Speciated VOC Methods – Overview

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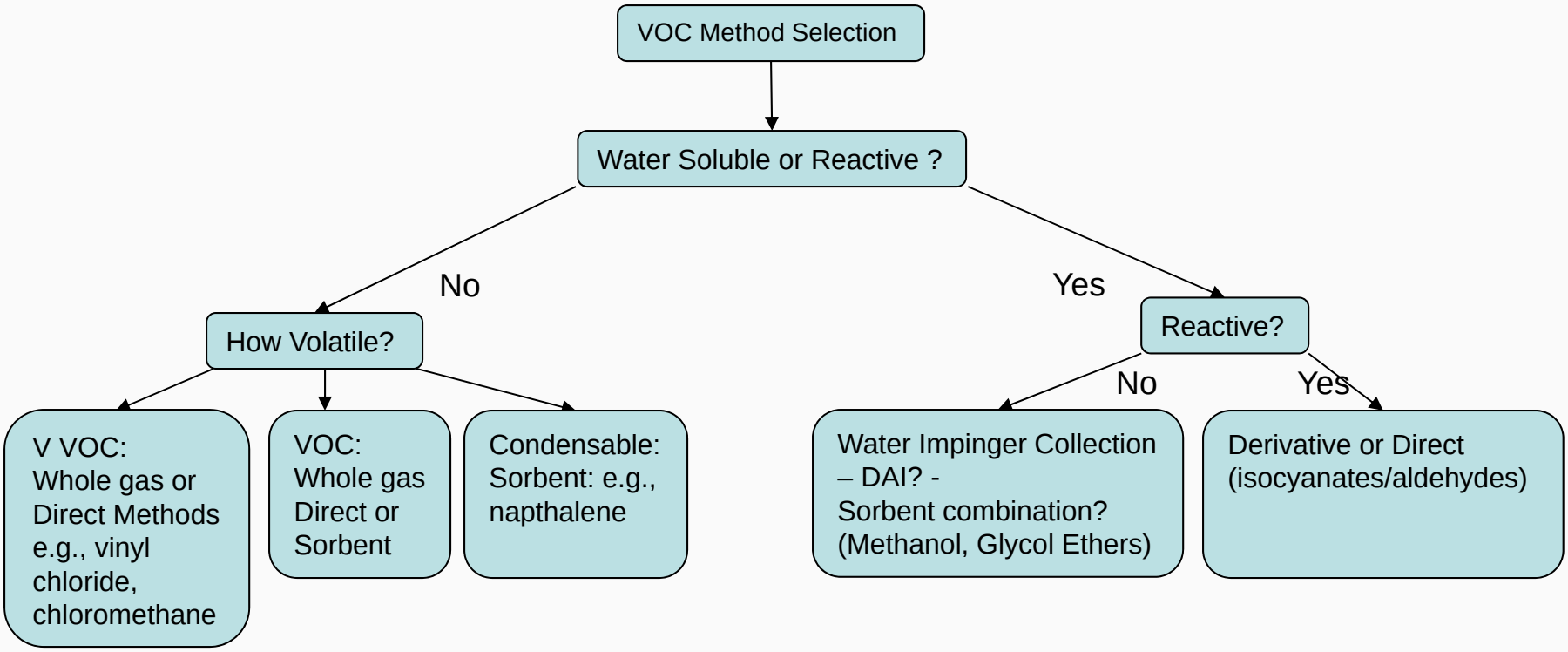
How do I choose a Method

(What does Ray think about when you ask him about a target VOC measurement?)

- ❑ Rule or permit mandated method?
- ❑ What do we know about the target VOC(s) physical and chemical behavior?
- ❑ Is this a field measurement or a collected sample lab analysis?
- ❑ Are there methods for this target already?

  (EPA/ASTM/NIOSH/OSHA)

Ray's Decision Tree for VOC



VOC Physical and Chemical Behavior

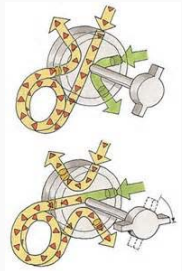
- Volatility
- Polarity/water solubility
- Reactivity
  - Stable, nonreactive
  - Reacts as condensate with water/pH
- Can I buy a certified standard?

How Volatile is your target VOC

- Very volatile organic compounds (VVOCs)

  It's about capturing a representative sample of an elusive gas e.g. vinyl chloride

  - ✓ Low molecular weight
  - ✓ Vapor pressures greater than 15 kPa at 25° C
  - ✓ Boiling points typically below 30° C.
  - ✓ Purgeable or not water soluble



- Very volatile compound measurement
  - ➢ Reference Methods
    - ✓ Whole gas sampling in bags with loop injections (Method 18)
    - ✓ Direct gas sampling with loop injection (Method 18)
    - ✓ Direct gas sampling into measurement cell (Method 320)

Note: Boiling Point/Vapor Pressure (see ASTM D6345 Standard Guide for Selection of Methods for Active, Integrative Sampling of VOC in Air)

How Volatile is your target VOC

- Volatile Organic Compounds (VOC)
  (It's about getting the target VOC to the detector. e.g., benzene, trichloroethylene)
  - Vapor pressures greater than 10^{-2} kPa at 25° C
  - Boiling points typically 30 to 180 ° C.
  - Purgeable or not water soluble
- Volatile compound measurement
  - Reference Methods
    - ✓ Sorbent sampling option (Method 18)*
    - ✓ Whole gas sampling in bags with loop injections (Method 18)
    - ✓ Direct gas sampling with loop injection (Method 18)
    - ✓Direct gas sampling into measurement cell (Method 320)

* Note the connection to NIOSH and OSHA sorbent methods.

How Volatile is your target VOC

- Condensable/Semivolatile/Non-Reactive

  (Its all about collecting/concentrating enough to measure e.g., napthalene)

  - Vapor pressures greater than 10^{-2} to 10-8 kPa at 25° C
  - Boiling points typically 180 to 350 ° C.

- Semivolatile compound measurement

  - Sorbent sampling (e.g., styrene, napthalene)

  (We are playing this one by ear)

  - ✓ Heated sampling lines – direct analysis
  - ✓ SW-826 Methods 0010/8270
  - ✓ Method 18 or other sorbent methods

Summary for
Methods for Non-Reactive Hydrophobic Volatile Organic Compounds

- Methods (Work Horses)
  - Reference Method 18
    - ✓ Very volatile compounds from Tedlar bags or direct interface
    - ✓ Volatile compounds – add sorbent sampling
  - Reference Method 320
    - ✓ Direct interface FTIR
    - ✓ Can I use a bag sample?

Why or Why Not Canisters for Non Reactive VOC?

- Canisters – Multiple Use
  - Combustion Matrix
    - ✓ Contamination/compromise
    - ✓ Acid gases
    - ✓ Water condensation
    - ✓ No visible inspection
    - ✓ Multiple use
- Bags
  - One time use
  - Blank contamination
  - Permeation
  - Water condensation
- What About Non-combustion gas ?
  - High concentration/safety
    - ✓ Fuels BTU Analysis
- What About Ambient Condition Source Gas
  - 2% or less moisture
  - Ambient temperature

How do I choose a Method

- Nonreactive, polar/water soluble VOC
  (Measurements are more challenging - e.g., methanol, ethanol, acetone, acetaldehyde, methyl ethyl ketone, ethers)
  - Manual sampling
  - Aqueous impinger with or without sorbent backup.
  - Direct aqueous analysis – not very sensitive
  - Extract derivative and analyze
- Nonreactive, polar/water soluble method examples
  - Water dropout, Method 323 (formaldehyde, others?)
    - ✓ Derivatization/analysis
  - Water dropout sorbent backup Method 308 (methanol, glycol ethers)
    - ✓ Water analysis
    - ✓ Sorbent analysis

How Do I choose a Method Reactive VOC Measurement

- Case by Case Basis
  - Does it react when cooled with the gas matrix during sampling?
    - ✓ Manual collection – stabilization/derivatization
      - – Isocyantes
    - ✓ Direct hot wet measurement
      - – Method 320?

Summary of Tools VOC Measurement Tools

- Manual Generic VOC Methods Regulatory Methods
  - Method 18 (GC with other Detectors)
    - ✓ Bags, Sorbents, Direct
  - Method 320 (FTIR)
- Manual Target Specific Compound Regulatory Methods
  - Method 207
  - Method 308
  - Method 323

- Other EPA Resources
  - ORCR HWI Methods (e.g.)
    - ✓ Method 0031/8260 VOC – Sorbent – GC/MS
    - ✓ Method 0010/8270 (Semivolatile)
- State Resources
  - CARB Methods
  - South Coast ARB Methods
- Industry Methods
  - NCASI
  - NIOSH
  - OSHA

Questions

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