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

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Outline

- 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

- 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

- 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

- The only method that defines “particulate matter” (PM)
  - PM mass is any material that condenses at or above the filter temperature of 120±14°C (248±25°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

- “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

- 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)

- 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

- 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

1. **EPA Method 29**

2. **ASTM D6784-02(2008) (Ontario-Hydro Method or OHM)**

3. **EPA Method 30B**
EPA Method 29

- 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°F ± 25
## Method 29 Generates Six Fractions for Mercury Analysis

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Filter</td>
</tr>
<tr>
<td>2</td>
<td>Nitric acid rinse of nozzle &amp; probe</td>
</tr>
<tr>
<td>3</td>
<td>Contents of impingers 1-3 plus nitric acid rinse</td>
</tr>
<tr>
<td>4</td>
<td>Contents of impinger 4 plus nitric acid rinse</td>
</tr>
<tr>
<td>5</td>
<td>Contents of impingers 5 and 6 plus potassium permanganate and distilled water rinses</td>
</tr>
<tr>
<td>6</td>
<td>Hydrochloric acid rinse of impingers 5 and 6</td>
</tr>
</tbody>
</table>
Common Problems with EPA Method 29

- **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)

- 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

- 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

- For measurement of total vapor phase mercury emissions
  - Elemental Hg
  - Oxidized forms of Hg (Hg$^{+2}$)

- 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

- **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

- 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

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

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

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

<table>
<thead>
<tr>
<th>Hg Fraction</th>
<th>Method 29</th>
<th>Ontario-Hydro</th>
<th>Method 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate Bound</td>
<td>5</td>
<td>6</td>
<td>NA</td>
</tr>
<tr>
<td>Oxidized(^1)</td>
<td>37</td>
<td>30</td>
<td>NA</td>
</tr>
<tr>
<td>Elemental</td>
<td>22</td>
<td>40</td>
<td>NA</td>
</tr>
<tr>
<td>Total</td>
<td>64</td>
<td>76</td>
<td>0.4(^a)</td>
</tr>
</tbody>
</table>

*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
\(^1\)Based on a 3.5 cubic meter flue gas sample volume and approximately 1-liter liquid sample volume
\(^a\)Vapor phase only
Questions?
Source Sulfuric Acid Emissions Measurement Methods
Measurement of Sulfuric Acid and/or Sulfuric Acid Mist

- 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

- 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

- 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

- The method is not isokinetic
- A quartz filter maintained at >500°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

- 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 $SO_2$ to form sulfate which will be reported as $H_2SO_4$
Questions?
HAPs Measured by FTIR

- 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

- 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

- 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

- 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

- 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

- 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

- 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

- 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

- 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?