CURRENT ISSUES AND METHODOLOGIES FOR DETERMINATION OF HAP EMISSIONS FROM WOOD PRODUCTS SOURCES

Derek Sain
NCASI
Overview

- List of approved methods
  - Pros, cons, what to watch for, etc.
- Issues
  - Regulators preferring one method over another – how do they compare?
  - FTIR sampling
- Comparison data
EPA Method 25A

- Measures THC using flame ionization analyzer
- Cannot resolve individual HAPs; measures almost all organics in gas steam
- Used as a surrogate for HAP destruction in PCWP MACT
- FIA has limited response to methanol and other oxygenated organic compounds
- FIA has no response to formaldehyde
- Some operating permits require results as WPP1 VOC
  - M25A with methanol and formaldehyde measured separately using approved method in PCWP MACT rule
- Negative bias for high moisture sources
- Only option for PCWP MACT sources demonstrating compliance by $\text{HAP}_{\text{THC}}$
EPA Method 18

- Measures gaseous organic compounds by gas chromatography
- Often used with Method 25A to measure methane
  - Methane can be subtracted from THC value
- Can measure individual HAP compounds
- Flexible method
- Most often GC/FID, but other detectors may be used
- Moderately rigorous QA
  - Must demonstrate spike recovery for each compound
EPA Method 308

- Methanol emissions from stationary sources
- Methanol collected in chilled impinger containing DI water and adsorbed on silica gel
- Requires extraction of methanol from silica gel
- Analysis of water sample and extracted silica gel sample on GC/FID
- Limited to only methanol
- Similar to NCASI CI/SG/PULP-94.03 which does not require silica gel
EPA Method 316

- Formaldehyde emissions from stationary sources
- Formaldehyde collected in chilled Greenburg/Smith glass impingers of DI water
- Method claims wide measurement range
  - 0.011 – 23,000 ppm
- Isokinetic sampling with relatively complex setup (adopted Method 5)
- Formaldehyde analyzed through colorimetric method
  - Modified pararosaniline method
  - Potential bias with dirty sample
- Limited to only formaldehyde
- Widely used in fiberglass industry
EPA Method 0011

- Sampling for select aldehyde and ketone emissions
  - Formaldehyde, acetaldehyde, propionaldehyde
  - Not applicable for acrolein
- Aldehydes derivatized with 2,4-nitrophenylhydrazine (DNPH)
- Formaldehyde detection limit of 90 ppb
- Isokinetic sampling with relatively complex procedure (modified Method 5)
- Analyzed by high performance liquid chromatography (HPLC)
- Method requires field and matrix spike
- Limited to only aldehydes (excluding acrolein)
- Acidic/reactive impinger solution can generate formaldehyde from cured resins
- DNPH depletion issues
- DNPH holding times are short
- Most wood products plants avoid this method if possible
“Chilled impinger” method to measure formaldehyde, methanol, and phenol

Compounds collected in chilled midget impingers of DI water

Methanol analyzed with GC/FID

Formaldehyde derivatized with acetylacetone and measured by colorimetric analysis

Simple setup and procedure

EPA Method 301 validated

Requires field blank, duplicate, and train spike/matrix spike
“Impinger/canister” method for selected HAPs and other compounds

Measures PCWP “total HAPs,” terpenes, and other organics

Polar compounds collected in chilled midget impingers containing DI water

Canister following impingers for collection of terpenes and breakthrough

Four different analyses
  - GC/FID(aqu), GC/MSD(can), GC/FID(can), acetylacetone procedure(form.)
NCASI 99.02 cont.

- Short hold time due to some volatile compounds (e.g., acrolein)
- Self validating method
  - Multiple QA requirements and restrictions
- Much more complicated than 98.01
- Had a time and place once, but not used much anymore
  - For PCWP HAPs, can now be replaced with “BHA method”
- Still used by industry mostly due to benzene sampling requirements
“BHA” impinger method for selected aldehydes, ketones, and polar compounds

Designed for measurement of PCWP MACT total HAPs

Chilled impingers with aqueous solution of o-benzylhydroxylamine (BHA) to derivatize aldehydes and ketones and capture polar compounds

Analysis of aldehyde oximes with GC/NPD

Analysis of alcohols with GC/FID
Aldehydes stable for longer time in derivatized form

Self-validating method

- Multiple QA requirements and restrictions

Setup and analysis less complicated than 99.02 since there is no canister

Typical detection limits are about 500 ppb

- Can be “pushed” down to about 50 ppb (just aldehydes)
EPA Method 320/ASTM Method D 6348-03

- Measurement of gaseous compounds by extractive FTIR spectroscopy
- Uses IR spectroscopy to analyze compounds absorbing in the mid-IR wavelength range
- Capable of measuring PCWP total HAPs and other gaseous compounds
- Measurement of all analytes on single instrument
- If analysis method is already established can obtain instantaneous results
  - Process monitoring, engineering testing
Establishing analysis method is difficult

- Must define target analytes, interfering compounds, analysis areas
- Requires knowledge of gas stream composition

Detection limit levels based on instrument and accuracy of analysis method

QA spiking required

- Analyte spiking can be used to evaluate analysis method
- Should use spike compounds with analysis areas similar to target compounds
## Method Comparison

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<th>18</th>
<th>308</th>
<th>316</th>
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FTIR vs. 98.01

- Facility failed 98.01 QA requirement for methanol and formaldehyde
  - RTO, TCO, Board Cooler
- State strongly suggested the use of FTIR
- FTIR analysis was significantly more expensive for facility
- Facility wanted comparison data to justify the continued use of 98.01
- Contractor – FTIR
- NCASI – 98.01
FTIR vs. 98.01: Methanol

The chart compares FTIR results with 98.01 ppmvd limits for RTO, TCO, and Board Cooler categories.

- **RTO**: FTIR ppmvd close to 98.01 limit.
- **TCO**: Lower ppmvd level than FTIR.
- **Board Cooler**: Significant difference with 98.01 limit.
FTIR vs. 98.01: Formaldehyde

- RTO
- TCO
- Board Cooler
FTIR vs. Speciation Trains

- NCASI developed sampling system to speciate VOC from wood products sources
  - TB 991 – Southern pine results
- Gas streams speciated using BHA and impinger/charcoal setups
  - Chilled impinger/charcoal was a modified 99.02 using a charcoal tube in place of the canister
  - Impinger/charcoal – Alcohols, organic acids, non-polar organic compounds
  - BHA – Aldehydes
- FTIR used initially as additional screening train
- QA for speciation trains according to A105.01
- No dynamic field spiking for FTIR
FTIR vs. Speciation Trains – Sources

- Southern pine
  - Small scale kiln
  - OSB (2), particleboard, plywood
    - Batch press/PCD outlet (3)
    - Green dryer/PCD inlet (2) and outlet (2)
    - Dry dryer/PCD outlet
    - Blender (3)
    - Sander

- Hardwood
  - OSB (2)
    - Green dryer/PCD inlet and outlet (2)
    - Former
    - Batch press/PCD outlet
    - Boiler/PCD outlet
FTIR vs. Speciation Trains – Analytes

- Methanol, Ethanol
- Acetic acid, Formic acid
- Formaldehyde, Acetaldehyde, Hexanal
- Alpha-pinene, Beta-pinene
FTIR vs. Speciation Trains: Uncontrolled Dryer Exhaust

Methanol
Formaldehyde
α-Pinene

OSB1  OSB2  Ply
FTIR
Lab
ND
FTIR vs. Speciation Trains: Controlled Dryer Exhaust

- Methanol
- Formaldehyde
- α-Pinene

ppmvd

FTIR vs. Lab
FTIR vs. Speciation Trains: Controlled Press Exhaust

- Methanol
- Formaldehyde
- α-Pinene

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<td>Part.</td>
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FTIR vs. Speciation Trains: Miscellaneous Sources

- Methanol
- Formaldehyde
- \(\alpha\)-Pinene

**Graph:**
- Y-axis: ppmvd
- Bars for Blend2, Blend3, Sand, and Boiler
- Two sets of bars: FTIR and Lab
- ND indicates not detected

**Data Points:**
- Blend2: Lab - ND, FTIR - ND
- Blend3: Lab - ND, FTIR - ND
- Sand: Lab - ND, FTIR - ND
- Boiler: Lab - ND, FTIR - ND
FTIR vs. Speciation Trains: Miscellaneous Sources cont.

- Methanol
- Formaldehyde
- α-Pinene

Blends:
- Blend 1
- Blend 4

Comparison between FTIR and Lab results.
FTIR Summary

- In field study FTIR showed good agreement to 98.01 results, with lower detection limits
- Small-scale kiln results showed good agreement for 9 compounds in complex gas stream
- Mill results showed FTIR compared reasonably well to other methods
- FTIR can be attractive solution for HAPs sampling
  - Multiple compounds, low detection limits (with the right conditions), instantaneous preliminary data
- FTIR results are only as good as the operator
  - Accurate results depend on how well analysis method is set up
- Any contractor selected for FTIR sampling should have:
  - Experience with instrument
  - Experience with methods and QA spiking
  - Knowledge of process and gas stream characteristics
Questions?

- Contact information
  - Rob Crawford – rcrawford@src-ncasi.org
  - Derek Sain – dsain@src-ncasi.org