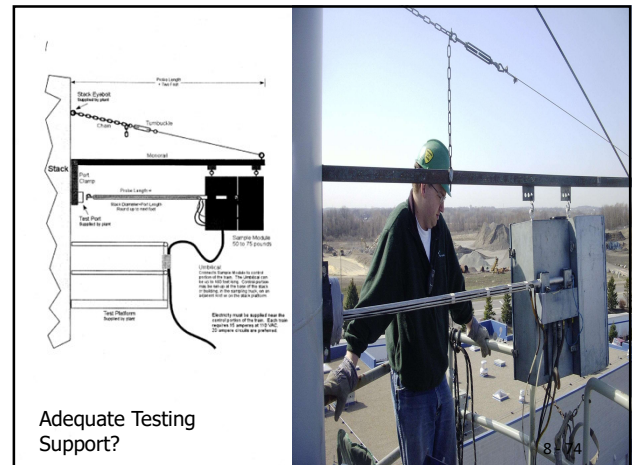
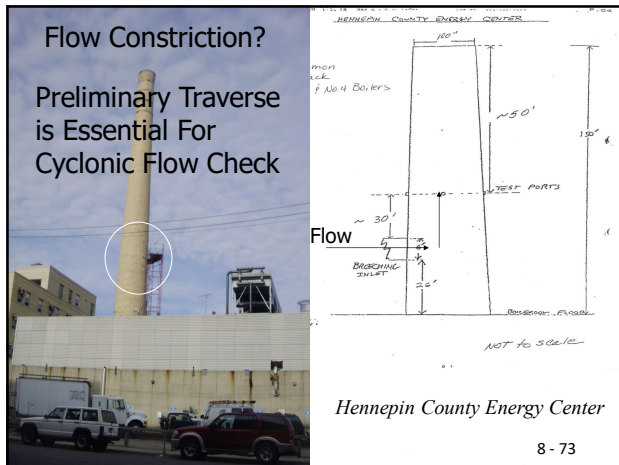
# APTI #450/468 Compliance Test and Source Test Observation Lesson 8: Role of the Agency Inspector



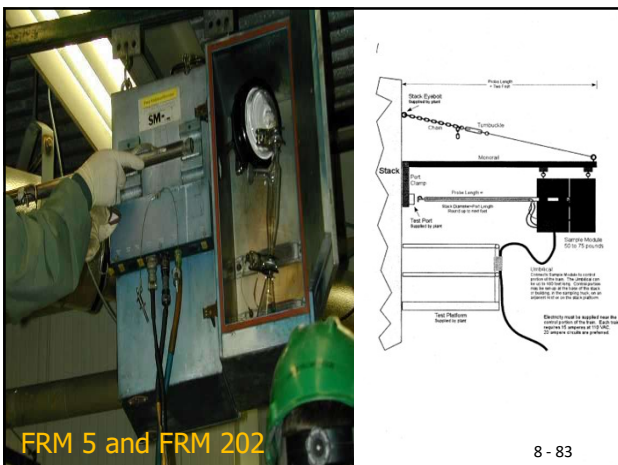
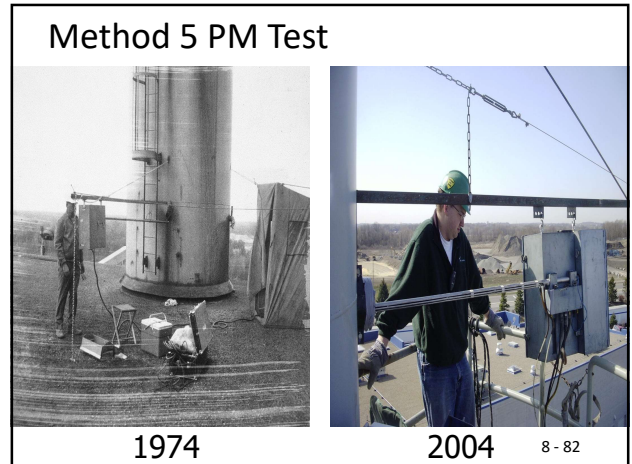


## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector



# APTI #450/468 Compliance Test and Source Test Observation Lesson 8: Role of the Agency Inspector





# APTI #450/468 Compliance Test and Source Test Observation Lesson 8: Role of the Agency Inspector

*Inspector Presence*

*"Be There"*






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

8 - 85




Times Have Changed...The Need to Test Hasn't

1974

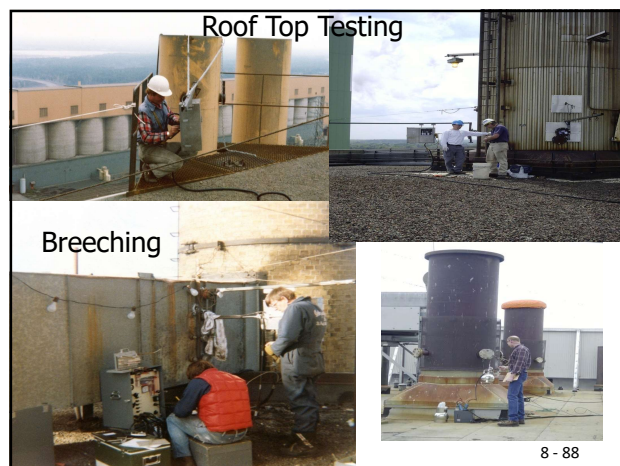


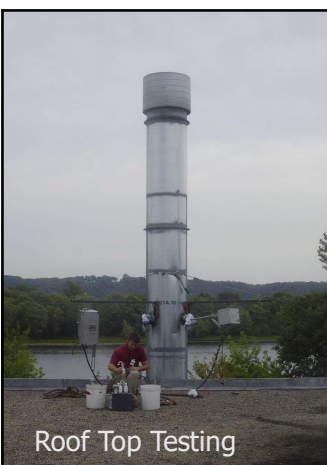
2004




*On-site presence is essential!*

8 - 87



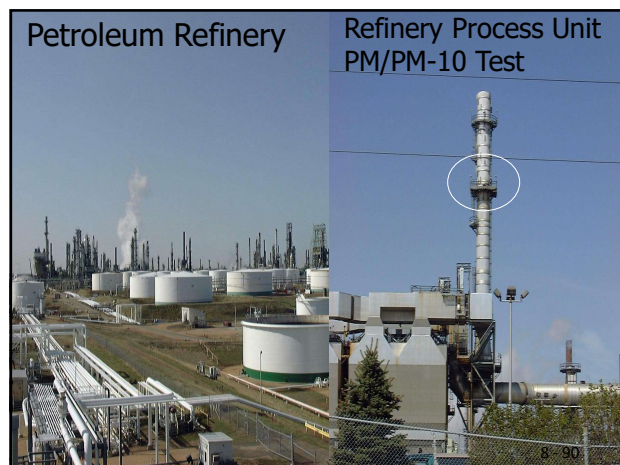


Roof Top Testing



Mobile Lab

8 - 89





# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector

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"*



8 - 93

Operations - Data Acquisition, You  
Have To Be There!



Load, production limits  
and temperatures



8 - 94

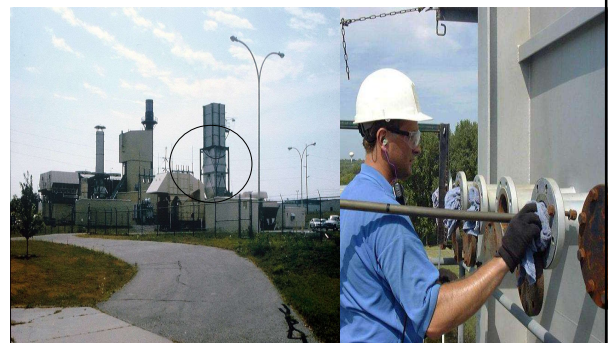


On Stack

Clean Room

8 - 95

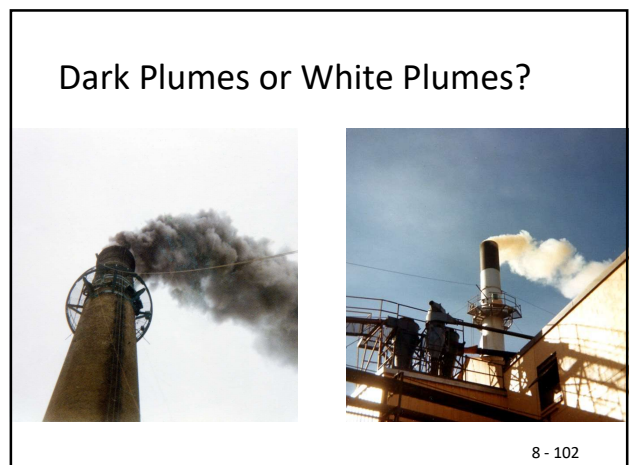
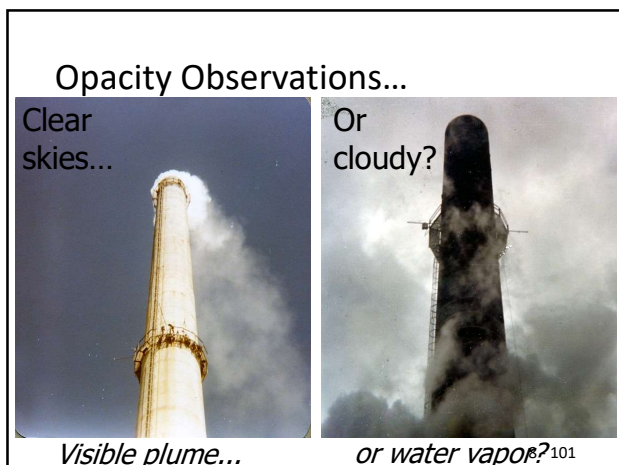
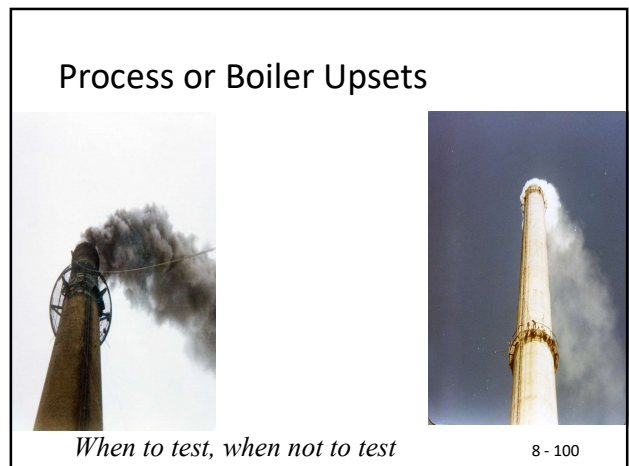
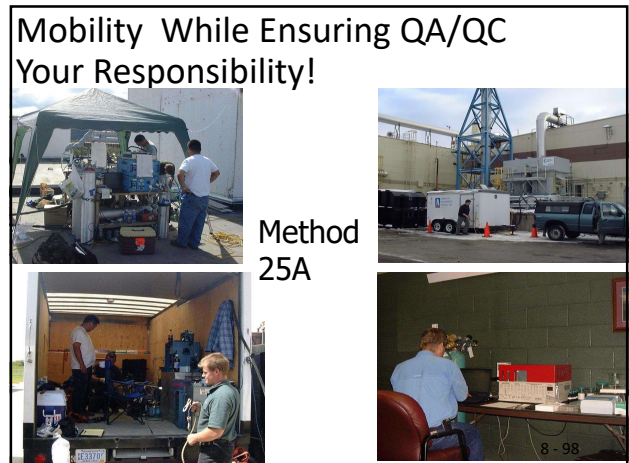
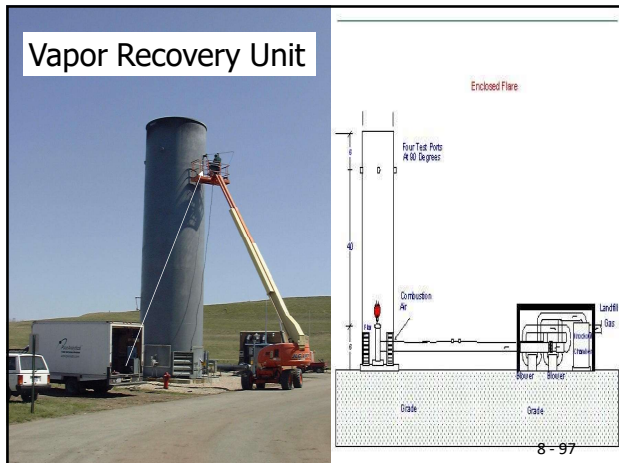
Combustion Turbines - MACT



Method 20

8 - 96

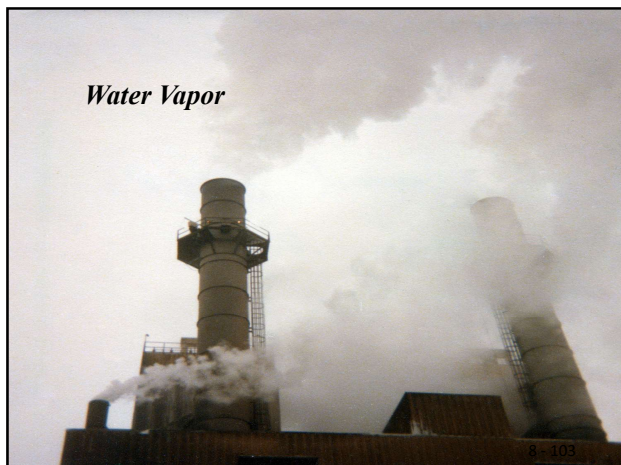
# APTI #450/468 Compliance Test and Source Test Observation Lesson 8: Role of the Agency Inspector





## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector



#### Testing Issues

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

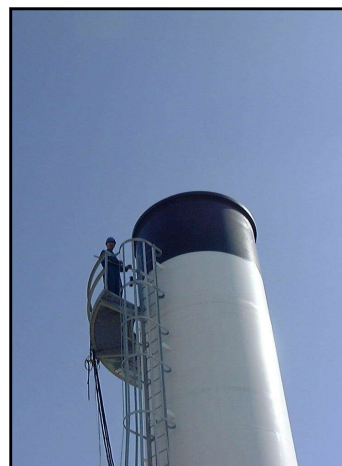
8 - 104

Safety...



How do YOU stack up?

8 - 105



A hard hat?

Nomex suit?

Safety glasses?

Safety Shoes?

(OSHA 29 CFR 1910.23)

8 - 106

Distance  
up  
equals...



...Distance  
down!

(OSHA 29 CFR 1910.23)

8 - 107

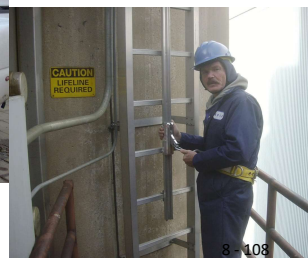
Be Prepared



Buckle Up...

Hook Up...

Lock Up!



8 - 108



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector

Weather is Critical  
Dress Accordingly



Ladder + Cable + Cage



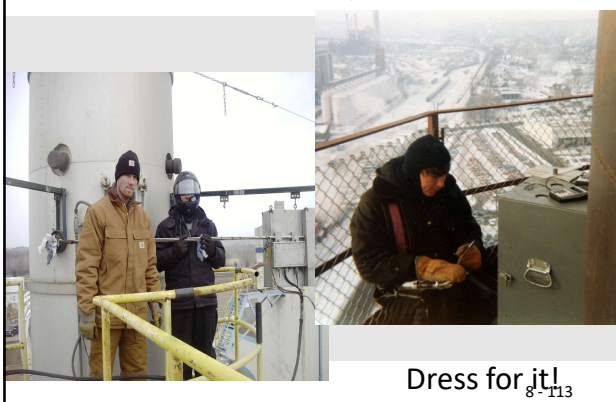
Safety...Always



8 - 111



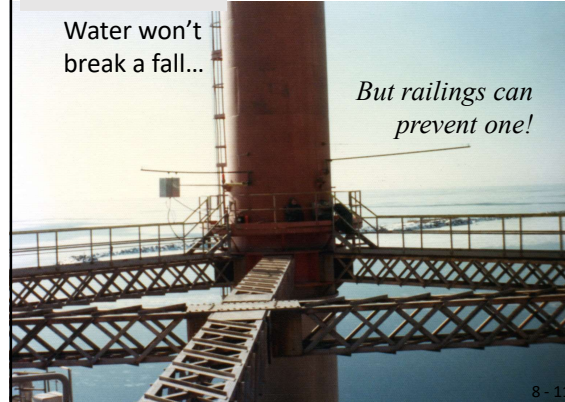
Cold Weather Testing



8 - 113

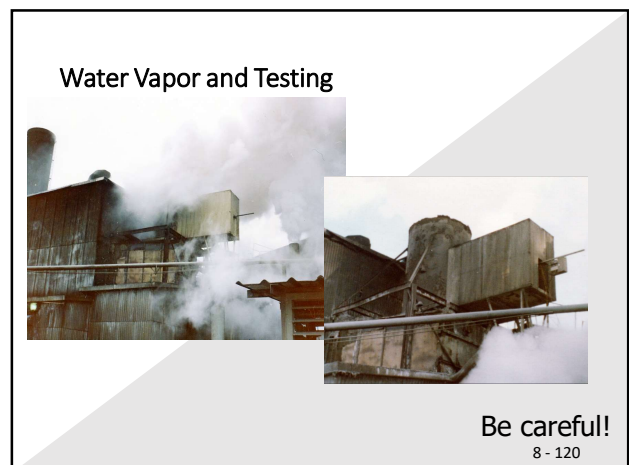
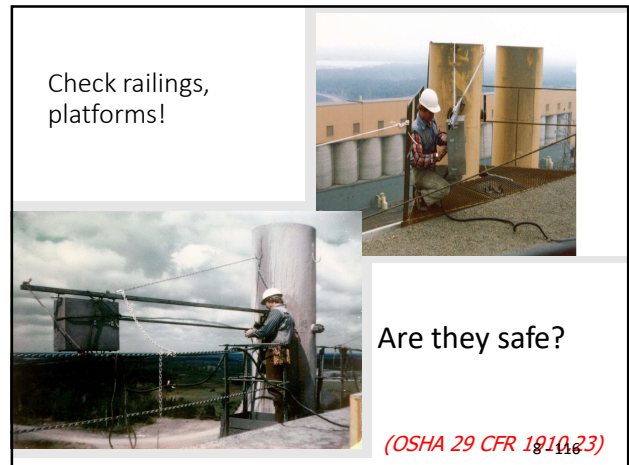
Water won't  
break a fall...

But railings can  
prevent one!



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 8: Role of the Agency Inspector



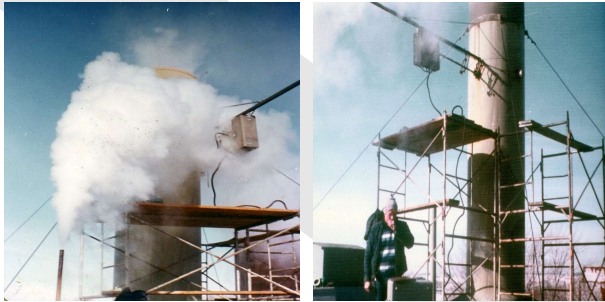


## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 8: Role of the Agency Inspector

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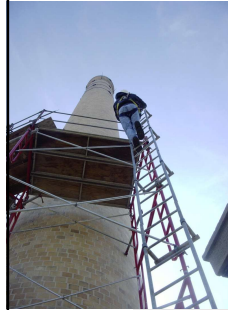
Communications are Essential



Make time for ***SAFETY!***

8 - 121

Testers use Harnesses!



State inspectors should too!

8 - 122

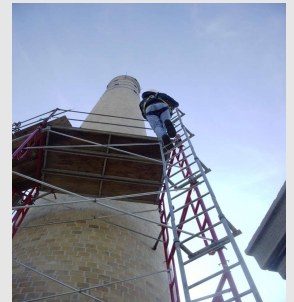
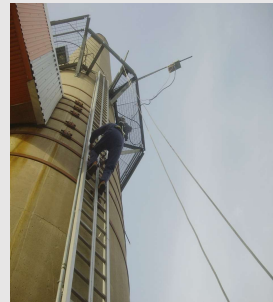
Respirators...



Are helpful!

8 - 123

Scaffolding or Ladders



Always Buckle Up!

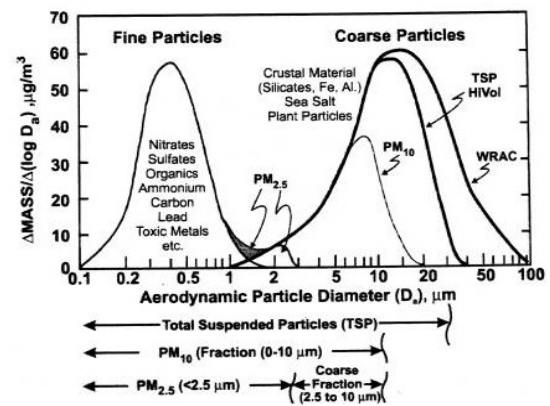
8 - 124

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 9: FRM 201-201A For PM-10 and PM-2.5**

**U.S. EPA APTI  
 Compliance Test and  
 Source Test Observation  
 FRMs 201/201A  
 For PM-10 and PM-10/2.5**

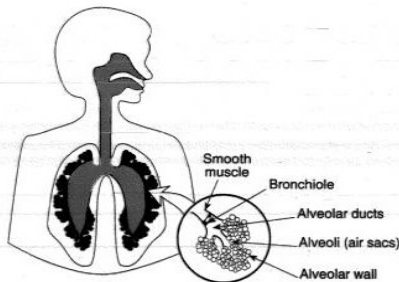


9 - 1



9 - 2

**Particles  $\leq 1 \mu\text{m}$  collect in most  
 remote portions of lungs –  
 the air sacs (or alveoli)**



9 - 3

**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!

9 - 4

**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

9 - 5

**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

9 - 6

### 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

9 - 7

### 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

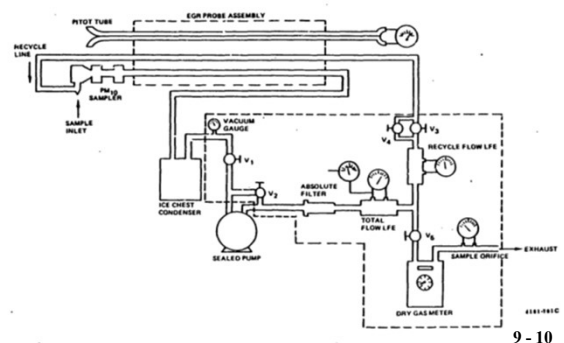
9 - 8

### FRM 201 Exhaust Gas Recirculation (EGR)

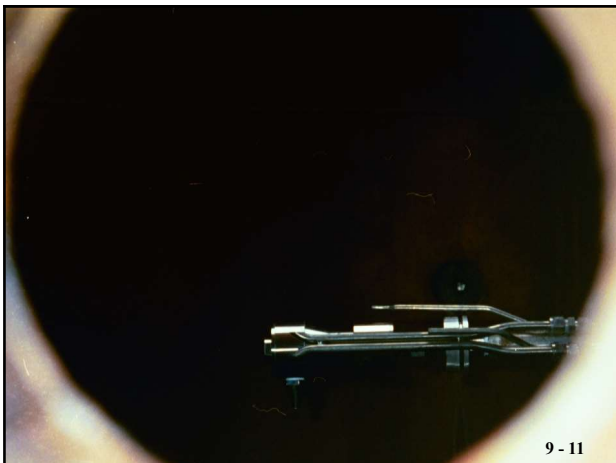
- Cyclone does have to be calibrated
- Must leak-check: positive and negative
- Can use condenser rather than FRM 5
- Each point isokinetically and same dwell time

9 - 9

### Schematic of EGR Sampling Train



9 - 10



9 - 11

### 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)

9 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 9: FRM 201-201A For PM-10 and PM-2.5

### 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.

9 - 13

### 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

9 - 14

### FRM 201A

#### Constant Sampling Rate (CSR)




- A 4-inch port should be adequate for the single PM<sub>10</sub> or PM<sub>2.5</sub> 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.

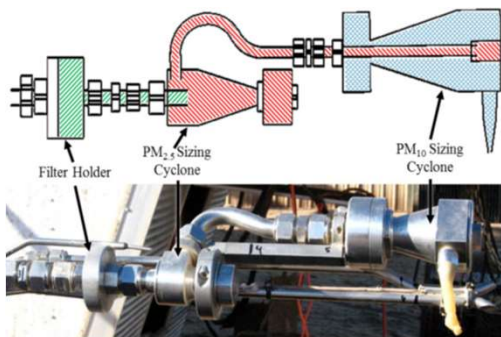
9 - 15

### PM – 10 Sampling at Cotton Gins

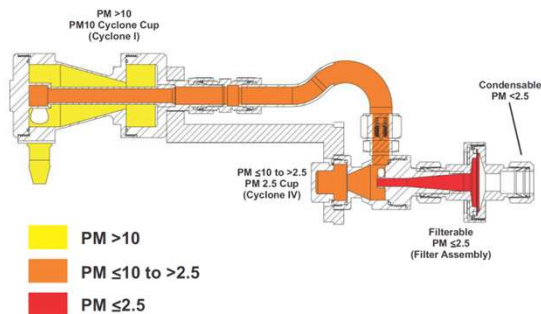


16

EPA Method 201A PM<sub>10</sub> and PM<sub>2.5</sub> sizing cyclones and in-stack filter holder schematic (CFR, 2010) and photograph (   $\leq 2.5 \mu\text{m}$   10 to  $2.5 \mu\text{m}$ ,   $> 10 \mu\text{m}$  ).



9 - 17



9 - 18



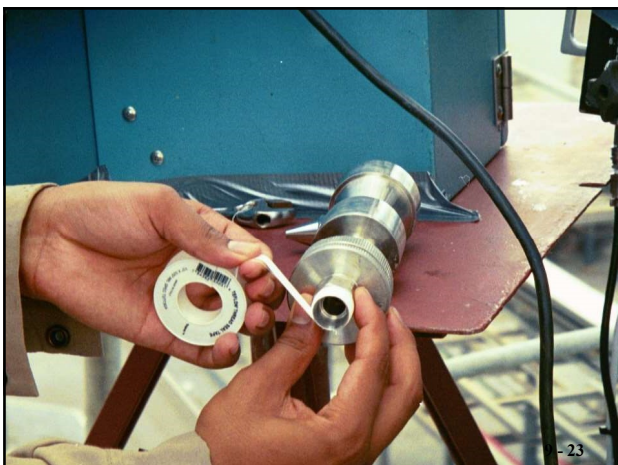
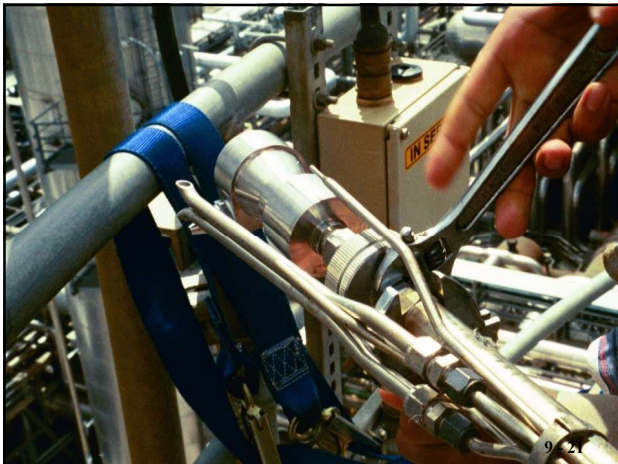
**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 9: FRM 201-201A For PM-10 and PM-2.5**

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**FRM 201/201A Review**

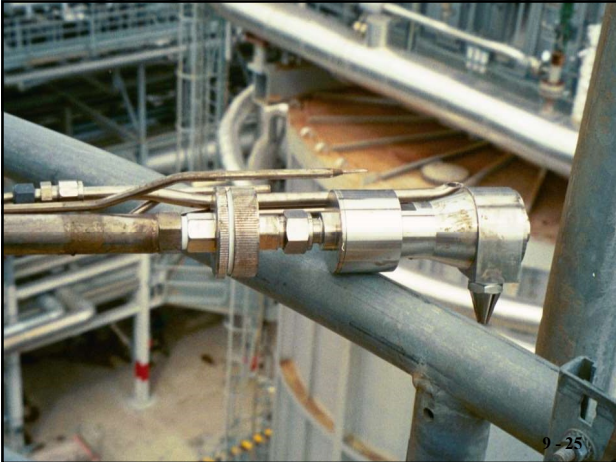
- Both methods measure PM-10 in-stack
- EGR new technology, CSR uses standard test equipment (i.e., FRM 5)

9 - 19



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 9: FRM 201-201A For PM-10 and PM-2.5**

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**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

9 - 26

**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

9 - 27

**FRM 201/201A Review**

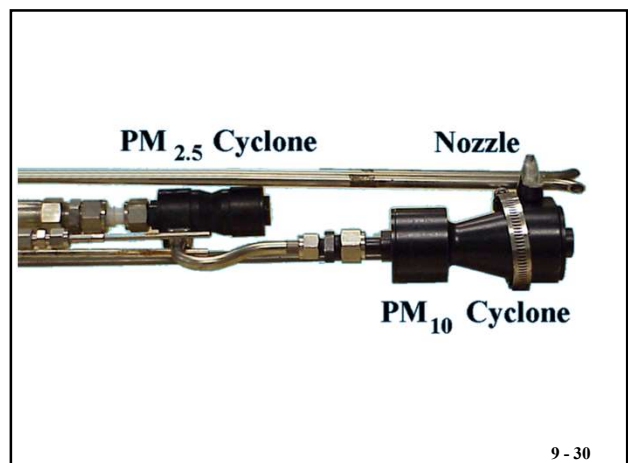
- CSR calibration of metering system and leak check procedures same as FRM 5
- CSR requires constant sampling rate and dwell time is proportional to stack gas velocity
- EGR is isokinetically and sampling time same as FRM 5

9 - 28

**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

9 - 29



9 - 30

### **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

9 - 31

### **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

9 - 32

### **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

9 - 33

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

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

9 - 34

### **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

9 - 35

### **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.

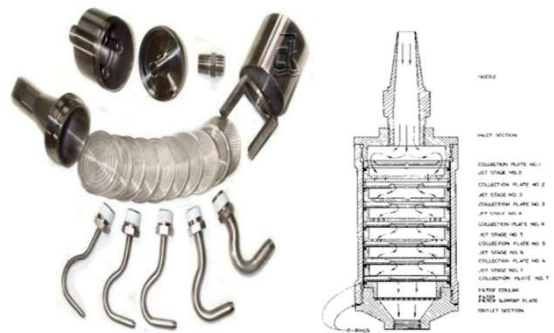
9 - 36

## 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.

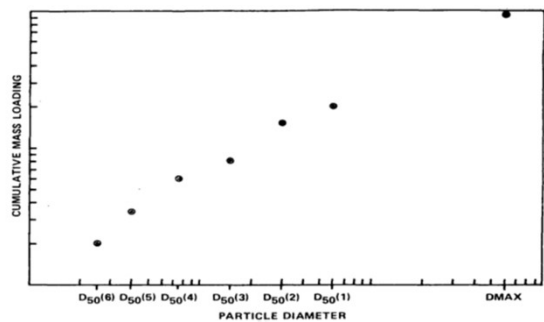
9 - 37

## Cascade Impactors



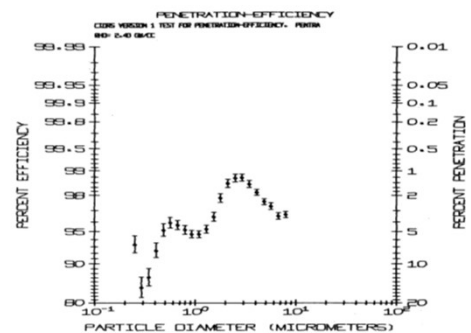
9 - 38

## Cumulative Size Distribution from Raw Impactor Data



9 - 39

### Control Device Penetration Curve with Confidence Limits



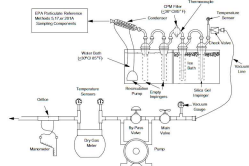
**9 - 40**



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 10: FRM 202 Condensable PM

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

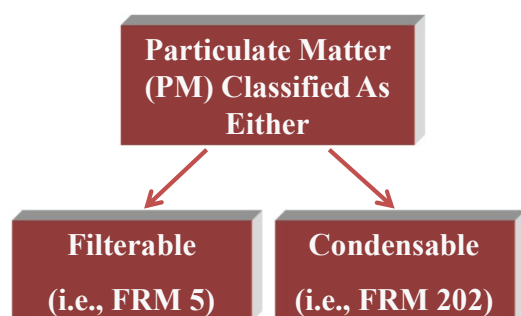


10 - 1

## 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)."*

10-2



10 - 3

## 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<sub>10</sub>/PM<sub>2.5</sub> particulate matter using FRM 201/201A

**10 - 4**

## 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

**10 - 5**

## 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<sub>2.5</sub> and PM<sub>10</sub> Emissions at Low Concentrations by Dilution Sampling (Constant Sampling Rate Procedure)

**10 - 6**



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

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### Regulatory Background CPM

- FRM 8 (1971): New source measurement method for  $\text{SO}_3/\text{H}_2\text{SO}_4$  emissions
- $\text{PM}_{10}$  NAAQS (1987): EPA acknowledges the effect of  $\text{PM}_{10}$  on human health
- FRM 201/201A (1990): New source measurement methods for  $\text{PM}_{10}$  for quantifying emissions

10 - 7

### 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

10 - 8

### Regulatory Background CPM

- $\text{PM}_{2.5}$  NAAQS (1997): EPA acknowledges that effect of fine particulate matter (i.e.,  $\text{PM}_{2.5}$ ) on human health
- Conditional Test Method 039 (2004): Measurement of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  Emissions by Dilution Sampling (Constant Sampling Rate Procedures)

10 - 9

### Regulatory Background CPM

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

10 - 10

### 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

10 - 11

### 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)

10 - 12

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

### Recent History

- Pre - PM<sub>10</sub> & PM<sub>2.5</sub> 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

10 - 13

### Why A Condensable Test Method?

- New NAAQS for particulate matter (PM<sub>2.5</sub>)
- New emission inventories required
- More comprehensive emission factors required

10 - 14

### 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

10 - 15

### Components of Direct PM<sub>2.5</sub>

- Filterable PM<sub>2.5</sub>
  - 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<sub>2.5</sub>
  - Vapor or gas at stack temperature
  - Condenses to liquid or solid at stack exit
  - Stable in atmosphere and collected on ambient sampler

10 - 16

### Precursors to Condensable PM

Ammonia	Nitrates
HCl	Organics
HF	Chlorides
Sulfates	

10 - 17

### List of Precursors Reactions to Condensable PM

- |                                     |   |
|-------------------------------------|---|
| • Condensable Organics              | • $H_xC_y(g) = H_xC_y(a)$                       |
| • SO <sub>3</sub>                   | • $SO_3(g) + H_2O(g) = H_2SO_4(a)$              |
| • SO <sub>3</sub> w/NH <sub>3</sub> | • $SO_3(g) + H_2O(g) + 2NH_3 = (NH_4)_2SO_4(s)$ |

10 - 18

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 10: FRM 202 Condensable PM

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#### List of Potential Precursors Reactions to Form Condensable PM

- HCl
- $\text{HCl(g)} + \text{H}_2\text{O(g)} = \text{HCl(l)}$
- HF
- $\text{HF(g)} + \text{H}_2\text{O(g)} = \text{HF(l)}$
- Trace Metals
- $\text{M(g)} = \text{M(l)} \text{ or } \text{M(s)}$
- Nitrates
- $\text{NO}_3\text{(g)} + \text{H}_2\text{O(g)} = \text{HNO}_3\text{(l)}$

10 - 19

#### FRM 202 for Measurement of CPM

- Needed to measure CPM instead of solid PM
- Allows the determination of both filterable and Condensable PM simultaneously

10 - 20

#### 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.)

10 - 21

#### Reasons to Consider Condensable $\text{PM}_{2.5}$ Emissions

- Condensable fraction of direct  $\text{PM}_{2.5}$  can be significant
  - 10 to 50 percent of  $\text{PM}_{2.5}$  emissions depending on control measures, temperature, other source-specific conditions

10 - 22

#### Reasons to Consider Condensable $\text{PM}_{2.5}$ Emissions

- Combustion, metallurgical & wood product sources emit large quantities of vapors that condense to form  $\text{PM}_{2.5}$ 
  - Acids (e.g., sulfuric acid from coal combustion)
  - Neutralized acids (e.g.,  $[\text{NH}_4]_2[\text{SO}_4]$ ,  $\text{NH}_4\text{Cl}$ )
  - Organic materials (e.g., alkanes, PAHs, PCBs, PCDDs, acids)
  - Metals (e.g., As, Se, Sb, Pb Compounds)

10 - 23

#### Reasons to Consider Condensable $\text{PM}_{2.5}$ Emissions

- A small fraction of point sources are responsible for the majority of condensable PM emissions

10 - 24

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

### Inventories and PM<sub>2.5</sub> Emissions

- Filterable PM
  - Historically only PM included in databases
  - Some States include filterable PM<sub>10</sub> or PM<sub>2.5</sub>
- Condensable PM
  - Current knowledge is spotty
  - Some SIP databases fail to include PM<sub>cond</sub> (even when required)
  - When PM<sub>cond</sub> included - calculated from emissions factors (e.g., AP-42) that are often based on incorrect test methods

10 - 25

### Inventories and PM<sub>2.5</sub> Emissions

- Inventories reflect database errors
  - Federal inventory includes some adjustments
  - Underestimate some sources' contributions, overestimate others

10 - 26

### Issues to Consider for CPM

- Most current regulations do not address PM<sub>cond</sub>
  - Effect on SIP Regulations
  - Focus on filterable PM
  - Force control technology towards filterable PM
- Some regulations do include PM<sub>cond</sub>, but with incorrect test methods

10 - 27

### Issues to Consider for CPM

- Final rule creates a transition period
  - Regulations addressing PM<sub>cond</sub> encouraged but not required
  - Develop more precise and accurate PM<sub>cond</sub> emissions for inventories and rules

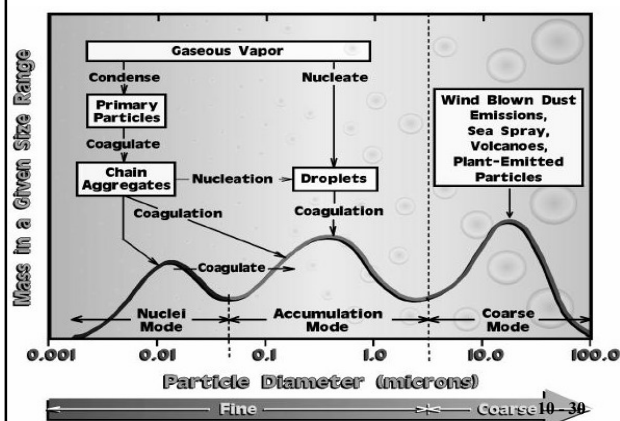
10 - 28

### CPM in Relation to Air Quality Issues

- Potential impacts on PSD review applicability for PM<sub>10</sub> and PM<sub>2.5</sub> (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

10 - 29

Size Distribution and Sources of Atmospheric Particles.



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

### 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

10 - 31

### 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

10 - 32

### 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

10 - 33

### 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

10 - 34

### 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)

10 - 35

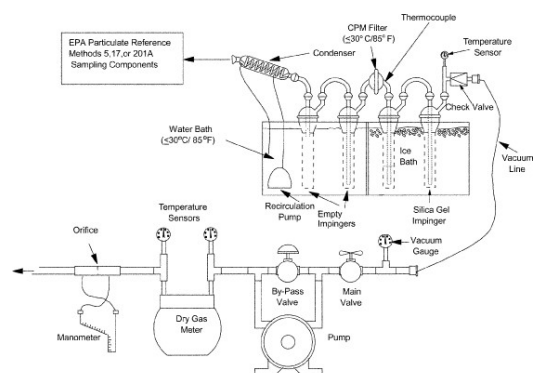


Figure 1. Schematic of Condensable Particulate Sampling Train

10 - 36



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

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### 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

10 - 37

### FRM 202 CPM Sampling Program

- Impinger portion of a FRM 17 type sampling train
- Nitrogen purge to remove dissolved SO<sub>2</sub>

10 - 38

### 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.

10 - 39

### 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.

10 - 40

### 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."

10 - 41

### 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.

10 - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 10: FRM 202 Condensable PM

### EPA FRM 202

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

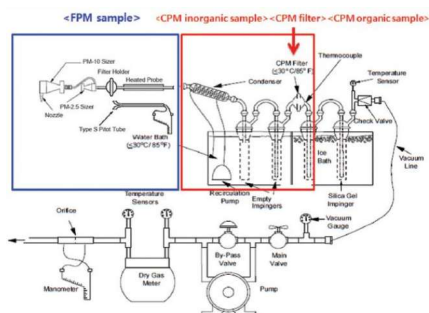
10 - 43

### 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

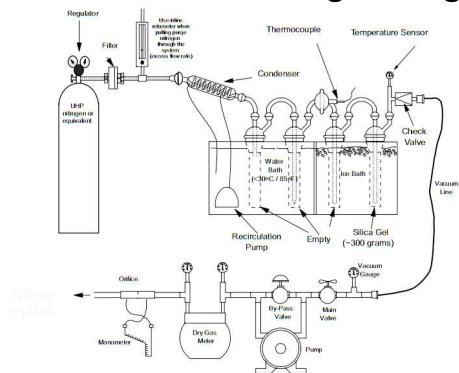
10 - 44

### FRM 202 Sampling Train



10 - 45

### FRM 202 Post Nitrogen Purge



10 - 46

### FRM 202 Biases

- Normally non-condensable gases may react with other gases or condensables to form condensable PM
- Oxidation of dissolved  $\text{SO}_2$  in the impinger water to form  $\text{H}_2\text{SO}_4$
- Stabilization of  $\text{H}_2\text{SO}_4$  with  $\text{NH}_4\text{OH}$  when pH of the impinger solution is  $> 4.5$

10 - 47

### FRM 202 Biases

- Use of water impingers to concentrate condensibles has bias given the potential to affect chemical reaction rate. Chemical reaction rates generally increase with concentration

10 - 48

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 10: FRM 202 Condensable PM

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#### % 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

10 - 49

#### Results of FRM 202 For Condensable PM

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

10 - 50

#### 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

10 - 51

#### 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<sub>10</sub> emissions from Fossil Fuel-Fired Steam Generators (FFSGs)

10 - 52

#### Special Considerations When Using Method 202

- May not be applicable at sources that emit high levels of ammonia
- If SO<sub>2</sub> is present, the sample must be purged with N<sub>2</sub>, but recent studies indicate that not all the SO<sub>2</sub> is purged from the impingers

10 - 53

#### Special Considerations When Using Method 202

EPA Method 202 Best Practices Handbook

- 8.1 What are the Method 202 requirements for the post-test nitrogen purge?
- Method 202 requires a post-test nitrogen purge at a minimum of 14 liters per minute (L/min) for 1 hour if water was collected in the sampling train.

10 - 54

#### EPA Activities to Resolve PM<sub>cond</sub> Test Methods Issues

- Recommending use of Method 202 with purge and use of condensable PM<sub>2.5</sub>  
(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

10 - 55

#### EPA Activities to Resolve PM<sub>cond</sub> 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

10 - 56

#### EPA Updated Method 202

- Recommending use of Method 201A (existing filterable PM<sub>10</sub> test method) with supplemental hardware for filterable PM<sub>2.5</sub> added to updated 202
- Revise Method 202 in Appendix M
  - Add filterable PM<sub>2.5</sub> measurement
  - Add condenser followed by dry impingers
  - First two impingers in water
  - Second two impingers in ice water
  - Promulgate 2008/2009

10 - 57

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 11: F-Factors and Units of the Standard**

---

**U.S. EPA APTI**  
**Compliance Test and Source Test**  
**Observation**  
**F-Factors and Units of the Standard**



11 - 1

**Emission Standards for Sources**

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

11 - 2

**Concentration of Stack Gas ( $c_s$ )**

Can be expressed in:

- ppm
- g/dscm
- gr/dscf

11 - 3

**For example:**

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

0.04 gr/dscf  $\Leftrightarrow$  90 mg/dscm

11 - 4

**Pollutant Mass Rate (pmr)**

Can be expressed in:

- lb/hr
- g/hr

11 - 5

**Pollutant Mass Rate (pmr)**

$\text{pmr} = \text{Concentration} \times \text{Stack gas volumetric flow rate}$

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

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

11 - 6



# **APTI #450/468 Compliance Test and Source Test Observation** **Lesson 11: F-Factors and Units of the Standard**

## **Emission Rate (E)**

**Can be expressed in:**

- lb/10<sup>6</sup> Btu heat input
- ng/joule heat input

11 - 7

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:

$$E = \frac{\text{pmr}}{Q_H} = \frac{c_s Q_s}{Q_H}$$

Where:

Q<sub>s</sub> = the stack gas volumetric flow rate (units of ft<sup>3</sup>/hr, m<sup>3</sup>/hr)

Q<sub>H</sub> = the heat input rate, the rate at which combusted fuel supplies heat to the boiler or other heat utilization system (Btu/hr, Kcal/hr)

11 - 8

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

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

11 - 9

## **For example:**

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

Particulate emissions limited to  
0.03 lb/10<sup>6</sup> Btu.

11 - 10

## **Reporting In Units Of The Standard: F Factor Methods**

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

1. Pollutant concentration, c<sub>s</sub>
  - a. Pollutant mass captured
  - b. Dry gas volume sampled
2. Effluent volumetric flow rate, Q<sub>s</sub>
  - a. Stack gas velocity
  - b. Stack temperature
  - c. Stack pressure

11 - 11

## **Reporting In Units Of The Standard: F Factor Methods**

- d. Dry gas composition (Orsat) %CO<sub>2</sub>, %O<sub>2</sub>, %N<sub>2</sub>
- e. Moisture content
3. Heat input rate, Q<sub>H</sub>
  - a. Fuel input rate
  - b. Proximate analysis of fuel

11 - 12

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 11: F-Factors and Units of the Standard**

---

**Process Weight Rate (E)**

**Can be expressed in:**

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

11 - 13

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

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

11 - 14

**For Example:**

The NSPS for sulfuric acid plants is:

SO<sub>2</sub> emissions limited to 2 kg

SO<sub>2</sub>/ metric ton H<sub>2</sub>SO<sub>4</sub> produced.

11 - 15

**Concentration Corrected To  
Standard Conditions**

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

11 - 16

**Correcting Concentration to 12% CO<sub>2</sub>**

$$\bar{C}_{s_{12\text{CO}_2}} = \bar{C}_s \frac{12}{\% \text{CO}_2}$$

11 - 17

**Correcting Concentration to 6% O<sub>2</sub>**

$$\bar{C}_{s_{6\% \text{O}_2}} = \frac{\bar{C}_s (20.9 - 6.0)}{20.9 - \% \text{O}_2}$$

11 - 18

### Correcting Concentration to 3% O<sub>2</sub>

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

11 - 19

### Excess Air Correction Factor

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

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

11 - 20

## Method 19 F Factor Methods

11 - 21

### 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<sup>6</sup> Btu).
- An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel.

11 - 22

### 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.

11 - 23

### Reporting in Units of Standard: F factor Methods

- All of the quantities for c<sub>s</sub> and Q<sub>s</sub> are obtained in a source test
- Q<sub>H<sub>2</sub></sub> 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

11 - 24

### 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:
- $E = c_s F_d \left( \frac{20.9}{20.9 - \%O_2} \right)$
- Where:  $F_d$  is the dry F factor
- The F factor essentially replaces the ratio OS/OH and the term in brackets is merely an

11 - 25

### 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.
- $F_d$  factors and its variants ( $F_c$  and  $F_w$  factors) are useful in reporting continuous monitoring data in terms of lb/10<sup>6</sup> Btu heat input

11 - 26

### 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

11 - 27

### 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.
- 

11 - 28

### 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<br>2. % ash<br>3. % volatile matter<br>4. % fixed carbon | } | Total<br>100% | 5. % sulfur<br>6. Heating value (BTU/lb)<br>7. Ash fusion temperature |
|--|---|---------------|---|

11 - 29

### 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.”

11 - 30

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 11: F-Factors and Units of the Standard

### Reporting in Units of Standard: F factor Methods

$$\frac{Q_s}{Q_H} = (\text{correction air excess}) \frac{V_t}{GCV}$$

Dimensionally, this says

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

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

11 - 31

### Reporting in Units of Standard: F factor Methods

■ Remembering the first equation given in this lesson,

$$\text{■ } E = c_s Q_s / Q_H$$

■ and through substitution

$$\text{■ } E = \frac{c_s V_t}{GCV} \frac{1}{(\text{excess air correction})}$$

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

11 - 32

### 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:

$$\text{■ } (20.9 - \% O_2) / 20.9$$

■ and the equation to be used for calculating emissions for Method 5 is:

$$\text{■ } E = (c_s F_d)(20.9/20.9 - \% O_2)$$

11 - 33

### 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:

$$\text{■ } E = (c_{ws} F_d) ((20.9/20.9(1 - B_{ws}) - \% O_2))$$

■ *Note:* The subscript w stands for measurements made on a wet basis.

11 - 34

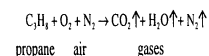
F Factors Table

Factor	Excess Air Units	Measurement Required for Emissions Determination	Calculations	Comments
$F_d$	$\frac{\text{dscf}}{10^6 \text{Btu}}$	$\%O_2$ (dry basis)	$E = c_s F_d \left[ \frac{20.9}{20.9 - \%O_{2d}} \right]$	$c_s$ determined on dry basis
$F_c$	$\frac{\text{dscf}}{10^6 \text{Btu}}$	$\%CO_2$ (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
$F_w$	$\frac{\text{wscf}}{10^6 \text{Btu}}$	$\%O_2$ (wet basis)	$E = c_{ws} F_w \left[ \frac{20.9}{20.9(1 - B_{ws}) - \%O_{2w}} \right]$	The "wet" F factor, $c_{ws}$ and $\%O_2$ on wet basis $B_{ws}$ = average moisture content of ambient air
$F_o$	—	—	$F_o = \frac{20.9 F_d}{100 F_c} = \frac{20.9 - \%O_2}{\%CO_2}$	Miscellaneous factor useful for checking Orsat data <b>11 - 35</b>

### 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



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.

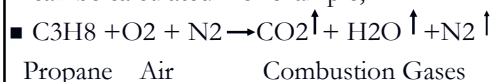
11 - 36

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 11: F-Factors and Units of the Standard

### 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,



For each pound of fuel undergoing perfect combustion, a known amount of gaseous products will result. 11 - 37

### Calculation and Tabulation of F Factors

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

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

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

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

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

$$F_w = \frac{10^6 [5.56 (\%H) + 1.53 (\%C) + 0.57 (\%S) + 0.14 (\%N) - 0.46 (\%O) + 0.21 (\%H_2O)]}{GCV_w} \quad 11 - 38$$

### 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

11 - 39

### 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  $F_d$  factor can be calculated to within a  $\pm 3\%$  deviation and the  $F_c$  factor can be calculated to within a  $\pm 5.9\%$  deviation. The calculated factors are given in the Table below.

11 - 40

### F Factors for Various Fuels

Fuel Type	$F_d$		$F_w$		$F_c$	
	dscm/j	dscf/10 <sup>6</sup> Btu	wscm/j	wscf/10 <sup>6</sup> Btu	scm/j	scf/10 <sup>6</sup> Btu
Coal:						
Anthracite <sup>2</sup> -----	2.71x10 <sup>-7</sup>	10,100	2.83x10 <sup>-7</sup>	10,540	0.530x10 <sup>-7</sup>	1,970
Bituminous <sup>2</sup> -----	2.63x10 <sup>-7</sup>	9,780	2.86x10 <sup>-7</sup>	10,640	0.484x10 <sup>-7</sup>	1,800
Lignite -----	2.65x10 <sup>-7</sup>	9,860	3.21x10 <sup>-7</sup>	10,950	0.513x10 <sup>-7</sup>	1,910
Oil <sup>3</sup> :	2.47x10 <sup>-7</sup>	9,190	2.77x10 <sup>-7</sup>	10,320	0.383x10 <sup>-7</sup>	1,420
Gas:						
Natural -----	2.43x10 <sup>-7</sup>	8,710	2.85x10 <sup>-7</sup>	10,610	0.287x10 <sup>-7</sup>	1,040
Propane -----	2.34x10 <sup>-7</sup>	8,710	2.74x10 <sup>-7</sup>	10,200	0.321x10 <sup>-7</sup>	1,190
Butane -----	2.34x10 <sup>-7</sup>	8,710	2.79x10 <sup>-7</sup>	10,390	0.337x10 <sup>-7</sup>	1,250
Wood -----	2.48x10 <sup>-7</sup>	9,240			0.492x10 <sup>-7</sup>	1,830
Wood bark -----	2.58x10 <sup>-7</sup>	9,600			0.516x10 <sup>-7</sup>	1,920
Municipal -----	2.57x10 <sup>-7</sup>	9,570			0.488x10 <sup>-7</sup>	1,820
Solid waste -----						

<sup>1</sup> Determined at standard conditions: 20°C (68°F) and 760 mmHg (29.92 in. Hg)

<sup>2</sup> As classified according to ASTM D388-77

<sup>3</sup> Crude, residual, or distillate

11 - 41

### 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 O<sub>2</sub> for the excess air correction may be used in the calculation. The  $F_c$  and  $F_w$  factors may not be used.

11 - 42



### 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.

11 - 43

### 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.

11 - 44

### 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.

11 - 45

### Other Uses for F Factors

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

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

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

11 - 46

### Other Uses for F Factors

- If after calculating  $F_d$ ,  $F_c$ , or  $F_w$ , a large discrepancy exists between the calculated value and the corresponding value in the table, the original data for  $Q_s$ ,  $Q_H$ , and the Orsat data should be checked. This is an easy way of conducting a material balance check.
- 1. Using a tabulated value for  $F_d$ ,  $F_c$ , or  $F_w$  and the data obtained during the stack test for  $Q_s$  and  $\%O_2$ , a value of  $Q_H$  may be obtained from the equations.

11 - 47

### 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.

11 - 48

### 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 %O<sub>2</sub> and %CO<sub>2</sub> values.
- Failure to have complete combustion of the fuel (complete combustion is assumed in the derivation of all of the F factor methods).

11 - 49

### Errors and Problems in the Use of F Factors

- Loss of carbon dioxide when wet scrubbers are used affecting the F<sub>d</sub>, F<sub>c</sub> and F<sub>w</sub> factors.
- Addition of carbon dioxide when lime or limestone scrubbers are used, affecting the F<sub>c</sub> factor.
- 

11 - 50

### 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:

11 - 51

### 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% CO<sub>2</sub> and 50% excess air may introduce sizeable errors in the corrected particulate loading...”

11 - 52

### 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 CO<sub>2</sub> or O<sub>2</sub> concentration can be made, which would minimize this error, if the % CO is determined in the flue gas.

11 - 53

### 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<sub>2</sub> or O<sub>2</sub> concentration, a combustion source having 11% CO<sub>2</sub>, 1 % CO, and 6% O<sub>2</sub> will result in about plus 9% error for the F<sub>c</sub> Factor Method and about plus 3% for the F<sub>d</sub> Factor and F<sub>w</sub> Factor Methods.

11 - 54

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 11: F-Factors and Units of the Standard

## Errors in Source Sampling and Factor Examples

[illegible]

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.

<sup>a</sup>Error due to calculation and combined isokinetic bias.<sup>b</sup>Error due to calculation and combined isokinetics bias.  
<sup>c</sup>See effect on the measured value.

<sup>d</sup>Lb/10<sup>4</sup> Btu is actually a concentration

<sup>0</sup>N/A - not applicable.

**11 - 55**

## Example F Factor Problem

- The Bradshaw Furniture Company has an industrial steam generating unit of greater than  $250 \times 10^6$  Btu/hr heat input. The unit fires Bituminous coal and has an extractive  $\text{CO}_2$  monitor. Recent testing showed an effluent  $\text{SO}_2$  concentration of 750 ppm (wet basis) and 12.8 %  $\text{CO}_2$ (dry basis). The average stack moisture content is 7%  $\text{H}_2\text{O}$ .
- What is the emission rate in  $\text{lb}/10^6 \text{ BTU}$

What is the emission rate in lb/10<sup>6</sup> BTU

- Use  $F_C$  and convert  $C_{SO_2}$  from ppm to lb/dscf

$$(750 \text{ ppm}) \times \frac{10^{-6} \text{ ft}^3 \text{ SO}_2}{\text{ft}^3 \text{ air/ppm}} \times \frac{(64 \text{ lb SO}_2)}{\text{lb-mole}} \times \frac{(\text{lb-mole})}{392.75 \text{ ft}^3} = 1.22 \times 10^{-4} \text{ lb/dscf}$$

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

$$E = C_s F_C 100/\text{CO}_2 = 1.31 \times 10^{-4} \text{ lb/dscf } (1800 \text{ ft}^3/10^6 \text{ BTU})$$

$$(100/12.8)$$

$$= 1.85 \text{ lb SO}_2/10^6 \text{ BTU}$$

11 - 57

## Combination of Fuels F-factor

- A fossil-fired steam generator burns the following combination of fuels:
- Natural gas 30 %
- Oil 20 %
- Bituminous coal 50 %

**A stack test of the unit yielded the following:**

**Particulate matter concentration =  $1.5 \times 10^{-5}$  lb/dscf**

**What is the PM emissions in lbs/10<sup>6</sup> BTU?**

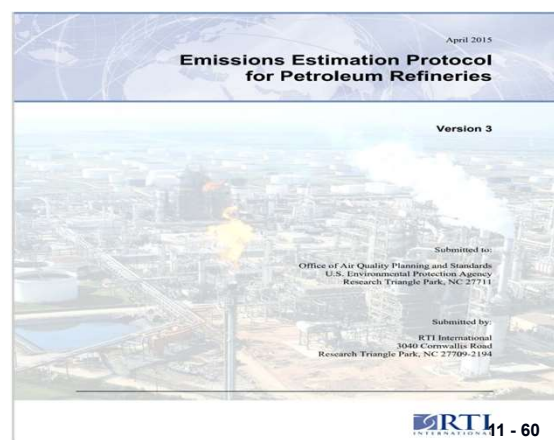
11 - 58

## Combination of Fuels F-factor

- $F_d$  natural gas =  $8710 \times 0.3 = 2613$
- $F_d$  Oil =  $9190 \times 0.2 = 1838$
- $F_d$  Bituminous coal =  $9780 \times 0.5 = \underline{4890}$
- Total Sum =  $9341 \text{ lb}/10^6 \text{ BTU}$

$$\begin{aligned} E &= c_s F_d [20.9/20.9 - \% O_2] \\ &= 1.5 \times 10^{-5} \text{ lb/dscf } (9341 \text{ lb}/10^6 \text{ BTU } [20.9/20.9 - 6.2]) \\ &= 2.0 \text{ lb}/10^6 \text{ BTU} \end{aligned}$$

11 - 59



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 11: F-Factors and Units of the Standard

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

The CEMS measures SO<sub>2</sub> and O<sub>2</sub> 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<sub>d</sub> factor (scf/MMBtu). The F<sub>d</sub> 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<sub>d</sub> as follows:

$$F_d = K \times [(X_{CH_4} \times MEV_{CH_4}) + (X_{C_2H_6} \times MEV_{C_2H_6}) + (X_{H_2} \times MEV_{H_2}) + (X_{C_3H_8} \times MEV_{C_3H_8}) + (X_{C_4H_{10}} \times MEV_{C_4H_{10}}) + (X_{C_2H_4} \times MEV_{C_2H_4}) + (X_{C_4H_8} \times MEV_{C_4H_8}) + (X_{C_2H_2} \times MEV_{C_2H_2}) + (X_{C_3H_4} \times MEV_{C_3H_4}) + (X_{C_4H_6} \times MEV_{C_4H_6}) + (X_{C_4H_{10}} \times MHC_{C_4H_{10}}) + (X_{C_3H_8} \times MHC_{C_3H_8}) + (X_{C_2H_6} \times MHC_{C_2H_6}) + (X_{C_2H_4} \times MHC_{C_2H_4}) + (X_{C_2H_2} \times MHC_{C_2H_2}) + (X_{C_3H_4} \times MHC_{C_3H_4}) + (X_{C_4H_6} \times MHC_{C_4H_6}) + (X_{inerts} \times MHC_{inerts})]$$

$$F_d = 10^6 \times [(0.44 \times 7.28) + (0.04 \times 12.94) + (0.06 \times 1.61) + (0.01 \times 11.34) + (0.2 \times 18.61) + (0.03 \times 17.01) + (0.17 \times 24.28) + (0.01 \times 22.67) + (0.04 \times 0.85)] \div [(0.44 \times 842) + (0.04 \times 1475) + (0.06 \times 269) + (0.01 \times 1335) + (0.2 \times 2100) + (0.03 \times 1947) + (0.17 \times 2717) + (0.01 \times 2558) + (0.04 \times 0)]$$

$$= 10^6 \times 12.55 \div 1425$$

$$= 8,809 \text{ dscf/MMBtu}$$

11 - 61

### 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<sub>2</sub> concentration is 20 ppmv (dry basis), the measured O<sub>2</sub> 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:

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

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

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

Use this value of Q<sub>e</sub> in Equation 4-1 without the temperature, pressure, and moisture correction terms to estimate hourly emissions as follows:

$$E_{SO_2} = (Q_e) \times [1 - (F_{H_2O})] \times \left( \frac{C_{SO_2}}{100\%} \right) \times \frac{MW_{SO_2}}{MW_{O_2}} \times M_N \times K$$

$$E_{SO_2} = 8,031 \times 1 \times (20 \div 1,000,000) \times 64.06 \div 32.06 \times 60 \times 2.2046 = 1.6 \text{ lb/hr}$$

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

Given the same measurements as Example 4-3, calculate hourly SO<sub>2</sub> 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<sub>2</sub> concentration in ppm by 1.660 × 10<sup>-7</sup> 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:

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

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

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

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.

11 - 62

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

### Defining Volatile Organic Compounds (VOCs)

12 - 1

## How Do We Define HAPs

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

12 - 2

## 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

12 - 3

## 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

12 - 4

## 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

12 - 5

## 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

12 - 6

### 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)

12 - 7

### 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

12 - 8

### 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.

12 - 9

### 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.

12 - 10

### 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)

12 - 11

### General Classification of VOCs

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

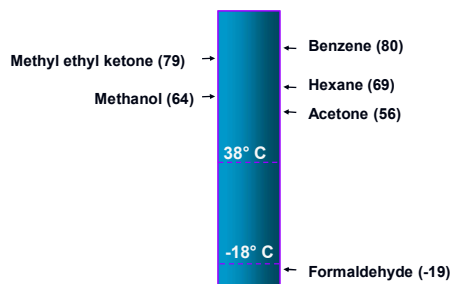
12 - 12



# APTI #450/468 Compliance Test and Source Test Observation

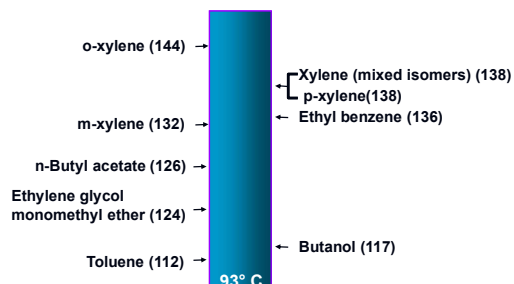
## Lesson 12: Defining Volatile Organic Compounds (VOCs)

### Boiling Points of Volatile Organic Compounds



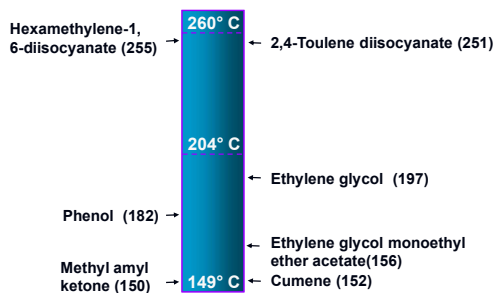
12 - 13

### Boiling Points of Volatile Organic Compounds



12 - 14

### Boiling Points of Semi-volatile Organic Compounds



12 - 15

### 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

12 - 16

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

4. The characteristics of the effluent (i.e., temperature, moisture, %CO<sub>2</sub> etc.)
5. The advantages and disadvantages of each of the test methods
6. The state and federal testing requirements documented in their regulations

12 - 17

### 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

12 - 18

### Methods Associated with Monitoring VOCs

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

12 - 19

### 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

12 - 20

### 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

12 - 21

### Definitions

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

12 - 22

### 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  $\text{MeCl}_2$

12 - 23

### 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

12 - 24

# APTI #450/468 Compliance Test and Source Test Observation Lesson 12: Defining Volatile Organic Compounds (VOCs)

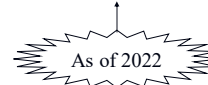
## Definitions

- 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)

12 - 25

## Definitions

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



12 - 26

## 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	

12 - 27

## Applicability of Methods

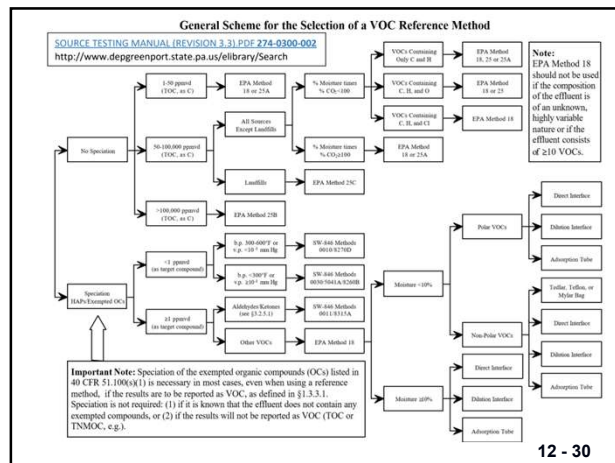
	FRM 18	FRM 25	FRM 25A
Measures...	VOCs	TGNMO	THC
Principle...	GC/MD	GC/FID	FID
Carbon Resp...	1:1	1:1	Var.
Results Exp As..	VOC	As C	Cal Gas

12 - 28

## Applicability of Methods

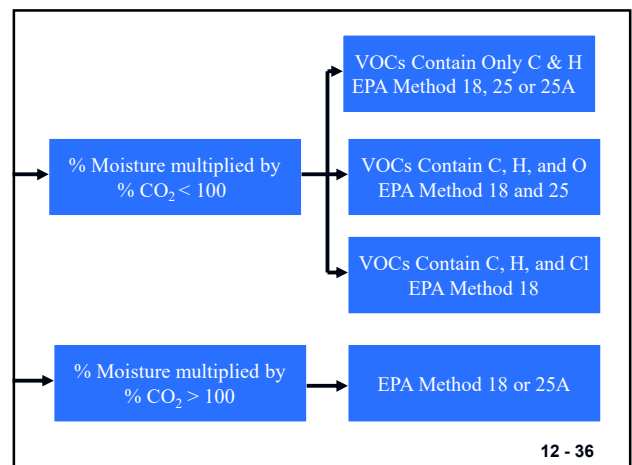
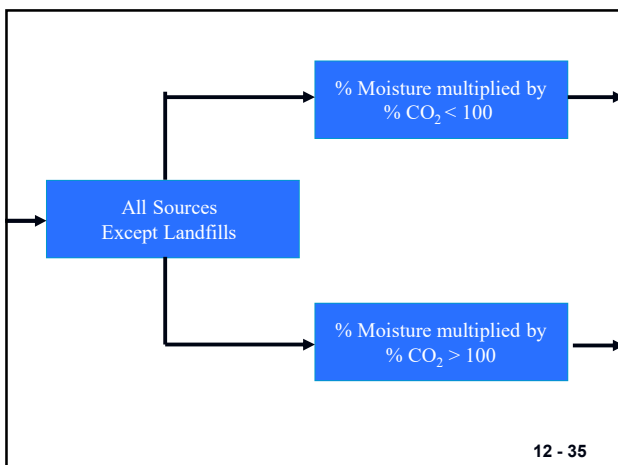
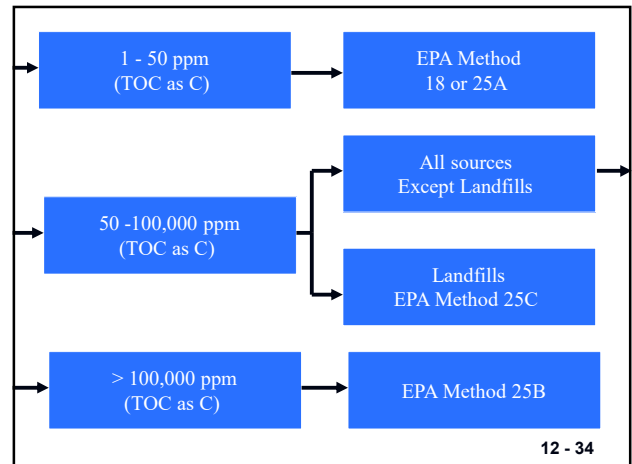
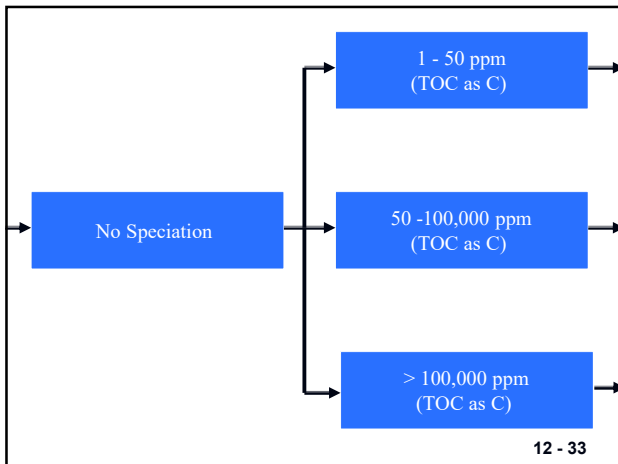
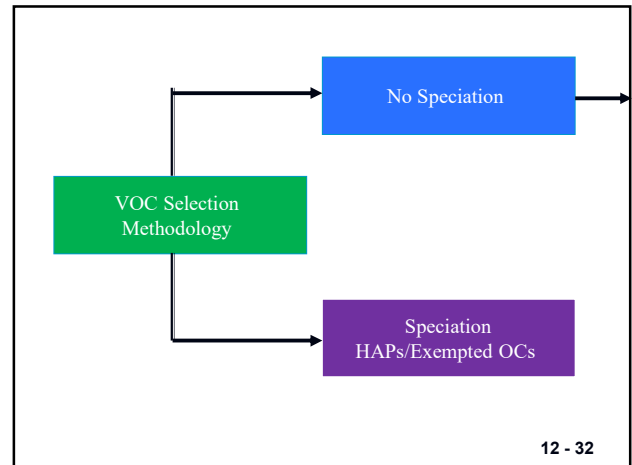
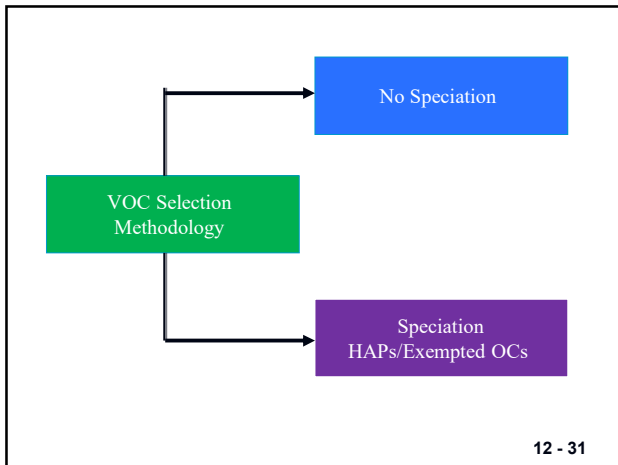
Nature of Emission	Report Emission As	Affected Facility
VOCs unknown/variable	Propane	Asphalt Plants
Single VOC > 75 %	That single VOC	Cement Plants Resource Recovery Bakeries
Single VOC < 75 %	Surrogate	SOCMI Surface Coat Graphite Art

12 - 29

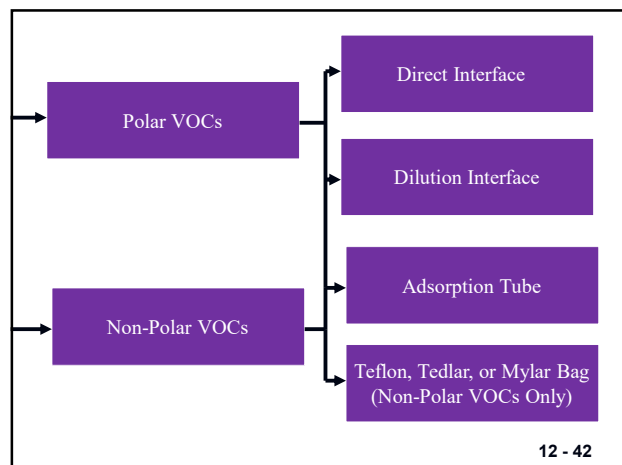
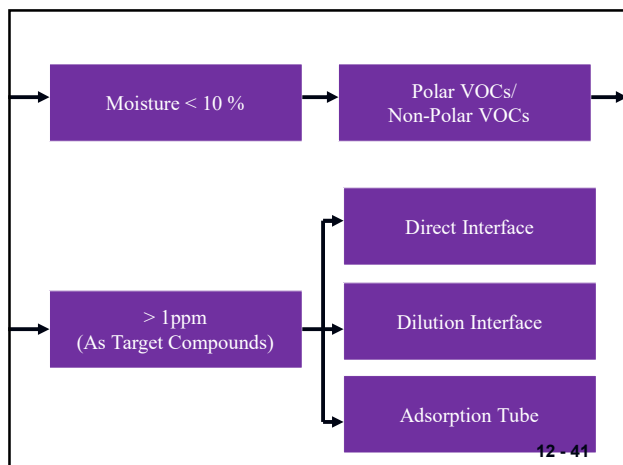
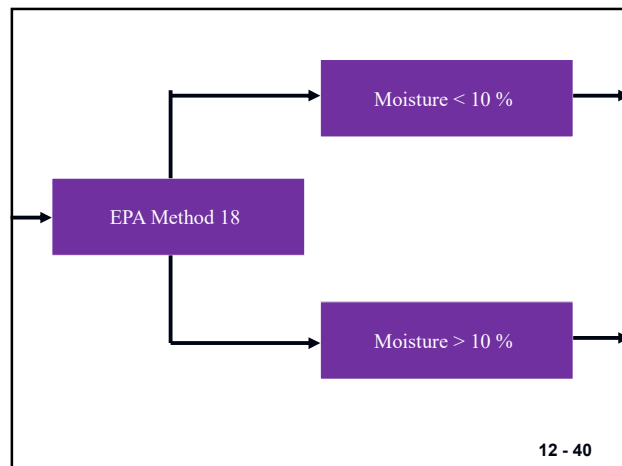
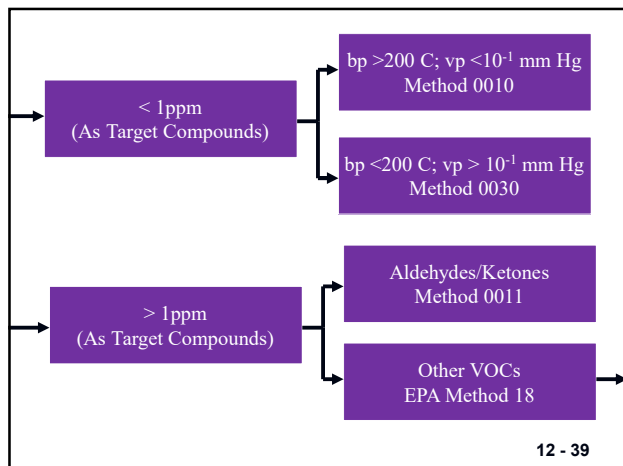
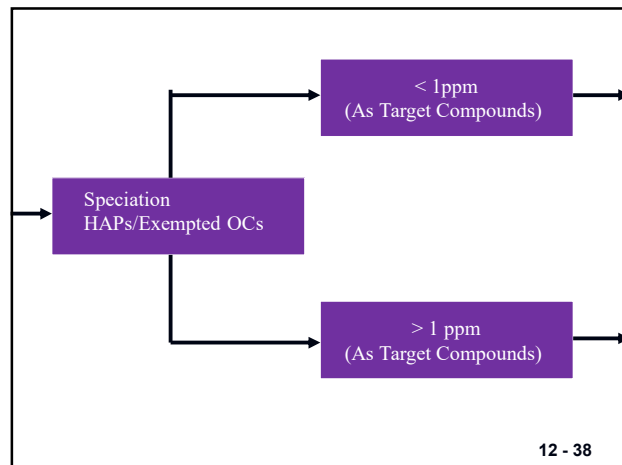
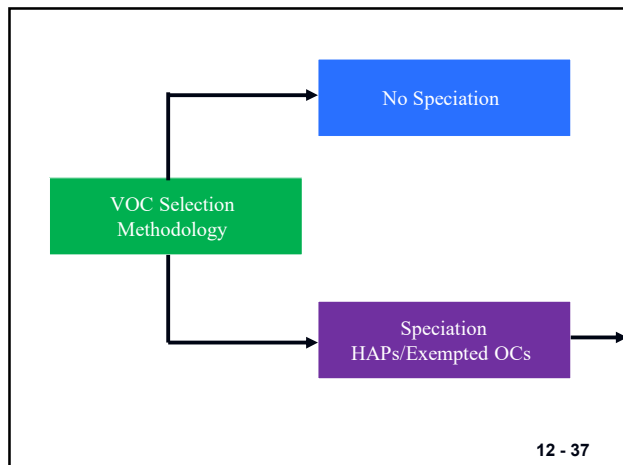


# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 12: Defining Volatile Organic Compounds (VOCs)



# **APTI #450/468 Compliance Test and Source Test Observation** **Lesson 12: Defining Volatile Organic Compounds (VOCs)**



### Reporting of Emissions?

- “As Carbon?”
- “As TGNMOCs?”
- “As Propane?”
- “As VOCs?”
- “As THC?”
- “As.....What?”

12 - 43

### 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) .

12 - 44

### 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.

12 - 45

### 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.

12 - 46

### 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

12 - 47

### 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.

12 - 48



# APTI #450/468 Compliance Test and Source Test Observation Lesson 12: Defining Volatile Organic Compounds (VOCs)

## 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

12 - 49

## 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.)

12 - 50

## 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., SOCM 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.)

12 - 51

## 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.”

12 - 52

## 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.

12 - 53

## Reporting of Emissions

### Example Calculation 1

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

$$\left( \frac{\text{ppmvw as } C_3H_8}{(1 - B_{wt})} \right) (K_{MESA}) (MW_C) (Q_{sc}) \left( \frac{MW_{C_2H_5OH}}{(\# \text{ C atoms } C_2H_5OH) (MW_C)} \right) \left( \frac{RRF_{C_2H_5OH}}{RRF_{C_3H_8}} \right) = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

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

12 - 54

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 12: Defining Volatile Organic Compounds (VOCs)

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#### 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...

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

12 - 55

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18

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

### Federal Reference Method 18 General GC Methodology (Work Horse for VOCs Speciation Detection)

13A - 1

Direct Interface  
Direct Interface/Dilution  
Solid Adsorbent  
Tedlar Bags



13A - 2

Survey Canister Sampling



13A - 3

### 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

13A - 4

### 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!”

13A - 5

### 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)

13A - 6

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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

13A - 7

#### 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 %

13A - 8

#### 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

13A - 9

#### 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 ( $\text{CH}_3\text{OH}$ , MW=32)  $100 \text{ ppm} \times 32 = 3200$
  - FRM 25 (C, MW=12)  $100 \text{ ppm} \times 12 = 1200$
  - Error: 62 %

13A - 10

#### 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

13A - 11

#### 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

13A - 12

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### Overview Items

- FRM 18 requires determination of recovery study for all methodologies
  - Direct interface: Mid-level gas at probe then analyzer/2 injections ( $\pm 10\%$ )
  - 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

13A - 13

#### 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

13A - 14

#### 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

13A - 15

#### 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

13A - 16

#### 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

13A - 17

#### 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.

13A - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18

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### Interferences

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

13A - 19

### Interferences

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

13A - 20

### 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

13A - 21

### 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

13A - 22

### 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)

13A - 23

### FRM 18 Sampling Methods

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

13A - 24



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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

13A - 25

#### FRM 18 Sampling Methods

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

13A - 26

#### 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., % H<sub>2</sub>O, stack temperature, part. loading etc.)
  - Perform survey with direct injection, Tedlar bags or canisters and identify all TICs with peaks > 5 %

13A - 27

#### 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)**

13A - 28

#### 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.

13A - 29

#### 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

13A - 30

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18

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### 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

13A - 31

### 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

13A - 32

### 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

13A - 33

### 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

13A - 34

### 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

13A - 35

### Purge Flask Sampling Procedure

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

13A - 36

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 13A: Federal Reference Method 18**

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Purge Flask  
Sampling Procedure

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

13A - 37

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

13A - 38

Flexible Bag  
Sampling Procedure

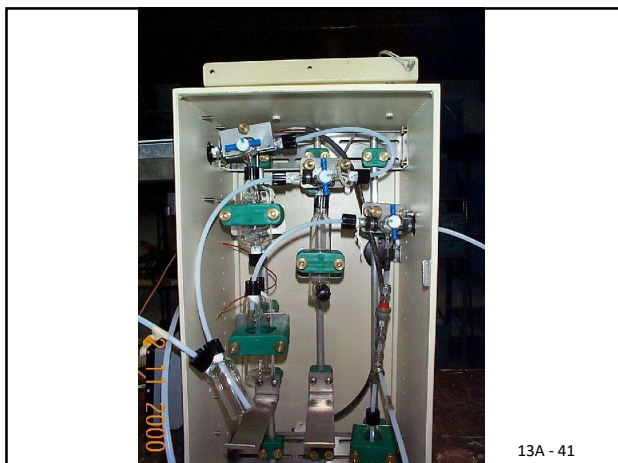
- Check for contamination by filling with nitrogen
- Analyze 24 hours later with GC

13A - 39

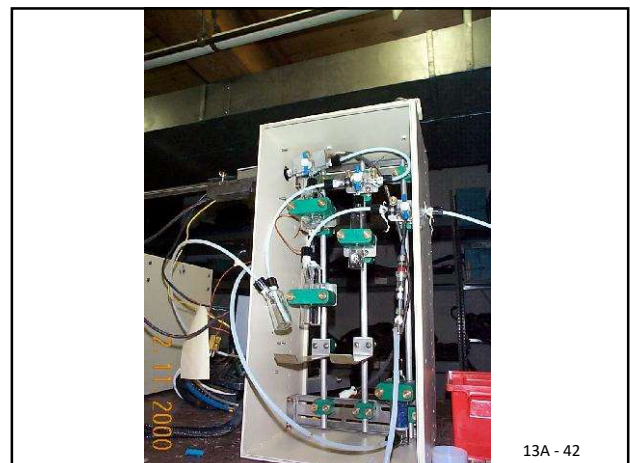
Bag Sampling

- 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

13A - 40



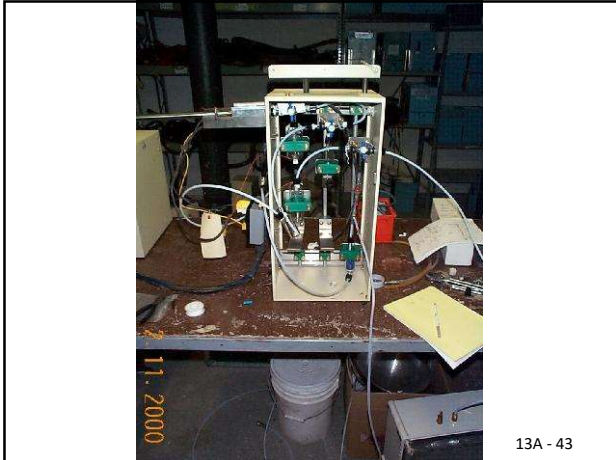
13A - 41



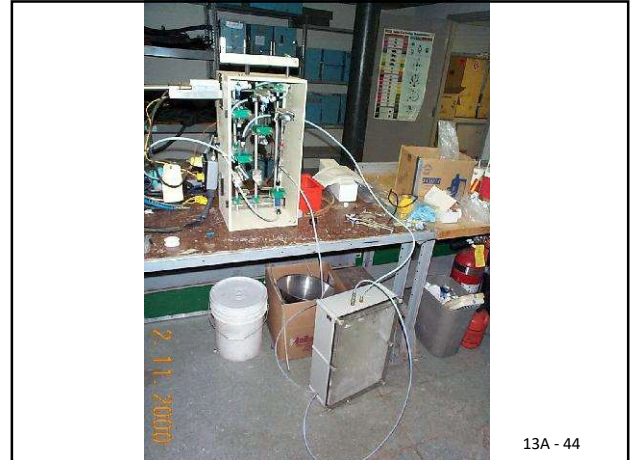
13A - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18



13A - 43



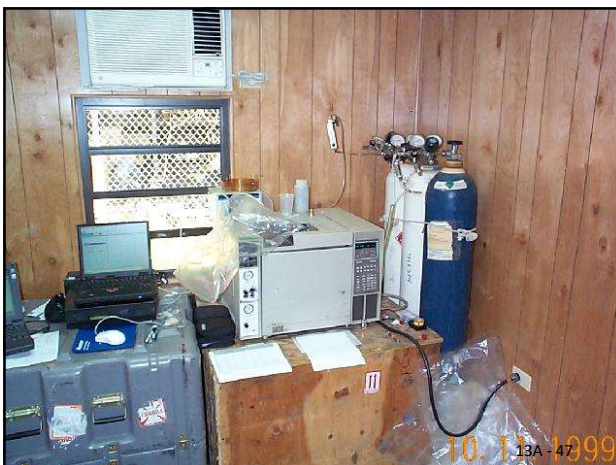
13A - 44



### 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

13A - 46



13A - 47

### 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%

13A - 48

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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)

13A - 49

#### 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

13A - 50

#### Direct Interface Sampling and Analysis

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

13A - 51

#### 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 %

13A - 52

#### 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

13A - 53

#### 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

13A - 54

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

---

#### 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

13A - 55

#### 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.)

13A - 56

#### 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  $\pm 10\%$

13A - 57

#### Nature of Ideal Adsorbents

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

13A - 58

#### Nature of Ideal Adsorbents

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

13A - 59

#### Advantages of Adsorbent Technology

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

13A - 60



**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 13A: Federal Reference Method 18**

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Typical Adsorbents

- Organic polymer adsorbent
- Inorganic adsorbent
- Carbon adsorbents

13A - 61

Classification of Adsorbents

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

13A - 62

Typical Organic  
Polymeric Adsorbents

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

13A - 63

Weaknesses of  
Tenax® Adsorbent

- Poor desorption of highly polar compounds
- Possibly retains O<sub>2</sub> leading to sample oxidation
- Limited to specific range of VOCs

13A - 64

Weaknesses of  
Tenax® Adsorbent

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

13A - 65

Weaknesses of  
XAD® Series Adsorbent

- Thermal stability questionable
- Breakthrough extensive for < C7

13A - 66

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 13A: Federal Reference Method 18**

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Inorganic Adsorbents

- Silica gel
- Alumina
- Fluorisil
- Carbon molecular sieves

13A - 67

Weaknesses of  
Silica Gel Adsorbent

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

13A - 68

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

13A - 69

Carbon Adsorbent

- Activated carbon
- Carbon molecular sieve
- Carbonaceous polymeric adsorbents

13A - 70

Limitation of  
Carbon Base Adsorbents

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

13A - 71

Limitation of  
Carbon Base Adsorbents

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

13A - 72

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18

### Common Adsorbents Used in Air Pollution Studies

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

13A - 73

### Common Adsorbents Used in Air Pollution Studies

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

13A - 74

### 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

13A - 75

### 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

13A - 76

### Supelco Carbotrap® 300

Carbotrap C®	Carbonaceous material	Heavy Organics (> C <sub>12</sub> )
Carbotrap	Carbonaceous material	C <sub>5</sub> to C <sub>12</sub>
Carbosieve S-III®	Carbon molecular sieve	C <sub>2</sub> to C <sub>6</sub>

13A - 77

### Adsorbent Recovery Two Process Recoveries

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

13A - 78

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18

### Adsorbent Recovery Solvent Extraction

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

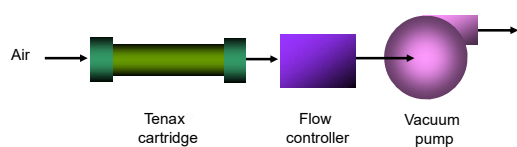
13A - 79

### 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

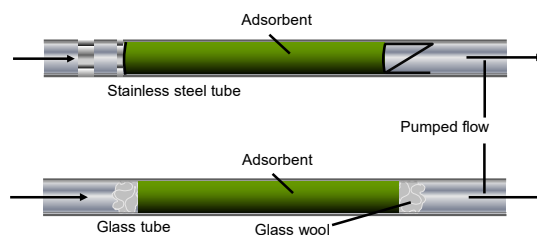
13A - 80

### Active Sampling System Utilizing Solid Adsorbents



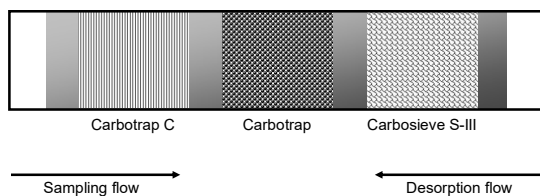
13A - 81

### Single Tube Design-Glass/Stainless Steel



13A - 82

### Multi-bed Adsorbent Trap



13A - 83



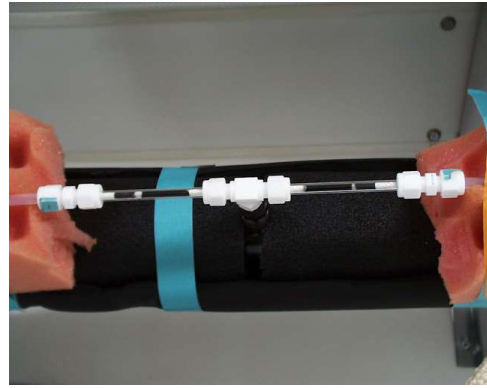
13A - 84

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18



13A - 85



13A - 86



13A - 87

#### Adsorbent Tube Sampling

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

13A - 88

#### Adsorbent Tube Sampling

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

13A - 89

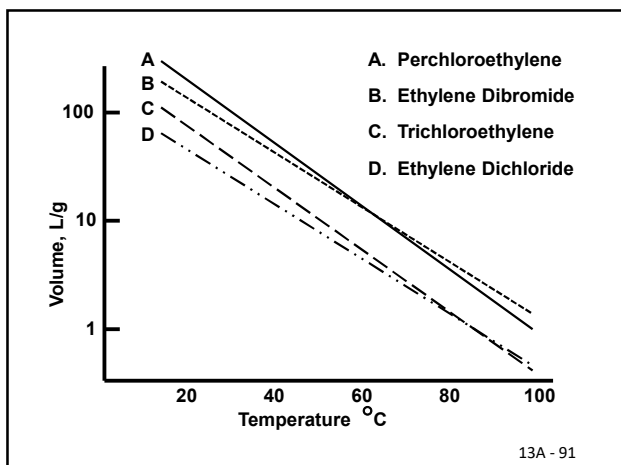
#### Breakthrough Volume

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

13A - 90

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13A: Federal Reference Method 18



### 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

13A - 92

### 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

13A - 93

### 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

13A - 94

### 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

13A - 95

### 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)

13A - 96



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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  $\pm 10\%$

13A - 97

#### 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  $100^{\circ}\text{C}$  and organics suitable for GC analysis

13A - 98

#### Direct Interface Sampling

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

13A - 99

#### 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

13A - 100

#### Tedlar® Bag Sampling

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

13A - 101

#### Recovery Studies

- Direct Interface: Mid-level calibration point for 1 analysis ( $\pm 10\%$ ) repeated twice ( $\pm 5\%$ )
- 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

13A - 102

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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

13A - 103

#### 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

13A - 104

#### FRM 18 Adsorbent Tube Sampling

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

13A - 105

#### FRM 18 Adsorbent Tube Sampling

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

13A - 106

#### FRM 18 Adsorbent Tube Sampling

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

13A - 107

#### FRM 18 Adsorbent Tube Sampling

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

13A - 108

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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

13A - 109

#### 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

13A - 110

#### 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

13A - 111

#### 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

13A - 112

#### FRM 18 Pre-survey Requirements

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

13A - 113

#### 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

13A - 114

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 13A: Federal Reference Method 18**

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FRM 18 Pre-survey  
Sample Analysis

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

13A - 119

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

13A - 120

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### Criteria for Pre-survey and Sample Analysis

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

13A - 121

#### 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])

13A - 122

#### Preparation of Calibration Standards

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

13A - 123

#### 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

13A - 124

#### Preparation of Calibration Standards

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

13A - 125

#### 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)

13A - 126

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### FRM 18 Final Sampling and Analysis Procedure

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

13A - 127

#### 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

13A - 128

#### FRM 18 Compliance Test Direct/Dilution Interface

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

13A - 129

#### FRM 18 Compliance Test Direct/Dilution Interface

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

13A - 130

#### FRM 18 Compliance Test Direct/Dilution Interface

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

13A - 131

#### 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

13A - 132



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13A: Federal Reference Method 18

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#### 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

13A - 133

#### FRM 18 Reporting Results

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

13A - 134

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25

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



13B - 1

### 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

13B - 2

### 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

13B - 3

### 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

13B - 4

### 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 |

13B - 5

### 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<sub>2</sub> X % H<sub>2</sub>O > 100
  - As water freezes in the trap, CO<sub>2</sub> is trapped out prematurely. The CO<sub>2</sub>, when reduced to methane, is counted as VOCs in the analytical system

13B - 6

### 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

13B - 7

### 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

13B - 8

### 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

13B - 9



### 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

13B - 11

### 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

13B - 12

### 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)

13B - 13

### 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)

13B - 14

### 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

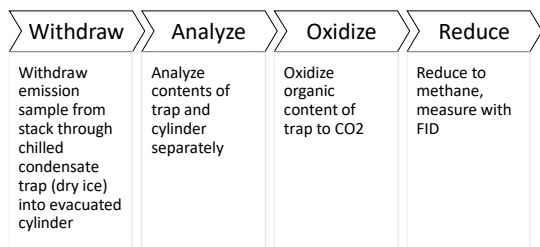
13B - 15

### 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<sub>2</sub> together can cause interference
  - ( $\%CO_2$ )x( $\%H_2O$ )>100 gives potential high bias (EPA Guidelines)

13B - 16

### Method 25 Summary



13B - 17

### Method 25 Summary

- Inject portion of cylinder sample into GC to separate non-methane organics, oxidize NMO to CO<sub>2</sub>, reduce to methane, and measure with FID
- Combine results (condensable and non-condensable) and report as total gaseous nonmethane organics (TGNMO)

13B - 18

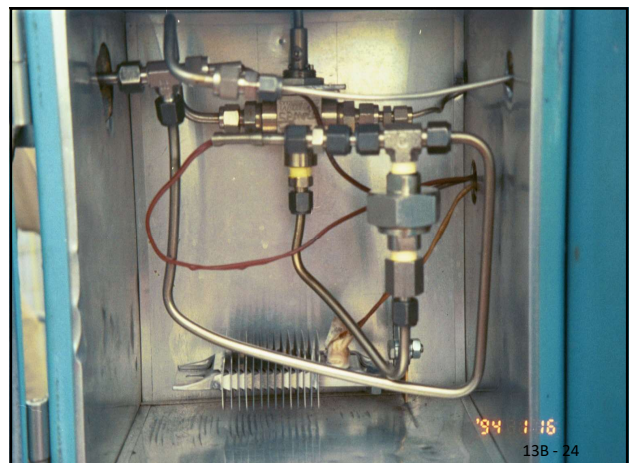
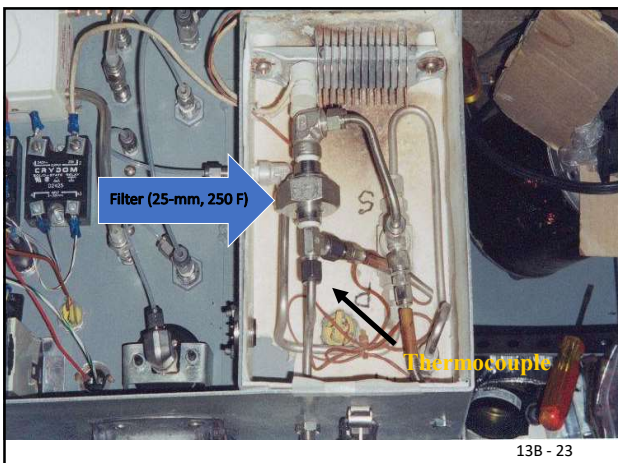
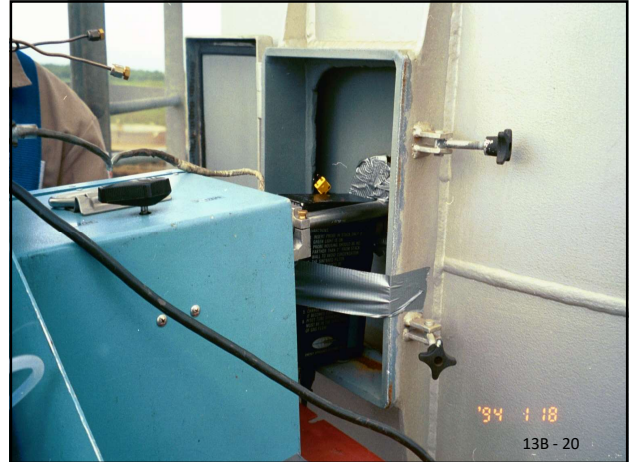
# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25

### Method 25 Apparatus

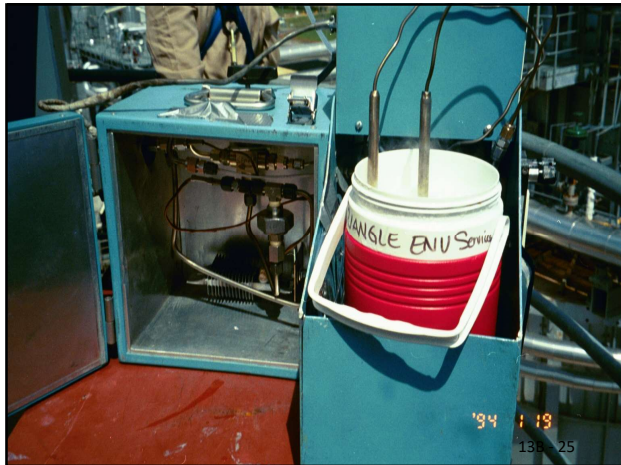
- Sampling System
  - Probe (260 °C)
  - Filter (250 °C  $\pm$  5 °C)
  - Condensate trap (-78 °C) for condensables
  - Flow control system
  - Sample tank for non-condensables

13B - 19





APTI #450/468 Compliance Test and Source Test Observation  
Lesson 13B: Federal Reference Method 25





# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25



### 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)

13B - 36

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13B: Federal Reference Method 25

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#### 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

13B - 37

#### Method 25 Sampling Train Preparation

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

13B - 38

#### 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

13B - 39

#### Method 25 Train Preparation

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

13B - 40

#### 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  $\Delta P$ . Vacuum should not change more than 2 mm to be acceptable

13B - 41

#### Method 25 Train Preparation

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

13B - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25

### 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

13B - 43

### 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

13B - 44

### Method 25 Sampling

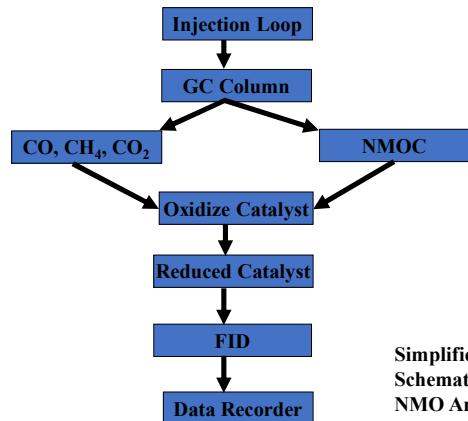
- Record sample tank vacuum, flow meter settings, and temperatures at 5 - minute intervals on FTDS
- Adjust the flow rate as necessary to maintain a constant rate,  $\pm 10\%$  over duration
- Sampling rate between 60-100 mL/min (i.e., 3.6 to 6.0 L of total sample acquired)
- After sampling, record final readings

13B - 45

### 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

13B - 46



Simplified  
Schematic of  
NMO Analyzer  
13B - 47

### Method 25 Sample Analysis

- Condensable organics in the trap are vaporized and oxidized to CO<sub>2</sub> and collected in a separate (#2) evacuated tank
- The CO<sub>2</sub> (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

13B - 48

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13B: Federal Reference Method 25

#### 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<sub>2</sub>, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO<sub>2</sub>, reduced to methane and detected with an FID

13B - 49

#### Method 25 Apparatus

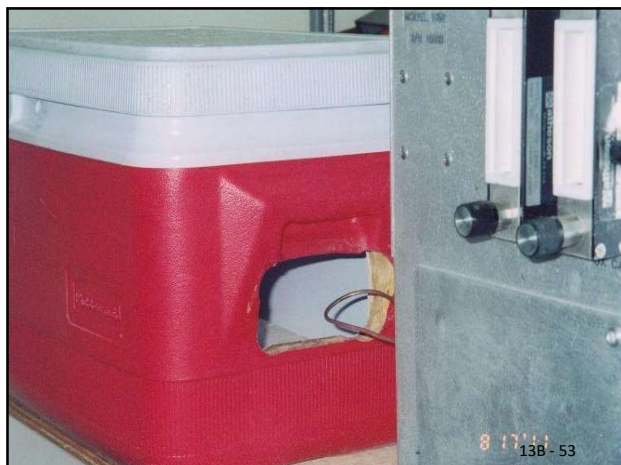
- Analytical System
  - Oxidation system for recovery and conditioning of condensate trap contents
    - Heat source
    - Oxidation catalyst (chromia @ 650 °C)
    - Non-dispersive infrared analyzer (NDIR)
    - Intermediate evacuated canister (#2)

13B - 50

#### Method 25 Apparatus

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

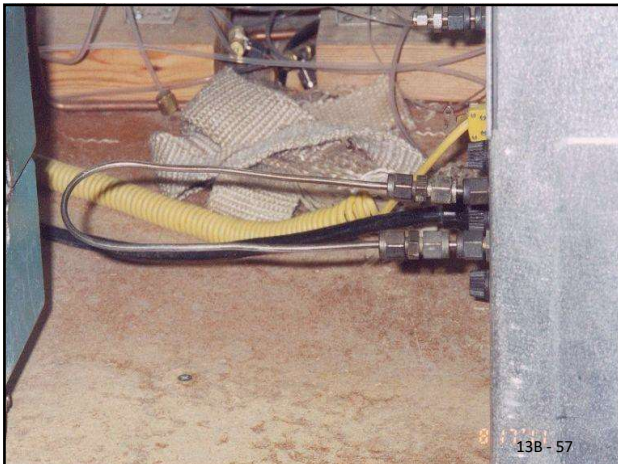
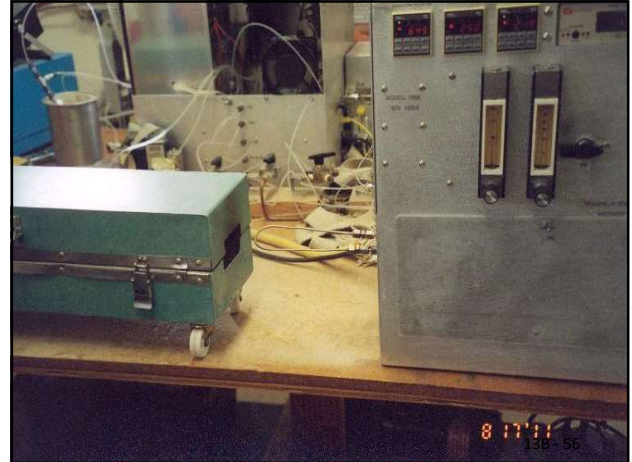
13B - 51





**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 13B: Federal Reference Method 25**

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# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25



### Initial Performance Check of Condensate Recovery and Conditioning Apparatus

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

138 - 63

### Daily Performance Tests

1

#### Condensable organic recovery system

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

2

#### NMO analyzer daily calibration

- CO<sub>2</sub> response calibration (CO<sub>2</sub>/methane)
- NMO response calibration (Propane)

138 - 64

### Condensable Organic Fraction Recovery

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

138 - 65

### 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

138 - 66



### Condensable Organic Fraction Recovery

- Measure sample tank pressure
- Immerse the condensate trap in crushed dry ice
- Observe IR response to CO<sub>2</sub> to minimum level of < 5 ppm
- Pressurize sample tank (#1) to 1060 mm Hg absolute pressure and detach

13B - 67

### 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

13B - 68

### 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

13B - 69

### Condensable Organic Fraction Recovery

- Recovery of condensable organics
  - After NDIR analyzer indicates a CO<sub>2</sub> concentration of < 10,000 ppm, begin heating the tubing that connects the condensate trap to the oxidation catalyst with a heat gun

13B - 70

### Condensable Organic Fraction Recovery

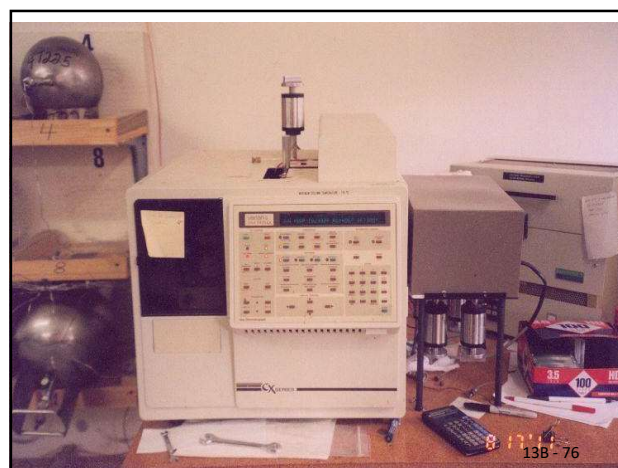
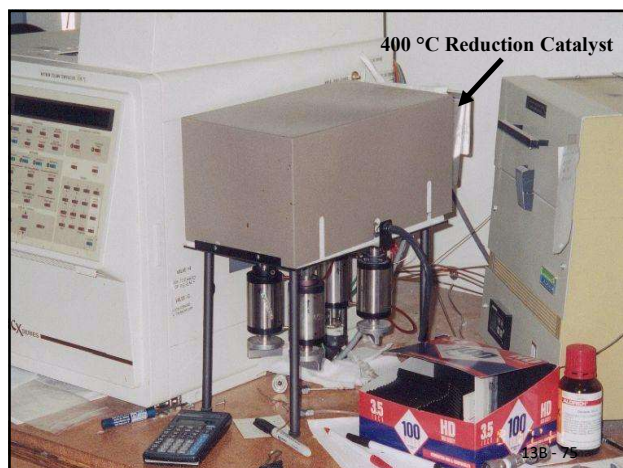
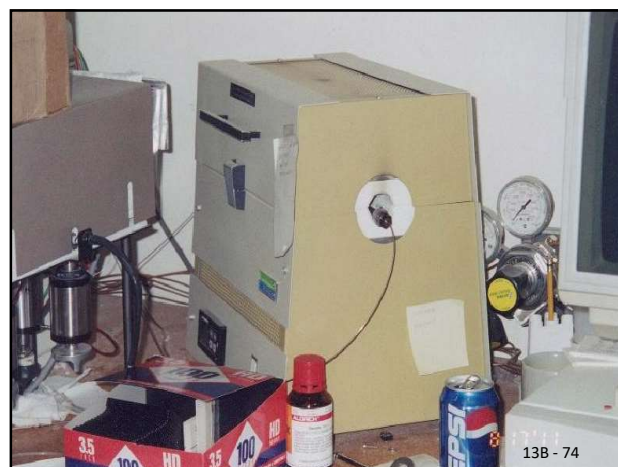
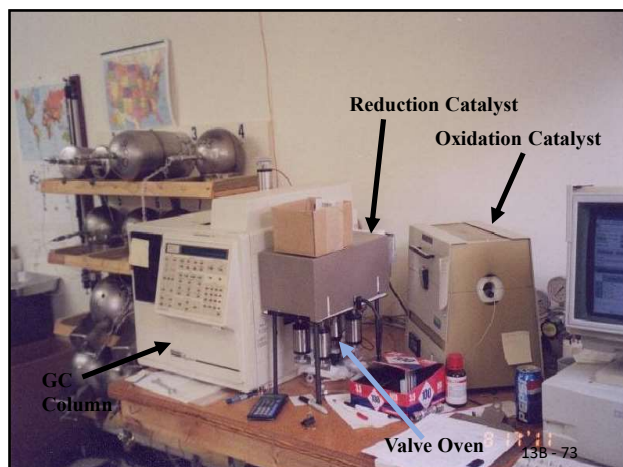
- Continue trap heating and purging until the CO<sub>2</sub> concentration is below 10 ppm
- Pressurize the ICV (i.e., #2) to approximately 1060 mm Hg

13B - 71



13B - 72

APTI #450/468 Compliance Test and Source Test Observation  
Lesson 13B: Federal Reference Method 25



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25

### Method 25 Apparatus

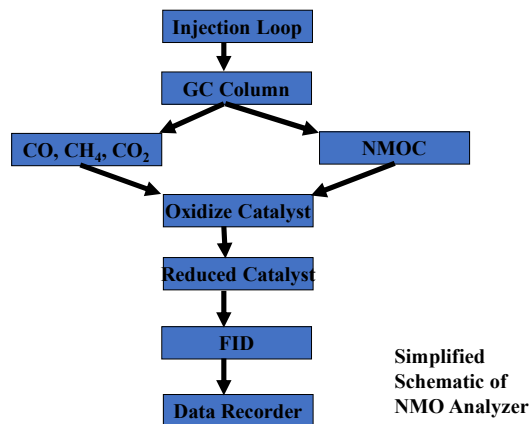
- Method 25 NMO Analyzer Apparatus
  - GC with back-flush capability
  - Oxidizing catalyst (19 % chromia on alumina @ 650 °C)
  - Reducing catalyst (Ni @ 400 °C)
  - FID

13B - 79

### 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<sub>2</sub>, and NMOC are separated, and the NMOC fraction is then back-flushed, oxidized to CO<sub>2</sub>, reduced to methane, and detected with an FID
  - Original tank (#1) only NMO quantified

13B - 80



13B - 81

### 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<sub>2</sub> peak, back-flush and increase column oven temperature

13B - 82

### Method 25 Analysis

- After detection of any NMOC, return column oven temperature to 85°C
- Record the CO<sub>2</sub> peak area and NMO peak area
- Repeat analysis two additional times

13B - 83

### 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

13B - 84



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13B: Federal Reference Method 25

### Method 25 Calculations

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

13B - 85



### Method 25 QC Checks

#### 1. Oxidation Catalyst Efficiency Test

1 % CH<sub>4</sub>

Oxid./Red. Cat. Unheated (R1)

Oxid Cat. Heated (R2)

Oxid. Cat. Eff. =  $R1 - R2 / R1 \times 100$

13B - 91

### Method 25 QC Checks

#### 2. Reduction Catalyst Efficiency Test

1 % CH<sub>4</sub>

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

Oxid./Red. Cat. Heated (R3)

Red. Cat. Eff. =  $R4 / R3 \times 100$

13B - 92

### 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

13B - 93

### Method 25 QC Checks

#### 4. CO<sub>2</sub> Response Linearity Test and Initial Calibration

50, 500, 10,000 ppm CO<sub>2</sub> standard

Response Factor (RF) within 10 % over range, then linear response

13B - 94

### Method 25 QC Checks

#### 5. NMO Analyzer Performance (ppmC)

Std #1: 50 ppm CO, 50 ppm CH<sub>4</sub>, 2 % CO<sub>2</sub>, 20 ppm Propane

Std #2: 50 ppm Hexane

Std #3: 20 ppm Toluene

Std #4: 100 ppm Methanol

Criteria:  $\pm 5\%$

13B - 95

### 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

13B - 96

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13B: Federal Reference Method 25

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#### 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<sub>2</sub>)
3. Oxidation catalyst efficiency check
4. CO<sub>2</sub> analyzer response
5. NMO response check

13B - 97

#### 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

13B - 98

#### Method 25 QC Checks

##### EPA Audit Sample (2)

Between 50 % below standard and 100 % above standard ± 20% of known concentration

13B - 99

#### 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

13B - 100

#### 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

13B - 101

#### Method 25 Guide

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

13B - 102



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13B: Federal Reference Method 25

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#### 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)

13B - 103

#### 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

13B - 104

#### 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

13B - 105

#### 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

13B - 106

#### 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)

13B - 107

#### 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)

13B - 108

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13B: Federal Reference Method 25

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#### 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

13B - 109

#### Method 25 Guide

- However, this increases analytical cost and may increase the positive bias from trapping CO<sub>2</sub>
- This approach does appear to limit sampling problems

13B - 110

#### 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 affects final volume sampled
- Do not over tighten swage-lock fittings as part of the sample train

13B - 111

#### 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

13B - 112

#### 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

13B - 113

#### 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

13B - 114

### Observations

- If you are sampling a source with high moisture (> 20%) and high CO<sub>2</sub> (>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

13B - 115

**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)

13C - 1

**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

13C - 2

**Method 25A Timeline**

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

13C - 3

**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

13C - 4

**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)

13C - 5

**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)

13C - 6

### 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

13C - 7

### 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

13C - 8

### Applicability

- FRM 25A “...*can only be used where an appropriate response factor for the stack gas can be determined*”

13C - 9

### 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

13C - 10

### 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

13C - 11

### 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

13C - 12

#### FRM 25A Items

- Calibration for FRM 25A should be done using EPA Traceability Protocol gas standards, preferably propane
- The sample line should be heated ( $\geq 110^{\circ}\text{C}$ ) to prevent any condensation. Heating above 400 F is not required.

13C - 13

#### 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

13C - 14

#### 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.

13C - 15

#### 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

13C - 16

#### 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

13C - 17

#### 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 %)

13C - 18



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13C: Federal Reference Method 25A

### Wet Bases to Dry Bases

- Wet bases measurement emissions to dry bases measurement emissions:

$$C_{s(dry)} = \frac{C_{s(wet)}}{(1-Bws)}$$

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

13C - 19

### 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  $\geq 110^{\circ}\text{C}$  ( $220^{\circ}\text{F}$ )
- The flame ionization detector block shall be heated  $>120^{\circ}\text{C}$  ( $250^{\circ}\text{F}$ ).

13C - 20

### 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

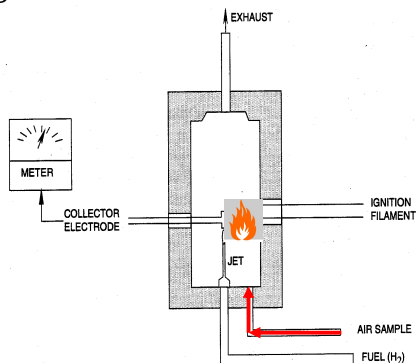
13C - 21

### 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  $\text{H}_2\text{O}$  and  $\text{CO}_2$

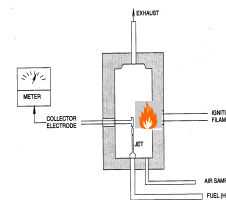
13C - 22

### Diagram of FID



13C - 23

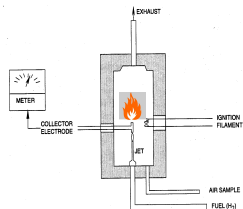
### Flame Ionization Detection



- Advantages
  - Wide dynamic and linear range (0-10,000 ppm)
  - Highly sensitive to hydrocarbon vapors
  - Very stable and repeatable
  - Unaffected by ambient levels of  $\text{CO}$ ,  $\text{CO}_2$  and water vapor

13C - 24

### Flame Ionization Detection



#### •Disadvantages

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

13C - 25

### 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

13C - 26

### 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

13C - 27

### 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

13C - 28

### 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<sub>2</sub> (> 16 %) for combustion in the FID

13C - 29

### 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

13C - 30

### 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

13C - 31

### FRM 25A Sampling System

- Sample Line: Heated ( $> 250^{\circ}\text{F}$ ) stainless steel or Teflon<sup>®</sup> tubing
- All components must be heated  $> 250^{\circ}\text{F}$  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

13C - 32

### Sampling System

- Calibration Valve Assembly:  
A heated ( $> 250^{\circ}\text{F}$ ) 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 ( $> 250^{\circ}\text{F}$ ) glass fiber filter assembly
- Pump: A heated ( $> 250^{\circ}\text{F}$ ) leak-free diaphragm type

13C - 33

### Sampling System

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

13C - 34

### FRM 25A Gases

- Fuel: 40%  $\text{H}_2$ /60% He or 40%  $\text{H}_2$ /60%  $\text{N}_2$
- Zero Air: High purity air with less than 0.1 ppmv of organic material (propane or carbon equivalent)
  - Most systems use 100%  $\text{H}_2$  as the fuel which makes for a hotter flame

13C - 35

### Gases

- Calibration Gases (i.e., propane in air/ $\text{N}_2$ )
  - 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

13C - 36

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13C: Federal Reference Method 25A

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#### 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<sub>2</sub> may yield inaccurate results!)

13C - 37

#### 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):  $\pm$  5% of calibration gas value

13C - 38

#### 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):  $\pm$  3% of span value

13C - 39

#### Pre-test Requirements

- Sampling Site: Located as required by the specific regulations (i.e., exhaust stack, inlet line etc.)
- Method 1

13C - 40

#### Pre-test Requirements

- Assemble the sampling system following manufacturer's specification
- Prepare sample interface from stack to extraction system
- Make system operable

13C - 41

#### 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

13C - 42

### 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

13C - 43

### Pre-test Requirements

- After leak test of system, place probe at centroid of stack, pipe, or duct and is sealed tightly

13C - 44

### 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

13C - 45

### 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

13C - 46

### 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

13C - 47

### 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

13C - 48

### 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)

13C - 49

### 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%

13C - 50

### 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

13C - 51

### 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

13C - 52

### 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

13C - 53

### 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!!!

13C - 54



### 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

13C - 55

### 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!

13C - 56

### Organic Concentration Calculations

- Calculated as ppm<sub>v</sub> 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

13C - 57

### 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!

13C - 58

### 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

13C - 59

### 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<sub>2</sub>)(H<sub>2</sub>O) > 100 %
- Set-up instrument in environmentally controlled room to minimize instrument drift

13C - 60

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13C: Federal Reference Method 25A

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#### 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!

13C - 61

#### 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

13C - 62

#### 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

13C - 63

#### 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

13C - 64

#### 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<sub>2</sub>O etc.)
  - The results (lbs/hour) at both the inlet and outlet must be on the same bases (as propane or as VOCs)

13C - 65

#### Method 25A Notes (Contd)

- The actual emissions should be determined if at a VOC coating source:

$$\text{Emission Rate} = \{(\text{Coating Usage}) \times (\text{Coating Usage}) \times (1 - \text{DE}) \times (\text{CE})\} + \{(\text{Coating Usage}) \times (\text{VOC Content}) \times (1 - \text{CE})\}$$

13C - 66

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

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

#### Weakness/Strengths FRMs 18, 25, & 25A



13D - 1

#### Lecture Objectives



13D - 2

#### Background

- FRM 25 - measures total VOC
- FRM 25A - measures total hydrocarbons (THC)
- FRM 18 - measures individual organic compounds

13D - 3

#### 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

13D - 4

#### 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

13D - 5

#### Background

- FRM 25
  - Samples are time integrated
  - Analysis is completed off site
- FRM 25A
  - Sampling is continuous
  - Analysis is done on site

13D - 6

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

---

### Background

- FRM 18
  - Samples can be time integrated or semi-continuous
  - Analysis can be on site or off site

13D - 7

### 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

13D - 8

### Background

- FRM 18
  - Each compound is separated and measured individually with an FID

13D - 9

### 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

13D - 10

### FRM 25 & 25A

- Where only one compound is known to exist
- When the organic compounds consist of only hydrogen and carbon

13D - 11

### 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

13D - 12

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

---

#### 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)

13D - 13

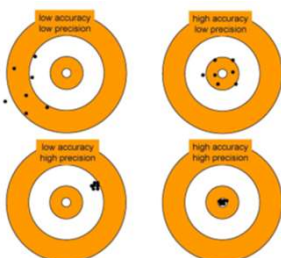
#### Advantages: FRM 25

- Measures only VOC (excludes Methane)
- Responds equally to all VOC

13D - 14

#### Disadvantages: FRM 25

- Potential positive bias that may vary according to source category
- Relatively poor precision



13D - 15

#### Advantages: FRM 25A

- Very good precision
- Real time analysis
- Relatively low detection limit

13D - 16

#### Disadvantages: FRM 25A

- Does not respond equally to all VOC
- Requires a separate measurement of Methane to convert THC to VOC

13D - 17

#### Advantages: FRM 18

- Good precision
- Low detection limits
- Can exclude methane

13D - 18

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

---

### Disadvantages: FRM 18

- Measures individual organic compounds - not total VOC
- Requires calibration standards for all measured compounds

13D - 19

### General Guidance

USEPA Guidance Document 033

([www3.epa.gov/ttn/emc/guidlnd/gd-033.pdf](http://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

13D - 20

### 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

13D - 21

### 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

13D - 22

### 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

13D - 23

### 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

13D - 24



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

---

#### 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

13D - 25

#### 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”

13D - 26

#### 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

13D - 27

#### 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)

13D - 28

#### Case Study

- Using the MW of carbon for mass emission rate calculation
- Consider Propylene Glycol ( $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ )
- Molecular Weight is 76.10
- Assume: Concentration = 100ppm
- Qsd of 100,000 dscfm

13D - 29

#### Case Study

- lb/hr “as carbon” ( $\text{MW}=12$ ) = 18.7 lb/hr.
- lb/hr “as VOC” ( $\text{MW}=76.1/3$ ) = 39.57 lb/hr.
- An error in excess of 100% due only to MW

13D - 30

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 13D: Weakness - Strengths of FRM 18, 25, 25A

---

### 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

13D - 31

### 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

13D - 32

### 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

13D - 33

### FRM 18 Reporting

- Difficulties
  - Sources claim that they only need to measure “total VOCs” - not speciated
  - What to do with a “soup” of VOCs?

13D - 34

### 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)

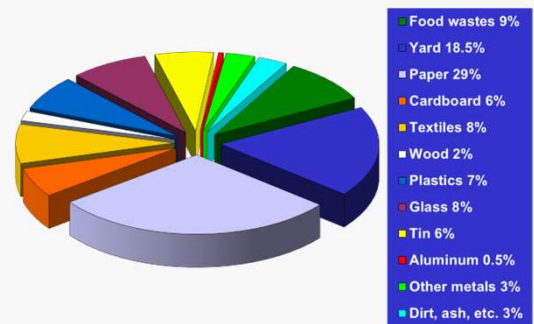
13D - 35

## Compliance Test and Source Test Observation

### Landfill FRM Sampling Methods



## Landfill Composition



14 - 2

## What is Landfill Gas(LFG)?

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

14 - 3

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

- ◆ 45 - 58% methane ( $\text{CH}_4$ )
- ◆ 35 - 45% carbon dioxide ( $\text{CO}_2$ )
- ◆ <1 - 5% oxygen ( $\text{O}_2$ )
- ◆ <1 - 20% nitrogen ( $\text{N}_2$ )

14 - 4

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

- ◆ <1 - 5% hydrogen ( $\text{H}_2$ )
- ◆ 1 - 5% water vapor
- ◆ <1 - 3% trace constituents

14 - 5

## LFG is typically composed of:

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

14 - 6

### LFG is typically composed of:

- ◆ Nonorganic species
  - Hydrogen sulfide
  - Mercury
  - Particulate matter

14 - 7

### 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

14 - 8

### Landfill Gases

- ◆ Carbon Dioxide (CO<sub>2</sub>)
  - By-product of both aerobic and anaerobic decomposition
  - Colorless, odorless gas
  - Heavier than air, noncombustible
  - Soluble in water and decreases water pH

14 - 9

### Landfill Gases

- ◆ Oxygen (O<sub>2</sub>) and Nitrogen (N<sub>2</sub>)
  - 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

14 - 10

### Landfill Gases

- ◆ Hydrogen (H<sub>2</sub>)
  - Typically produced during aerobic decomposition and early stages of anaerobic decomposition
  - Should have only trace concentrations in a mature landfill

14 - 11

### Landfill Gases

- ◆ Water Vapor (H<sub>2</sub>O)
  - LFG typically saturated with water vapor
  - Water in landfill entrained in the gas

14 - 12

## 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%

14 - 13

## Landfill Gases

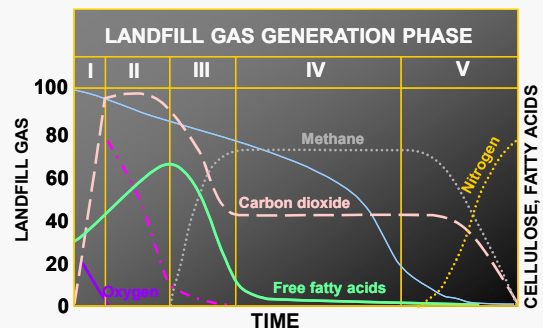
- Over 150 different organic gases have been identified
- Contaminants of potential concern (COPCs) in LFG

14 - 14

## Landfill Gas Generation Stages

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

14 - 15



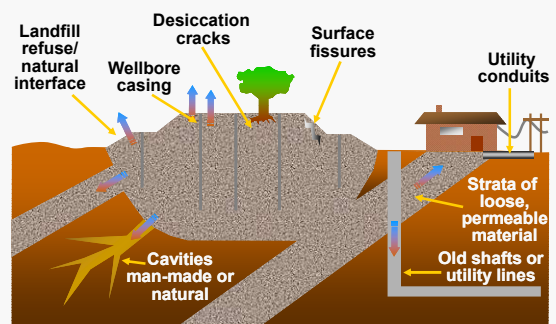
14 - 16

## 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

14 - 17

## Path of Least Resistance



14 - 18

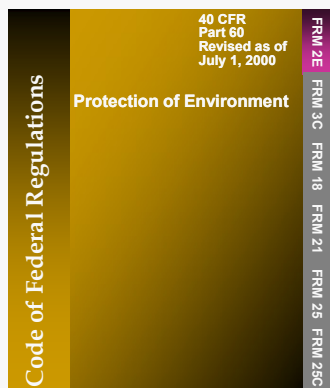
### Depends Upon the Path of Least Resistance

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

14 - 19

### Federal Reference Method 2E Determination of Landfill Gas Production Flow Rate

14 - 20



14 - 21

### 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

14 - 22

### 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

14 - 23

### Principle

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

14 - 24



### Apparatus

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

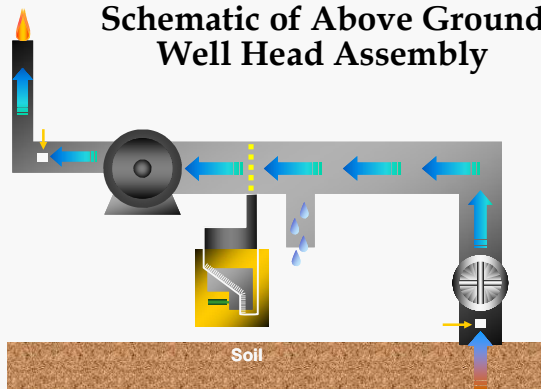
14 - 25

### Apparatus

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

14 - 26

### Schematic of Above Ground Well Head Assembly



14 - 27

### 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

14 - 28

### 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

14 - 29

### Extraction Well Pipe Configuration

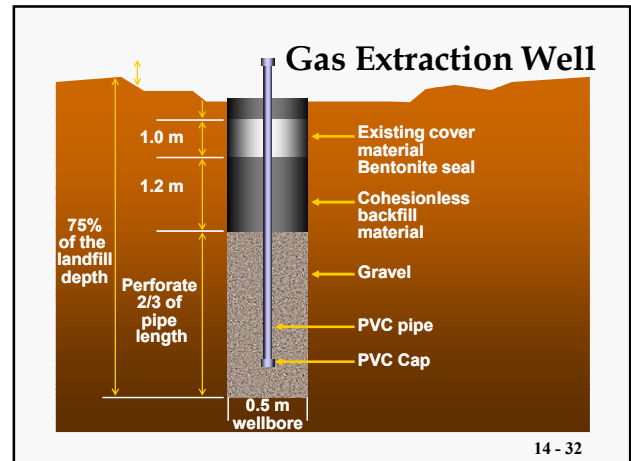
- ◆ PVC, HDPE, fiberglass, stainless steel or other materials of construction
- ◆ Minimum diameter of 0.075 meters

14 - 30

### 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

14 - 31



14 - 32

### 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

14 - 33

### 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

14 - 34

### Pressure Probe Configuration

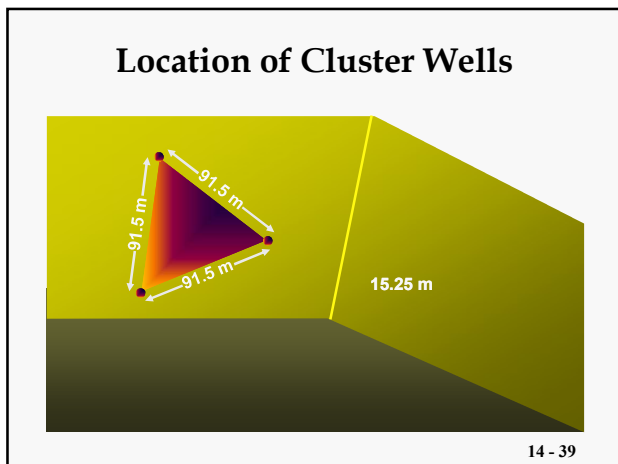
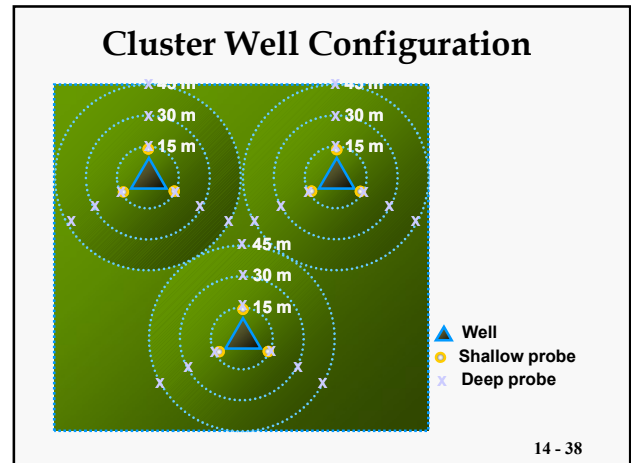
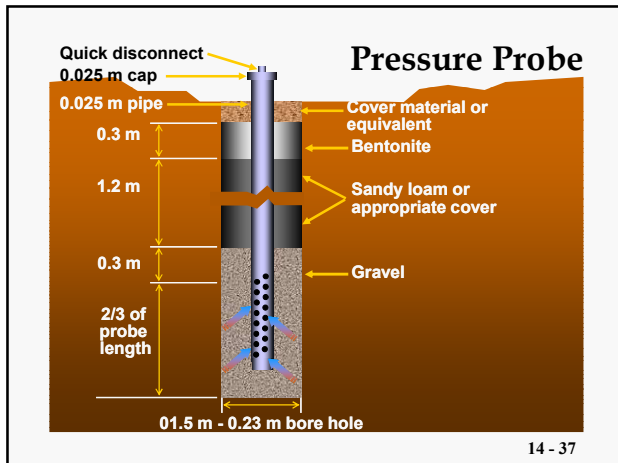
- ◆ PVC or stainless steel, 0.025 meter
- ◆ Bottom two-thirds of pipe perforated
  - Four 6-mm diameter holes
  - Placed 90 degrees apart
  - Every 0.15 meters

14 - 35

### 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

14 - 36



## **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**

14 - 41

# 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

14 - 42

### LFG Static Testing

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

14 - 43

### 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

14 - 44

### 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

14 - 45

### 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

14 - 46

### Short Term Testing

- ◆ LFG temperature  $> 55^\circ\text{C}$
- ◆ 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

14 - 47

### Short Term Testing

- ◆ Then reduce blower vacuum until nitrogen  $< 20\%$ , shallow probes are positive, or LFG temperature  $< 55^\circ\text{C}$
- ◆ 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:  $Q_s$

14 - 48

### 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 ( $P_{fa}$ )

14 - 49

### Short Term Testing

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

14 - 50

### 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:
  - $D_{st} = WD + R_{ma}^2$

14 - 51

### 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

14 - 52

### 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

14 - 53

### Long Term Testing

- Calculate  $V_t$ , the total volume of landfill gas extracted:

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

14 - 54

## Calculating NMOC mass emission rate

$$Q_t = 2kL'_o C_{NMOC} (3.595 \times 10^{-9}) \sum_{i=1}^n M_i e^{-[(k)(t_i)]}$$

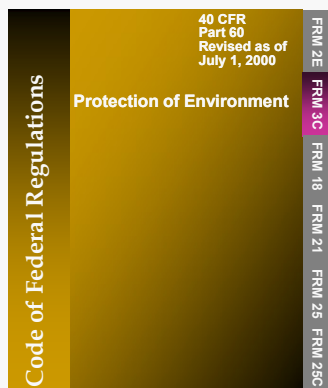
Eq. 2E-14

14 - 55

## Federal Reference Method 3C

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

14 - 56



14 - 57

## Applicability

- ◆ This method applies to the analysis of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), and oxygen (O<sub>2</sub>) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart

14 - 58

## Principle

- ◆ A portion of the sample is injected into a gas chromatograph (GC) and the CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and O<sub>2</sub> concentrations are determined by using a thermal conductivity detector (TCD) and integrator

14 - 59

## 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

14 - 60



### GC System and Analytical Apparatus



14 - 61

### 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

14 - 62

### Sample Collection

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

14 - 63

### Whole Air Flask/canister at Extraction Well



14 - 64

### 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)

14 - 65

### Analytical System Standardization

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

14 - 66

## Analytical System Standardization

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

14 - 67

## Sample Analysis

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

14 - 68

## Method 3C Calculations

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

14 - 69

## Concentration of Sample Components

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

14 - 70

## Federal Reference Method 25C

14 - 71



14 - 72

### Applicability

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

14 - 73

### 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

14 - 74

### 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<sub>2</sub>, and CH<sub>4</sub>

14 - 75

### Principle

- ◆ The NMOC from the separation is oxidized to CO<sub>2</sub>, reduced to CH<sub>4</sub>, and measured by a flame ionization detector (FID)

14 - 76

### 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

14 - 77

### 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

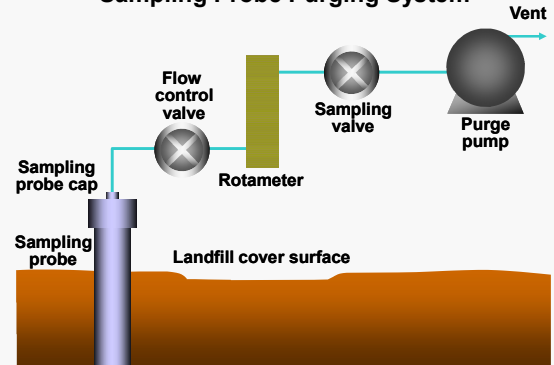
14 - 78

## 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

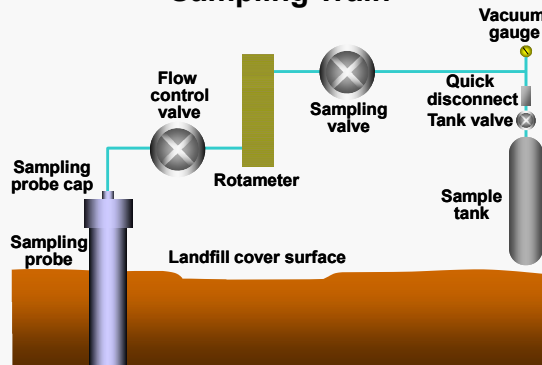
14 - 79

## Sampling Probe Purging System



14 - 80

## Sampling Train



14 - 81

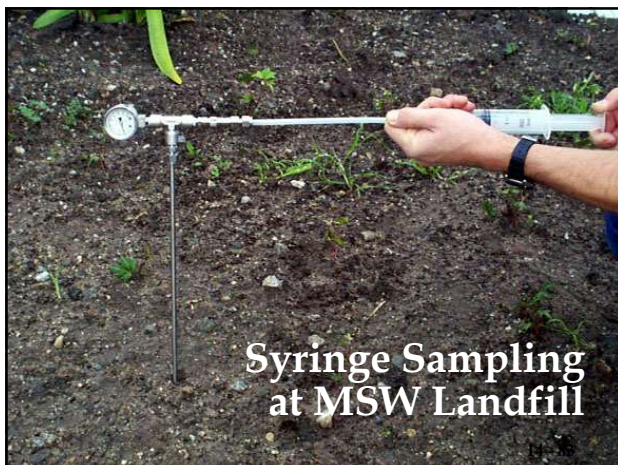


14 - 82

## Tank Sampling Procedure

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

14 - 84



## 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

14 - 85

## 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

14 - 86

## Pitot Probe Sampling Procedure

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

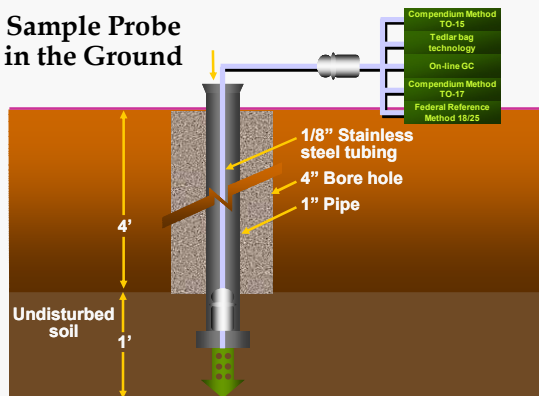
14 - 87

## 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

14 - 88

### Sample Probe in the Ground

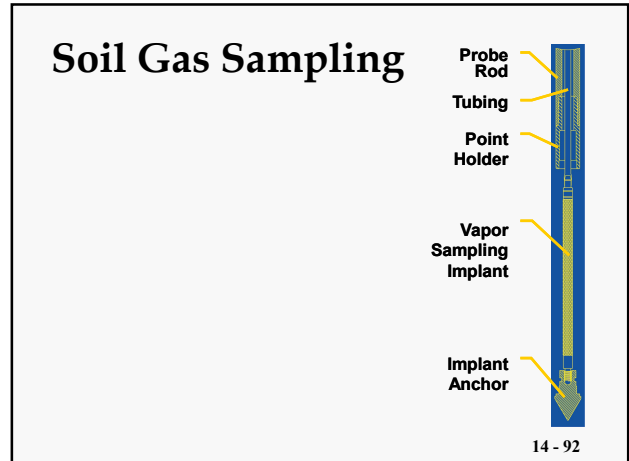
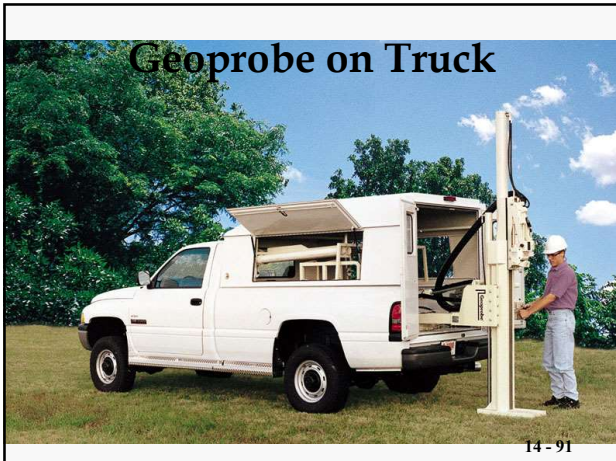


14 - 89



14 - 90





### 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

14 - 93

### Sampling Procedure

- Record final pressure (may also be pressurized in the laboratory)
- Landfill gas sample is acceptable if N<sub>2</sub> is < 20%

14 - 94

### 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<sub>2</sub>)

14 - 95

### Federal Reference Method 25C Analysis

- ◆ **NMO Analyzer daily calibration**
- ◆ **NMO response factor**

14 - 96



### NMOC Concentration

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

14 - 97

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 15A: Reciprocating Internal Combustion Engines (RICE)**

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Compliance Test and Source  
Test Observation

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

15A - 1

Stationary Engines - Video



15A - 2

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

---

#### Compliance Test and Source Test Observation

*FRMs 3A, 6C, 7E, 10 and 20 and ASTM 6522-00*



15B - 1



15B - 2

#### Applicability

- "...controlled and uncontrolled emissions from sources specified in the regulations..."
- Fossil fuel-fired boilers
- Municipal waste combustors
- ASTM 6522-00 "natural gas-fired reciprocating engines, combustion turbines, boilers, and process heaters"

15B - 3

#### Principle

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

15B - 4

#### How the Method Works

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

15B - 5

#### 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!

15B - 6

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

---

#### 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)
- Note: ASTM 6522-00 does not require bias check as  
all the calibrations is conducted through the entire  
system.

15B - 7

#### Eight Major Points (cont.)

4. Interference Check (SO<sub>2</sub> Analyzer): Use Modified  
Method 6 (3 Runs 1 L/min) vs. Analyzer at Vent  
(7%)
5. Converter Check (NO<sub>x</sub> Analyzer): Introduce CO @  
500 ppm, SO<sub>2</sub>@200 ppm, CO<sub>2</sub>@10% and  
O<sub>2</sub>@20.9%; < 2% of span response, pass

15B - 8

#### 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)
9. ASTM 6522-00 Does not specify a minimum  
allowable drift or bias.

15B - 9

#### 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%

15B - 10

#### Interesting Points

- Span of instrument: Emission standard at 30% of  
span
  - ASTM 6522-00 > 25% of span
- Calibration gases can be SO<sub>2</sub>/N<sub>2</sub>, SO<sub>2</sub>/Air, SO<sub>2</sub>/CO<sub>2</sub>, or  
SO<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>
- Emission data corrected with determined bias  
number
- No EPA Method 6 audit vial required due to  
"Interference Check"

15B - 11

#### 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!

15B - 12

APTI #450/468 Compliance Test and Source Test Observation  
Lesson 15B: Federal Reference Method 6C-7E-3A and 20



15B - 13

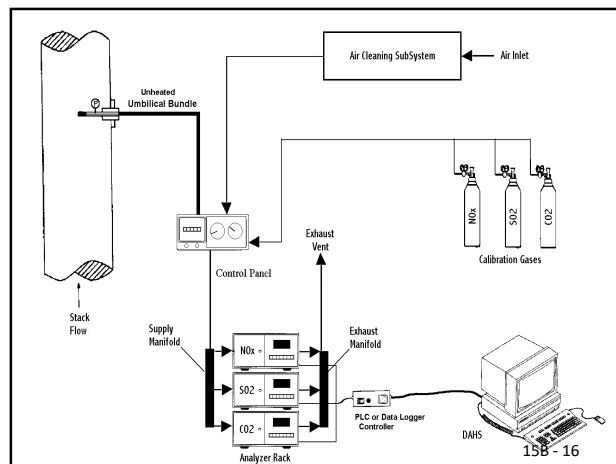


15B - 14

Method 6C  
Typical Analytical Methods

- Ultraviolet Absorption (UV)
  - Nondispersive Infrared (NDIR)
  - Fluorescence
  - FTIR
- Analyzer must meet the performance requirements of this method.

15B - 15



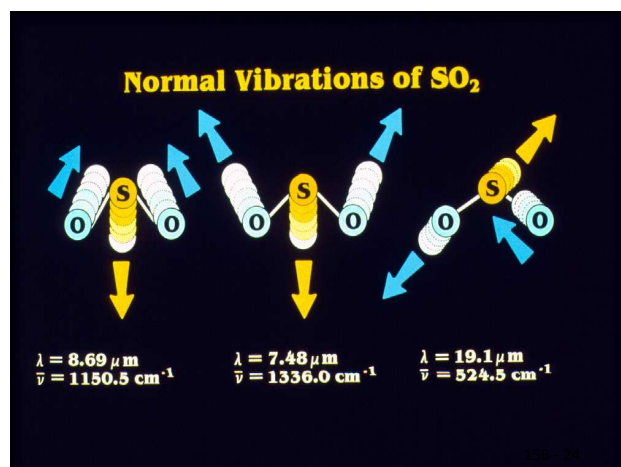
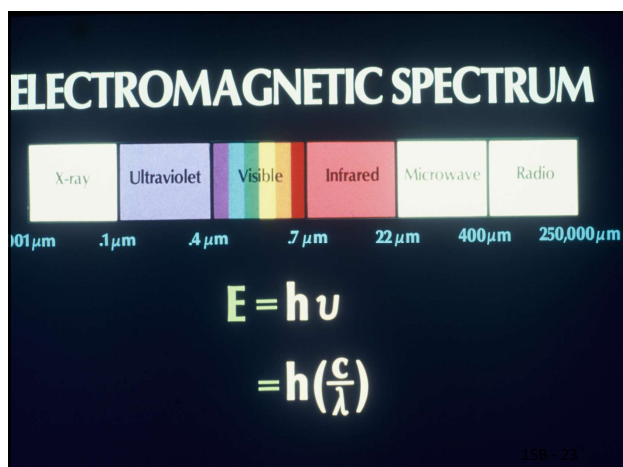
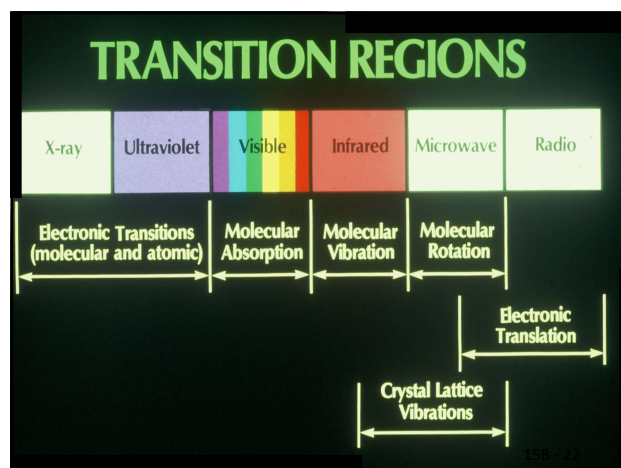
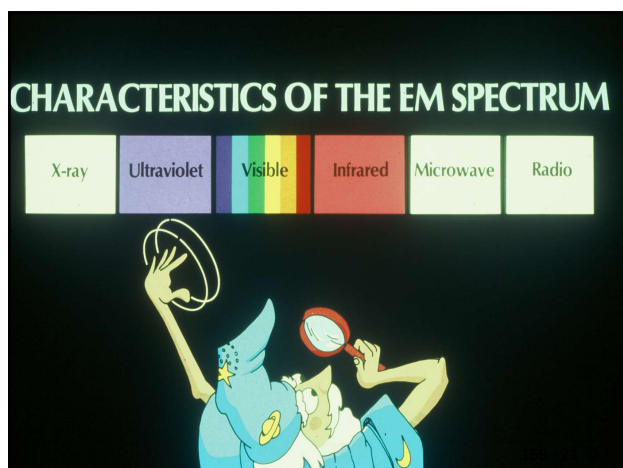
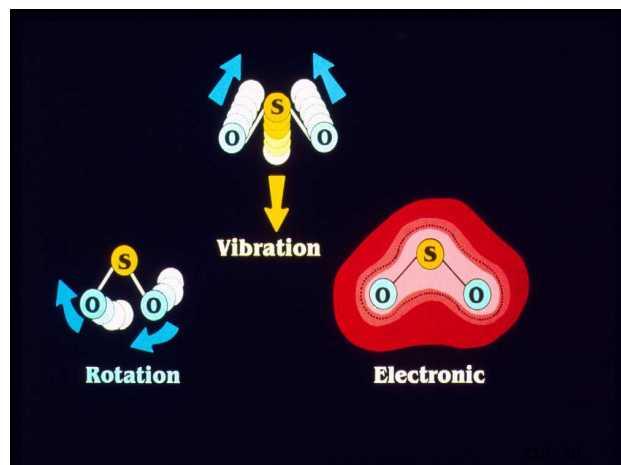
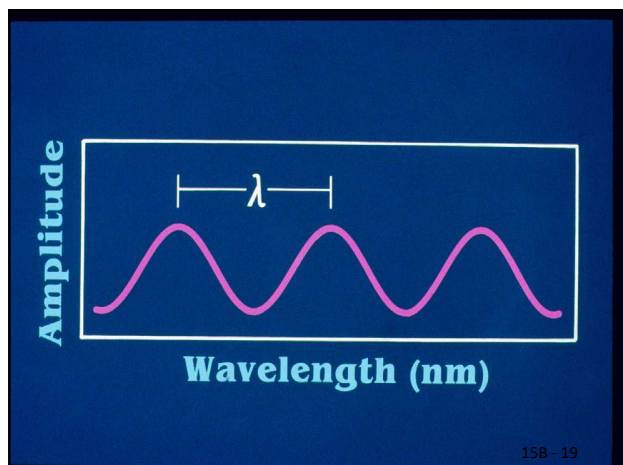
15B - 16



15B - 17



15B - 18



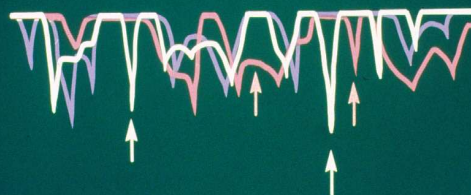


### Molecules Absorb Light at Specific Wavelengths

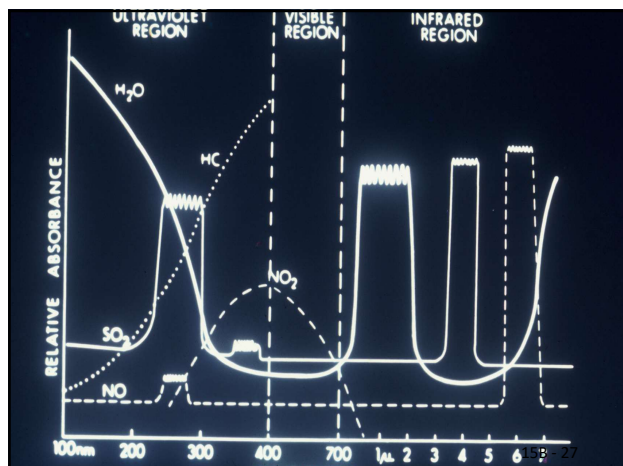


15B - 25

### Spectra of Different Molecules Can Overlap



15B - 26



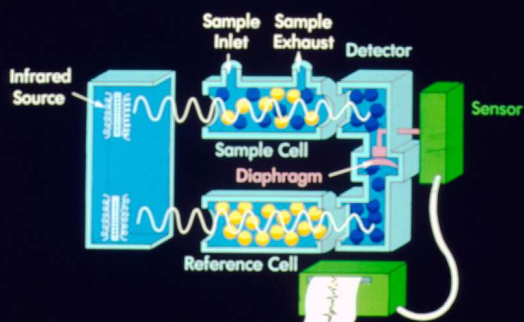
15B - 27

Light  $\rightarrow E = h\nu \rightarrow$  Absorption  $\rightarrow$  Beer-Lambert Law  $\rightarrow$  Instrument



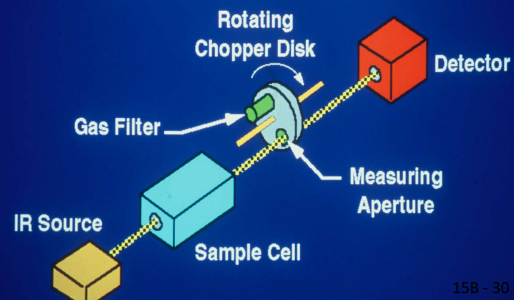
15B - 28

### NDIR ANALYZER FOR CO



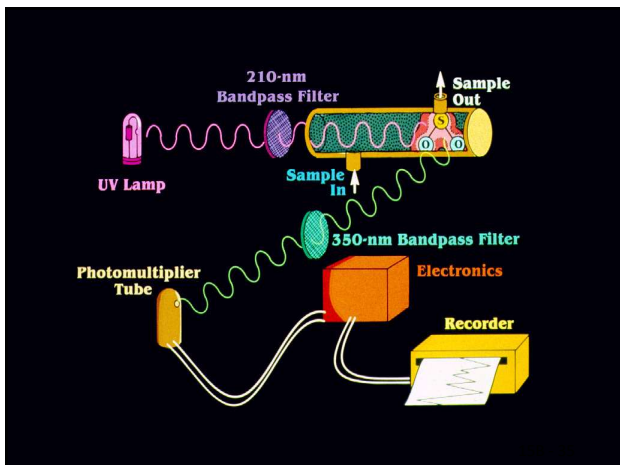
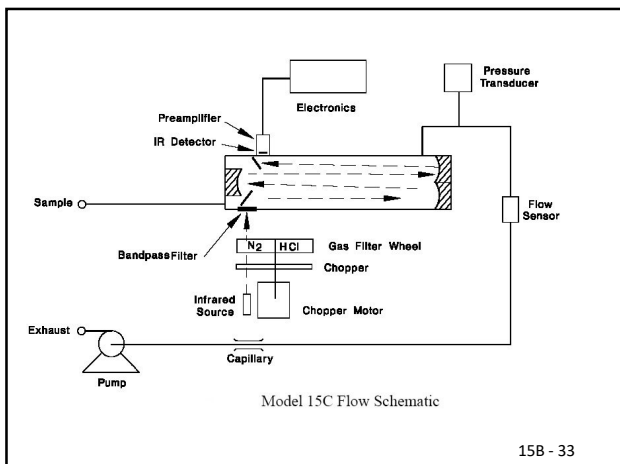
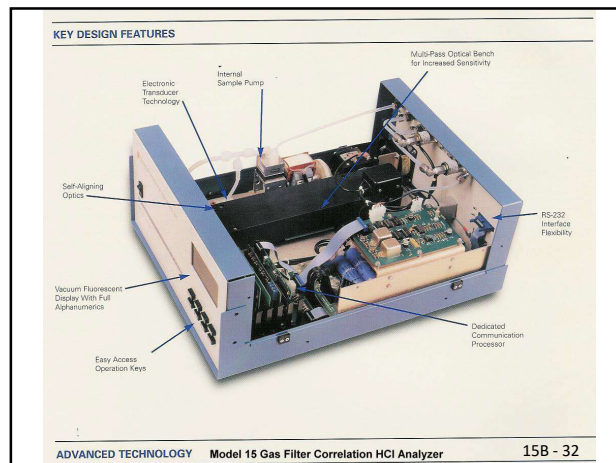
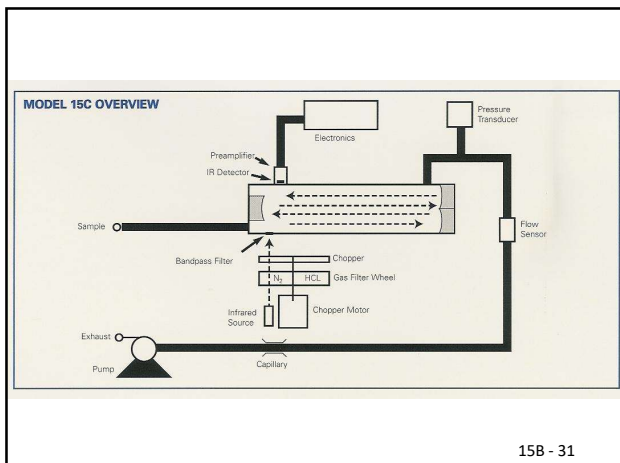
15B - 29

### Extractive Type Gas Filter Cell Correlation Analyzer



15B - 30

# APTI #450/468 Compliance Test and Source Test Observation Lesson 15B: Federal Reference Method 6C-7E-3A and 20



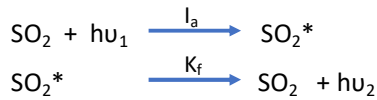
**MODEL 43C- SO<sub>2</sub> ANALYZER**

- Microprocessor control
- SO<sub>2</sub> Specific
- Reflective U.V. filtering
- Hermetically sealed U.V. lamp
- No consumables

15B - 36

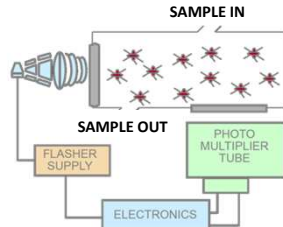
# APTI #450/468 Compliance Test and Source Test Observation Lesson 15B: Federal Reference Method 6C-7E-3A and 20

## MODEL 43C-SO<sub>2</sub> Analyzer



$$I_a = I_0[1 - e^{-\{ax(\text{SO}_2)\}}]$$

$$I_f = I_0ax(\text{SO}_2) \text{ or } K(\text{SO}_2)$$



15B - 37

## Thermo Model 43C SO<sub>2</sub> Analyzer

### Pulsed Fluorescence SO<sub>2</sub> 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<sub>2</sub> 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 programmable measurement ranges and SO<sub>2</sub> concentration value storage by date and time.

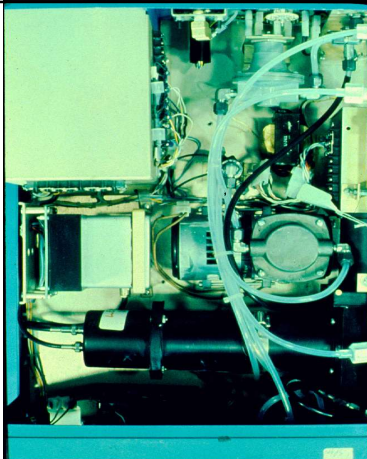


#### MODEL 43C SPECIFICATIONS

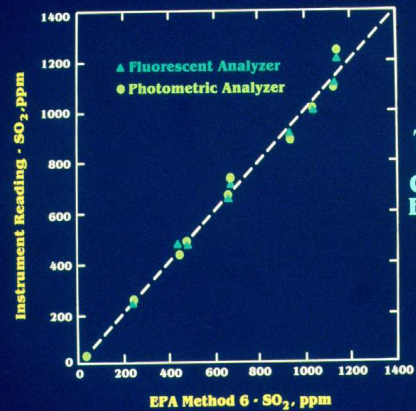
Ranges	0-50, 100, 200, 500, 1000 ppb and 0-5, 10, 20, 50, 100 ppm
Zero/Noise	1.0 ppb RMS (10 second averaging time) 0.5 ppb RMS (60 second averaging time) 0.2 ppb RMS (300 second averaging time)
Lower Detectable Limit	21.0 ppb RMS (10 second averaging time) 1.0 ppb RMS (60 second averaging time) 0.5 ppb RMS (300 second averaging time)

Analyze • Detect • Measure • Control™  
Thermo  
ELECTRON CORPORATION

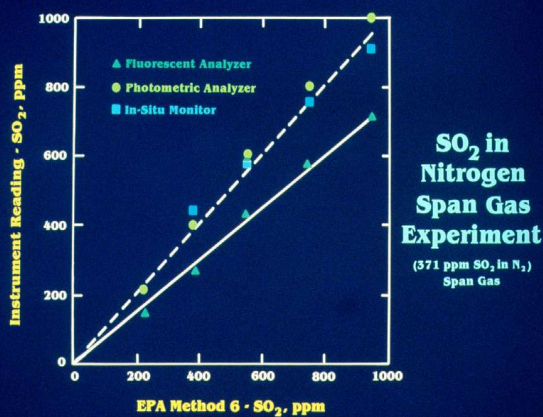
15



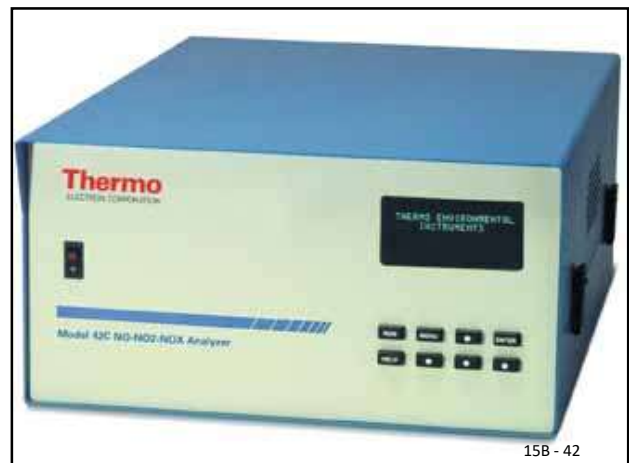
15B - 39



15B - 40



15B - 41



15B - 42



## HOW IS NO MEASURED?

Chemiluminescence Technique



Intensity of emitted light is proportional to NO concentration

15B - 43

## Chemiluminescent

Reduction of NO<sub>2</sub> to NO

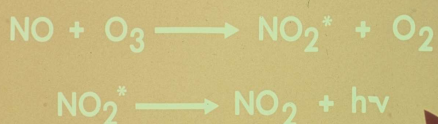


A molybdenum catalyst, heated to ~325°C, is used to Convert NO<sub>2</sub> to NO

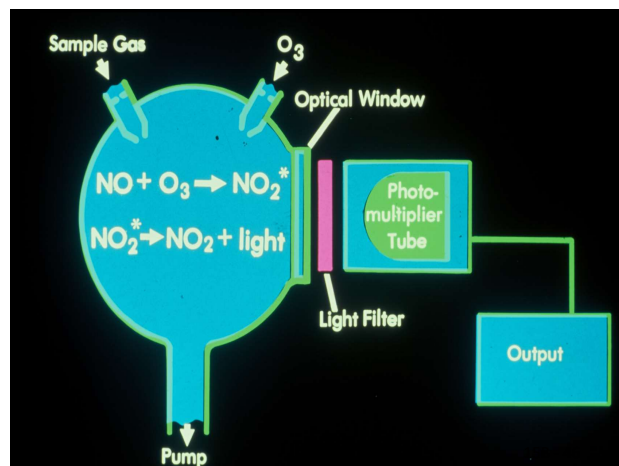
15B - 44

## Measurement Principle

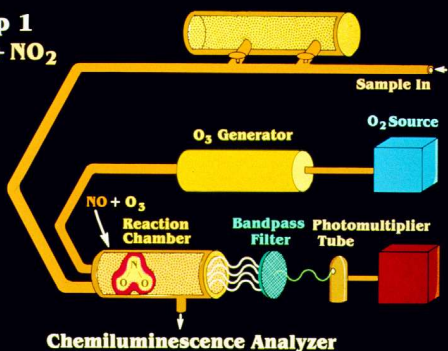
### CHEMILUMINESCENCE



15B - 45

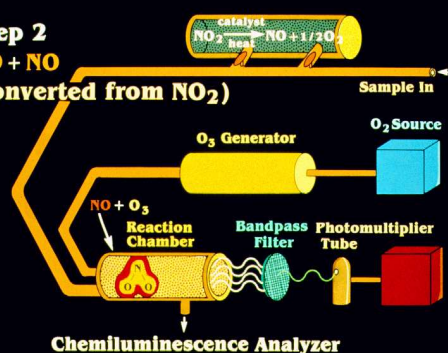


### Step 1 NO + NO<sub>2</sub>

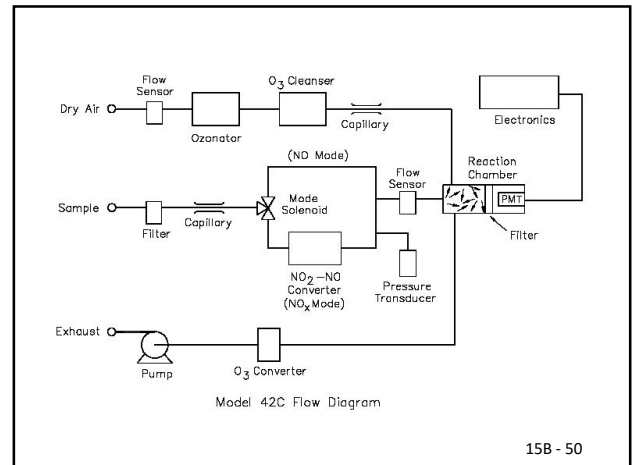
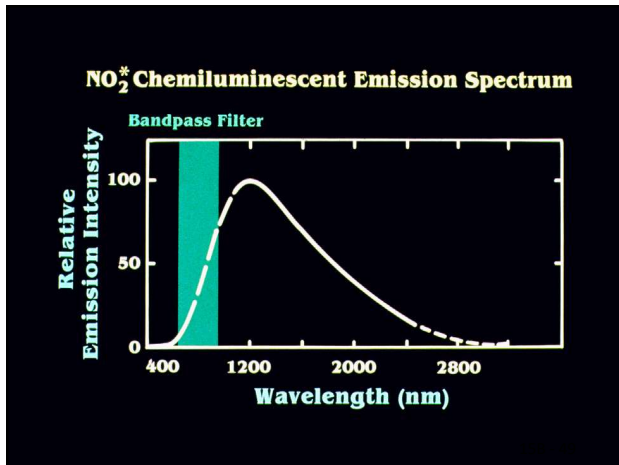


### Step 2

NO + NO  
(Converted from NO<sub>2</sub>)



# APTI #450/468 Compliance Test and Source Test Observation Lesson 15B: Federal Reference Method 6C-7E-3A and 20



15B - 50



15B - 51



15B - 52

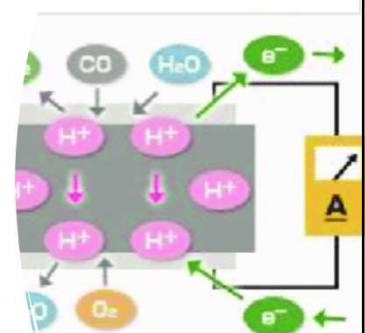
## Analytical Range

- "...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."

15B - 53

## ASTM 6522-00 In carbon monoxide

- Electrochemical Cells
- CO gas reaches the working electrode, it is oxidized with the participation of a water molecules from the surrounding air.
- $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

---

#### 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  $\pm 2\%$  of span for zero, mid, and high-range gases

15B - 55

#### 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.

15B - 56

#### 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.

15B - 57

#### Performance Specifications

- Sampling system bias
  - Less than  $\pm 5\%$  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  $\pm 3\%$  of span over the period of the run

15B - 58

#### Calibration Gases

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

15B - 59

#### Calibration Gases

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

15B - 60



### Measurement System Performance Test Procedures

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

15B - 61

### 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

15B - 62

### Recommended Sampling System Design Criteria

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

15B - 63

### 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

15B - 64

### 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)

15B - 65

### Moisture Removal Condensers

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

15B - 66

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

---

#### Moisture Removal Condensers

- Continuously remove condensate from traps to further reduce contact with sample and limit absorption of SO<sub>2</sub> and NO<sub>2</sub>

15B - 67

#### Other Methods of Lowering Sample Dew Point

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

15B - 68

#### 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

15B - 69

#### Three Suggested Ways to Introduce Calibration Gases

- Straight Tee
- Closed Loop
- Closed Loop with Vent

15B - 70

#### 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

15B - 71

#### 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

15B - 72

#### 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

15B - 73

#### 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

15B - 74

#### Analyzer Calibration Error

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

15B - 75

#### Sampling System Bias Check

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

15B - 76

#### 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).

15B - 77

#### 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.

15B - 78

### 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

15B - 79

### 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

15B - 80

### If System Meets Bias Specification

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

15B - 81

### 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

15B - 82

### Emission Calculations

- Data corrected for errors observed in calibration error bias checks

15B - 83

### 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.

15B - 84

### 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.

15B - 85

### Known SO<sub>2</sub> Analyzer Interferences

- Some earlier model NDIR SO<sub>2</sub> 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<sub>2</sub> concentrations were high relative to the SO<sub>2</sub> concentrations

15B - 86

### Known SO<sub>2</sub> Analyzer Interferences

- Fluorescence analyzers suffer from quenching effects from CO<sub>2</sub> and O<sub>2</sub>

15B - 87

### Sampling in the Presence of Ammonia

- Ammonia reacts with SO<sub>2</sub> in the condenser causing a low bias
- Amount of bias depends on the relative concentrations of SO<sub>2</sub> and ammonia

15B - 88

### 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

15B - 89

### 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.

15B - 90

#### 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.

15B - 91

#### Calibration Gas - Dilution Systems

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

15B - 92

#### Method 7E - NO<sub>x</sub>

- ? No field interference check (use Method 20 laboratory interference test)
- NO<sub>2</sub> to NO converter efficiency test (same as Method 20)

15B - 93

#### Method 7E - Ammonia (NH<sub>3</sub>) Interference Problems

- Use low temperature (molybdenum or activated carbon) NO<sub>2</sub> to NO converter to prevent conversion of NH<sub>3</sub> to NO
- Molybdenum converters lose efficiency quickly and need to be regenerated often

15B - 94

#### Method 7E - High NO<sub>2</sub>/NO Ratio in Sample

- NO<sub>2</sub> is readily absorbed by the sampling system, causing low bias
- Most NO<sub>x</sub> calibration gases contain little NO<sub>2</sub>

15B - 95

#### Method 7E - High NO<sub>2</sub>/NO Ratio in Sample

- NO<sub>2</sub> to NO converter efficiency becomes much more important
- Tester should perform NO/NO<sub>2</sub> balance adjustment

15B - 96



## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

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#### Method 3A - O<sub>2</sub> and CO<sub>2</sub>

- Any analytical technique
- Less rigorous sampling system material specification
- Option to substitute low-range check for zero gas for O<sub>2</sub> analyzers
- Laboratory interference check same as Method 20

15B - 97

#### 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.

15B - 98

#### 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<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and/or O<sub>2</sub> concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

15B - 99

#### Method 20

- In this method, NO<sub>x</sub>, O<sub>2</sub> (or CO<sub>2</sub>), and SO<sub>x</sub> 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).

15B - 100

#### 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.

15B - 101

#### 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.

15B - 102

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 15B: Federal Reference Method 6C-7E-3A and 20**

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ASTM-6522-00

• **Summary**

- A gas sample is continuously extracted from a stack and conveyed to a portable analyzer for determination of NO, NO<sub>2</sub>, CO, and O<sub>2</sub> gas concentrations using electrochemical cells.

15B - 104

ASTM-6522-00

• **Interferences**

- NO and NO<sub>2</sub> can interfere with CO concentration measurements, and NO<sub>2</sub> can interfere with NO concentration measurements. The interference effects for the CO and NO emission measurements are quantified in 9.2 and shall not exceed 5 % of the measurement

15B - 105

ASTM-6522-00

- the minimum detectable limit should be less than 2 % of the nominal range
- The sampling system shall maintain the gas sample at a temperature above the dew point up to the moisture removal system.

15B - 106

ASTM-6522-00

• **Data Recorder**

- A strip chart recorder, computer, or digital recorder, for recording measurement data. The data recorder resolution (that is, readability) shall be at least 1 ppm for CO, NO, and NO<sub>2</sub>; 0.1 % O<sub>2</sub> for O<sub>2</sub>; and 1° (C or F) for temperature.

15B - 107

ASTM-6522-00

• **Calibration**

• **Protocol 1 Gas**

- CO and NO Span Gases—Choose a span gas concentration such that the average stack gas reading for each test run is greater than 25 % of the span gas concentration

15B - 108

**APTI #450/468 Compliance Test and Source Test Observation**  
**Lesson 15B: Federal Reference Method 6C-7E-3A and 20**

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ASTM-6522-00

- Calibration
- Protocol 1 Gas
- *Mid-Level Gases*—Select mid-level gas concentrations that are 40 to 60 % of the span gas concentrations.
- *Zero Gas*—Zero gas must have concentrations of less than 0.25 % of the span gas for each component.

15B - 109

ASTM-6522-00

- If concentration results exceed 125 % of the span gas at any time during the sampling run, then the test run for that channel is invalid.

15B - 110

ASTM-6522-00

- Linearity Check:
- Conduct the linearity check once for each nominal range that is to be used on each electrochemical cell (NO, NO<sub>2</sub>, CO, and O<sub>2</sub>) before each field test program.
- NO, CO and O<sub>2</sub> Cells  $\leq$  2.5 % of the span gas concentration.
- NO<sub>2</sub> Cells  $\leq$  3.0 % of the span gas concentration

15B - 111

ASTM-6522-00

- Stability Check:
- Conduct the stability check once for each nominal range that is to be used on each pollutant electrochemical cell (NO, NO<sub>2</sub>, and CO) before each field test program.

15B - 112

ASTM-6522-00

- Stability Check:
- After the analyzer response has stabilized, continue to flow the span gas for at least 30 min.
  - $\leq$  2.0 % of the span gas concentration.
- If the concentration reaches a peak value within 5 min, the data may be recorded for at least 15 min (rather than 30 min) following the peak.
  - $\leq$  1.0 % of the span gas concentration.

15B - 113

ASTM-6522-00

- Sampling Location:
- No closer than 1 m or three stack, duct, or pipe diameters (whichever is less) upstream of the gas discharge to the atmosphere.
- Use a minimum of three sampling points located at positions of 16.7, 50, and 83.3 % of the stack, duct, or pipe diameter.

15B - 114

## APTI #450/468 Compliance Test and Source Test Observation

### Lesson 15B: Federal Reference Method 6C-7E-3A and 20

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#### ASTM-6522-00

- Sampling Location:
- Alternative sampling location or sample from a single point in the center of the stack, duct, or pipe, if previous test data demonstrate that the stack, duct, or pipe gas concentration does not vary significantly across the duct diameter, or both.

15B - 115

#### ASTM-6522-00

- Conduct the calibration error check at the sampling location (near the sampling port) just prior to the start of an emissions test or test run.
- Determine the NO and CO response times by observing the time required to respond to 95 % of a step change in the analyzer response for both the zero and span gases. Note the longer of the two times as the response time. For NO<sub>2</sub> span gas record the time required to respond to 90 % of a step change

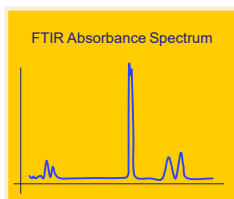
15B - 116

#### ASTM-6522-00

- Zero Calibration Error Specifications < 3 % of the span gas value for NO, NO<sub>2</sub>, and CO channels; < .3 % O<sub>2</sub> for the O<sub>2</sub> channel.
- Span Calibration Error Specifications < 5 % of the span gas value for NO, NO<sub>2</sub>, and CO channels; < 0.5 % O<sub>2</sub> for the O<sub>2</sub> channel.

15B - 117

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



16 - 1

### 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

16 - 2

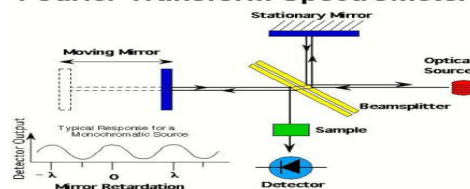
### Introduction to FTIR Operation

- 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

16 - 3

### FTIR Theory and Instrumentation

#### Typical Fourier Transform Spectrometer



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

16 - 4

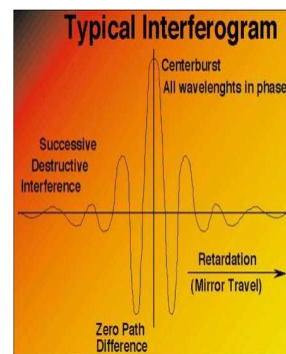
### FTIR Theory and Instrumentation

- 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

16 - 5

### 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.



16 - 6

### **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

16 - 7

### **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

16 - 8

### **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

16 - 9

### **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

16 - 10

### **FRM 320 (cont'd)**

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

16 - 11

### **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

16 - 12



### FRM 320 Sampling Types

- Screening
- Emission Test
- Validation

16 - 13

### 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

16 - 14

### 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  $\text{cm}^{-1}$  (2.5 to 2.5  $\mu\text{m}$ ). 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."*

16 - 15



16 - 16

### Infrared Spectroscopy

- Infrared light (IR) waves at discrete 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)

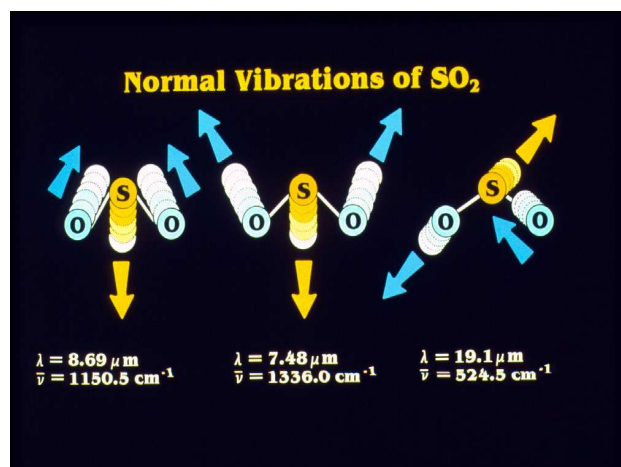
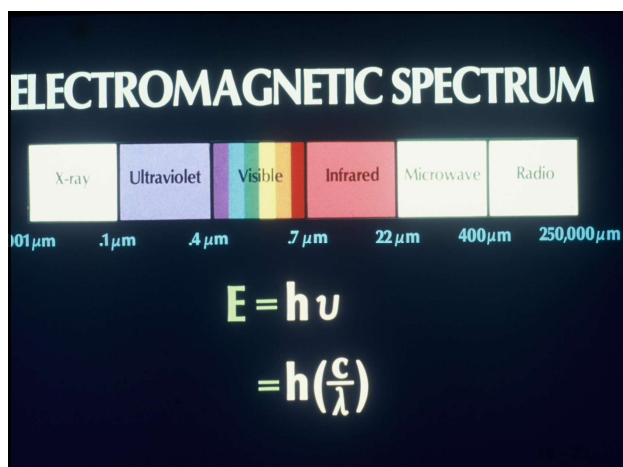
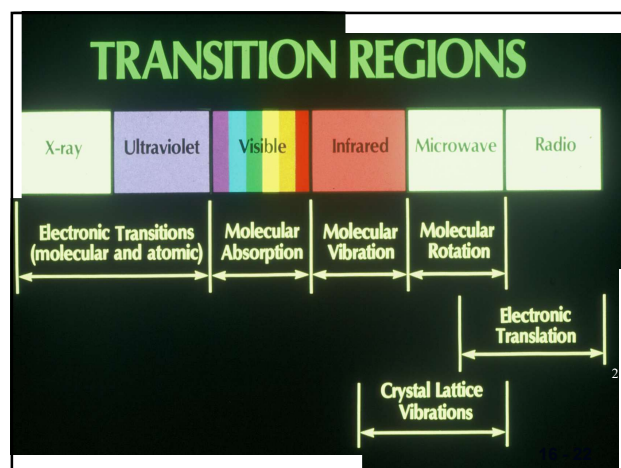
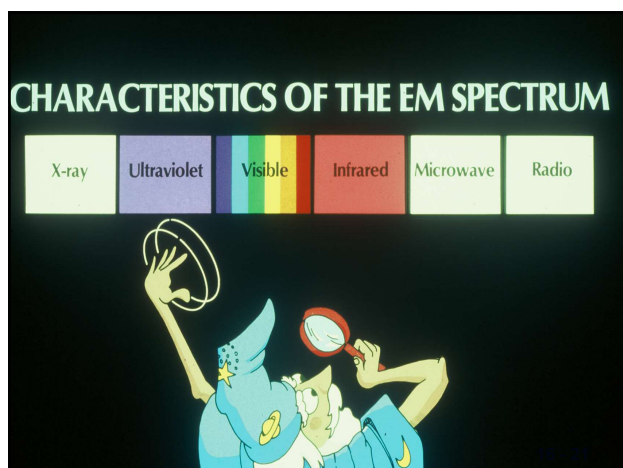
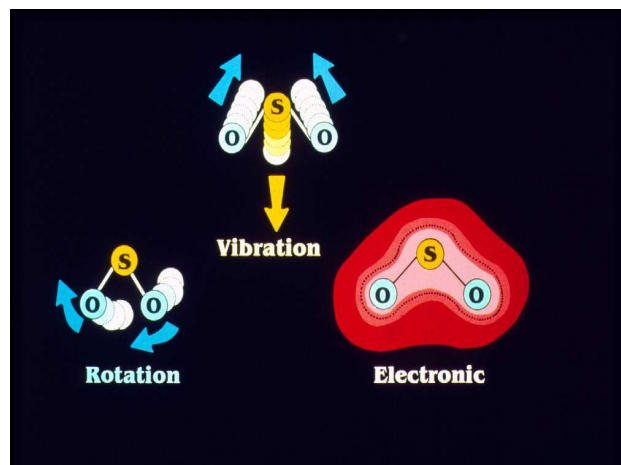
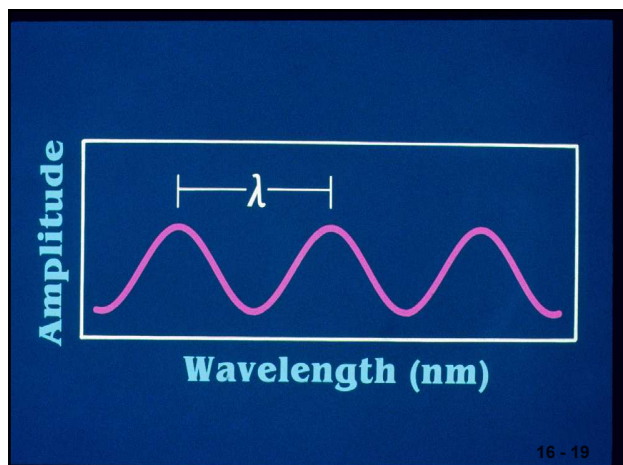
16 - 17

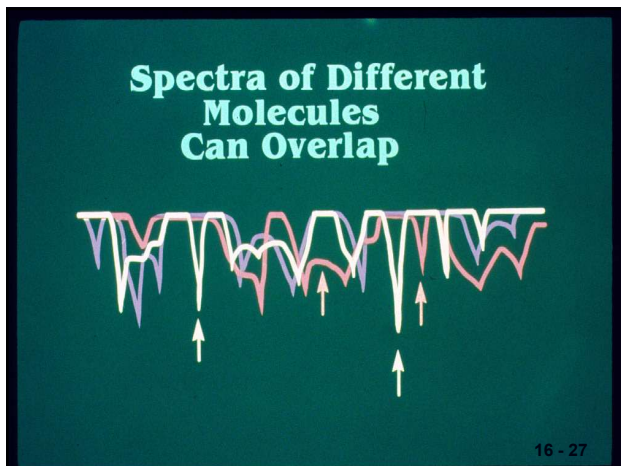
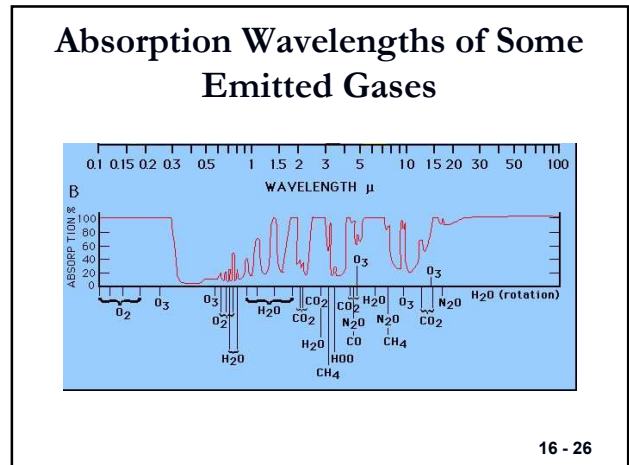
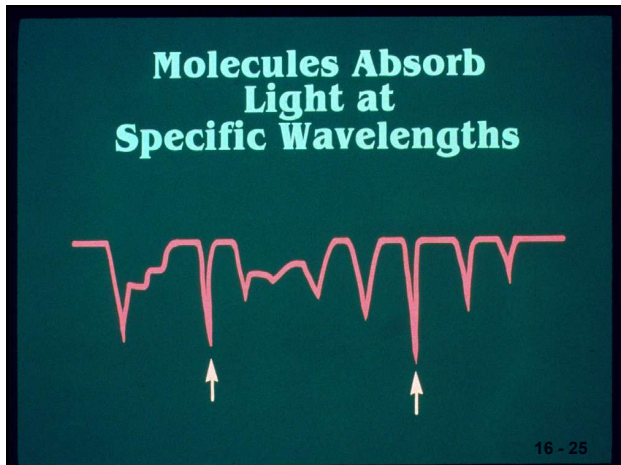
### Infrared Spectroscopy

- The energy absorbed by the bond at discrete frequencies is proportional to the number of molecules
- FTIR spectrum is a plot of decreased energy at discrete frequencies corresponding to the absorption bands of the compounds in the sample. High resolution 0.5  $\text{cm}^{-1}$

16 - 18

APTI #450/468 Compliance Test and Source Test Observation  
Lesson 16: FRM 320 FTIR





**Beer-Lambert Law**

$$I = I_0 e^{-\alpha c l}$$

$I$  = intensity of radiation through the sample  
 $I_0$  = intensity of radiation with  $c = 0$  or  $\alpha = 0$   
 $\alpha$  = absorption coefficient  
 $c$  = gas concentration  
 $l$  = pathlength of radiation through the gas

16 - 29

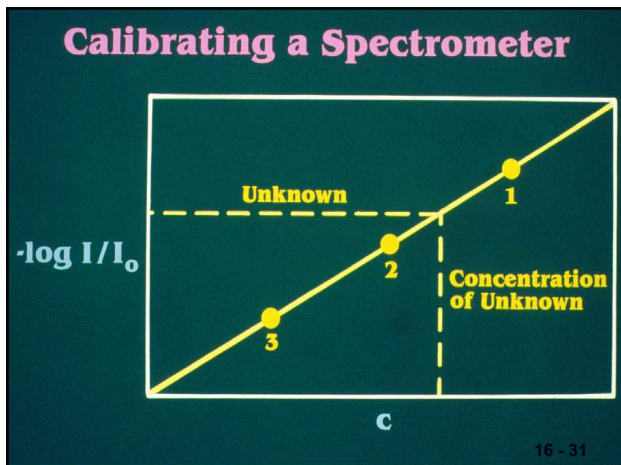
**From Beer-Lambert Law:**

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

**Direct Relationship**

16 - 30



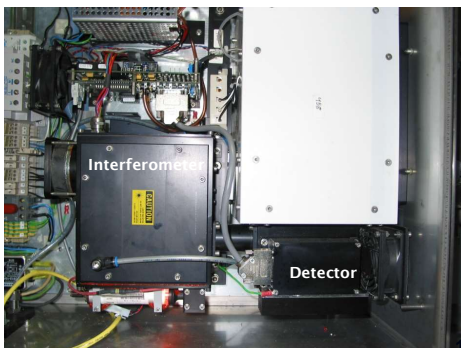


### Infrared Band Centers Of Some Common Gases

Gas	Band Center ( $\mu\text{m}$ )	Wave Number ( $\text{cm}^{-1}$ )
NO	5.0-5.5	1800-2000
NO <sub>2</sub>	5.5-20	500-1800
SO <sub>2</sub>	8-14	700-1250
H <sub>2</sub> O	3.1, 5-5.5, 7.1-10	1000-1400 1800-3200
CO <sub>2</sub>	2.7, 5.2, 8-12	850-3700
NH <sub>3</sub>	10.5	950

16 - 32

### FTIR Interferometer Cell



16 - 33

### Operation of the FTIR Spectrometer

- IR energy enters the spectrometer
- A beam splitter reflects back 50 percent and transmits 50 percent of the incoming infrared 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

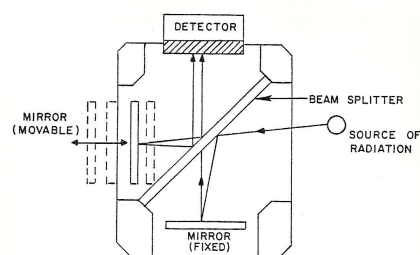
16 - 34

### 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

16 - 35

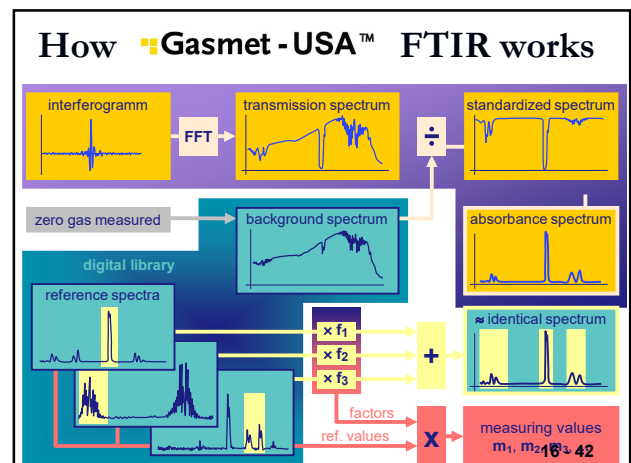
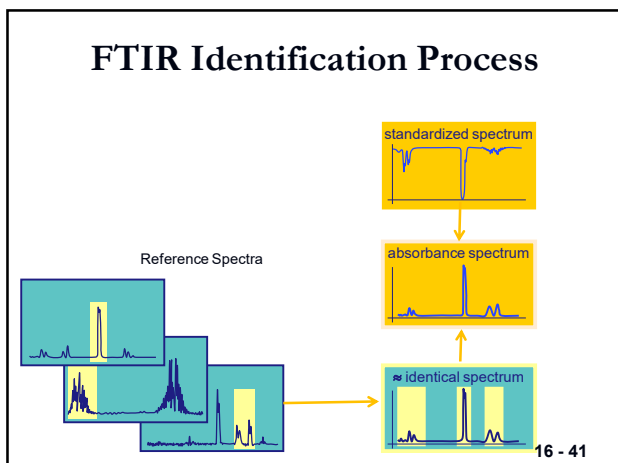
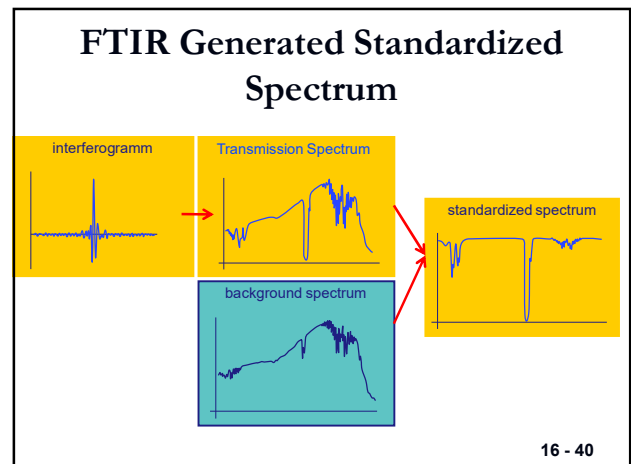
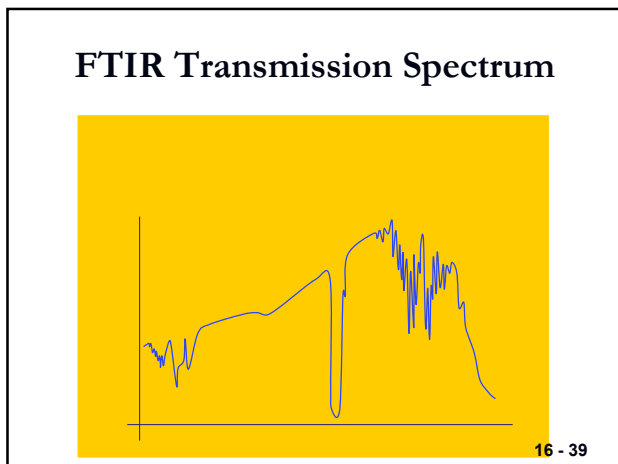
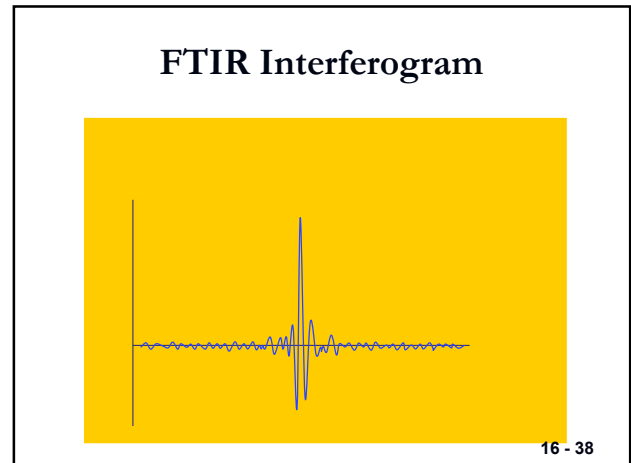
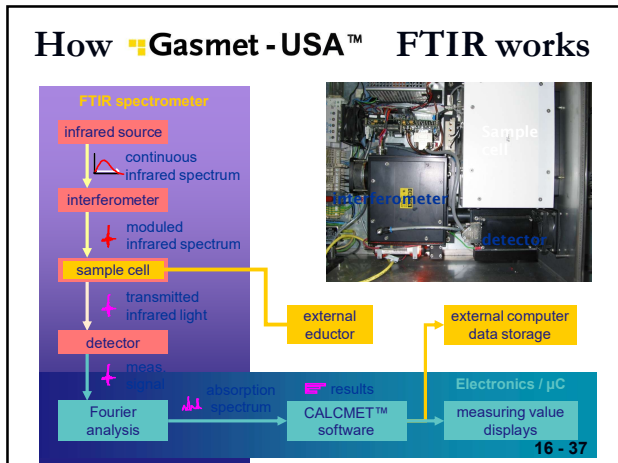
### Operation of the FTIR Mirror



16 - 36

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 16: FRM 320 FTIR





## Components of FRM 320

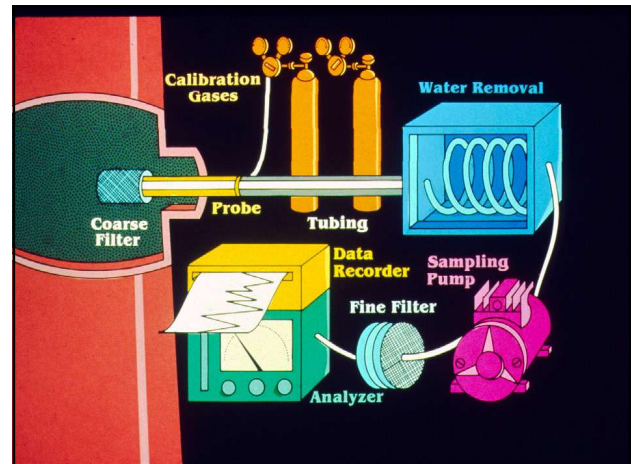
- **Sample probe:** Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating.
- **Particulate filter:** A glass wool plug inserted at the probe tip and a filter to remove particulate matter.
- **Heat trace sample line:** Heated sufficiently to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

16 - 44

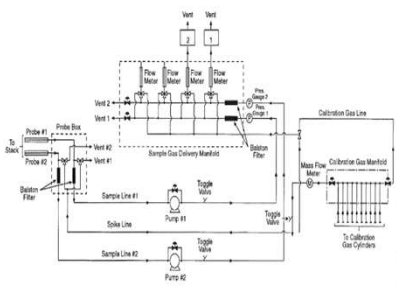
## Components of FRM 320

- **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**

**16 - 45**



## FRM 320 Extractive FTIR Sampling System



16 - 47

## 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 ( $FRU_i$ )

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# APTI #450/468 Compliance Test and Source Test Observation Lesson 16: FRM 320 FTIR

## 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

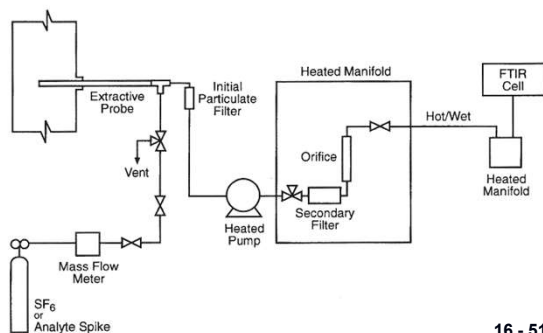
16 - 49

## 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  $\pm 2\%$  by manufacturer. Record spectra
  - QA Spike to probe to FTIR analytical bench using certified standard (70-130 % recovery)
- Begin Sampling

16 - 50

## FRM 320 FTIR Sampling/Spiking Configuration



16 - 51

## Sampling and Analysis Procedures

- Post-test QA
  - Verify instrument parameters
  - Perform post-test CTS spectra ( $\pm 5\%$ )

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## 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)-

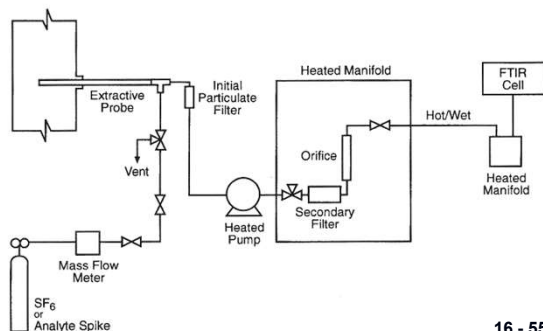
16 - 53

## 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

# APTI #450/468 Compliance Test and Source Test Observation Lesson 16: FRM 320 FTIR

## FRM 320 FTIR Sampling/Spiking Configuration



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## FRM 320 QA Activities

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

16 - 56

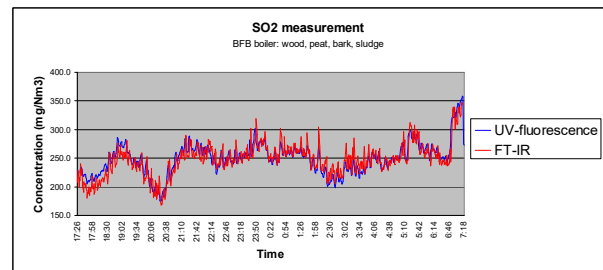
## FRM 320 Interferences

- 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.

16 - 57

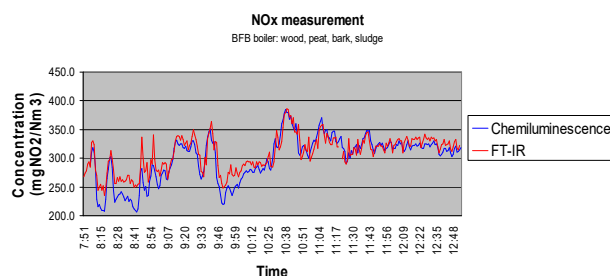
## GASMET CEMS APPLICATIONS

### Gasmet CEMS and reference measurements:



16 - 58

## Gasmet CEM'S Applications

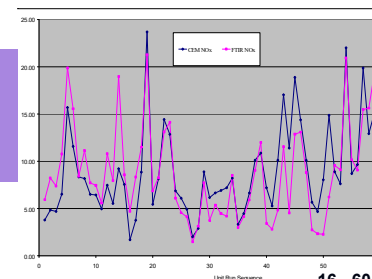


16 - 59

## Austin Energy Sandhill

### Unit #1 Demonstration Results

	CEM	FTIR	FTIR
	NOx	NOx	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



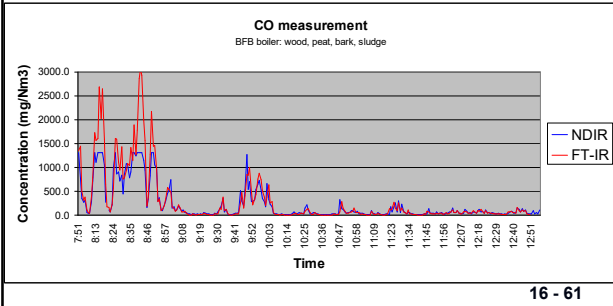
16 - 60

# APTI #450/468 Compliance Test and Source Test Observation

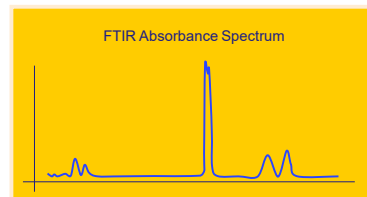
## Lesson 16: FRM 320 FTIR

### GASMET CEMS APPLICATIONS

Gasmeter CEMS and reference measurements:



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



## Part 75

CONTINUOUS EMISSION MONITORING

17 - 1

### Purpose

- Establish requirements for the monitoring, recordkeeping, and reporting of sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and carbon dioxide (CO<sub>2</sub>) emissions, volumetric flow, and opacity data from affected units under the Acid Rain Program

17 - 2

### Scope

- General requirements for the installation, certification, operation, and maintenance of continuous emission or opacity monitoring systems and specific requirements for the monitoring of SO<sub>2</sub> emissions, volumetric flow, NO<sub>x</sub> emissions, opacity, CO<sub>2</sub> emissions and SO<sub>2</sub> emissions.
- Statistical estimation procedures for missing data are included in appendix C to this part. Optional protocols for estimating SO<sub>2</sub> mass emissions from gas-fired or oil-fired units and NO<sub>x</sub> emissions from gas-fired peaking or oil-fired peaking units are included in appendices D and E, respectively.

17 - 3

### Subpart A General (75.3)

- (a) [§ 72.2](#) (Definitions);
- (b) [§ 72.3](#) (Measurements, Abbreviations, and Acronyms);
- (c) [§ 72.4](#) (Federal Authority);
- (d) [§ 72.5](#) (State Authority);
- (e) [§ 72.6](#) (Applicability);
- (f) [§ 72.7](#) (New Unit Exemption);
- (g) [§ 72.8](#) (Retired Units Exemption);
- (h) [§ 72.9](#) (Standard Requirements);
- (i) [§ 72.10](#) (Availability of Information); and
- (j) [§ 72.11](#) (Computation of Time).

17 - 4

### Subpart B Monitoring Provisions

- **§ 75.10 General operating requirements.**
- (a) **Primary Measurement Requirement.** The owner or operator shall measure opacity, and all SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub> emissions for each affected units.

17 - 5

### Subpart B Monitoring Provisions

- **§ 75.10 General operating requirements.**
- (g) **Minimum recording and recordkeeping requirements.** The owner or operator shall record and the designated representative shall report the hourly, daily, quarterly, and annual information collected under the requirements of this part as specified in [subparts F](#) and [G of this part](#).

17 - 6

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

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### Subpart C Operation and Maintenance Requirements

- **§ 75.20 Initial certification and recertification procedures.**
- (a) **Initial certification approval process.** The owner or operator shall ensure that each continuous emission or opacity monitoring system required by this part meets the initial certification requirements of this section and shall ensure that all applicable initial certification tests under [paragraph \(c\)](#) of this section.

17 - 7

### Subpart C Operation and Maintenance Requirements

- **40 CFR 75.20(a)(1) Notification of initial certification test dates.** The owner or operator or designated representative shall submit a written notice of the dates of initial certification testing at the unit as specified in [§ 75.61\(a\)\(1\)](#).

17 - 8

### Subpart C Operation and Maintenance Requirements

- **40 CFR 75.20(a)(2) Certification application.** The owner or operator shall apply for certification of each continuous emission or opacity monitoring system used under the Acid Rain Program. The owner or operator shall submit the certification application in accordance with [§ 75.60](#) and each complete certification application shall include the information specified in [§ 75.63](#).

17 - 9

### Subpart C Operation and Maintenance Requirements

- **40 CFR 75.20(a)(3) Provisional approval of certification (or recertification) applications.** Upon the successful completion of the required certification (or recertification) procedures of this section, each continuous emission or opacity monitoring system shall be deemed provisionally certified (or recertified) for use under the Acid Rain Program for a period not to exceed 120 days following receipt by the Administrator of the complete certification (or recertification) application under [paragraph \(a\)\(4\)](#) of this section.

17 - 10

### Subpart C Operation and Maintenance Requirements

- **40 CFR 75.20(a)(4) Certification (or recertification) application formal approval process.** The Administrator will issue a notice of approval or disapproval of the certification (or recertification) application to the owner or operator within 120 days of receipt of the complete certification (or recertification) application. In the event the Administrator does not issue such a notice within 120 days of receipt, each continuous emission or opacity monitoring system which meets the performance requirements of this part and is included in the certification (or recertification) application will be deemed certified (or recertified) for use under the Acid Rain Program.

17 - 11

### Subpart C Operation and Maintenance Requirements

- **40 CFR 75.20(c) Initial certification and recertification procedures.** Prior to the deadline in [§ 75.4](#), the owner or operator shall conduct initial certification tests and in accordance with [§ 75.63](#), the designated representative shall submit an application to demonstrate that the continuous emission or opacity monitoring system and components thereof meet the specifications in appendix A to this part.

17 - 12

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1) For each SO<sub>2</sub> pollutant concentration monitor, each NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined under [§ 75.71\(a\)\(2\)](#), and each NO<sub>x</sub>-diluent continuous emission monitoring system:

17 - 13

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1)(i) A 7-day calibration error test, where, for the NO<sub>x</sub>-diluent continuous emission monitoring system, the test is performed separately on the NO<sub>x</sub> pollutant concentration monitor and the diluent gas monitor;

17 - 14

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1)(ii) A linearity check, where, for the NO<sub>x</sub>-diluent continuous emission monitoring system, the test is performed separately on the NO<sub>x</sub> pollutant concentration monitor and the diluent gas monitor;

17 - 15

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1)(iii) A relative accuracy test audit. For the NO<sub>x</sub>-diluent continuous emission monitoring system, the RATA shall be done on a system basis, in units of lb/mmBtu. For the NO<sub>x</sub> concentration monitoring system, the RATA shall be done on a ppm basis;

17 - 16

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1)(iv) A bias test;

17 - 17

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(c)(1)(v) A cycle time test, (where, for the NO<sub>x</sub>-diluent continuous emission monitoring system, the test is performed separately on the NO<sub>x</sub> pollutant concentration monitor and the diluent gas monitor); and
- 40 CFR 75.20(c)(2) For each flow monitor:
- 40 CFR 75.20(c)(3) The initial certification test data from an O<sub>2</sub> or a CO<sub>2</sub> diluent gas monitor
- 40 CFR 75.20(c)(4)

17 - 18



### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(g) **Initial certification and recertification procedures for excepted monitoring systems under appendices D and E.** The owner or operator of a gas-fired unit, oil-fired unit, or diesel-fired unit using the optional protocol under appendix D or E to this part shall ensure that an excepted monitoring system under appendix D or E to this part meets the applicable general operating requirements of [§ 75.10](#), the applicable requirements of appendices D and E to this part, and the initial certification or recertification requirements of this paragraph.

17 - 19

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(g)(1)(i) ... the owner or operator shall provide data from a flowmeter accuracy test (or shall provide a statement of calibration if the flowmeter meets the accuracy standard by design) for each fuel flowmeter, according to [section 2.1.5.1](#) of appendix D to this part. ...

17 - 20

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(g)(2) **Initial certification, recertification, and QA testing notification.** The designated representative shall provide initial certification testing notification, recertification testing notification, and routine periodic quality-assurance testing, as specified in [§ 75.61](#). Initial certification testing notification, recertification testing notification, or periodic quality assurance testing notification is not required for an excepted monitoring system under appendix D to this part.

17 - 21

### Subpart C Operation and Maintenance Requirements

- 40 CFR 75.20(g)(3) **Monitoring plan.** The designated representative shall submit an initial monitoring plan in accordance with [§ 75.62\(a\)](#).
- 40 CFR 75.20(g)(4) **Initial certification or recertification application.** The designated representative shall submit an initial certification or recertification application in accordance with [§§ 75.60](#) and [75.63](#).

17 - 22

### Subpart C Operation and Maintenance Requirements

40 CFR § 75.21 Quality assurance and quality control requirements.

- (a) Continuous emission monitoring systems.** The owner or operator of an affected unit shall operate, calibrate and maintain each continuous emission monitoring system used to report emission data under the Acid Rain Program.
- 1) The owner or operator shall operate, calibrate and maintain each primary and redundant backup continuous emission monitoring system according to the quality assurance and quality control procedures in appendix B of this part.

17 - 23

### Subpart D Missing Data Substitution Procedures

- **§ 75.30 General provisions.**
- (a) Except as provided in [§ 75.34](#), the owner or operator shall provide substitute data for each affected unit using a continuous emission monitoring system according to the missing data procedures in this subpart whenever the unit combusts any fuel and:

17 - 24

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(1) A valid, quality-assured hour of SO<sub>2</sub> concentration data (in ppm) has not been measured and recorded for an affected unit by a certified SO<sub>2</sub> pollutant concentration monitor, or by an approved alternative monitoring method under [subpart E of this part](#), except as provided in [paragraph \(d\)](#) of this section; or

17 - 25

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(2) A valid, quality-assured hour of flow data (in scfh) has not been measured and recorded for an affected unit from a certified flow monitor, or by an approved alternative monitoring system under [subpart E of this part](#); or

17 - 26

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(3) A valid, quality-assured hour of NO<sub>x</sub> emission rate data (in lb/mmBtu) has not been measured or recorded for an affected unit, either by a certified NO<sub>x</sub>-diluent continuous emission monitoring system or by an approved alternative monitoring system under [subpart E of this part](#); or

17 - 27

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(4) A valid, quality-assured hour of CO<sub>2</sub> concentration data (in percent CO<sub>2</sub>, or percent O<sub>2</sub> converted to percent CO<sub>2</sub> using the procedures in appendix F to this part) has not been measured and recorded for an affected unit, either by a certified CO<sub>2</sub> continuous emission monitoring system or by an approved alternative monitoring method under [subpart E of this part](#); or

17 - 28

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(5) A valid, quality-assured hour of NO<sub>x</sub> concentration data (in ppm) has not been measured or recorded for an affected unit, either by a certified NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in [§ 75.71\(a\)\(2\)](#), or by an approved alternative monitoring system under [subpart E of this part](#); or

17 - 29

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(a)(6) A valid, quality-assured hour of CO<sub>2</sub> or O<sub>2</sub> concentration data (in percent CO<sub>2</sub>, or percent O<sub>2</sub>) used for the determination of heat input has not been measured and recorded for an affected unit, either by a certified CO<sub>2</sub> or O<sub>2</sub> diluent monitor, or by an approved alternative monitoring method under [subpart E of this part](#); or

17 - 30

### Subpart D Missing Data Substitution Procedures

- 40 CFR 75.30(b) However, the owner or operator shall have no need to provide substitute data according to the missing data procedures in this subpart if the owner or operator uses SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, or O<sub>2</sub> concentration, flow rate, percent moisture, or NO<sub>x</sub> emission rate data recorded from either a certified redundant or regular non-redundant backup CEMS, a like-kind replacement non-redundant backup analyzer, or a backup reference method monitoring system when the certified primary monitor is not operating or is out-of-control.

17 - 31

### Subpart D Missing Data Substitution Procedures

- § 75.31 Initial missing data procedures.
- § 75.32 Determination of monitor data availability for standard missing data procedures.
- § 75.33 Standard missing data procedures for SO<sub>2</sub>, NO<sub>x</sub>, and flow rate.
- § 75.34 Units with add-on emission controls.
- § 75.35 Missing data procedures for CO<sub>2</sub>.
- § 75.36 Missing data procedures for heat input rate determinations.
- § 75.37 Missing data procedures for moisture.

17 - 32

### Subpart E Alternative Monitoring Systems

- § 75.40 General demonstration requirements.
- 40 CFR 75.40(a) The owner or operator of an affected unit, or the owner or operator of an affected unit and representing a class of affected units which meet the criteria specified in § 75.47, required to install a continuous emission monitoring system may apply to the Administrator for approval of an alternative monitoring system (or system component) to determine average hourly emission data for SO<sub>2</sub>, NO<sub>x</sub>, and/or volumetric flow by demonstrating that the alternative monitoring system has the same or better precision, reliability, accessibility, and timeliness as that provided by the continuous emission monitoring system.

17 - 33

### Subpart F Recordkeeping Requirements

- § 75.53 Monitoring plan.
- The owner or operator of an affected unit shall prepare and maintain a monitoring plan.
- ECPMS
  - <https://www.epa.gov/power-sector/ecmps-reporting-instructions>
  - <https://ecmps.camdsupport.com/downloads.shtml>
  - [https://ecmps.camdsupport.com/learn\\_tutorials.shtml](https://ecmps.camdsupport.com/learn_tutorials.shtml)
- Whenever the owner or operator makes a replacement, modification, or change in the certified CEMS, continuous opacity monitoring system, the owner or operator shall update the monitoring plan, by the applicable deadline specified in § 75.62 or elsewhere in this part.

17 - 34

### Subpart F Recordkeeping Requirements

- 40 CFR 75.53(e) **Contents of the monitoring plan.** Each monitoring plan shall contain the information in paragraph (e)(1) of this section in electronic format and the information in paragraph (e)(2) of this section in hardcopy format. Electronic storage of all monitoring plan information, including the hardcopy portions, is permissible provided that a paper copy of the information can be furnished upon request for audit purposes.
- Electronic
- Hardcopy

17 - 35

### Subpart F Recordkeeping Requirements

- 40 CFR 75.57 General recordkeeping provisions.
- 40 CFR 75.57(a) **Recordkeeping requirements for affected sources.** The owner or operator of any affected source subject to the requirements of this part shall maintain for each affected unit a file of all measurements, data, reports, and other information required by this part at the source in a form suitable for inspection for at least three (3) years from the date of each record.

17 - 36

### Subpart F Recordkeeping Requirements

- 40 CFR 75.57(b) **Operating parameter record provisions.** The owner or operator shall record for each hour the following information on unit operating time, heat input rate, and load, separately for each affected unit and also for each group of units utilizing a common stack and a common monitoring system or utilizing a common pipe header and common fuel flowmeter:

17 - 37

### Subpart F Recordkeeping Requirements

- 40 CFR 75.57(b)
  - 1) Date and hour;
  - 2) Unit operating time
  - 3) Hourly gross unit load
  - 4) Operating load range corresponding to hourly gross load
  - 5) Hourly heat input rate
  - 6) Identification code for formula used for heat input
  - 7) For CEMS units only, F-factor for heat input

17 - 38

### Subpart G Reporting Requirements

- Subpart G—Reporting Requirements
- 40 CFR 75.60(a) The designated representative for any affected unit subject to the requirements of this part shall comply with all reporting requirements in this section and with the signatory requirements of [§ 72.21 of this chapter](#) for all submissions.
- 40 CFR 75.60(b) **Submissions.** The designated representative shall submit all reports and petitions (except as provided in [§ 75.61](#)) as follows:

17 - 39

### Subpart G 40 CFR 75.60(b) Reporting Requirements

- 40 CFR 75.60(b) The designated representative shall submit
  - 1) Initial certifications
  - 2) Recertifications
  - 3) Monitoring plans
  - 4) Electronic quarterly reports
  - 5) Other petitions and communications
  - 6) Semiannual or annual RATA reports (If requested in writing (or by electronic mail) by the applicable EPA Regional Office, appropriate State, and/or appropriate local air pollution control agency)

17 - 40

### Subpart G Reporting Requirements

- 40 CFR 75.60(b) The designated representative shall submit
  - 7) Routine appendix E retest reports (If requested)

17 - 41

### Subpart G Reporting Requirements

- § 75.61 Notifications.
- 40 CFR 75.61(a) **Submission.** The designated representative for an affected unit (or owner or operator, as specified) shall submit notice to the Administrator, to the appropriate EPA Regional Office, and to the applicable State and local air pollution control agencies for the following purposes, as required by this part.

17 - 42

# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

### Subpart G Reporting Requirements

- 40 CFR 75.61(a)(1) ... submit written notification of initial certification tests and revised test dates as specified in [§ 75.20](#)...
- 40 CFR 75.61(a)(1)(i) shall be submitted not later than 21 days prior to the first scheduled day of certification or recertification testing.
  - emergency situations:
    - notice shall be sufficient if provided within 2 business days following the date when testing is scheduled
    - notice of the new date is provided either in writing or by telephone or other means at least 7 days prior to the original scheduled test date

17 - 43

### Subpart G Reporting Requirements

- 40 CFR 75.61(a)(1)(ii) **Notification of certification retesting, and partial recertification testing.** For retesting required following a loss of certification under [§ 75.20\(a\)\(5\)](#) or for partial recertification testing required under [§ 75.20\(b\)\(2\)](#), notice of the date of any required RATA testing or any required retesting under [section 2.3](#) in appendix E to this part shall be submitted either in writing or by telephone at least 7 days prior to the first scheduled day of testing; except that in emergency situations when testing is required following an uncontrollable failure of equipment that results in lost data, notice shall be sufficient if provided within 2 business days following the date when testing is scheduled. Testing may be performed on a date other than that already provided in a notice under this subparagraph as long as notice of the new date is provided by telephone or other means at least 2 business days prior to the original scheduled test date or the revised test date, whichever is earlier.

17 - 44

### Subpart G Reporting Requirements

- 40 CFR 75.61(a)(1)(iii) Notwithstanding the above notice requirements, the owner or operator may elect to repeat a certification or recertification test immediately, without advance notification, whenever the owner or operator has determined during the certification or recertification testing that a test was failed or must be aborted, or that a second test is necessary in order to attain a reduced relative accuracy test frequency.

17 - 45

### Subpart G Reporting Requirements

- 40 CFR 75.61(a)(1)(iv) The Administrator, the appropriate EPA Regional Office, or the applicable State or local air pollution control agency may issue a waiver from the notification requirement of [paragraph \(a\)\(1\)\(iii\)](#) of this section, for a unit or a group of units, for one or more recertification tests or other retests.

17 - 46

### Subpart G Reporting Requirements

- 40 CFR 75.61(a)(5) Periodic relative accuracy test audits, appendix E retests, and low mass emissions unit retests.
  - 21 days prior to the first scheduled day of testing.
  - Testing may be performed on a date other than that already provided in a notice under this subparagraph as long as notice of the new date is provided either in writing or by telephone or other means acceptable to the respective State agency or office of EPA, and the notice is provided as soon as practicable after the new testing date is known, but no later than twenty-four (24) hours in advance of the new date of testing.

17 - 47

### Subpart G Reporting Requirements

- 40 CFR § 75.62 Monitoring plan submittals.
- 40 CFR 75.62(a)(1) Electronic
  - no later than 21 days prior to the initial certification tests
- 40 CFR 75.62(a)(2) Hardcopy no later than 21 days prior to the initial certification tests
  - no later than 21 days prior to the initial certification test; with any certification or recertification application, if a hardcopy monitoring plan change is associated with the certification or recertification event; and within 30 days of any other event with which a hardcopy monitoring plan change is associated

17 - 48

### Subpart G Reporting Requirements

- 40 CFR § 75.63 Initial certification or recertification application.
- (a) **Submission.** The designated representative for an affected unit or a combustion source shall submit applications and reports as follows:
- (1) Initial certifications.
- (1)(i) For CEM systems or excepted monitoring systems under appendix D or E to this part, within 45 days after completing all initial certification tests, submit:
- (1)(i)(B) To the applicable EPA Regional Office and the appropriate State and/or local air pollution control agency, the hardcopy information required by [paragraph \(b\)\(2\)](#) of this section.

17 - 49

### Subpart G Reporting Requirements

- 40 CFR 75.63(a)(2) Recertifications and diagnostic testing.
- (i) Within 45 days after completing all recertification tests under [§ 75.20\(b\)](#), submit to the Administrator the electronic information required by [paragraph \(b\)\(1\)](#) of this section. Except for subpart E applications for alternative monitoring systems or unless specifically requested by the Administrator, do not submit a hardcopy of the test data and results to the Administrator.

17 - 50

### Subpart G Reporting Requirements

- 40 CFR 75.63(a)(2)(ii) Within 45 days after completing all recertification tests under [§ 75.20\(b\)](#), submit the hardcopy information required by [paragraph \(b\)\(2\)](#) of this section to the applicable EPA Regional Office and the appropriate State and/or local air pollution control agency. The applicable EPA Regional Office or appropriate State or local air pollution control agency may waive the requirement to provide hardcopy recertification test and data results. The applicable EPA Regional Office or the appropriate State or local air pollution control agency may also discontinue the waiver and reinstate the requirement of this paragraph to provide a hardcopy report of the recertification test data and results.

17 - 51

### Subpart G Reporting Requirements

- 40 CFR § 75.64 **Quarterly reports.**
- 40 CFR 75.64(a) **Electronic submission.** The designated representative for an affected unit shall electronically report the data and information in [paragraphs \(a\), \(b\), and \(c\)](#) of this section to the Administrator quarterly,
- 40 CFR 75.64(b) The designated representative shall affirm that the component/system identification codes and formulas in the quarterly electronic reports, submitted to the Administrator pursuant to [§ 75.53](#), represent current operating conditions.

17 - 52

### Subpart G Reporting Requirements

- 40 CFR 75.64(c) **Compliance certification.** The designated representative shall submit a certification in support of each quarterly emissions monitoring report based on reasonable inquiry of those persons with primary responsibility for ensuring that all of the unit's emissions are correctly and fully monitored.

17 - 53

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR § 75.70 NO<sub>x</sub> mass emissions provisions.
- 40 CFR 75.70(a) **Applicability.** The owner or operator of a unit shall comply with the requirements of this subpart to the extent that compliance is required by an applicable State or federal NO<sub>x</sub> mass emission reduction program that incorporates by reference, or otherwise adopts the provisions of, this subpart.

17 - 54



### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.70(d) Initial certification and recertification procedures.
- 1) The owner or operator of an affected unit that is subject to an Acid Rain emissions limitation shall comply with the initial certification and recertification procedures in [§ 75.20 of this part](#), except that the owner or operator shall meet any additional requirements set forth in an applicable State or federal NO<sub>x</sub> mass emission reduction program that adopts the requirements of this subpart.

17 - 55

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.70(e) **Quality assurance and quality control requirements.** For units that use continuous emission monitoring systems to account for NO<sub>x</sub> mass emissions, the owner or operator shall meet the applicable quality assurance and quality control requirements in [§ 75.21](#), appendix B to this part, and [§ 75.74\(c\)](#) for the NO<sub>x</sub>-diluent continuous emission monitoring systems, flow monitoring systems, NO<sub>x</sub> concentration monitoring systems, moisture monitoring systems, and diluent monitors required under [§ 75.71](#)

17 - 56

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.70(f) **Missing data procedures.** Except as provided in [§ 75.34, paragraph \(g\)](#) of this section, and [§ 75.74\(c\)\(7\)](#), the owner or operator shall provide substitute data from monitoring systems required under [§ 75.71](#) for each affected unit as follows:
- 40 CFR 75.70(f)(1) For an owner or operator using a continuous emissions monitoring system, substitute for missing data in accordance with the applicable missing data procedures in [§§ 75.31](#) through [75.37](#) whenever the unit combusts fuel and:

17 - 57

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.70(f)(2) For an owner or operator using an excepted monitoring system under appendix D or E of this part, substitute for missing data in accordance with the missing data procedures in [section 2.4](#) of appendix D to this part or in [section 2.5](#) of appendix E to this part whenever the unit combusts fuel and:

17 - 58

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.70(g) **Reporting data prior to initial certification.** If the owner or operator of an affected unit has not successfully completed all certification tests required by the State or federal NO<sub>x</sub> mass emission reduction program that adopts the requirements of this subpart by the applicable date required by that program, he or she shall determine, record and report hourly data prior to initial certification using one of the following procedures, consistent with the monitoring equipment to be certified:

17 - 59

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR § 75.73 Recordkeeping and reporting.
- 40 CFR 75.73(a) **General recordkeeping provisions.** The owner or operator of any affected unit shall maintain for each affected unit and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#) a file of all measurements, data, reports, and other information required by this part at the source in a form suitable for inspection for at least three (3) years from the date of each record.

17 - 60

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(b) **Certification, quality assurance and quality control record provisions.** The owner or operator of any affected unit shall record the applicable information in [§ 75.59](#) for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#).
- 40 CFR 75.73(c) **Monitoring plan recordkeeping provisions —**
- 1) **General provisions.** The owner or operator of an affected unit shall prepare and maintain a monitoring plan for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#).

17 - 61

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(c) **Monitoring plan recordkeeping provisions —**
- 2) **Monitoring plan updates.** Whenever the owner or operator makes a replacement, modification, or change in the certified continuous emission monitoring system
- 3) **Contents of the monitoring plan.** Each monitoring plan shall contain the information in [§ 75.53\(g\)\(1\)](#) in electronic format and the information in [§ 75.53\(g\)\(2\)](#) in hardcopy format. In addition, to the extent applicable, each monitoring plan shall contain the information in [§ 75.53\(h\)\(1\)\(i\)](#) and [\(h\)\(2\)\(i\)](#) in electronic format and the information in [§ 75.53\(h\)\(1\)\(ii\)](#) and [\(h\)\(2\)\(ii\)](#) in hardcopy format.

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### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(d) General reporting provisions.
- 40 CFR 75.73(d)(1) The designated representative for an affected unit shall comply with all reporting requirements in this section and with any additional requirements set forth in an applicable State or federal NO<sub>x</sub> mass emission reduction program that adopts the requirements of this subpart.

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### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(d)(2) The designated representative for an affected unit shall submit the following for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#):
- (i) Initial certification and recertification applications in accordance with [§ 75.70\(d\)](#);
- (ii) Monitoring plans in accordance with [paragraph \(e\)](#) of this section; and
- (iii) Quarterly reports in accordance with [paragraph \(f\)](#) of this section.

17 - 64

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(d)(4) **Quality assurance RATA reports.** If requested by the permitting authority, the designated representative of an affected unit shall submit the quality assurance RATA report for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#) by the later of 45 days after completing a quality assurance RATA according to [section 2.3](#) of appendix B to this part or 15 days of receiving the request. The designated representative shall report the hardcopy information required by [§ 75.59\(a\)\(9\)](#) to the permitting authority.

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### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(d)(5) **Notifications.** The designated representative for an affected unit shall submit written notice to the permitting authority according to the provisions in [§ 75.61](#) for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#).

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# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(e) **Electronic submission.**
- 40 CFR 75.73(e)(1) The designated representative for an affected unit shall submit to the Administrator a complete, electronic, up-to-date monitoring plan file for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#), no later than 21 days prior to the initial certification test

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### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(e)(2) **Hardcopy submission.** The designated representative of an affected unit shall submit all of the hardcopy information required under [§ 75.53](#), for each affected unit or group of units monitored at a common stack and each non-affected unit under [§ 75.72\(b\)\(2\)\(ii\)](#), to the permitting authority prior to initial certification. Thereafter, the designated representative shall submit hardcopy information only if that portion of the monitoring plan is revised. The designated representative shall submit the required hardcopy information as follows: no later than 21 days prior to the initial certification test; with any certification or recertification application, if a hardcopy monitoring plan change is associated with the recertification event; and within 30 days of any other event with which a hardcopy monitoring plan change is associated, pursuant to [§ 75.53\(b\)](#). Electronic submittal of all monitoring plan information, including hardcopy portions, is permissible provided that a paper copy of the hardcopy portions can be furnished upon request.

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### Subpart H NO<sub>x</sub> Mass Emissions Provisions

- 40 CFR 75.73(f) **Quarterly reports —**
- (1) **Electronic submission.** The designated representative for an affected unit shall electronically report the data and information in this [paragraph \(f\)\(1\)](#) and in [paragraphs \(f\)\(2\)](#) and [\(3\)](#) of this section to the Administrator quarter.
- (2) **Verification of identification codes and formulas.** The designated representative shall certify that the component and system identification codes and formulas in the quarterly electronic reports submitted to the Administrator pursuant to [paragraph \(e\)](#) of this section represent current operating conditions.

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### Appendix A to Part 75 Specifications and Test Procedures

- 1.1 Gas Monitors
- 1.1(a) Following the procedures in section 8.1.1 of Performance Specification 2 in appendix B to [part 60 of this chapter](#), install the pollutant concentration monitor or monitoring system at a location where the pollutant concentration and emission rate measurements are directly representative of the total emissions from the affected unit.

17 - 70

### Appendix A to Part 75 Specifications and Test Procedures

- 1.1.1 Point Monitors
- Locate the measurement point (1) within the centroidal area of the stack or duct cross section, or (2) no less than 1.0 meter from the stack or duct wall.

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### Appendix A to Part 75 Specifications and Test Procedures

- 1.2 Flow Monitors
- Install the flow monitor in a location that provides representative volumetric flow over all operating conditions.

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# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

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### Appendix A to Part 75 Specifications and Test Procedures

- 1.2.1 Acceptability of Monitor Location
  - minimum siting criteria of method 1 in appendix A to [part 60 of this chapter](#)
  - the results of a flow profile study, if performed, are acceptable (i.e., there are no cyclonic (or swirling) or stratified flow conditions)
  - If the flow monitor is installed in a location that does not satisfy these physical criteria, but nevertheless the monitor achieves the performance specifications of this part, then the location is acceptable, notwithstanding the requirements of this section

17 - 73

### Appendix A to Part 75 Specifications and Test Procedures

- 1.2.2 Alternative Monitoring Location
- Administrator may approve an interim alternative flow monitoring methodology and an extension to the required certification date for the flow monitor.
- the owner or operator may petition the Administrator for an alternative method for monitoring flow.

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### Appendix A to Part 75 Specifications and Test Procedures

- 2. Equipment Specifications
- 2.1 Instrument Span and Range
- In implementing sections 2.1.1 through 2.1.6 of this appendix, set the measurement range for each parameter (SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, O<sub>2</sub>, or flow rate) high enough to prevent full-scale exceedances from occurring, yet low enough to ensure good measurement accuracy and to maintain a high signal-to-noise ratio.

17 - 75

### Appendix A to Part 75 Specifications and Test Procedures

- 2.1.2 NO<sub>x</sub> Pollutant Concentration Monitors
- Determine, as indicated in sections 2.1.2.1 through 2.1.2.5 of this appendix, the span and range value(s) for the NO<sub>x</sub> pollutant concentration monitor so that all expected NO<sub>x</sub> concentrations can be determined and recorded accurately.

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### Appendix A to Part 75 Specifications and Test Procedures

- 2.1.2.1 Maximum Potential Concentration
- (a) The maximum potential concentration (MPC) of NO<sub>x</sub> for each affected unit shall be based upon whichever fuel or blend combusted in the unit produces the highest level of NO<sub>x</sub> emissions.

17 - 77

### Appendix A to Part 75 Specifications and Test Procedures

- 2.1.2.1 Maximum Potential Concentration
- Make an initial determination of the MPC using the appropriate option as follows:
  - Option 1: Use 800 ppm for coal-fired and 400 ppm for oil- or gas-fired units as the maximum potential concentration of NO<sub>x</sub> (if an MPC of 1600 ppm for coal-fired units or 480 ppm for oil- or gas-fired units was previously selected under this section, that value may still be used, provided that the guidelines of section 2.1 of this appendix are met); For cement kilns, use 2000 ppm as the MPC. For process heaters, use 200 ppm if the unit burns only gaseous fuel and 500 ppm if the unit burns oil;

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### Appendix A to Part 75 Specifications and Test Procedures

- Option 2: Use the specific values based on boiler type and fuel combusted, listed in Table 2–1 or Table 2–2; For a new gas-fired or oil-fired combustion turbine, if a default MPC value of 50 ppm was previously selected from Table 2–2, that value may be used until March 31, 2003;
- Option 3: Use NO<sub>x</sub> emission test results;
- Option 4: Use historical CEM data over the previous 720 (or more) unit operating hours when combusting the fuel or blend with the highest NO<sub>x</sub> emission rate; or
- Option 5: If a reliable estimate of the uncontrolled NO<sub>x</sub> emissions from the unit is available from the manufacturer, the estimated value may be used.

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 2.1.2.1(b)
- For the purpose of providing substitute data during NO<sub>x</sub> missing data periods in accordance with §§ 75.31 and 75.33 and as required elsewhere under this part, the owner or operator shall also calculate the maximum potential NO<sub>x</sub> emission rate (MER), in lb/mmBtu, by substituting the MPC for NO<sub>x</sub> in conjunction with the minimum expected CO<sub>2</sub> or maximum O<sub>2</sub> concentration (under all unit operating conditions except for unit startup, shutdown, and upsets)

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 2.1.2.1(c)
- Report the method of determining the initial MPC and the calculation of the maximum potential NO<sub>x</sub> emission rate in the monitoring plan for the unit. Note that whichever MPC option in paragraph 2.1.2.1(a) of this appendix is selected, the initial MPC value is subject to periodic review under section 2.1.2.5 of this appendix. If an MPC value is found to be either inappropriately high or low, the MPC shall be adjusted in accordance with section 2.1.2.5, and corresponding span and range adjustments shall be made, if necessary.

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 2.1.2.1(d)
- For units with add-on NO<sub>x</sub> controls (whether or not the unit is equipped with low-NO<sub>x</sub> burner technology), or for units equipped with dry low-NO<sub>x</sub> (DLN) technology, NO<sub>x</sub> emission testing may only be used to determine the MPC if testing can be performed either upstream of the add-on controls or during a time or season when the add-on controls are not in operation or when the DLN controls are not in the premixed (low-NO<sub>x</sub>) mode

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 2.1.2.1(e)
- If historical CEM data are used to determine the MPC, the data must, for uncontrolled units or units equipped with low-NO<sub>x</sub> burner technology and no other NO<sub>x</sub> controls, represent a minimum of 720 quality-assured monitor operating hours from the NO<sub>x</sub> component of a certified monitoring system, obtained under various operating conditions including the minimum safe and stable load, normal load (including periods of high excess air at normal load), and maximum load.

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 2.1.2.2(a)
- Make an initial determination of the maximum expected concentration (MEC) of NO<sub>x</sub> during normal operation for affected units with add-on NO<sub>x</sub> controls of any kind (e.g., steam injection, water injection, SCR, or SNCR) and for turbines that use dry low-NO<sub>x</sub> technology. Determine a separate MEC value for each type of fuel (or blend) combusted in the unit, except for fuels that are only used for unit startup and/or flame stabilization.

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### Appendix A to Part 75

#### Specifications and Test Procedures

- Calculate the MEC of NO<sub>x</sub> using Equation A-2, if applicable, inserting the maximum potential concentration, as determined using the procedures in section 2.1.2.1 of this appendix. Where Equation A-2 is not applicable, set the MEC either by:
  - (1) measuring the NO<sub>x</sub> concentration using the testing procedures in this section;
  - (2) using historical CEM data over the previous 720 (or more) quality-assured monitor operating hours; or
  - (3) if the unit has add-on NO<sub>x</sub> controls or uses dry low NO<sub>x</sub> technology, and has a federally-enforceable permit limit for NO<sub>x</sub> concentration, the permit limit may be used as the MEC.

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### Appendix A to Part 75

#### Specifications and Test Procedures

- 3. Performance Specifications
- 3.1 Calibration Error
  - (a) The calibration error performance specifications in this section apply only to 7-day calibration error tests under sections 6.3.1 and 6.3.2 of this appendix and to the offline calibration demonstration described in section 2.1.1.2 of appendix B to this part. The calibration error limits for daily operation of the continuous monitoring systems required under this part are found in section 2.1.4(a) of appendix B to this part.

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### Appendix A to Part 75

#### Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 3.1(b)
- The calibration error of SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors shall not deviate from the reference value of either the zero or upscale calibration gas by more than 2.5 percent of the span of the instrument, as calculated using Equation A-5 of this appendix.
- Alternatively, where the span value is less than 200 ppm, calibration error test results are also acceptable if the absolute value of the difference between the monitor response value and the reference value,  $|R-A|$  in Equation A-5 of this appendix, is  $\leq 5$  ppm

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### Appendix A to Part 75

#### Specifications and Test Procedures

- 3.2 Linearity Check
- For SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors, the error in linearity for each calibration gas concentration (low-, mid-, and high-levels) shall not exceed or deviate from the reference value by more than 5.0 percent (as calculated using equation A-4 of this appendix)

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### Appendix A to Part 75

#### Specifications and Test Procedures

- 3.2 Linearity Check
- For SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors, the error in linearity for each calibration gas concentration (low-, mid-, and high-levels) shall not exceed or deviate from the reference value by more than 5.0 percent (as calculated using equation A-4 of this appendix)

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### Appendix A to Part 75

#### Specifications and Test Procedures

- 3.3.2 Relative Accuracy for NO<sub>x</sub>-Diluent Continuous Emission Monitoring Systems
- (a) The relative accuracy for NO<sub>x</sub>-diluent continuous emission monitoring systems shall not exceed 10.0 percent.
- (b) For affected units where the average of the reference method measurements of NO<sub>x</sub> emission rate during the relative accuracy test audit is less than or equal to 0.200 lb/mmBtu, the difference between the mean value of the continuous emission monitoring system measurements and the reference method mean value shall not exceed  $\pm 0.020$  lb/mmBtu, wherever the relative accuracy specification of 10.0 percent is not achieved.

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### Appendix A to Part 75 Specifications and Test Procedures

- 3.3.4 Relative Accuracy for Flow Monitors
- (a) The relative accuracy of flow monitors shall not exceed 10.0 percent at any load (or operating) level at which a RATA is performed (i.e., the low, mid, or high level, as defined in section 6.5.2.1 of this appendix).

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### Appendix A to Part 75 Specifications and Test Procedures

- 3.4 Bias
- 3.4.1 SO<sub>2</sub> Pollutant Concentration Monitors, NO<sub>x</sub> Concentration Monitoring Systems and NO<sub>x</sub>-Diluent Continuous Emission Monitoring Systems
- SO<sub>2</sub> pollutant concentration monitors, NO<sub>x</sub>-diluent continuous emission monitoring systems and NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions, as defined in [§ 75.71\(a\)\(2\)](#), shall not be biased low as determined by the test procedure in section 7.6 of this appendix

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### Appendix A to Part 75 Specifications and Test Procedures

- 3.5 Cycle Time
- The cycle time for pollutant concentration monitors, oxygen monitors used to determine percent moisture, and any other monitoring component of a continuous emission monitoring system that is required to perform a cycle time test shall not exceed 15 minutes.

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### Appendix A to Part 75 Specifications and Test Procedures

- 4. Data Acquisition and Handling Systems
- (a) Automated data acquisition and handling systems shall read and record the entire range of pollutant concentrations and volumetric flow from zero through full-scale and provide a continuous, permanent record of all measurements and required information in an electronic format.
- continuous readout of pollutant emission rates or pollutant mass emissions (as applicable) in the appropriate units (e.g., lb/hr, lb/mmBtu, tons/hr).

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### Appendix A to Part 75 Specifications and Test Procedures

- 5. Calibration Gas
- 5.1 Reference Gases
- For the purposes of part 75, calibration gases include the following:

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.1.1 Standard Reference Materials (SRM)
- These calibration gases may be obtained from the National Institute of Standards and Technology (NIST) at the following address: Quince Orchard and Cloppers Road, Gaithersburg, MD 20899-0001.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.1.2 SRM-Equivalent Compressed Gas Primary Reference Material (PRM)
- Contact the Gas Metrology Team, Analytical Chemistry Division, Chemical Science and Technology Laboratory of NIST, at the address in section 5.1.1, for a list of vendors and cylinder gases.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.1.3 NIST Traceable Reference Materials
- Contact the Gas Metrology Team, Analytical Chemistry Division, Chemical Science and Technology Laboratory of NIST, at the address in section 5.1.1, for a list of vendors and cylinder gases that meet the definition for a NIST Traceable Reference Material (NTRM) provided in [§ 72.2](#).

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.1.4 EPA Protocol Gases
- (a) An EPA Protocol gas is a calibration gas mixture prepared and analyzed according to Section 2 of the "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," September 1997, as amended on August 25, 1999, EPA-600/R-97/121 (incorporated by reference, see [§ 75.6](#)) or such revised procedure as approved by the Administrator.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.2.1 Zero-level Concentration
- 0.0 to 20.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.2.2 Low-level Concentration
- 20.0 to 30.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.2.3 Mid-level Concentration
- 50.0 to 60.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

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### Appendix A to Part 75 Specifications and Test Procedures

- 5.2.4 High-level Concentration
- 80.0 to 100.0 percent of span, including span for high-scale or both low-and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6. Certification Tests and Procedures
- 6.1.2 Requirements for Air Emission Testing
- (a) On and after March 27, 2012, all relative accuracy test audits (RATAs) of CEMS under this part, and stack testing under [§ 75.19](#) and Appendix E to this part ***shall be conducted by an Air Emission Testing Body (AETB)***

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 6.1.2(e)
- All relative accuracy testing performed pursuant to [§ 75.74\(c\)\(2\)\(ii\)](#), section 6.5 of appendix A to this part or section 2.3.1 of appendix B to this part, and stack testing under [§ 75.19](#) and Appendix E to this part shall be overseen and supervised on site by at least one Qualified Individual

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.2 Linearity Check (General Procedures)
- Check the linearity of each SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitor while the unit, or group of units for a common stack, is combusting fuel at conditions of typical stack temperature and pressure; it is not necessary for the unit to be generating electricity during this test

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 6.2(a)
- For the initial certification of a CEMS, data from the monitoring system are considered invalid until all certification tests, including the linearity test, have been successfully completed, unless the conditional data validation procedures in [§ 75.20\(b\)\(3\)](#) are used. When the procedures in [§ 75.20\(b\)\(3\)](#) are followed, the words "initial certification" apply instead of "recertification," and complete all of the initial certification tests by the applicable deadline in [§ 75.4](#), rather than within the time periods specified in [§ 75.20\(b\)\(3\)\(iv\)](#) for the individual tests.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.3 7-Day Calibration Error Test
- 6.3.1 Gas Monitor 7-Day Calibration Error Test
- The following monitors and ranges are exempted from the 7-day calibration error test requirements of this part: the SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub> and O<sub>2</sub> monitors installed on peaking units (as defined in [§ 72.2 of this chapter](#)); and any SO<sub>2</sub> or NO<sub>x</sub> measurement range with a span value of 50 ppm or less.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.4 Cycle Time Test
- Perform cycle time tests for each pollutant concentration monitor and continuous emission monitoring system while the unit is operating, according to the following procedures.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5 Relative Accuracy and Bias Tests (General Procedures)
- Perform the required relative accuracy test audits (RATAs) as follows for each CO<sub>2</sub> emissions concentration monitor (including O<sub>2</sub> monitors used to determine CO<sub>2</sub> emissions concentration), each SO<sub>2</sub> pollutant concentration monitor, each NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, each flow monitor, each NO<sub>x</sub>-diluent CEMS, each O<sub>2</sub> or CO<sub>2</sub> diluent monitor used to calculate heat input, and each moisture monitoring system.

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 6.5(a) Except as otherwise provided in this paragraph or in [§ 75.21\(a\)\(5\)](#), perform each RATA while the unit (or units, if more than one unit exhausts into the flue) is combusting the fuel that is a normal primary or backup fuel for that unit (for some units, more than one type of fuel may be considered normal, *e.g.*, a unit that combusts gas or oil on a seasonal basis).

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### Appendix A to Part 75 Specifications and Test Procedures

- 40 CFR Appendix-A-to-Part-75 6.5(e) Complete each single-load relative accuracy test audit within a period of 168 consecutive unit operating hours, as defined in [§ 72.2 of this chapter](#) (or, for CEMS installed on common stacks or bypass stacks, 168 consecutive stack operating hours, as defined in [§ 72.2 of this chapter](#)).

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.5 Reference Method Measurement Location
- Select a location for reference method measurements that is (1) accessible; (2) in the same proximity as the monitor or monitoring system location; and (3) meets the requirements of Performance Specification 2 in appendix B of [part 60 of this chapter](#) for SO<sub>2</sub> and NO<sub>x</sub> continuous emission monitoring systems, Performance Specification 3 in appendix B of [part 60 of this chapter](#) for CO<sub>2</sub> or O<sub>2</sub> monitors, or method 1 (or 1A) in appendix A of [part 60 of this chapter](#) for volumetric flow, except as otherwise indicated in this section or as approved by the Administrator.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.6 Reference Method Traverse Point Selection
- Select traverse points that ensure acquisition of representative samples of pollutant and diluent concentrations, moisture content, temperature, and flue gas flow rate over the flue cross section. To achieve this, the reference method traverse points shall meet the requirements of section 8.1.3 of Performance Specification 2 ("PS No. 2") in appendix B to [part 60 of this chapter](#) (for SO<sub>2</sub>, NO<sub>x</sub>, and moisture monitoring system RATAs), Performance Specification 3 in appendix B to [part 60 of this chapter](#) (for O<sub>2</sub> and CO<sub>2</sub> monitor RATAs), Method 1 (or 1A) (for volumetric flow rate monitor RATAs), Method 3 (for molecular weight), and Method 4 (for moisture determination) in appendix A to [part 60 of this chapter](#). The following alternative reference method traverse point locations are permitted for moisture and gas monitor RATAs:

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.6.1 Stratification Test
- (a) With the unit(s) operating under steady-state conditions at the normal load level (or normal operating level), as defined in section 6.5.2.1 of this appendix, use a traversing gas sampling probe to measure the pollutant (SO<sub>2</sub> or NO<sub>x</sub>) and diluent (CO<sub>2</sub> or O<sub>2</sub>) concentrations at a minimum of twelve (12) points, located according to Method 1 in appendix A to [part 60 of this chapter](#).

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### Appendix A to Part 75 Specifications and Test Procedures

- (b) Use Methods 6C, 7E, and 3A in appendix A to [part 60 of this chapter](#) to make the measurements. Data from the reference method analyzers must be quality-assured by performing analyzer calibration error and system bias checks before the series of measurements and by conducting system bias and calibration drift checks after the measurements, in accordance with the procedures of Methods 6C, 7E, and 3A.

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### Appendix A to Part 75 Specifications and Test Procedures

- c) Measure for a minimum of 2 minutes at each traverse point. To the extent practicable, complete the traverse within a 2-hour period

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### Appendix A to Part 75 Specifications and Test Procedures

- (d) If the load has remained constant ( $\pm 3.0$  percent) during the traverse and if the reference method analyzers have passed all of the required quality assurance checks, proceed with the data analysis.

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### Appendix A to Part 75 Specifications and Test Procedures

- (e) Calculate the average NO<sub>x</sub>, SO<sub>2</sub>, and CO<sub>2</sub> (or O<sub>2</sub>) concentrations at each of the individual traverse points. Then, calculate the arithmetic average NO<sub>x</sub>, SO<sub>2</sub>, and CO<sub>2</sub> (or O<sub>2</sub>) concentrations for all traverse points.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.6.3 Stratification Test Results and Acceptance Criteria
- (a) For each pollutant or diluent gas, the short reference method measurement line described in section 8.1.3 of PS No. 2 may be used in lieu of the long measurement line prescribed in section 8.1.3 of PS No. 2 if the results of a stratification test, conducted in accordance with section 6.5.6.1 or 6.5.6.2 of this appendix (as appropriate; see section 6.5.6(b)(3) of this appendix), show that the concentration at each individual traverse point differs by no more than  $\pm 10.0$  percent from the arithmetic average concentration for all traverse points. The results are also acceptable if the concentration at each individual traverse point differs by no more than  $\pm 5$ ppm or  $\pm 0.5$  percent CO<sub>2</sub> (or O<sub>2</sub>) from the arithmetic average concentration for all traverse points.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.9 Number of Reference Method Tests
- Perform a minimum of nine sets of paired monitor (or monitoring system) and reference method test data for every required (i.e., certification, recertification, diagnostic, semiannual, or annual) relative accuracy test audit.

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### Appendix A to Part 75 Specifications and Test Procedures

- 6.5.10 Reference Methods
- Method 1 or 1A
- Method 2
- Methods 3, 3A or 3B
- Method 4
- Methods 6, 6A or 6C
- Methods 7, 7A, 7C, 7D or 7E
  - When using Method 7E for measuring NO<sub>x</sub> concentration, total NO<sub>x</sub>, including both NO and NO<sub>2</sub>, must be measured

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### Appendix A to Part 75 Specifications and Test Procedures

- 7. Calculations
- 7.1 Linearity Check
- $LE = \frac{|R-A|}{R} \times 100$

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### Appendix A to Part 75 Specifications and Test Procedures

- 7.2 Calibration Error
- 7.2.1 Pollutant Concentration and Diluent Monitors
- For each reference value, calculate the percentage calibration error based upon instrument span for daily calibration error tests using the following equation:
- $CE = \frac{|R-A|}{S} \times 100$   
(Eq. A-5)

17 - 124

### Appendix A to Part 75 Specifications and Test Procedures

- 7.3 Relative Accuracy for SO<sub>2</sub> and CO<sub>2</sub> Emissions Concentration Monitors, O<sub>2</sub> Monitors, NO<sub>x</sub> Concentration Monitoring Systems, and Flow Monitors
- Analyze the relative accuracy test audit data from the reference method tests for SO<sub>2</sub> and CO<sub>2</sub> emissions concentration monitors, CO<sub>2</sub> or O<sub>2</sub> monitors used for heat input rate determination, NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions under [subpart H of this part](#), and flow monitors using the following procedures.

17 - 125

### Appendix A to Part 75 Specifications and Test Procedures

- 7.3.1 Arithmetic Mean
- Calculate the arithmetic mean of the differences of a data set as follows:
- $\bar{d} = \frac{1}{n} \sum_{i=1}^n d_i$

17 - 126



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

### Appendix A to Part 75 Specifications and Test Procedures

- 7.3.2 Standard Deviation
- Calculate the standard deviation,  $S_d$ , of a data set as follows:

$$S_d = \sqrt{\frac{\sum_i^n d_i^2 - \left[ \frac{(\sum_{i=1}^n d_i)^2}{n} \right]}{(n-1)}}$$

(Eq. A-8)

17 - 127

### Appendix A to Part 75 Specifications and Test Procedures

7.3.3 Confidence Coefficient  
 Calculate the confidence coefficient (one-tailed),  $cc$ , of a data set as follows.

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

(eq. A-9)

17 - 128

### Appendix A to Part 75 Specifications and Test Procedures

7.3.4 Relative Accuracy  
 Calculate the relative accuracy of a data set using the following equation.

$$RA = \frac{|Q| + |cc|}{RR} \times 100$$

(Eq. A-10)

17 - 129

### Appendix A to Part 75 Specifications and Test Procedures

- 7.6.5 Bias Adjustment
- (a) If the monitor or monitoring system fails to meet the bias test requirement, adjust the value obtained from the monitor using the following equation:

$$CEM_i^{Adjusted} = CEM_i^{Monitor} \times BAF$$

17 - 130

### Appendix A to Part 75 Specifications and Test Procedures

- BAF = Bias adjustment factor, defined by:

$$BAF = 1 + \frac{|\bar{d}|}{CME_{avg}}$$

17 - 131

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

Quality Assurance/Quality Control Program

- Develop and implement a quality assurance/quality control (QA/QC) program for the continuous emission monitoring systems, excepted monitoring systems approved under appendix D or E to this part, and alternative monitoring systems under [subpart E of this part](#), and their components.

17 - 132

# APT1 #450/468 Compliance Test and Source Test Observation

## Lesson 17: Part 75

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

Test	Basic QA test frequency requirements		
	Daily *	Quarterly *	Semiannual or annual *
Calibration Error Test (2 pt.)	X		
Interference Check (flow)	X		
Flow-to-Load Ratio		X	
Leak Check (DP flow monitors)		X	
Linearity Check * (3 pt.)		X	
RATA (SO <sub>2</sub> , NO <sub>x</sub> , CO <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> O) <sup>1</sup>			X
RATA (flow) <sup>12</sup>			X

17 - 133

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

RATA <sup>y</sup>	Semiannual <sup>w</sup>	Annual <sup>w</sup>
SO <sub>2</sub> or NO <sub>x</sub> <sup>x</sup>	7.5% <RA ≤10.0% or ±15.0 ppm <sup>x</sup>	RA ≤7.5% or ±12.0 ppm <sup>x</sup>
NO <sub>x</sub> -diluent	7.5% <RA ≤10.0% or ±0.020 lb/mmBtu <sup>x</sup>	RA ≤7.5% or ±0.015 lb/mmBtu <sup>x</sup>
Flow	7.5% <RA ≤10.0% or ±2.0 fps <sup>x</sup>	RA ≤7.5% or ±1.5 fps <sup>x</sup>
CO <sub>2</sub> or O <sub>2</sub>	7.5% <RA ≤10.0% or ±1.0% CO <sub>2</sub> /O <sub>2</sub> <sup>x</sup>	RA ≤7.5% or ±0.7% CO <sub>2</sub> /O <sub>2</sub> <sup>x</sup>
Moisture	7.5% <RA ≤10.0% or ±1.5% H <sub>2</sub> O <sup>x</sup>	RA ≤7.5% or ±1.0% H <sub>2</sub> O <sup>x</sup>

17 - 134

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

- 2.1.1.1 Calibration Error Test
- Except as provided in section 2.1.1.2 of this appendix, perform the daily calibration error test of each gas monitoring system (including moisture monitoring systems consisting of wet- and dry-basis O<sub>2</sub> analyzers) according to the procedures in section 6.3.1 of appendix A to this part, and perform the daily calibration error test of each flow monitoring system according to the procedure in section 6.3.2 of appendix A to this part.

17 - 135

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

- 2.1.1.1.1 **On-line Daily Calibration Error Tests.** Except as provided in section 2.1.1.2 of this appendix, all daily calibration error tests must be performed while the unit is in operation at normal, stable conditions (i.e. "on-line").

17 - 136

### Appendix B to Part 75 Quality Assurance and Quality Control Procedures

- 2.1.1.1.2 **Off-line Daily Calibration Error Tests.** Daily calibrations may be performed while the unit is not operating (i.e., "off-line") and may be used to validate data for a monitoring system that meets the following conditions:
  - (1) An initial demonstration test of the monitoring system is successfully completed and the results are reported in the quarterly report required under [§ 75.64 of this part](#).
  - (2) For each monitoring system that has passed the off-line calibration demonstration, off-line calibration error tests may be used on a limited basis to validate data, in accordance with paragraph (2) in section 2.1.5.1 of this appendix.

17 - 137

### Appendix C to Part 75 Missing Data Estimation Procedures

- 1. Parametric Monitoring Procedure for Missing SO<sub>2</sub> Concentration or NO<sub>x</sub> Emission Rate Data
  - 1.1 Applicability
  - The owner or operator of any affected unit equipped with post-combustion SO<sub>2</sub> or NO<sub>x</sub> emission controls and SO<sub>2</sub> pollutant concentration monitors and/or NO<sub>x</sub> continuous emission monitoring systems at the inlet and outlet of the emission control system may apply to the Administrator for approval

17 - 138

### Appendix C to Part 75

#### Missing Data Estimation Procedures

- 2. Load-based Procedure for Missing Flow Rate, NO<sub>x</sub> Concentration, and NO<sub>x</sub> Emission Rate Data
- 2.1 Applicability
- This procedure is applicable for data from all affected units for use in accordance with the provisions of this part to provide substitute data for volumetric flow rate (scfh), NO<sub>x</sub> emission rate (in lb/mmBtu) from NO<sub>x</sub>-diluent continuous emission monitoring systems, and NO<sub>x</sub> concentration data (in ppm) from NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions.

17 - 139

### Appendix E to Part 75

#### Optional NO<sub>x</sub> Emissions Estimation Protocol for Gas-Fired Peaking Units and Oil-Fired Peaking Units

- 1. Applicability
- 1.1 Unit Operation Requirements
- This NO<sub>x</sub> emissions estimation procedure may be used in lieu of a continuous NO<sub>x</sub> emission monitoring system (lb/mmBtu) for determining the average NO<sub>x</sub> emission rate and hourly NO<sub>x</sub> rate from gas-fired peaking units and oil-fired peaking units as defined in [§ 72.2 of this chapter](#).

17 - 140

### Appendix E to Part 75

#### Optional NO<sub>x</sub> Emissions Estimation Protocol for Gas-Fired Peaking Units and Oil-Fired Peaking Units

- 2. Procedure
- 2.1 Initial Performance Testing
- Use the following procedures for: measuring NO<sub>x</sub> emission rates at heat input rate levels corresponding to different load levels; measuring heat input rate; and plotting the correlation between heat input rate and NO<sub>x</sub> emission rate, in order to determine the emission rate of the unit(s).

17 - 141

### Appendix E to Part 75

#### Optional NO<sub>x</sub> Emissions Estimation Protocol for Gas-Fired Peaking Units and Oil-Fired Peaking Units

- 2.1.3 Heat Input
- Measure the total heat input (mmBtu) and heat input rate during testing (mmBtu/hr) as follows:
- 2.1.3.1 When the unit is combusting fuel, measure and record the flow of fuel consumed. Measure the flow of fuel with an in-line flowmeter(s) and automatically record the data. If a portion of the flow is diverted from the unit without being burned, and that diversion occurs downstream of the fuel flowmeter, an in-line flowmeter is required to account for the unburned fuel.

17 - 142

### Appendix E to Part 75

#### Optional NO<sub>x</sub> Emissions Estimation Protocol for Gas-Fired Peaking Units and Oil-Fired Peaking Units

- 2.2 Periodic NO<sub>x</sub> Emission Rate Testing
- Retest the NO<sub>x</sub> emission rate of the gas-fired peaking unit or the oil-fired peaking unit while combusting each type of fuel (or fuel mixture) for which a NO<sub>x</sub> emission rate versus heat input rate correlation curve was derived, at least once every 20 calendar quarters.

17 - 143

### Appendix E to Part 75

#### Optional NO<sub>x</sub> Emissions Estimation Protocol for Gas-Fired Peaking Units and Oil-Fired Peaking Units

- 2.5 Missing Data Procedures
- Provide substitute data for each unit electing to use this alternative procedure whenever a valid quality-assured hour of NO<sub>x</sub> emission rate data has not been obtained according to the procedures and specifications of this appendix.

17 - 144

## Compliance Test and Source Test Observation

### Stack Testing Special Topics:



18 - 1

## Compliance Test and Source Test Observation

### *Stack Testing Special Topics:*

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

18 - 2

## 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

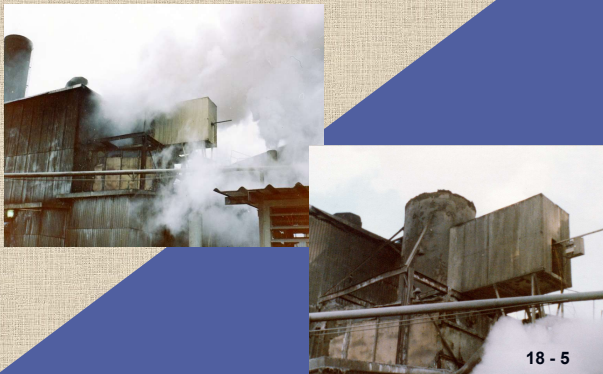
18 - 3

## The Problem

- High moisture in stack gas causes pitot tube to plug, thus poor  $\Delta p$  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

18 - 4

## Water Vapor and Testing



18 - 5

## High Moisture Potato Chip Fryer



18 - 6



### The Problem: FRM 5 Isokinetic Rate Equation

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

18 - 9

### 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

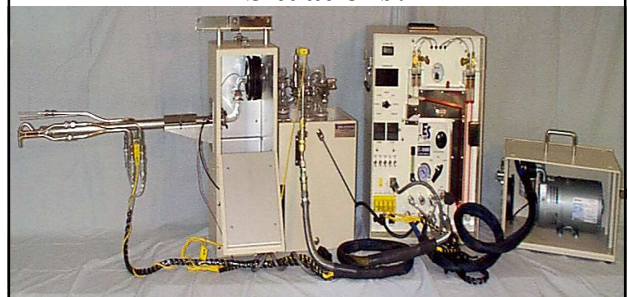
18 - 10

### 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

18 - 11

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



18 - 12

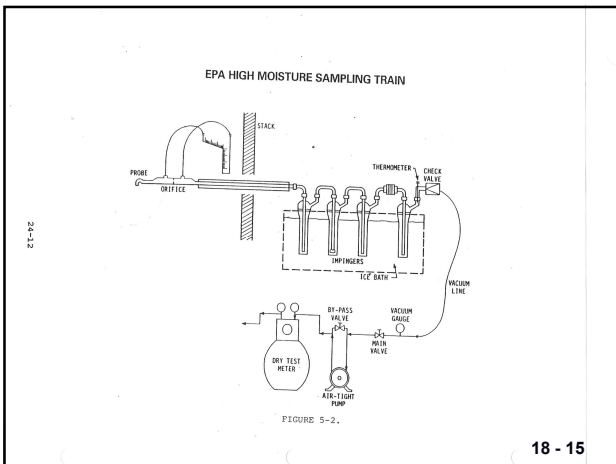
# **APTI #450/468 Compliance Test and Source Test Observation** **Lesson 18: Stack Testing Special Topics**



## **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

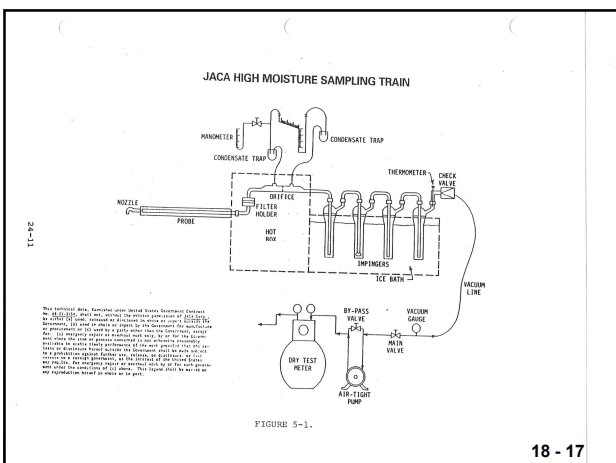
18 - 14



## **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

18 - 16



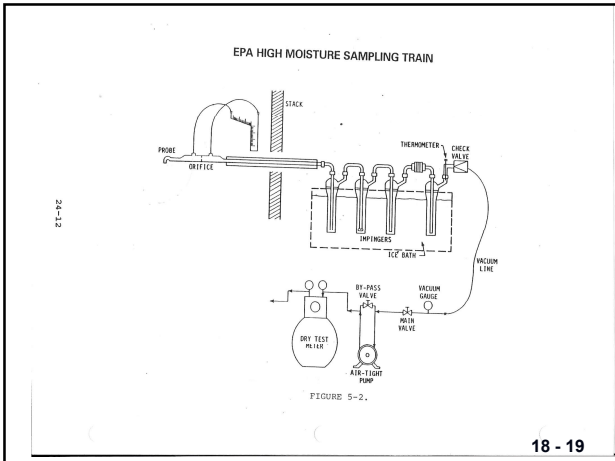
## **General Solution #3** **(In-situ Orifice with Changeable** **Orifice Plates)**

- 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

18 - 18



# APTI #450/468 Compliance Test and Source Test Observation Lesson 18: Stack Testing Special Topics



## 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

18 - 20

## 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 1<sup>st</sup> 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

18 - 21

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

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

18 - 22

## Problems Common To All Three Approaches

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

18 - 23

## 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)

18 - 24

## Compliance Test and Source Test Observation

### *Stack Testing Special Topics:*

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

18 - 25

## Stack Testing At High Pressure Sources

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

- Port Leakage
- Pressure Measurement Difficulties
- Sample Losses

18 - 27

### 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 )

18 - 28

### 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

18 - 29



18 - 30

### 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

18 - 31

### 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 manahelic gauge

18 - 32

### 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

18 - 33

### 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

18 - 34

### 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

18 - 35

### 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

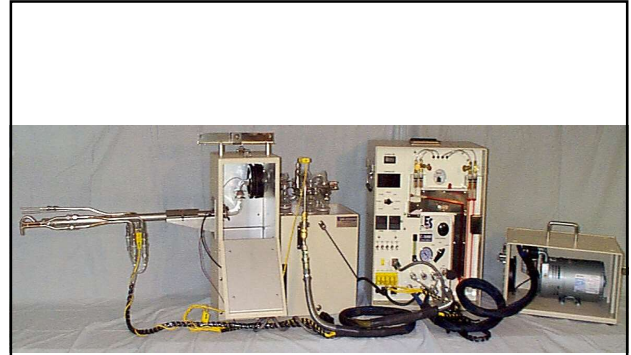
18 - 36

## Compliance Test and Source Test Observation

### *Stack Testing Special Topics:*

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

18 - 37



18 - 38

## Typical Sources With High Temperature In Stack

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

18 - 39



18 - 40



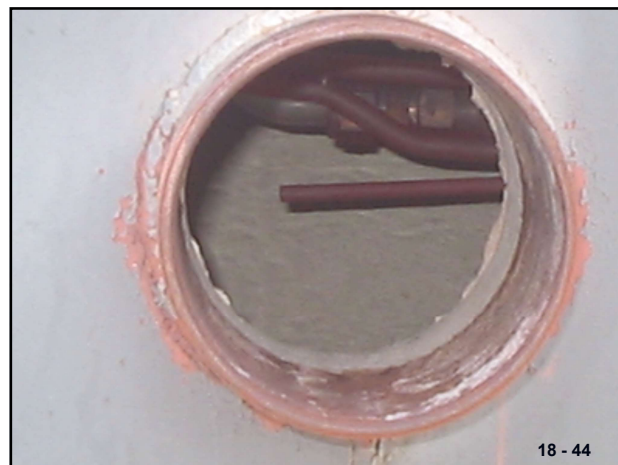
18 - 41



18 - 42

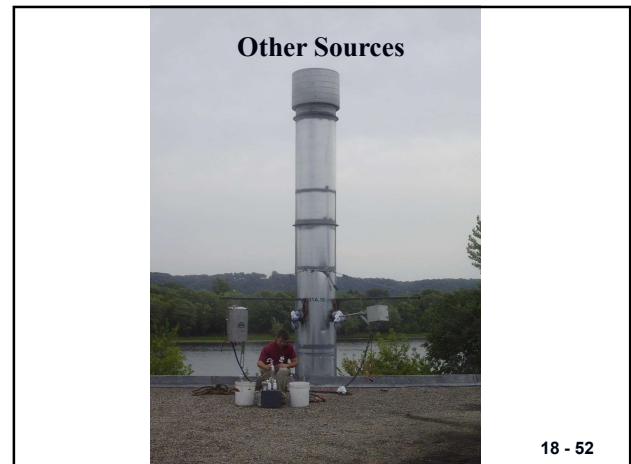
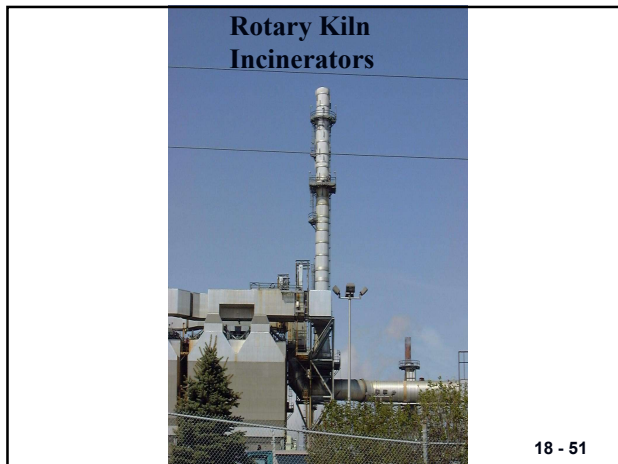
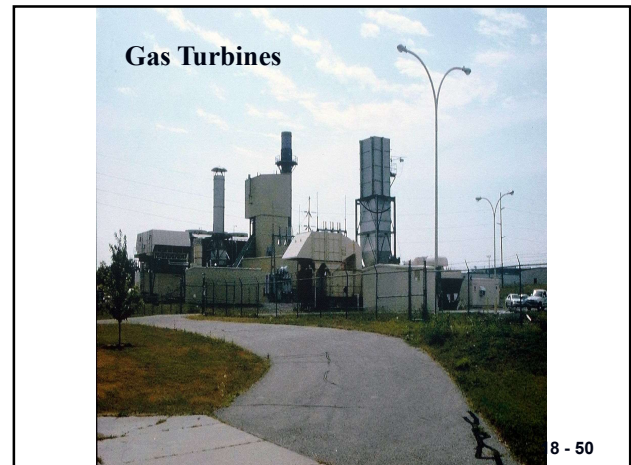
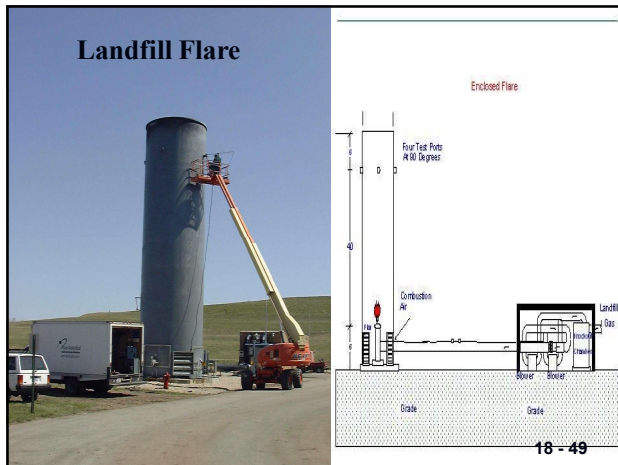


APTI #450/468 Compliance Test and Source Test Observation  
Lesson 18: Stack Testing Special Topics



# APTI #450/468 Compliance Test and Source Test Observation

## Lesson 18: Stack Testing Special Topics



### 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

18 - 53

### 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

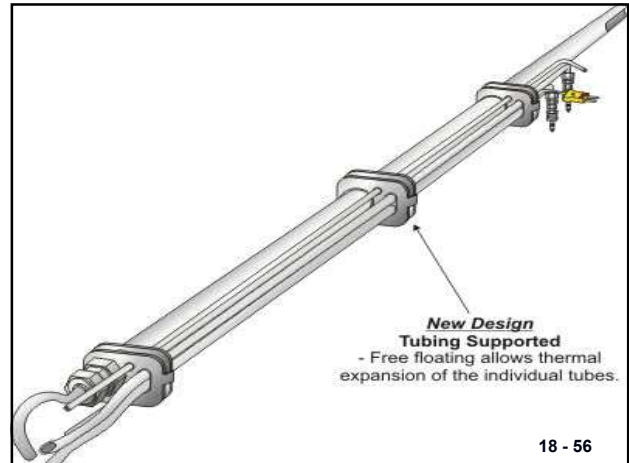
18 - 54



### Maximum Temperature of Various Materials

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

18 - 55

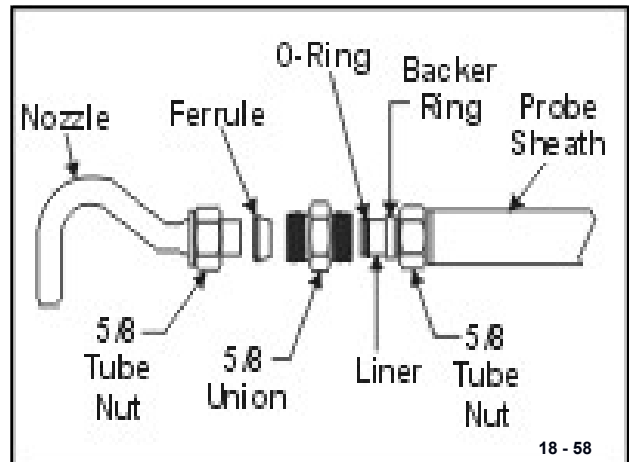


18 - 56

### 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.

18 - 57



18 - 58

### Sampling Problems

- Metal probes, at high temperatures, become catalyst (reactive surfaces) for substances in the stack gas (i.e., oxidation of metals,  $\text{SO}_2$  to  $\text{SO}_3$ , etc.)
- High effluent gas temperature could cause softening of the nozzle, probe and pitot tube
- Difficulty of maintaining filter box temperature at 248 °F

18 - 59

### 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)

18 - 60

**Solution #2  
(Construction of High  
Temperature Probes)**

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

18 - 61

**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

18 - 62

**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

18 - 63

**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

18 - 64

**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

18 - 65

**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

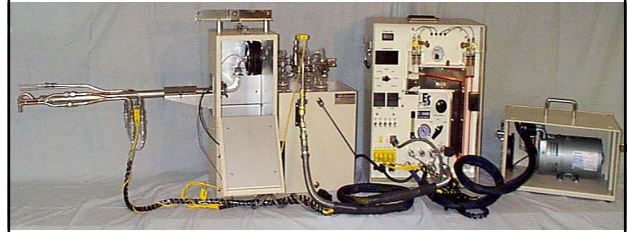
18 - 66

## Compliance Test and Source Test Observation

### *Stack Testing Special Topics:*

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

18 - 67



18 - 68

## 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

18 - 69

## Federal Reference Method 2 Average Velocity Over Cross-Section

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

18 - 70

## Average Stack Gas Dry Volumetric Flow Rate

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

18 - 71

## The Problem

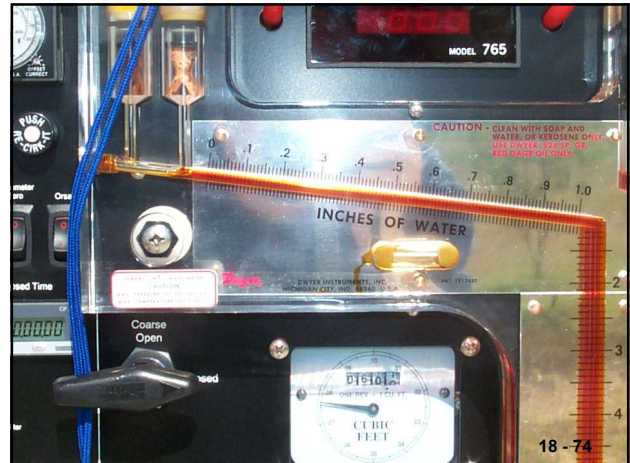
- Pressure differential devices insensitive below 17 ft/second
- Unreliable pitot tube accuracy below 7 ft/second

18 - 72

### The Problem

- FRM 5 typical incline manometer has incline range of 0-1 " H<sub>2</sub>O with 0.01 " divisions, and vertical range of 1-10 " H<sub>2</sub>O with 0.10 " divisions
- FRM 5 designed to monitor flows around 1.84 " H<sub>2</sub>O, not in the 0-0.5 " H<sub>2</sub>O range

18 - 73



18 - 74

### Federal Reference Method 2 Guidelines

- A differential pressure gauge other greater sensitivity shall be used:
  - The arithmetic average of all  $\Delta p$  readings at the traverse points  $< 0.05$  " H<sub>2</sub>O
  - For traverse of 12 or more points, more than 10 % of the individual  $\Delta p$  readings  $< 0.05$  " H<sub>2</sub>O
  - For traverse of  $< 12$  points, more than one  $\Delta p$  reading  $< 0.05$  " H<sub>2</sub>O

18 - 75

### 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.

18 - 76

### Determination of Sensitivity of Pressure Gauge

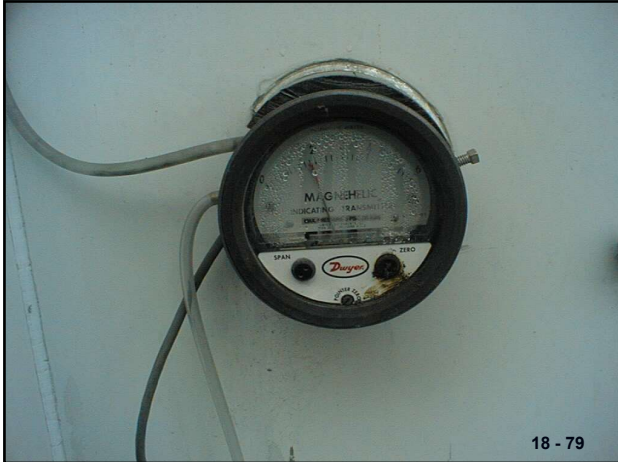
$$T = \frac{\sum_{i=1}^n \sqrt{\Delta p_i + K}}{\sum_{i=1}^n \sqrt{\Delta p_i}}$$

18 - 77

### 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  $\Delta p$  readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of  $\Delta p$  values in the stack.

18 - 78



### 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

18 - 80

### Techniques For Measurement of Low Flows

- Standard pitot tube with portable inclined manometer (0-0.25 " H<sub>2</sub>O with 0.005 " H<sub>2</sub>O scale divisions) or digital manometer
- Standard pitot tube with dual scale portable inclined manometer with 0-1.0 " H<sub>2</sub>O with 0.01 " H<sub>2</sub>O scale divisions and 0-10 " H<sub>2</sub>O with 0.10 " H<sub>2</sub>O scale divisions

18 - 81

### 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)

18 - 82

### Other Low Flow Techniques

- Venturi Meters
- Orifice Meters
- Mass Flow Meters

18 - 83

### Compliance Test and Source Test Observation

#### *Stack Testing Special Topics:*

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

18 - 84



# APTI #450/468 Compliance Test and Source Test Observation Lesson 19: FRM 23 & SW-846 Method 0023A Dioxins and Furans

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



19 - 1



19 - 2

### 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

19 - 3

### Dioxins and Furans

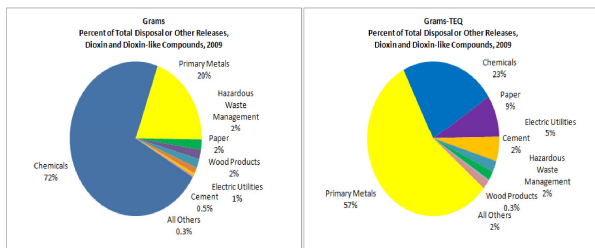
- Dibenzofurans and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) are listed on the 188 list
- EPA inventories all dioxins and furans
- Dioxins occur in the environment in complex mixtures of 210 congeners and have different toxicities
- Compounds can be grouped by 2,3,7,8 TCDD for Toxic Equivalents (TEQs)
- TEQs are multipliers for some dioxin and furan congeners to get to a common basis of toxicity
- For some air quality models, dioxins will require more refined inventory (not sufficient to report TEQs)

<http://www.epa.gov/tri/lawsandregs/teq/teqpfinalrule.html>

<http://www.greenfacts.org/en/dioxins/toolboxes/teq-explanations.htm>

19 - 4

### Summary Statistics – Persistent and Bioaccumulative and Toxic chemicals (PBTs)



#### Releases of dioxin and dioxin-like compounds

- Difference between dioxin grams and dioxin TEQs by sector (<http://www.epa.gov/tri/lawsandregs/teq/teqpfinalrule.html>)
- Total disposal or other releases in 2009 about 32,000 g
- Dioxin in grams decreased 18% from 2008 to 2009

19 - 5

### Sources of Dioxins and Dioxin-like Compounds (DLC's) in the Environment

- Combustion - DLCs are unintended byproducts of combustion, except for the dioxin-like PCBs.
- Combustion processes forming dioxins include waste incineration (e.g., municipal solid waste, sewage sludge, medical waste, and hazardous waste), burning of various fuels (e.g., coal, wood, and petroleum products), other high-temperature sources (e.g., cement kilns), and poor or uncontrolled combustion sources (e.g., forest fires, volcanic eruptions, building fires, and residential wood burning)

19 - 6



### **Formation of DLC's**

- DLCs are formed in chemical reactions that occur during the combustion of organic compounds in the presence of chlorinated materials.
- First, stack emissions of DLCs result from the incomplete destruction of DLC contaminants present in materials delivered to the combustion chamber.
- Not all of the DLC components are destroyed by the combustion system, thus allowing trace amounts of DLCs to be emitted from the stack.

19 - 7

### **Formation of DLC's**

- Second, the formation of DLCs from aromatic precursor compounds occurs in the presence of a chlorine donor.
- The general reaction in this formation pathway is an interaction between an aromatic precursor compound and chlorine promoted by a transition metal catalyst on a reactive fly ash surface.

19 - 8

### **Formation of DLC's**

- Last, de novo synthesis promotes formation of DLCs in combustion processes from the oxidation of carbon particulate catalyzed by a transition metal in the presence of chlorine. Intermediate compounds, which are precursors to DLC formation, are produced during de novo synthesis.
- The formation of DLCs via either the precursor or de novo synthesis pathways requires the availability of gaseous chlorine (The source of the chlorine is the materials (fuels or feed) in the combustion system.

19 - 9

### **Other Sources of DLC's**

- **Metals Smelting and Refining**
- There are several types of primary and secondary metal smelting and refining operations, including iron ore sintering, steel production, and scrap metal recovery.
- Such operations use both ferrous and nonferrous metals.

19 - 10

### **Other Sources of DLC's**

- Secondary smelting and refining of nonferrous metals such as aluminum, copper, lead, and zinc may result in formation of DLCs, due to combustion of organic impurities (e.g., plastic, paints, and solvents) in the metals and chlorine-containing chemicals (e.g., sodium chloride and potassium chloride) used in the smelting process (Aittola et al., 1992; EPA, 1987, 1997, as cited in EPA, 2000).

19 - 11

### **Other Sources of DLC's**

- **Chemical Manufacturing**
- Three types of chemical manufacturing processes—bleaching of wood pulp in paper manufacturing, chlorine and chlorine-derivative manufacturing, and halogenated organic chemical manufacturing—lead to the production of DLCs. DLCs, primarily the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) congeners.

19 - 12

### **Other Sources of DLC's**

- DLC are present in effluent and sludge from pulp and paper mills that employ the bleached kraft process.
- From 1988 to 1992, there was a 90 percent reduction in TEQs generated by pulp and paper mills for 2,3,7,8-TCDD and 2,3,7,8-TCDF (NCASI, 1993, as cited in EPA, 2000).

19 - 13

### **Other Sources of DLC's**

- To help reduce DLCs in effluents from pulp and paper mills, EPA promulgated effluent limitations guidelines and standards for certain segments of the pulp, paper, and paperboard industries (EPA, 1998, as cited in EPA, 2000).
- These industries are responsible for more than 90 percent of the bleached-chemical pulp production in the United States.

19 - 14

### **Applicability of Method 23**

- 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

19 - 15

### **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

19 - 16

### **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<sup>3</sup>
- FRM 23 is used to quantify PCDD's and PCDF's from stationary sources

19 - 17

### **Method 23 Revisions (3/20/2023)**

- The primary focus for the Method 23 revisions is to change the method from a prescriptive method to a method which allows users to have flexibility in implementing the method (e.g., choice of gas chromatograph (GC) column, the procedures used for sample cleanup).
- The method must also meet performance criteria that the EPA believes are necessary for demonstrating and documenting the quality of the measurements for the target compounds.

19 - 18

### Method 23 Revisions (3/20/2023)

- The third major focus for the EPA's final revisions to Method 23 is to include options for combining sampling and analysis of PCDD/PCDF with sampling and analysis of PAH and PCB to allow the measurement of these toxic semi-volatile organic compounds (SVOC).
- Therefore, PCB and PAH were added to the list of target compounds measured by Method 23.

19 - 19

### Method 23 Revisions (3/20/2023)

- The EPA's second focus for the final revisions is to modify the method to allow isotope dilution with isotopically labeled compounds for each target compound. Quantitation is based on isotope dilution, moving from nine to 17 labeled compounds for 17 target toxic 2,3,7,8-substituted PCDD/PCDF.

19 - 20

### Structure



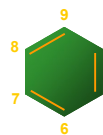
p-Dioxin



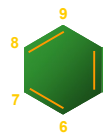
Furan

19 - 21

### Structures of Dioxins and Furans



Dibenzo-p-Dioxin



Dibenzofuran

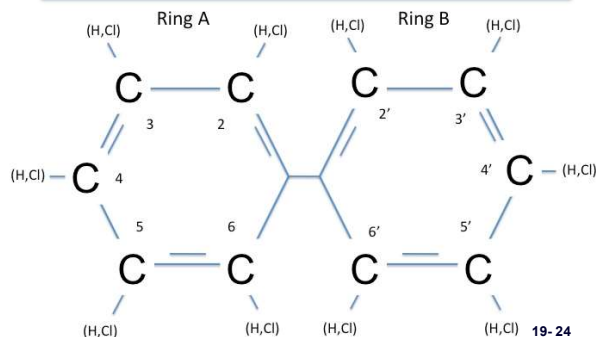
19 - 22

### Polychlorinated Biphenyl Structure



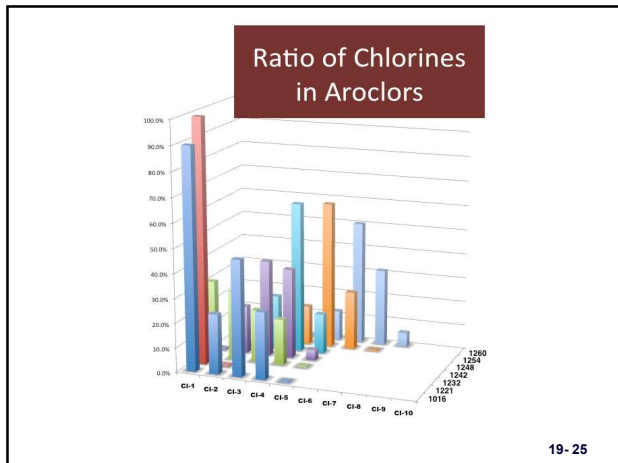
19 - 23

### Structure of PCB (Polychlorinated Biphenyl)



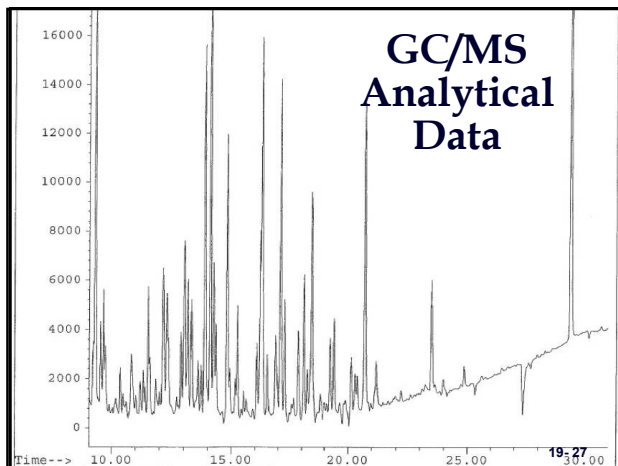
19 - 24

# APTI #450/468 Compliance Test and Source Test Observation Lesson 19: FRM 23 & SW-846 Method 0023A Dioxins and Furans



**Chlorine Distribution in Aroclors**

	1016	1221	1232	1242	1248	1254	1260
CI-1	90.0%	99.4%	31.5%	0.6%			
CI-2	24.3%	0.6%	28.2%	19.5%	0.7%		
CI-3	47.1%		21.5%	39.1%	22.0%		
CI-4	27.3%		18.7%	36.7%	61.3%	16.0%	0.3%
CI-5	0.4%		0.4%	4.2%	16.3%	59.9%	12.2%
CI-6						23.8%	50.3%
CI-7						0.4%	31.4%
CI-8							5.9%
CI-9							
CI-10							19 - 26



**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

19 - 28

**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

19 - 29

**Levels of Chlorination**

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

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# APTI #450/468 Compliance Test and Source Test Observation Lesson 19: FRM 23 & SW-846 Method 0023A Dioxins and Furans

## 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

19 - 31

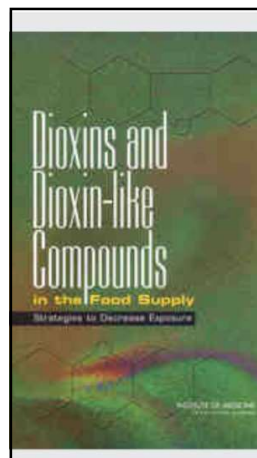
■ 2,3,7,8-Tetrachlorodibenzo-p-Dioxin	1
■ 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin	0.5
■ 2,3,4,7,8-Pentachlorodibenzofuran	0.5
■ 1,2,3,4,7,8-Hexachlorodibenzofuran	0.1
■ 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	0.1
■ 1,2,3,7,8,9-Hexachlorodibenzofuran	0.1
■ 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	0.1
■ 1,2,3,6,7,8-Hexachlorodibenzofuran	0.1
■ 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	0.1
■ 2,3,7,8-Tetrachlorodibenzofuran	0.1
■ 2,3,4,6,7,8-Hexachlorodibenzofuran	0.1
■ 1,2,3,7,8-Pentachlorodibenzofuran	0.05
■ 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	0.01
■ 1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01
■ 1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01
■ Octachlorodibenzofuran	0.001
■ Octachlorodibenzo-p-Dioxin	0.001

19 - 32

## How TEQs Are Calculated

- In order to calculate a TEQ, a toxic equivalent factor (TEF) is assigned to each member of the dioxin and dioxin-like compounds category. The TEF is the ratio of the toxicity of one of the compounds in this category to the toxicity of the two most toxic compounds in the category, which are each assigned a TEF of 1: 2,3,7,8-tetrachlorodibenzo-p-dioxin (commonly referred to as dioxin) and 1,2,3,7,8-pentachlorodibenzo-p-dioxin. TEFs that have been established through international agreements currently range from 1 to 0.0001.
- A TEQ is calculated by multiplying the actual grams weight of each dioxin and dioxin-like compound by its corresponding TEF (e.g., 10 grams X 0.1 TEF = 1 gram TEQ) and then summing the results. The number that results from this calculation is referred to as grams TEQ.
- For example, consider the following 60g mixture:  
10g of compound A, with a TEF of 1  
20g of compound B, with a TEF of 0.5  
30g of compound C, with a TEF of 0.2.
- The TEQ of this mixture would be:  
 $(10g \times 1) + (20g \times 0.5) + (30g \times 0.2) = 26g \text{ TEQ}$
- In other words, this mixture of 60g of various compounds would be as toxic as 26g of either of the two most toxic compounds.

19 - 33



## Further Reading:

<http://nap.edu/10763>

19 - 34

## 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

19 - 35

## Aroclor PCBs

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

19 - 36

### **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

19 - 37

### **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

19 - 38

### **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

19 - 39

### **Interferences**

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

19 - 40

### **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)

19 - 41

### **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)

19 - 42



### 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

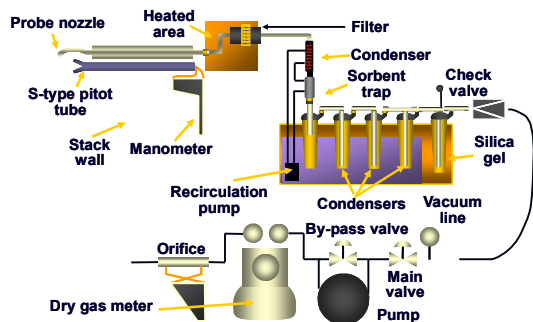
19 - 43

### FRM 23 and SW-846 Method 0023A Sampling Train

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

19 - 44

### FRM 23/Method 0023A Sampling Train



19 - 45

### 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 m<sup>2</sup>/g  
Temp. Max: 190°C

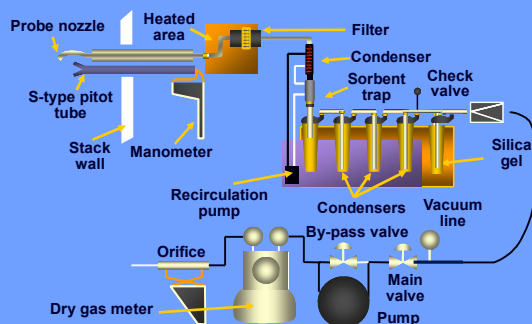
19 - 46

### Weaknesses of XAD-2 Resin

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

19 - 47

### FRM 23/Method 0023A Sampling Train



19 - 48

### Percent Phase Distribution of Dioxins in Sampling Train

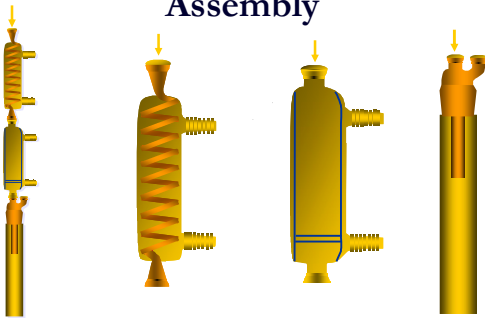
Phase	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Vapor	55	26	4	2	1
Particle	45	74	96	98	99

19 - 49

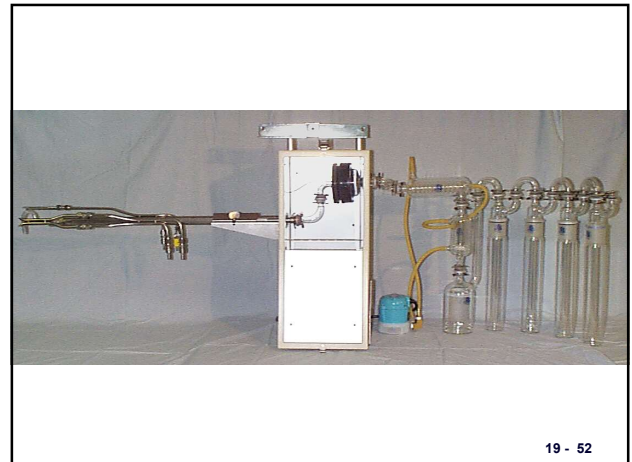


19 - 50

### Vertical Condenser/XAD-2 Trap Assembly

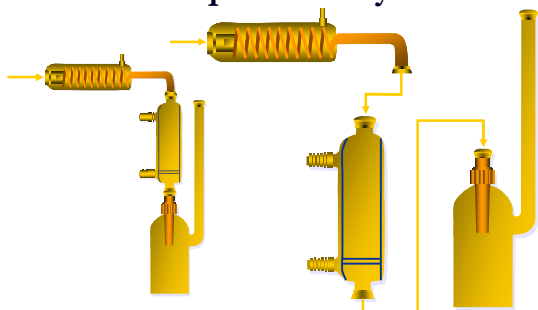


19 - 51



19 - 52

### Horizontal Condenser/ XAD-2 Trap Assembly



19 - 53

### 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  $0.010 \text{ pg/m}^3$

19 - 54

### XAD-2 Certification of Cleanliness

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

19 - 55

### 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)

19 - 56

### XAD-2 Certification of Cleanliness

- Wrap cartridge in hexane-rinsed aluminum foil

19 - 57

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

- Added to clean cartridge prior to field deployment
  - $^{37}\text{C}_4$ -2,3,7,8-TCDD
  - $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF
  - $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD
  - $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF
  - $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF

19 - 58

### Preparation Of Sample Train

- Clean glassware thoroughly before using.
- Section 8.1.1 provides a recommended procedure, but any protocol that consistently results in contamination-free glassware meeting the Laboratory Method Blank (LMB) criteria in Section 13.1 of this method is acceptable.

19 - 59

### Preparation of Sample Train

- Soak all glassware in hot soapy water (Alconox® or equivalent)
- Rinse with hot tap water.
- Rinse with deionized/distilled water.
- Rinse with methanol.
- Rinse with toluene.
- Baking glassware up to 400 °C (752°F) for a minimum of 2 hours may be necessary to remove contaminants or interferents from particularly dirty samples.
- Allow glassware to cool after baking.

19 - 60

### **FRM 23/Method 0023A Glassware Preparation**

- Cover glassware with cleaned glass fitting caps or aluminum foil
- Rinse glassware immediately before use with acetone and toluene

19 - 61

### **FRM 23/Method 0023A Glassware Preparation**

- Heavily soiled glassware needs additional cleaning with a strong oxidizing strong acid
- Repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb target compounds.

19 - 62

- For heavily soiled glassware, remove surface residuals from the glassware by soaking in hot soapy water, rinsing with hot water, then soaking with a non-chromic acid oxidizing cleaning reagent in a strong acid (e.g., NOCHROMIX® prepared according to manufacturer's directions).
- After the acid soak, rinse with hot water and repeat the cleaning procedures in Section 8.1.1.1 of the method.

19 - 63

### **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

19 - 64

### **FRM 23/Method 0023A Operational Requirements**

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

19 - 65

### **Calculation of Sample Duration**

- Minimum sample time =  
$$\text{Analytical Detection Limit} / [(\text{Sample Rate}) \times (\text{Desired Gas Concentration Detection Limit})]$$

19 - 66

### Example Calculation

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

19 - 67

### Example Calculation

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

19 - 68

### FRM 23/Method 0023A Record Keeping Requirements

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

19 - 69

### FRM 23/Method 0023A Record Keeping Requirements

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

19 - 70

### 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

19 - 71

### Preliminary Field Determination

- Determine total length of sampling based upon method detection limits
- Establish sampling time per point based upon calculation (8.1.2.2)
- This method recommends sampling a minimum of 2.5 dry standard cubic meters (dscm).

19 - 72

### **Adsorbent Module Preparation**

- **Adsorbent Module.** Load the modules in a clean area to avoid contamination (8.1.1.2).
- **Fill a module with 20 to 40 g of XAD-2.** Spike modules before the sampling event, but do not spike the modules in the field.
- **Add the pre-sampling adsorbent standard to the top quarter of the adsorbent bed rather than onto the top or bottom of the adsorbent bed.**

19 - 73

### **Adsorbent Module Preparation**

- **Add sufficient spike (picograms (pg)/module) to result in the final sample theoretical concentrations specified in Tables 23-7, 23-8, and 23-9 of this method for PCDD/PCDF, PAH, and PCB, respectively.**
- **For samples with known or anticipated target compound concentration significantly higher or lower than the specified concentration in these tables.**

19 - 74

### **Adsorbent Module Preparation**

- **Adjust the pre-sampling adsorbent standard concentration to the expected native compound concentration.**
- **However, no less than 10 times the method detection limit (MDL).**
- **Follow the XAD-2 with cleaned glass wool and tightly cap both ends of the module.**
- **For analysis that includes PAH, use spiked modules within 14 days of preparation.**
- **Refer to Table 23-10 of this method for storage conditions.**

19 - 75

### **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**

19 - 76

### **Preparation of Sample Train**

- **Filter.** Check each filter against light for irregularities and flaws or pinhole leaks.
- **Pack the filters flat in a clean glass container.**
- **Do not mark filters with ink or any other contaminating substance.**

19 - 77

### **Preparation of Sample Train**

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

19 - 78



### Preparation of Sample Train

- Weigh each impinger and the adsorbent module, including the fitting caps, to the nearest 0.5 g using the field balance and record the weight for moisture determination.
- Remove the aluminum foil from the adsorbent module before weighing.
- Keep the module out of direct sunlight and rewrap the module with foil immediately after recording the module weight.

19 - 79

### Preparation of Sample Train

- Using tweezers or clean disposable surgical gloves, place a filter in the filter holder.
- Filter should be properly centered, and the gasket properly placed, to prevent the sample gas stream from circumventing the filter.
- Check the filter for tears after completing the assembly.

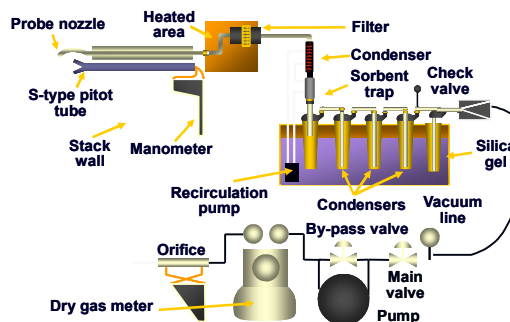
19 - 80

### Preparation of Sample Train

- Install selected nozzle and mark probe
- Assemble sample train  
(no silicone grease upstream of organic module)
- Place crushed ice around impingers

19 - 81

### FRM 23/Method 0023A Sampling Train



19 - 82

### Preparation of Sample Train

- Sample Volume. Unless otherwise specified in an applicable rule, regulation, or permit, sample for a minimum of 2 minutes at each traverse point.
- This method recommends sampling a minimum of 2.5 dry standard cubic meters (dscm).

19 - 83

### Preparation of Sample Train

- For continuously operating processes:
- Use the same sampling time at each traverse point.
- To avoid timekeeping errors, use an integer, or an integer plus one-half minute, for each traverse point.

19 - 84

### Preparation of Sample Train

- For batch processes, determine the minimum operating cycle duration, dividing the sampling time evenly between the required numbers of traverse points. 8.1.2.3
- After sampling all traverse points once, sample each point again for the same duration of time per sampling point in reverse order until the operating cycle is completed.
- Sample all traverse points at least once during each test run.

19 - 85

### Preparation of Sample Train

- Turn on filter/probe heating systems
- Turn on sorbent and condenser coil coolant recirculating pumps (must maintain resin bed at  $< 20^{\circ}\text{C}$ )

19 - 86

### Preparation of Sample Train

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

19 - 87

### 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

19 - 88

### Sample Train Operation

- Begin sampling when all temperatures are at required settings:
  - Probe/Filter:  $120 \pm 14^{\circ}\text{C}$
  - Sorbent Bed:  $< 20^{\circ}\text{C}$
  - Exit Silica Gel Impinger:  $< 20^{\circ}\text{C}$

19 - 89

### Sample Train Operation

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

19 - 90

### 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 ( $\Delta H = K\Delta p$ )

19 - 91

### 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

19 - 92

### 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

19 - 93

### Sample Train Recovery by FRM 23/Method 0023A

- Filter (Container #1: FRM 23/Method 0023A) Recover in pre-clean aluminum foil or container

19 - 94

### Sample Train Recovery by FRM 23/Method 0023A

- Adsorbent Module Recovery;
- Spike the adsorbent with the appropriate pre-extraction standard
- Review Tables 23-7, 23-8, and 23-9 of the method for final extraction concentrations, as applicable.
- Standard is spiked into the adsorbent, not on top of the adsorbent.

19 - 95

### Sample Train Recovery

- Transfer the adsorbent material to the glass extraction thimble in the glass solvent rinse catch beaker.
- Rinse the module into the thimble in the beaker with the contents of Container No. 1.

19 - 96

### Sample Train Recovery

- Alternatively, suspend the adsorbent module directly over the extraction thimble in a beaker, then, using a wash bottle containing methanol;
- Flush the XAD-2 into the thimble onto the filter.
- Thoroughly rinse the interior of the glass module that contained the XAD-2 with toluene.

19 - 97

### Sample Train Recovery

- Container No. 2 (Acetone and Toluene Rinses).
- Concentrate the sample to a volume of no less than 5 mL.
- Concentrate samples containing toluene using a heating mantle and three-ball Snyder column or a rotary evaporator.

19 - 98

### Sample Train Recovery

- Rinse sample Container No. 2 three times with small portions of toluene and add these to the concentrated solution and concentrate further to no less than 5 mL.
- This residue contains particulate matter removed in the rinse of the train probe and nozzle.

19 - 99

### Sample Train Recovery

- Rinse the concentrated material from Container No. 2 into the glass extraction thimble containing the filter and the XAD-2 resin.

19 - 100

### Sample Train Recovery

- Front Half Rinse (Container #2/Method 0023A) and Back Half Rinse with Acetone & toluene (FRM 23)
  - Nozzle, probe liner, filter housing with no less than 5 ml, then
  - (FRM 23/Method 0023A)
  - 2X with toluene (SW-846, Method 0023)
  - Rinse the concentrated material from container #2 into glass extraction thimble with the filter and XAD-2 resin

19 - 101

### Sample Train Recovery by FRM 23/Method 0023A

- XAD-2 sorbent trap (Container # 3/Method 0023A).
  - 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 acetone, 2X methylene chloride, 2X toluene

19 - 102

### Sample Train Recovery by FRM 23/Method 0023A

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

19 - 103

### 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)

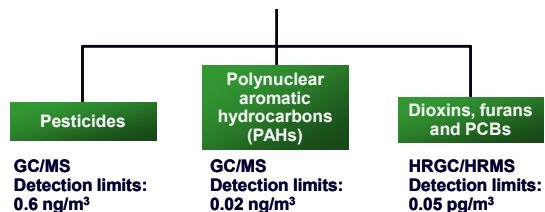
19 - 104

### 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%

19 - 105

### Analysis



19 - 106

### HRGC/HRMS Analysis

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

19 - 107

### HRGC/HRMS Analysis

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

19 - 108

### Ions Monitored by HRGC/HRMS

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

19 - 109

### Ions Monitored by HRGC/HRMS

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

19 - 110

### Ions Monitored by HRGC/HRMS

- OCDD
  - 394.7742
  - 457.7377
  - 459.7347

19 - 111

### Analysis For FRM 23

- Analysis by FRM 23 combines filter and XAD-2 resin as one analysis (11.1.3)
- 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)

19 - 112

### Analysis For FRM 23

- Rinse the back half of the filter holder three times with acetone followed by three rinses with toluene.
- Rinse the sample transfer line between the filter and the condenser three times with acetone followed by three rinses with toluene.
- Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

19 - 113

### Analysis For FRM 23

- Weigh the adsorbent module, impingers, and silica gel impinger to within  $\pm 0.5$  g using the field balance and record the weights.
- This information is required to calculate the moisture content of the effluent gas.
- For PCDD/PCDF-only measurements, discard the liquid after measuring and recording the weight.

19 - 114



### Analysis For FRM 23

- Container No. 3.
- Save and analyze impinger water samples if PAH and/ or PCB are the target compounds.
- Collect impinger water and rinses in Container No. 3 and mark the level of the liquid on the container.

19 - 115

### Analysis For FRM 23

- Store all field samples temporarily in cool ( $\leq 20^{\circ}\text{C}$ ,  $68^{\circ}\text{F}$ ) and dark conditions prior to transport to the laboratory.
- Ship samples cool ( $\leq 20^{\circ}\text{C}$ ,  $68^{\circ}\text{F}$ ), shielded from ultraviolet light. In addition, follow the procedures in American Society for Testing and Materials (ASTM) D6911-15

19 - 116

- Follow the chain of custody procedures in ASTM D4840-99(2018)e1 (Standard Guide for Sample Chain-of- Custody Procedures) for all samples (including field samples and blanks)

19 - 117

### Method 0023A Laboratory Surrogates

- ◆ Added to filter prior to extraction
  - $^{37}\text{C}_4$ -2,3,7,8-TCDD
  - $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF
  - $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD
  - $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF
  - $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF

19 - 118

### Analysis

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

19 - 119

### 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

19 - 120

### **Design a Column Cleanup Chromatography**

- You may use any number of permutations found in the referenced literature for this cleanup if the pre- extraction standard recoveries from field and LMB samples meet the associated performance criteria in Section 13 of this method.
- Alternatively, you may use an automated cleanup approach that meets the labeled spike recovery requirements in Section 13 of this method.

19 - 121

### **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

19 - 122

### **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

19 - 123

### **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

19 - 124

### **Both Method Analysis**

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

19 - 125

### **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

19 - 126

### 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

19 - 127

### Calculation

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

19 - 128

### 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

19 - 129

### Both Method Acceptance Criteria

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

19 - 130

### 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

19 - 131

### Both Method Key Points

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

19 - 132

### Both Method Key Points

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

19 - 133

### 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

19 - 134

### 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

19 - 135

### 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

19 - 137

### Applications Dioxin/Furan Emissions

- Municipal Incinerators
- Hazardous Waste Incinerators
- Hospital Waste Incinerators
- Sewage Sludge Incinerators
- Other Combustion Sources

19 - 138

### **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

19 - 139

### **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

19 - 140

### **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

19 - 141

### **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

19 - 142

### **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.

19 - 143

### **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

19 - 144

### **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

19 - 145

### **AMESA & DMS SAMPLING EQUIPMENT**

- Measures Stack Gas Velocity, Temperature, & Pressure
- Optional System Can Measure O<sub>2</sub> & CO<sub>2</sub>
- Sampling Range – 0.0001 to 10 ng/m<sup>3</sup>
- Condensate Can Be Collected & Analyzed For AMESA

19 - 146

### **AMESA & DMS SAMPLING PROTOCOL**

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

19 - 147

### **AMESA & DMS SAMPLE MULTIPLE ANALYSES**

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

19 - 148

### **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

19 - 149

### **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)

19 - 150



### DMS SUMMARY

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

19 - 151

### 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

19 - 152

### 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.

19 - 153

### AMESA & DMS AS ALTER. TEST METHODS

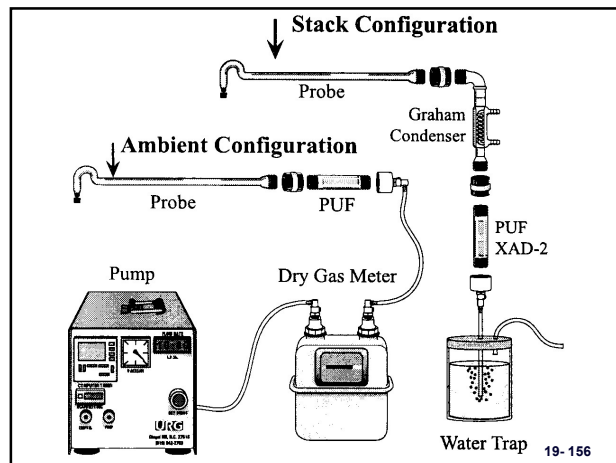
- Must Meet M 301 Acceptance Criteria as Compared With EPA Method 23
- Procedures Could be Approved
  - As alternative compliance test method
    - At specific industry category
    - Facility by Facility approval (each emission point must be evaluated)

19 - 154

### 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

19 - 155



19 - 156

### AmbStack Dioxin Sampling

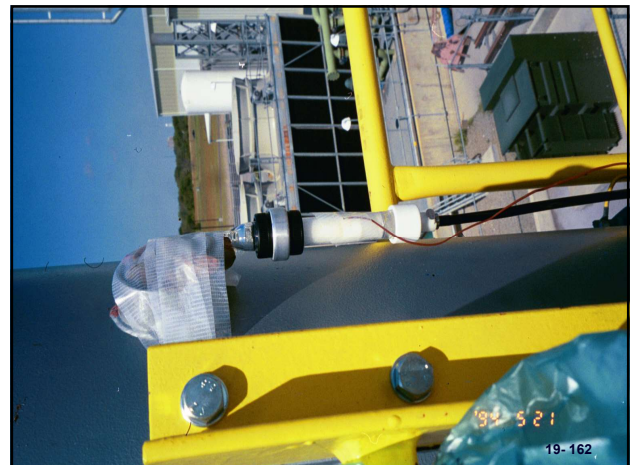
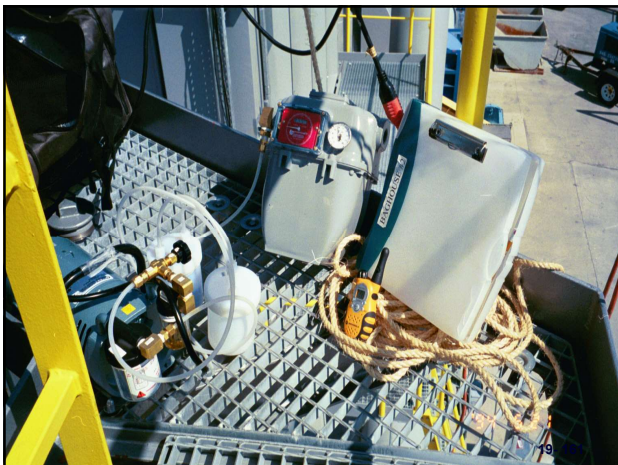
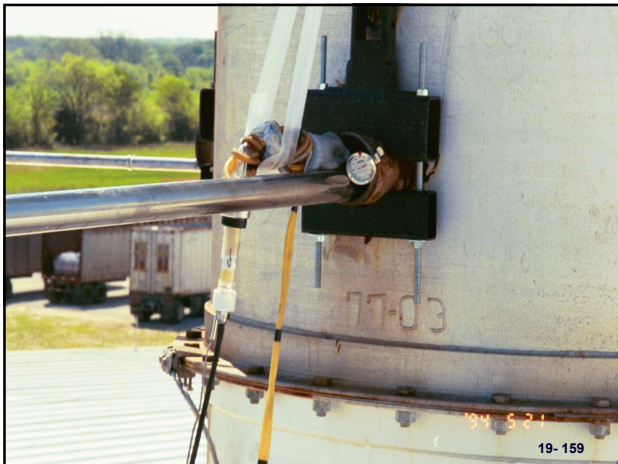
- System operated non-isokinetically and at a constant rate ( $\sim 2\text{L/min}$ ) at a single point (average velocity) in the stack. Sampling typically 3 hours
- Assay uses genetically engineered cells with the Luciferase gene under control of a dioxin-responsive promoter

19 - 157

### 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

19 - 158



APTI #450/468 Compliance Test and Source Test Observation  
Lesson 19: FRM 23 & SW-846 Method 0023A Dioxins and Furans

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