



# Air Emissions Measurement Methods – Issues, Limitations and Watch-outs

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# Outline

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- ▶ Introduction
- ▶ Methods 5, 5B and 5I for particulate
- ▶ Methods 29 and 30B for mercury
- ▶ Method 8 and CTM-013 (NCASI Method 8A) for sulfuric acid
- ▶ Method 320 and ASTM 6348 for HAPS using FTIR



## Source Sampling – Selecting the “Right” Method

# The “Right” Emission Test Method May Mean Many Things

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- ▶ Method specified in the air permit
- ▶ Method that provides representative results
- ▶ Method that is “appropriate” for the source
- ▶ Why does this matter?
  - ▶ Reference Methods for the same parameter do not necessarily yield the same results
  - ▶ i.e., if “inappropriate” method is specified in your permit, you may be in for a surprise



# Methods for Measuring Source Particulate Emissions

# Methods for Measuring Particulate Emissions

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- ▶ **First need to specify the type of particulate**
  - ▶ “Particulate matter” (PM) is exclusively defined by Method 5
  - ▶ Filterable and condensable PM are defined by other methods
- ▶ **PM can be further subdivided for specific applications as per Method 5A, B, D, E, F , & I**
- ▶ **Relative to FPI, you might come across:**
  - ▶ Method 5I: originally developed to evaluate continuous emission monitoring systems (CEMS) and is now used to determine low level PM emissions from stationary sources
  - ▶ Method 5B: used where sulfuric acid is not to be counted as PM

# EPA Method 5

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- ▶ The only method that defines “particulate matter” (PM)
  - ▶ PM mass is any material that condenses at or above the filter temperature of  $120\pm 14^{\circ}\text{C}$  ( $248\pm 25^{\circ}\text{F}$ )
    - ▶ or such other temperature as specified by an applicable subpart of the standard
    - ▶ or approved by the Administrator for a particular application
- ▶ Applicable to high moisture and/or high temperature sources
- ▶ Promulgated with several NSPS sources

# The Pitfalls of Method 5

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- ▶ “Total PM” is old terminology that still causes confusion
- ▶ PM defined specifically by filter temperature so important to maintain correct temperature during test
- ▶ Although interferences are not listed in M5, experience has shown that:
  - ▶ Condensed sulfuric acid mist (SAM) can collect on the filter and be counted as PM
  - ▶ Hygroscopic PM collected on filter can absorb water and cause problems with determining filter weights



# EPA Method 5I

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- ▶ Applicable for the determination of low level PM from stationary sources
  - ▶ Most effective for “total PM” catches of 50 mg or less
- ▶ Setup and operation essentially identical to M5 with specific measures designed to improve system performance at low levels:
  - ▶ Improved sample handling
  - ▶ Lightweight sample filter assembly
  - ▶ Use of low residue grade acetone
  - ▶ Other steps to minimize systemic errors associated with sample handling and weighing procedures

# Pitfalls of Method 5I

(when compared to Method 5)

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- ▶ Requires more sampling personnel expertise
- ▶ More time and equipment required to sample
- ▶ More quality control steps
- ▶ Gas stream characteristics must be considered (i.e., moisture, VOCs, etc.)

# EPA Method 5B

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- ▶ Measures a subset of PM called:
  - ▶ “Non-Sulfuric Acid” PM
- ▶ Same sampling train as Method 5 except that the filter temperature is maintained at 320°F
- ▶ The collected filter is also conditioned at 320°F for 6 hours to volatilize any condensed sulfuric acid
- ▶ Can be used only where specified by an applicable subpart of the regulation or where approved by the Administrator for a particular application

# Questions?



# Source Mercury Emissions Measurement Methods

# Three Methods Available for Measurement of Mercury Emissions

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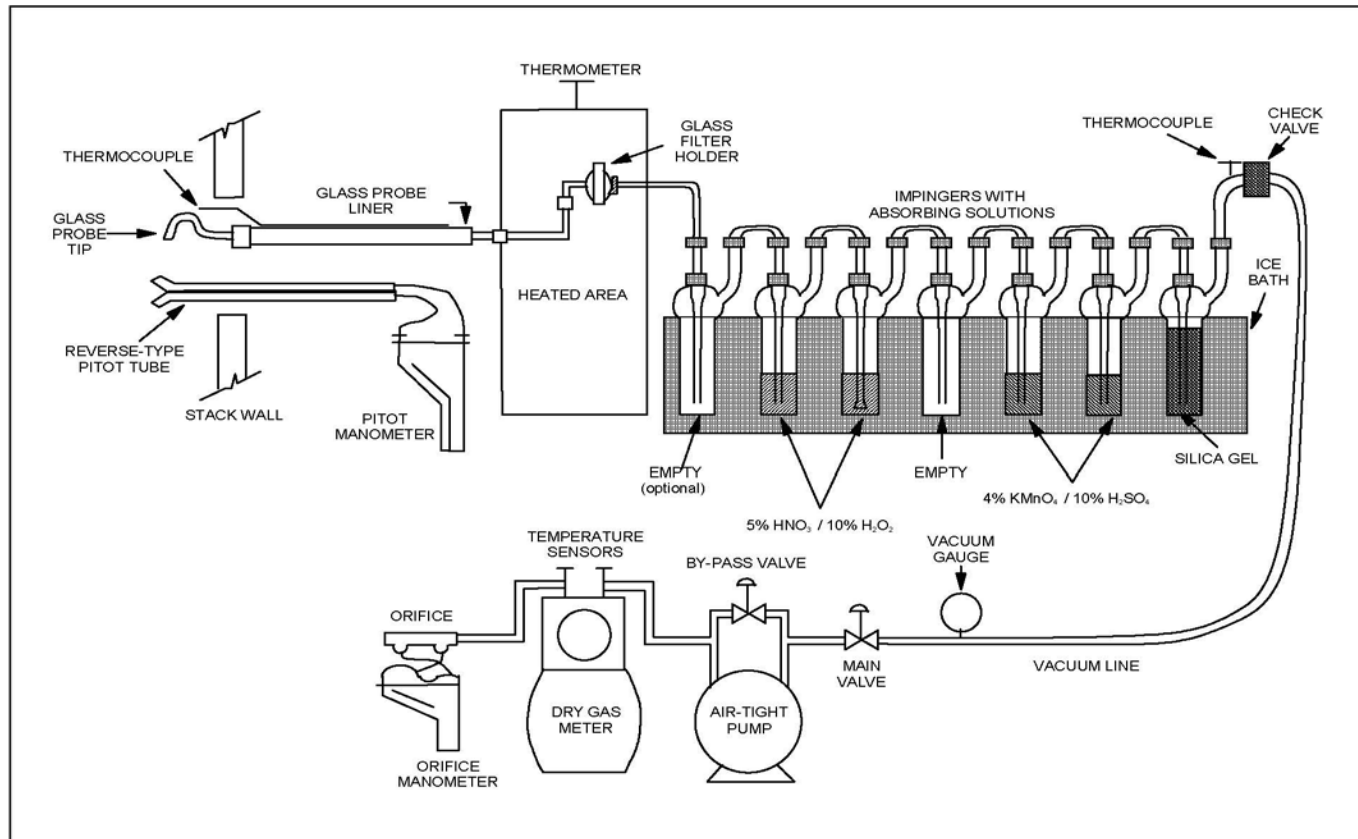
1. **EPA Method 29**
2. **ASTM D6784-02(2008)** (Ontario-Hydro Method or OHM)
3. **EPA Method 30B**

# EPA Method 29

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- ▶ Used to determine total Hg emissions (CAS 7439-97-6)
  - ▶ Also applicable for the measurement of other metals:
    - ▶ Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mg, Ni, P, Se, Ag, Tl, Zn (and others)
- ▶ Based on EPA Method 5 Train with back-half modifications
- ▶ Isokinetic sampling
- ▶ Filter temperature maintained at  $248^{\circ}\text{F} \pm 25$

# EPA Method 29 Train Schematic



**EPA METHOD 29  
MULTI-METALS SAMPLING TRAIN**



# Method 29 Generates Six Fractions for Mercury Analysis

Fraction	Description
1	Filter
2	Nitric acid rinse of nozzle & probe
3	Contents of impingers 1-3 plus nitric acid rinse
4	Contents of impinger 4 plus nitric acid rinse
5	Contents of impingers 5 and 6 plus potassium permanganate and distilled water rinses
6	Hydrochloric acid rinse of impingers 5 and 6

# Common Problems with EPA Method 29

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- ▶ **M29 is used for total Hg**
  - ▶ Does delineate mercury fractions but there can be detection limit issues and matrix stability problems
  - ▶ As a consequence, the Ontario-Hydro method is a better method for speciating mercury
  
- ▶ **M29 labor intensive and tedious method**

# Common Problems with EPA Method 29 (Cont'd)

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- ▶ **High blanks and train contamination**
  - ▶ Requires high level of care in train preparation and recovery
  - ▶ Adequate rinsing of any residue
- ▶ **Filter media and absorbing solution quality affect background levels**
- ▶ **Sample packaging and shipping issues caused by potential pressure buildup in the acidic permanganate solution bottles**

# Ontario–Hydro Method

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- ▶ Is the preferred method for quantification of mercury fractions
  - ▶ Elemental, oxidized, particle-bound, and total mercury
- ▶ However, only applicable for coal-fired combustion sources that have relatively low particulate conditions
- ▶ Method description:
  - ▶ Can be used in either M5 or M17 configuration
  - ▶ Isokinetic sampling method
  - ▶ Filter temperature maintained at 248°F or stack temperature, **whichever is greater**
  - ▶ Same implementation and analysis issues as Method 29

# Questions?

# EPA Method 30B

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- ▶ For measurement of total vapor phase mercury emissions
  - ▶ Elemental Hg
  - ▶ Oxidized forms of Hg (Hg<sup>+2</sup>)
- ▶ Intended for coal-fired combustion sources that have relatively low particulate conditions (e.g. sampling after APCDs).
- ▶ Onsite thermal decomposition analysis can provide **near real time Hg data**

# EPA Method 30B

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## ▶ Method description:

- ▶ Continuous, constant rate sample extraction using paired trains
- ▶ Sampling is non-isokinetic. However, multiple traverse points required
- ▶ Mercury collected on activated carbon in sorbent tube
- ▶ Analysis by thermal decomposition or wet chemical methods

# Method 30B Establishes Method Performance Criteria

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- ▶ Pre- and Post-Test Leak Checks
- ▶ Analytical Bias
- ▶ Analyzer Calibration
- ▶ Minimum Sample Mass
- ▶ Sorbent Trap Breakthrough
- ▶ Paired Trap Agreement
- ▶ Field Recovery Test (Spike Test)



# Method 30B Analytical Options

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Each sorbent trap section is recovered and analyzed separately using:

1. Wet Chemical Analysis, EPA Method 1631
2. Thermal Decomposition, EPA Method 7473
3. Or any analytical method compatible with the sorbent that meets performance criteria

# Potential Issues with EPA Method 30B Implementation

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- ▶ The results must satisfy the performance criteria
  - ▶ Spiking levels, paired train agreement, and breakthrough can be most challenging

# Detection Limits

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## Average Detectable Mass of Hg by Method\* (nanograms)

Hg Fraction	Method 29	Ontario-Hydro	Method 30B
Particulate Bound	5	6	NA
Oxidized <sup>1</sup>	37	30	NA
Elemental	22	40	NA
Total	64	76	0.4 <sup>a</sup>

\*Detection limits are laboratory specific, average for 3 runs  
Method reporting limits = 10 x DL for lab that analyzed Method 29 and Ontario-Hydro samples

<sup>1</sup>Based on a 3.5 cubic meter flue gas sample volume and approximately 1-liter liquid sample volume

<sup>a</sup>Vapor phase only

# Questions?



# Source Sulfuric Acid Emissions Measurement Methods

# Measurement of Sulfuric Acid and/or Sulfuric Acid Mist

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- ▶ A concern for sources that process or burn sulfur containing materials
- ▶ EPA Method 8
  - ▶ Measures sulfuric acid and sulfur dioxide
- ▶ NCASI Method 8A
  - ▶ Measures sulfuric acid emissions from recovery furnaces

# EPA Method 8

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- ▶ Developed for measuring sulfuric acid (including  $\text{H}_2\text{SO}_4$  mist and  $\text{SO}_3$ ) and gaseous  $\text{SO}_2$
- ▶ Method measures all species of sulfate as sulfuric acid
- ▶ No particulate filter is required between the probe and first impinger
  - ▶ Although an option to add a particulate filter is allowed, insertion of one will affect results

# NCASI Developed Method 8A (CTM-013) to Sample Kraft Recovery Furnaces

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- ▶ Developed by NCASI specifically for testing kraft recovery furnaces because M8 is subject to significant interferences from sulfates and sulfur dioxide
  - ▶ M8A eliminates these interferences by:
    - ▶ Placing a filter before the first impinger to remove sulfate particulates
    - ▶ And using a controlled condensation technique to eliminate the potential for interference from sulfur dioxide



# NCASI Developed Method 8A (CTM-013) to Sample Kraft Recovery Furnaces

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- ▶ The method is not isokinetic
- ▶ A quartz filter maintained at  $>500^{\circ}\text{F}$  is used to remove particulate sulfate
- ▶ A condenser is used to condense and trap sulfuric acid
- ▶ Sulfur dioxide fraction is measured separately by the barium-thorin titration method

# NCASI Method 8A Has Pitfalls

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- ▶ The method is not an isokinetic sampling method
- ▶ Agency approval is required for use on emission sources other than recovery furnaces
- ▶ Ammonia may react with  $\text{SO}_2$  to form sulfate which will be reported as  $\text{H}_2\text{SO}_4$

# Questions?

# HAPs Measured by FTIR

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- ▶ Two primary methods used to measure hazardous air pollutants (HAP) by Fournier transform infrared (FTIR) spectroscopy:
  - ▶ EPA Method 320
  - ▶ ASTM 6348

# Components of FTIR Testing

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- ▶ Sample system: FTIR and associated sample delivery apparatus
- ▶ Computer with FTIR interface software
- ▶ Library of reference spectra for all targeted compounds and interferents (including water)
  - ▶ Reference spectra at different concentrations
- ▶ Analysis Method
  - ▶ Should be specific for each source
  - ▶ References the desired compound spectra in the library
  - ▶ Specifies which analysis region to use for each compound spectra to determine concentration

# Benefits of FTIR Testing

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- ▶ FTIR spectrometers have the ability to measure IR spectra which contain information on multiple gaseous compounds
- ▶ Computer software can analyze the IR spectra and report HAP specific concentrations in real time
  - ▶ This can facilitate the evaluation of process changes on HAP emissions
- ▶ Source sample run spectra can also be saved for follow-up evaluation

# EPA Method 320

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- ▶ **Considered dated by most FTIR testers**
  - ▶ Spectrometers and software have significantly improved since method was published in the late 1990s
    - ▶ The initial laboratory based spectrometers used have become more field hardy
    - ▶ Software analysis has become more refined
    - ▶ Compound libraries are now available for manufacture specific instruments

# Issues with EPA Method 320

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- ▶ Method QA requires single representative compound dynamic spiking
  - ▶ May not be adequate to ensure accurate analysis of all compounds
- ▶ Method 320 **does not** provide details as to how to properly set up a source specific analysis method



# ASTM 6348 FTIR Test Method

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- ▶ Reflects current technical capabilities of FTIR equipment and testing
  - ▶ Verify using current version
  - ▶ Currently on version 12
  - ▶ If referenced for use in a standard or regulation, might need to verify applicability of any updated method

# Issues with FTIR analysis

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- ▶ Interfering IR absorption peaks impact analysis resulting in inaccurate results
- ▶ Software must be configured to analyze for all target compounds as well as all interferents for proper analysis
  - ▶ Difficult to achieve with complex gas stream
- ▶ Quality of data heavily dependent on operator experience

# Issues with FTIR analysis

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- ▶ For process units that have variable emission characteristics
  - ▶ There is a potential issue with meeting single dynamic QA spike criteria using a single FTIR analyzer
    - ▶  $[\text{source} + \text{spike}] - [\text{source}] = [\text{spike}]$
    - ▶ If source varies then hard to meet spike recovery criteria when source concentration changes significantly between normal run and QA run
    - ▶ NCASI recommends bracketing the QA spike run with two source only runs then average source results
      - $[\text{Source}]_{\text{run}}$  followed by  $[\text{source} + \text{spike}]_{\text{run}}$  followed by  $[\text{source}]_{\text{run}}$

# Issues with FTIR analysis

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- ▶ Until an analysis method has been validated for a particular source, instantaneous results should be treated as preliminary (at best)
  - ▶ Improperly configured analysis method can give wildly inaccurate results
- ▶ FTIR may not be able to achieve the desired detection level
  - ▶ Impinger methods with extended run times may be a better alternative

# Questions?