



# Total Hydrocarbon Methods The Good, The Bad, and the Ugly

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**Ray Merrill**  
[merrill.raymond@epa.gov](mailto:merrill.raymond@epa.gov)  
**919-541-5225**

U.S. Environmental Protection Agency



# Fundamentals

## ☐ Tools – Reference Methods

- Method 25 (Nonmethane combustible carbon)
- Method 25A (Combustibles by FIA)
- Method 25B (Hydrocarbons by NDIR)
- Method 25C (Landfill Combustibles by FIA)
- Method 18 (Speciated Combustibles by FID)
- Method 320 (Speciated Combustibles by FTIR)



# Fundamentals

## ☐ Tools – Non-methane Alternative Methods

- ✓ Alt – 066 Alternative to Method 18 for Subpart JJJJ
- ✓ Alt – 078 Clarification to Alternative to Method 18 for Subpart JJJJ
- ✓ Alt – 096 TECO-55I for RICE
- ✓ Alt – 097 TECO-55C for Landfills
- ✓ Alt – 106 VOC Measurements for Engines



# Method 25 – Parts is Parts

## □ Method basics

- Heated filtered stack gas
- Separate CO<sub>2</sub> and Methane
- Condensate and VOC converted to methane
- Uniform response, results as carbon

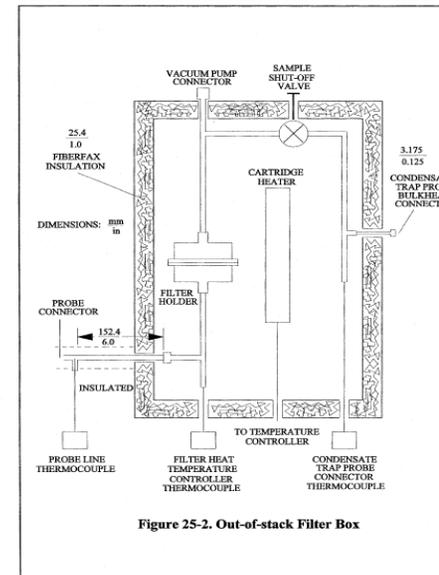


Figure 25-2. Out-of-stack Filter Box



# What to look for in report/results

## ❑ Method defined endpoint parameters

- Sampling line temperature – 121°C (250°F)
- Condensable trap desorb temperature 200°C (390°F)
- Carbon Dioxide interference – CO<sub>2</sub> purging
- Condensable trap Blanks – the detection limit driver
- Water interference

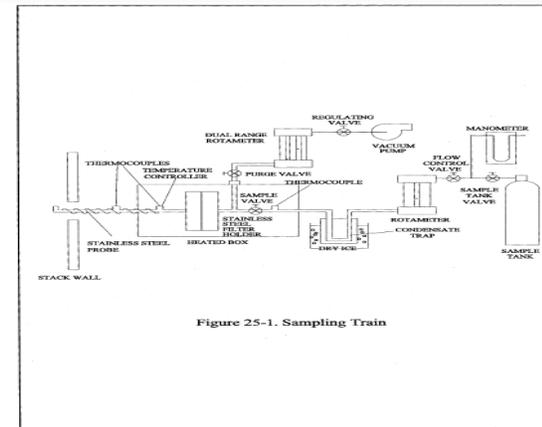


Figure 25-1. Sampling Train



- ❑ Why Choose Method 25 for NMOC?
  - The rule says so, somebody else figured out why.
  - Method 25 measures all collected VOC as carbon (methane)
    - Universal response regardless of the compound
    - Meets certain definitions of THC
- ❑ Why not Choose Method 25 for NMOC?
  - Limited to 50 ppm due to background/blank issues
  - Does not measure VOC mass  
(disregards heteroatoms – e.g., Oxygen, Nitrogen, Sulfur mass.)



## Method 25C (Landfill NMOC as Carbon)

### ☐ Method Basics – Method 25 without Condensate

- Specifies Sample Probe
  - ✓ Unheated
  - ✓ Penetrating (0.9 m)
  - ✓ Gas accumulation volume
  - ✓ No condensate trap
- Analysis = Method 25



## What to look for in Method 25C data.

- Nitrogen or Oxygen Correction
- Method 25 QC
- Remember landfill gas is often about 50% CO<sub>2</sub> and 50 % Methane



# Method 25A

## If it burns we count it

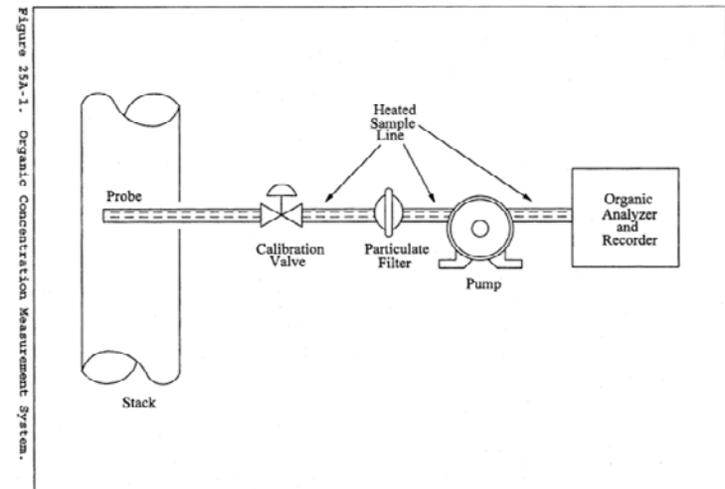
### □ Method Basics

#### ➤ If it makes it to the FIA

- ✓ Heated Filter and Transfer Line (Optional)  $\geq 110^{\circ}\text{C}$  ( $220^{\circ}\text{F}$ )

#### ➤ And burns, we count it.

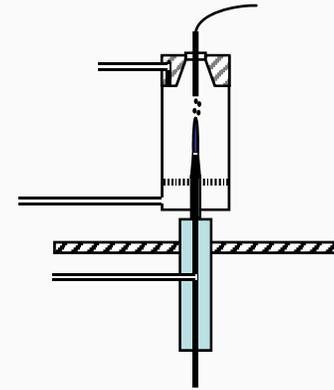
- ✓ Assume uniform response factor (propane)





# What to look for in results – M 25A

- Instrumental (CEMS) type QC
  - Calibration Error ( $\leq 5\%$  of cal gas value)
  - Calibration Drift ( $\leq 3\%$  of span)
  - Response Time
  - Water interference
- Response of polar VOC (oxygenates)
- Conversion to proper units of propane
  - ✓ Methane response factor used to convert to propane?
- What about NON-Methane VOC?





## What's Important to you – M 25A?

- Why choose Method 25A over Method 25
  - Detection limit,
    - ✓ Method 25 ~ 50 ppm
    - ✓ Method 25A ~ 0.1 ppm
  - Continuous THC Measurement
- Why not choose Method 25A
  - Rule does not specify, somebody else figured out why.
  - Does not measure or respond well to your VOC
    - Formaldehyde, methanol, ethanol, acetaldehyde.
    - Or, choose to calibrate with the predominant VOC if applicable.



## What's Important to you – M 25A? (cont.)

- ❑ How do I measure non-methane or non-ethane w/M-25A?
  - Method 18 gas separation and methane measurement
    - ✓ Make sure the units of measure are the same – (as propane)
    - ✓ High Methane results affect the confidence in NMOC difference
      - Error in Methane may be larger than final NMOC
      - Negative results for NMOC are possible.



## Other issues important to you – M 25A

- ❑ Why not choose Method 25A for VOC measurements?
  - Variable response to different VOC Classes
    - ✓ Nonresponsive to formaldehyde
    - ✓ Nonresponsive to per-chlorinated organic
    - ✓ Insensitive to other oxygenated compounds/water soluble
    - ✓ Does not measure true VOC mass



# Method 25B

## If I see it, it must be a VOC

- ❑ VOC that respond to IR in the hydrocarbon range
  - Used to measure VOC in hydrocarbon fuel
  - Response factors? – average response of propane
  - What about non-methane VOC from Method 25B?
    - ✓ Optical Speciation of Methane
    - ✓ Calibration with Methane and Propane
    - ✓ High Methane Interference



## CTM-042 for Bakeries (ICAC Method)

### ❑ Sample Inlet

- 375 F sampling line to avoid condensation/matches catalyst operating temperature.

### ❑ Catalytic Methane Cutter

- Methane by Method 25A
- Total by Method 25A
- NMOC by difference



# Methane Cutter Topics

## ❑ FID Calibration

- Methane Gas Standard(s)
- Ethanol Gas Standard(s) -Bakery Specific Response Factor

## ❑ Catalyst Efficiency

- Separate efficiency test using combined methane/ethanol cal gas is required.
- Efficiency is determined each time unit is calibrated.



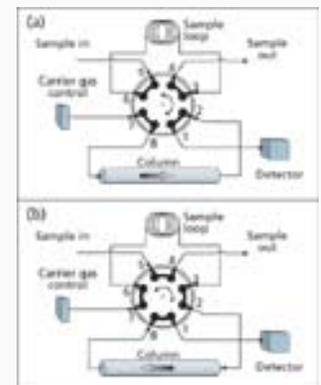
# Methane Cutter Topics

- ❑ Source Gas Composition Assumed
  - Mostly methane and ethanol
  - NMOC calculated by difference
    - ✓ High Methane, low NMOC calculation errors



## Other Methods for NMOC/NMEOC

- ❑ Methane Separation Methods (Alt106, 97a, 96,78,66)
  - TECO 55/VIG 200/Backflush GC
    - ✓ Methane passes through gas separation column to FID
    - ✓ Gas direction is reversed in column, residual sent to FIC
  - Calibration with Methane, Ethane, Propane
  - Semi-continuous Measurement by FID





## Why is this important to me?

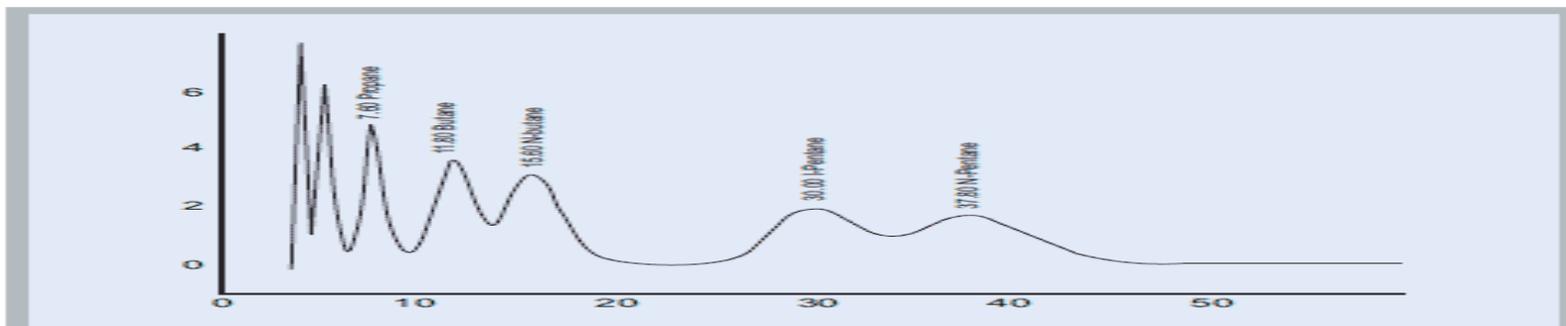
### ❑ Advantages

- Measures NMOC or NMEOC directly

### ❑ Disadvantages

- Ethylene/Acetylene included in NMEOC?

Typical Chromatogram



Fast NGA Analysis within 50 sec.



## Method 18

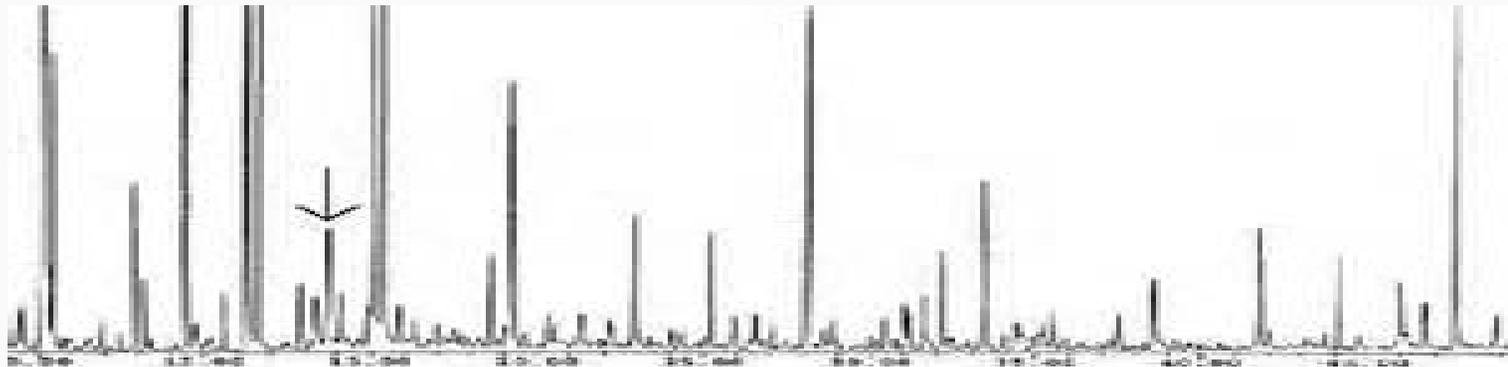
### An Ugly way to do total VOC (JJJJ)

- This is a VOC speciation method by Flame Detector
- Requires prior knowledge of the VOC to measure
  - Calibration and response factors
  - Complete VOC mass characterization
- Requires conversion to VOC as propane.



# What Compounds do I Measure?

- ❑ AP 42 lists may be applicable to identify VOC species
  - Requires Method 18 QC and spike recovery for each compound.





# Method 320

## Another Ugly way to do total VOC (JJJJ)

- ❑ This is a VOC speciation method by FT-Infrared Detector
  - Like Method 18
    - ✓ Requires calibration for each VOC species
    - ✓ Requires prior knowledge of the VOC to measure
    - ✓ AP 42 lists may be applicable to identify VOC species
    - ✓ VOC have widely varying response factors
    - ✓ Requires Method 320 QC and spike recovery (surrogate).
    - ✓ Requires conversion to VOC as propane.



## Method 18 or Method 320

- ❑ Questions on how and how not to do speciated VOC as propane!
  - Lets discuss what species to include as VOC to measure total VOC – Subpart JJJJ discussion
  - How many compounds can you practically do with Method 18 (Spike recovery on each compound)
  - How many compounds can you practically do with Method 320 (spike most difficult to recover- what's that about?).



## Method 18 or Method 320

- ❑ We have no systematic approach to know when “all” of VOC are measured to generate the total.
  - Method 18
    - ✓ Is accounting for 9X% of the chromatogram peak area enough?
    - ✓ Do I have to spike and show recovery on all compounds, even unknowns?
  - Method 320
    - ✓ Is accounting for 9X% of the IR spectrum features enough?
    - ✓ Is the error in water and CO<sub>2</sub> correction overwhelming to low concentration VOC measurement?
    - ✓ How do I quantitate the mass of unknown compounds from IR data?

