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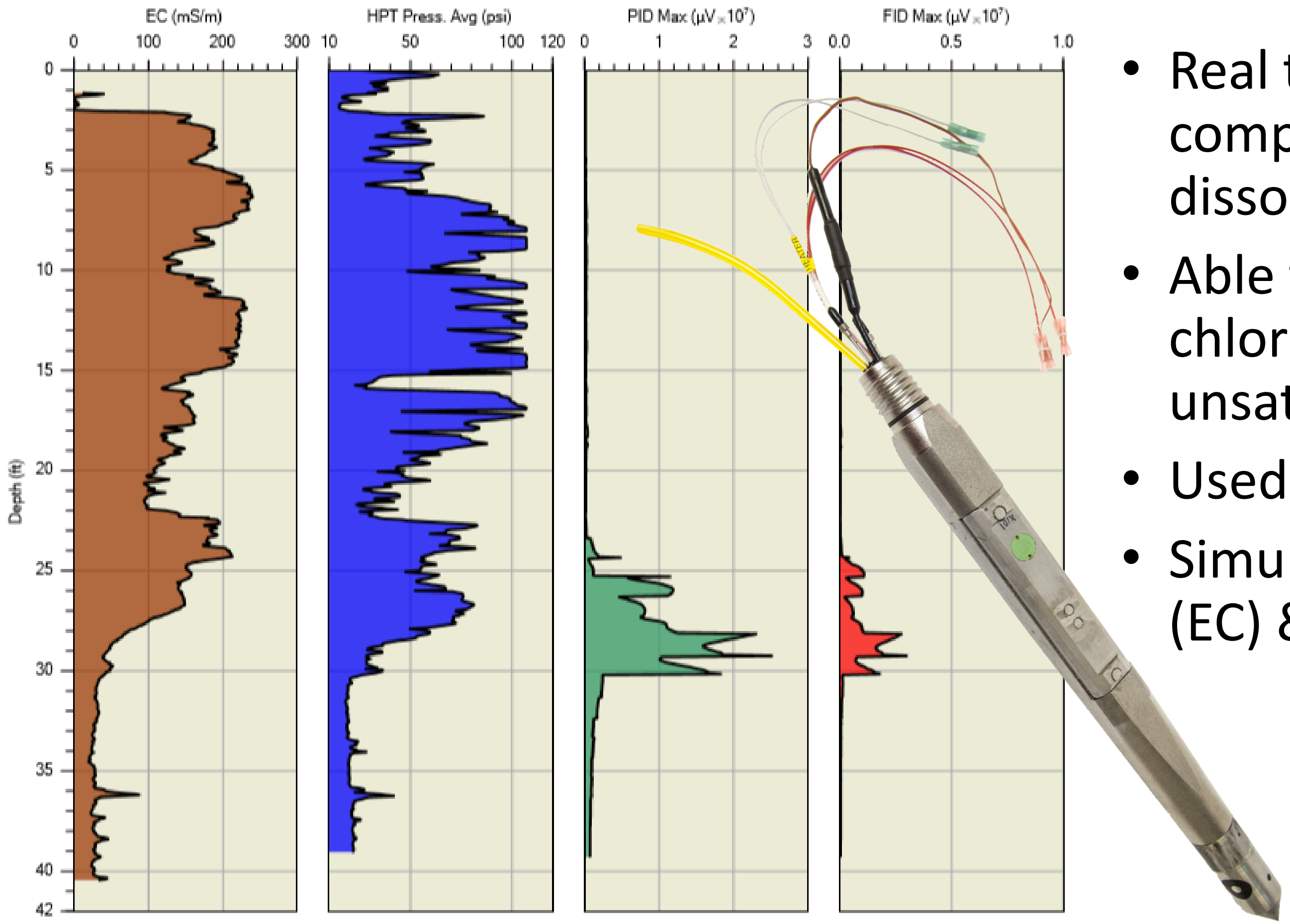
Factors Influencing In Situ Detection of Analytes with the Membrane Interface Probe

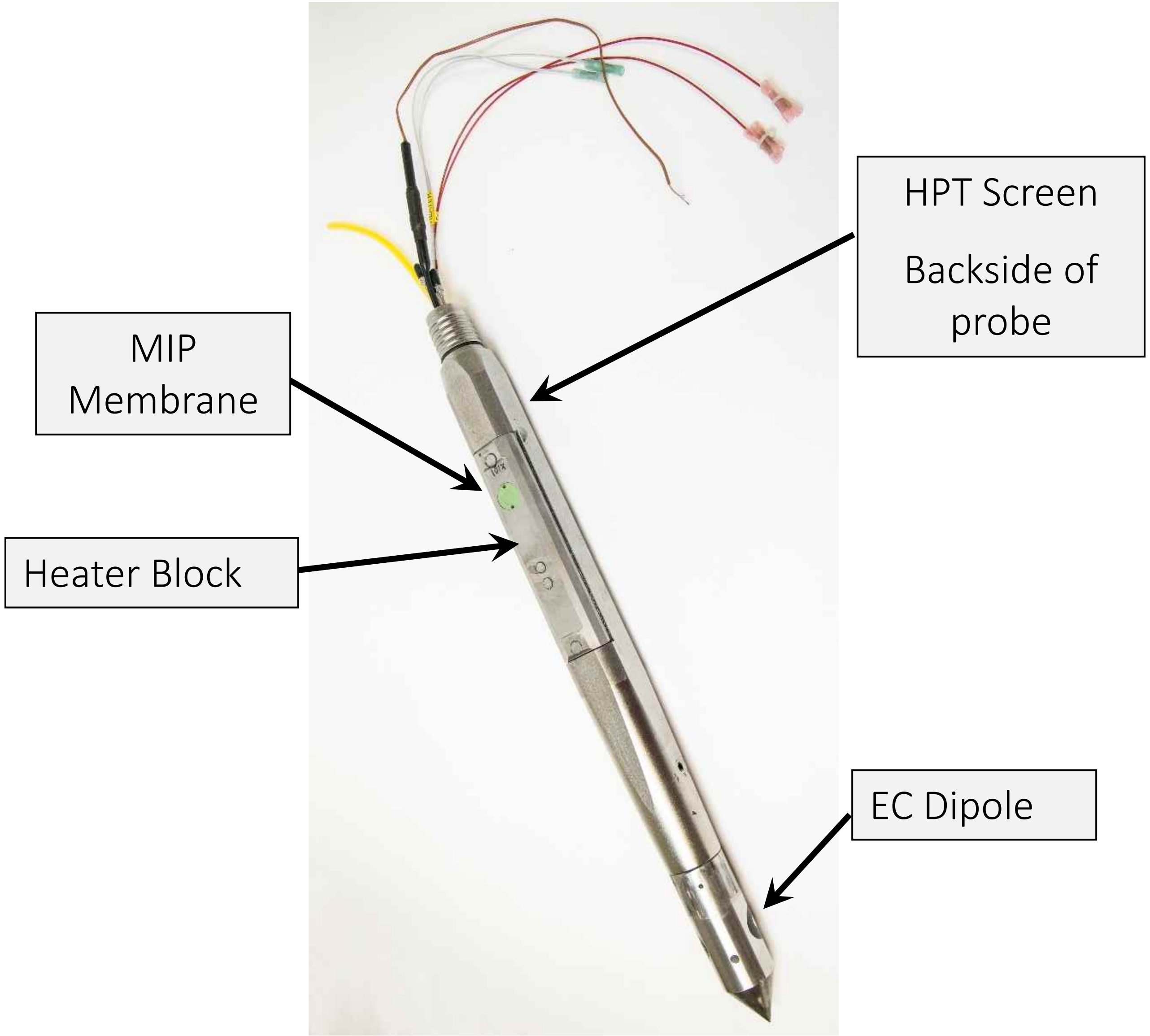
Daniel Pipp, Wes McCall, Nick Basore

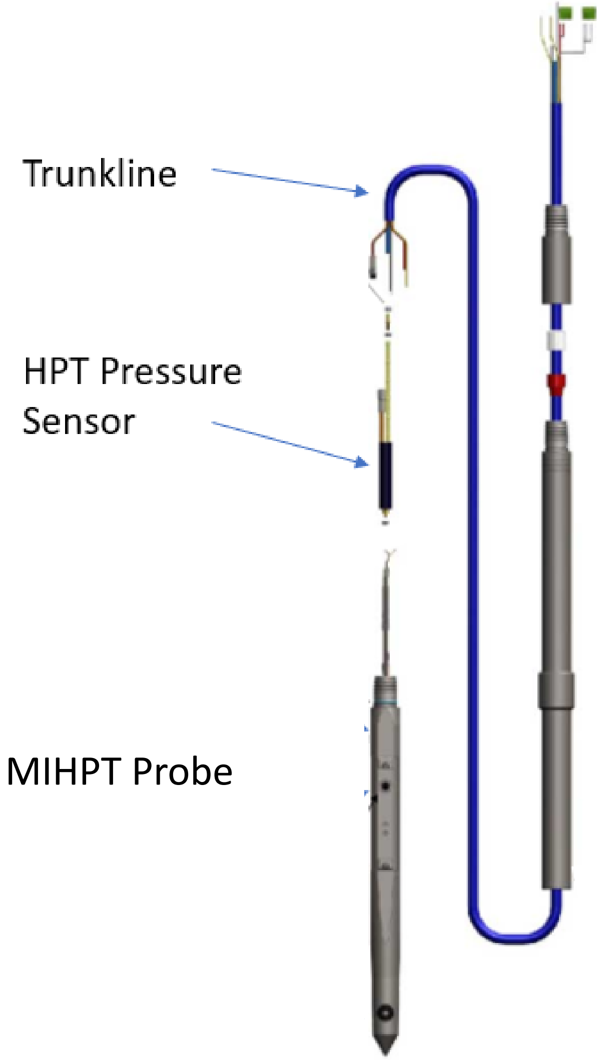
Membrane Interface Probe



- Real time mapping of volatile organic compounds (VOCs) at depth in the gaseous, dissolved, and free phases
- Able to map petroleum hydrocarbons (PVOCs), chlorinated hydrocarbons (TCE, PCE) & unsaturated hydrocarbons (methane)
- Used in the saturated and unsaturated zones
- Simultaneous log of soil electrical conductivity (EC) & HPT Injection Pressure

Membrane Interface Probe





Membrane Interface Probe

---FI6000---

- Real Time Data Acquisition
- Data Files Stored in Zip Files on field Laptop
- Circuitry for Electrical Conductivity

---MP6505---

- MIP Probe Heater Controller
- 110V Probe Heater Output
- Gas Flow Controller

---K6300---

- HPT Water Pump
- Flow Controller for Injection

---GC1000---

- 3 Gas Phase Detectors – PID, FID, XSD

Membrane Interface Probe

Gas Chromatograph (GC)

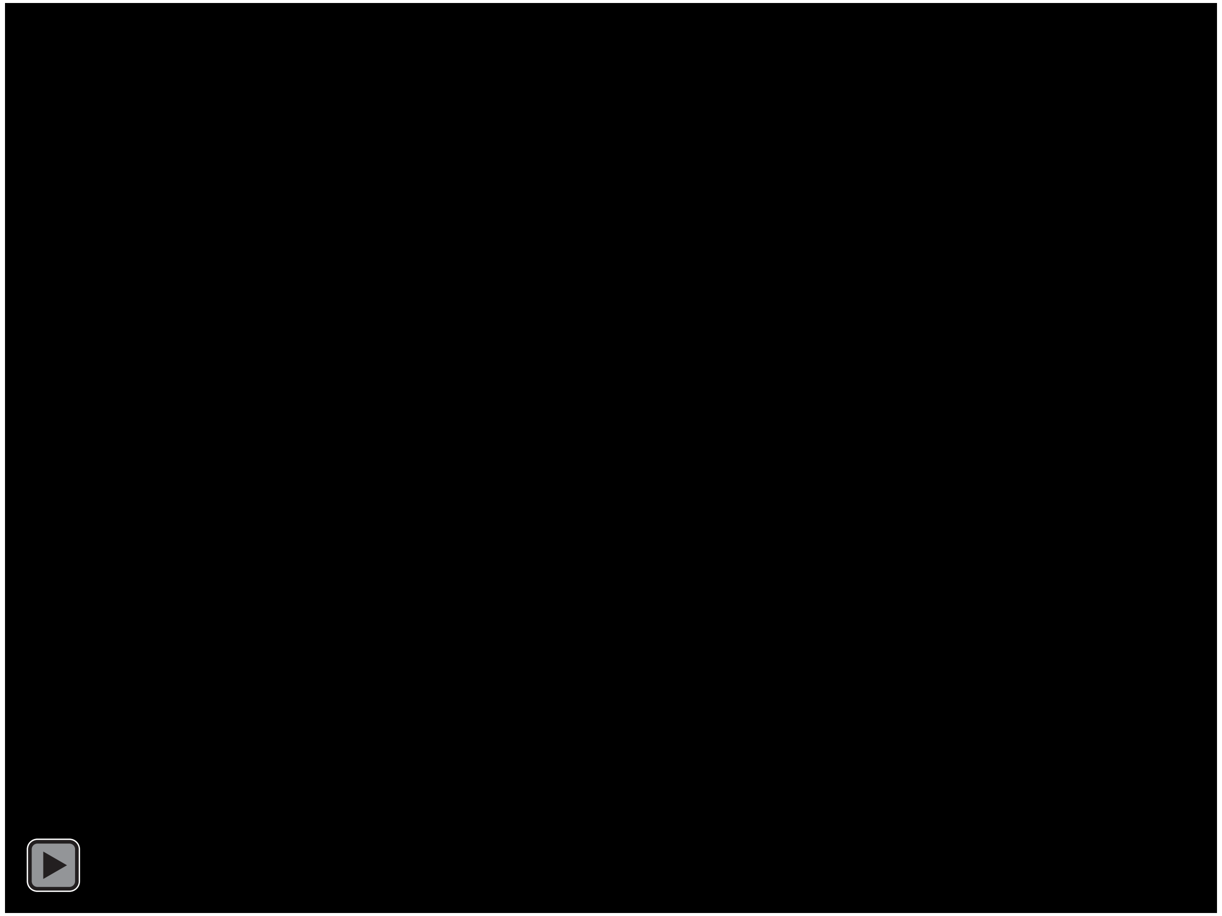
XSD FID PID

Gas Phase Detectors

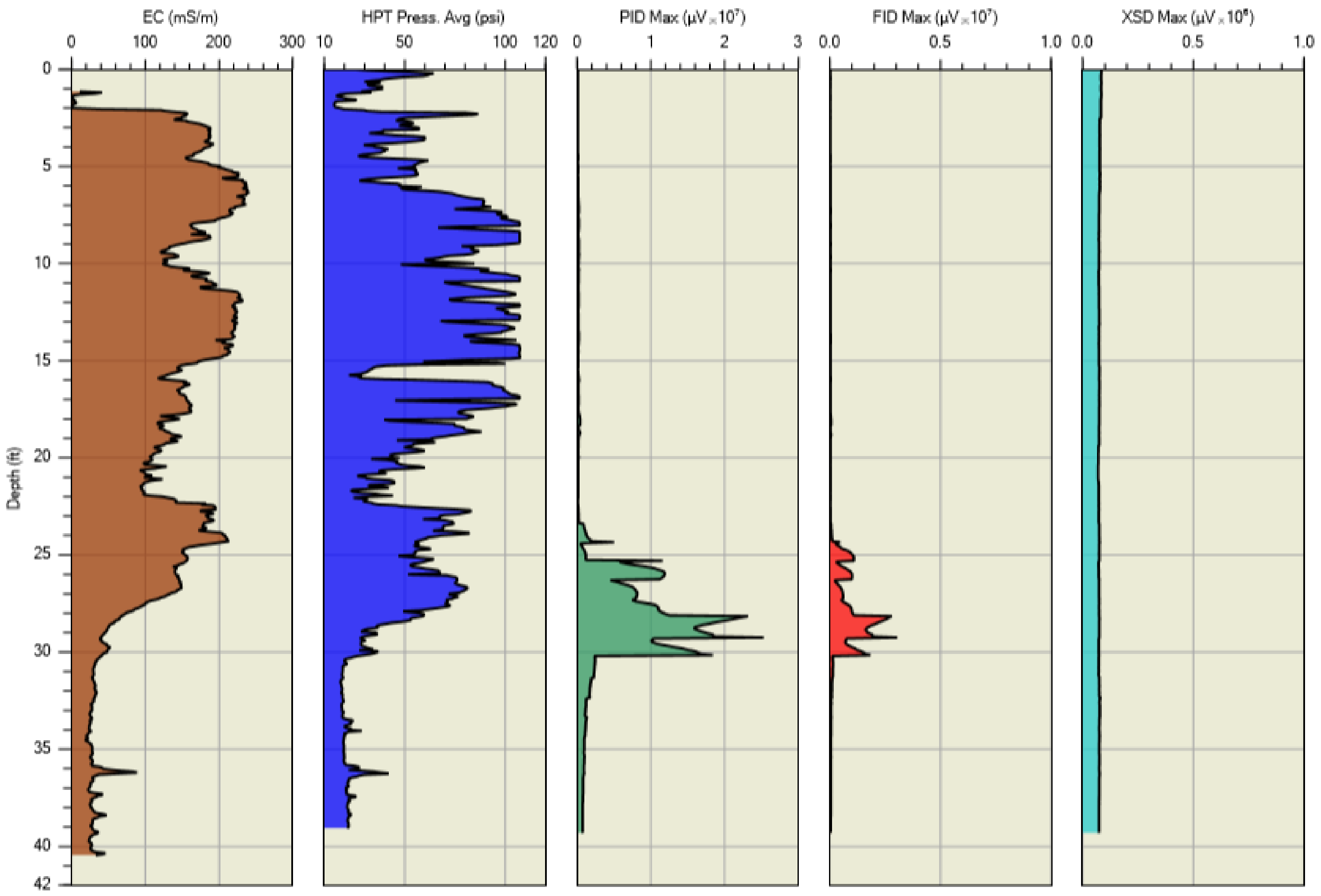
Membrane Interface Probe

MIP Theory of Operation

Under a concentration gradient VOCs move across the membrane via diffusion and then are transported to a series of detectors at the surface in an inert carrier gas.

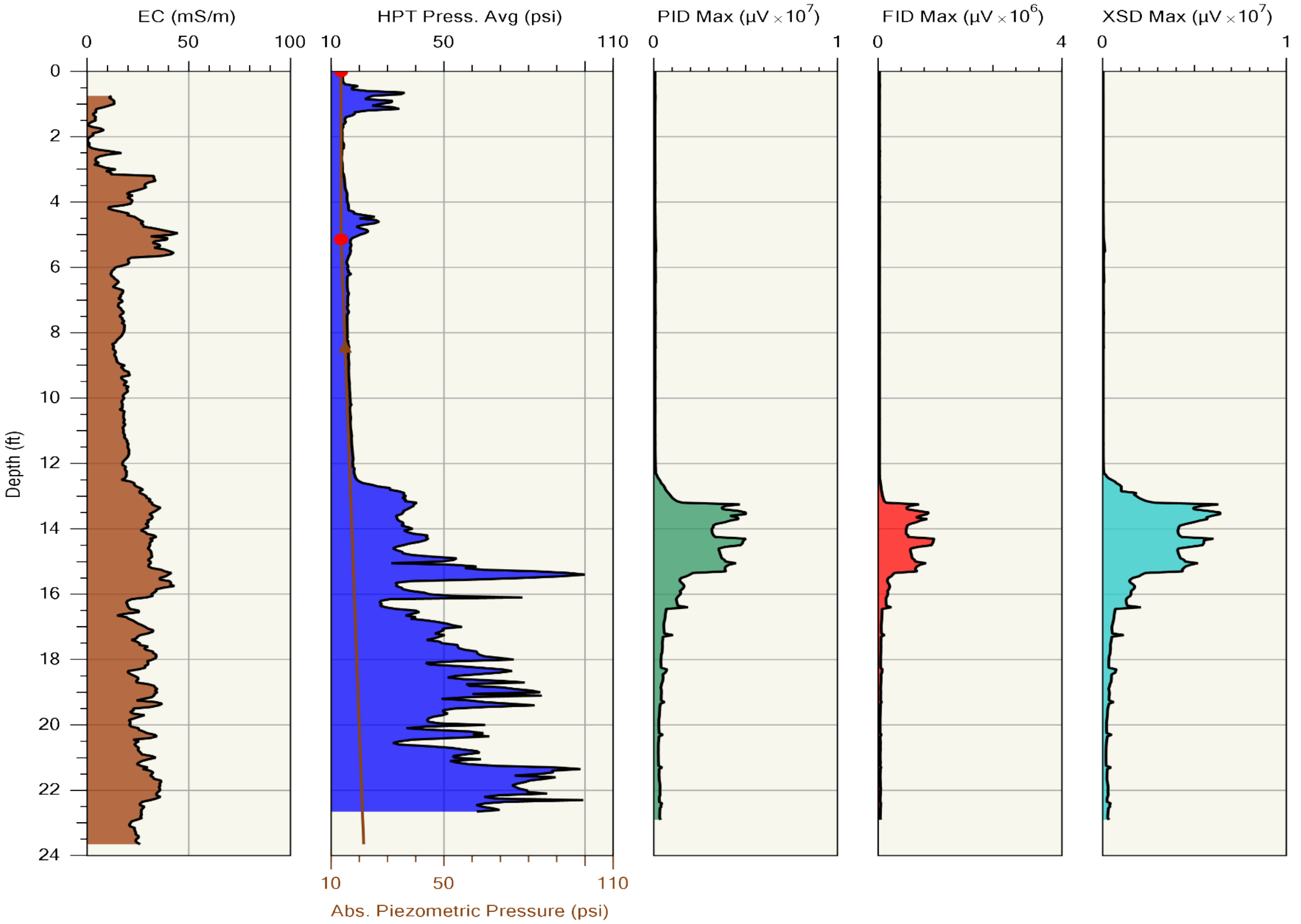


Membrane Interface Probe



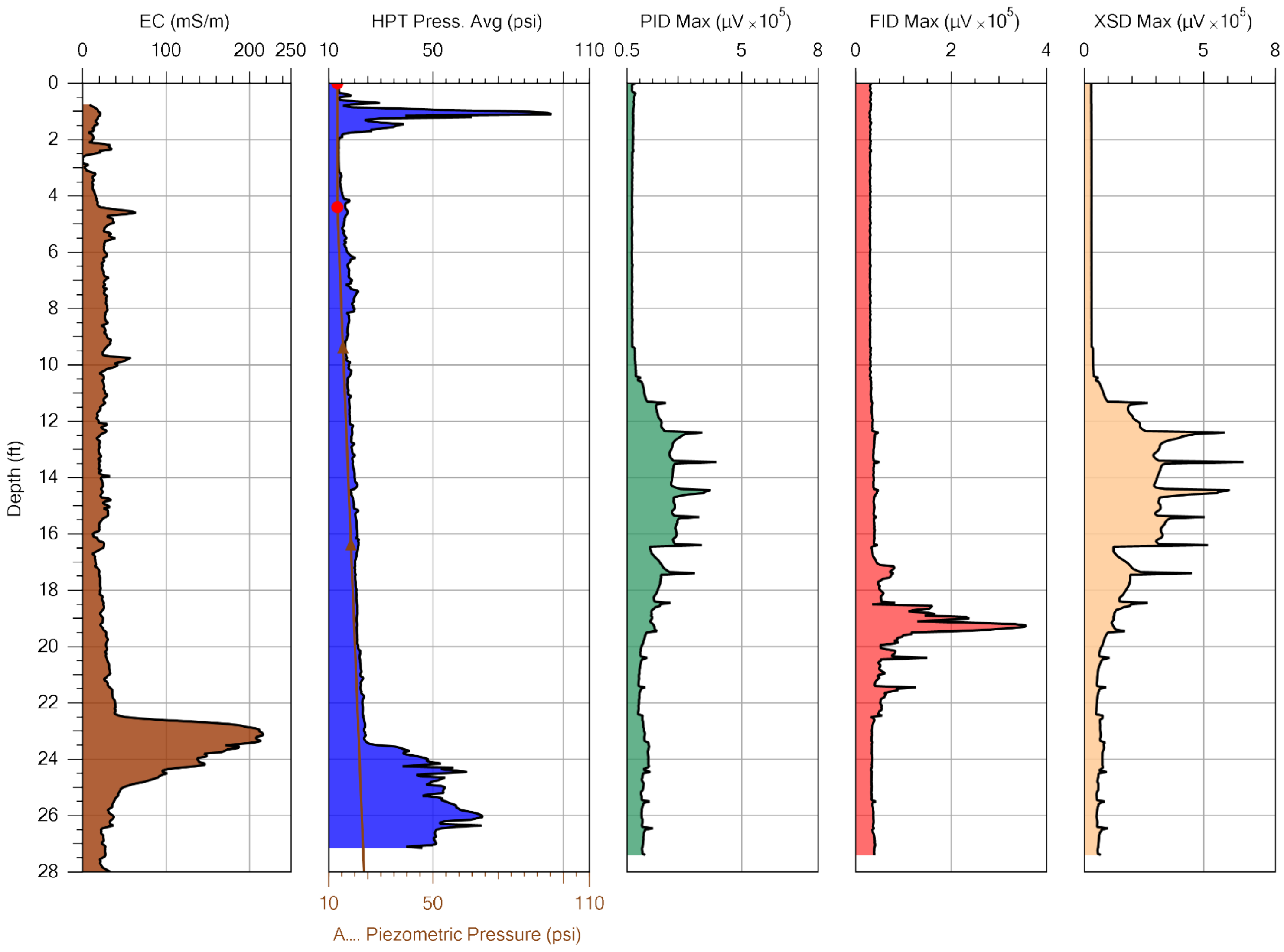
- Total VOC response within the log.
- Petroleum hydrocarbon PID-FID response without XSD response

Membrane Interface Probe



- Total VOC response within the log.
- Chlorinated solvent VOC response showing on all detectors PID-FID-XSD

Membrane Interface Probe



- Total VOC response within the log.
- Chlorinated solvent VOC response showing on all detectors PID-FID-XSD

Additionally showing a strong FID response not seen on the PID or XSD which is due to methane

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Detection Limits

- Standard MIP has detection limits in the ~250ppb range of Benzene/TCE compounds.
- Low Level MIP can reduce this as much as 10x lower.

- Detector Specific
  - Based upon the best overall detector for Benzene-TCE

  - Detector maintenance
  - Proper detectors being operated for analyte of interest

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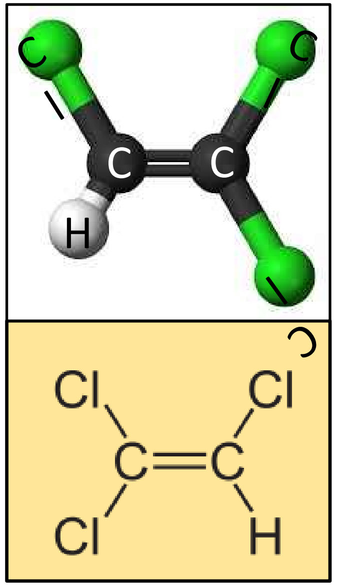
Factors within the tooling that influence analyte detection limits

- Back pressure of the trunkline
  - Length of trunkline
  - Carrier gas flow rate
- Wear of the membrane
- Usage of trunkline – sorbed contaminants to the gasline can create a chromatographic phase
- Temperature of the probe

Membrane Interface Probe

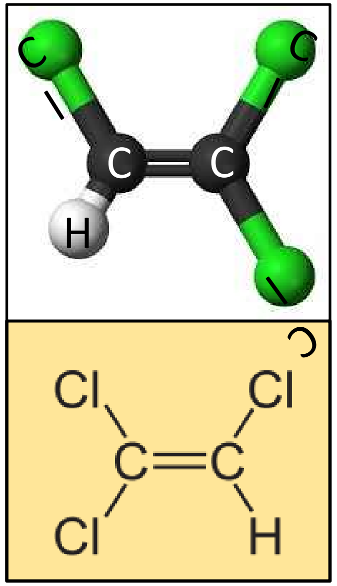


Trichloroethene (TCE)

C = Carbon
Cl = Chlorine
H = Hydrogen

How can I know what I am investigating for can be detected with the MIP ?

Membrane Interface Probe



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Boiling Point

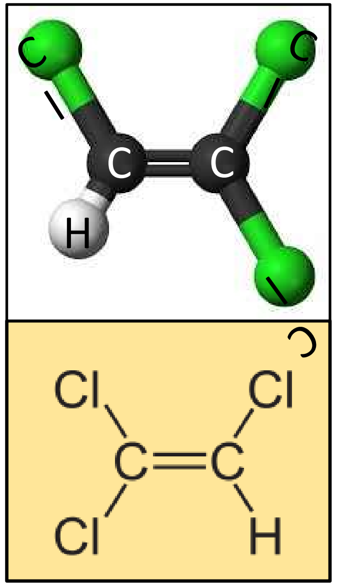
Vapor Pressure (volatility)

Water Solubility

Molecular Weight

Melting Point

Membrane Interface Probe



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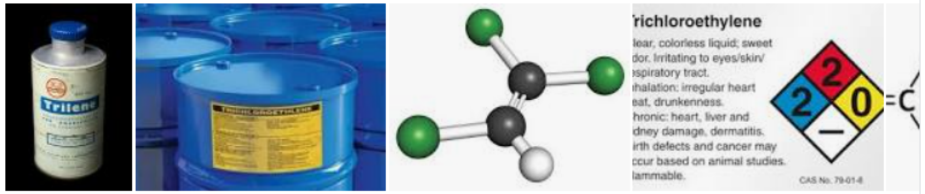
Membrane Interface Probe



Trichloroethylene (TCE) is a nonflammable, colorless liquid with a somewhat sweet odor and a sweet, burning taste. It is used mainly as a solvent to remove grease from metal parts, but it is also an ingredient in adhesives, paint removers, typewriter correction fluids, and spot removers.

pubchem.ncbi.nlm.nih.gov › compound › Trichloroethyl...

Trichloroethylene | ClCH=CCl2 - PubChem

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People also ask

- How dangerous is Trichloroethylene?
- Is Trichloroethylene still used?
- What is Trichloroethylene used for?
- When was Trichloroethylene banned?

Feedback

www.atsdr.cdc.gov › substances › toxsubstance

Trichloroethylene

The chemical compound trichloroethylene is a halocarbon commonly used as an industrial solvent. It is a clear, colourless non-flammable liquid with a chloroform-like sweet smell. It should not be confused with the similar 1,1,1-trichloroethane, which is commonly known as chlorothene. The IUPAC name is trichloroethene. Wikipedia

Molar mass: 131.4 g/mol

Boiling point: 189°F (87.2°C)

Formula: C_2HCl_3

Density: 1.46 g/cm³

IUPAC ID: Trichloroethene

Soluble in: Water

Flash point

Metabolism

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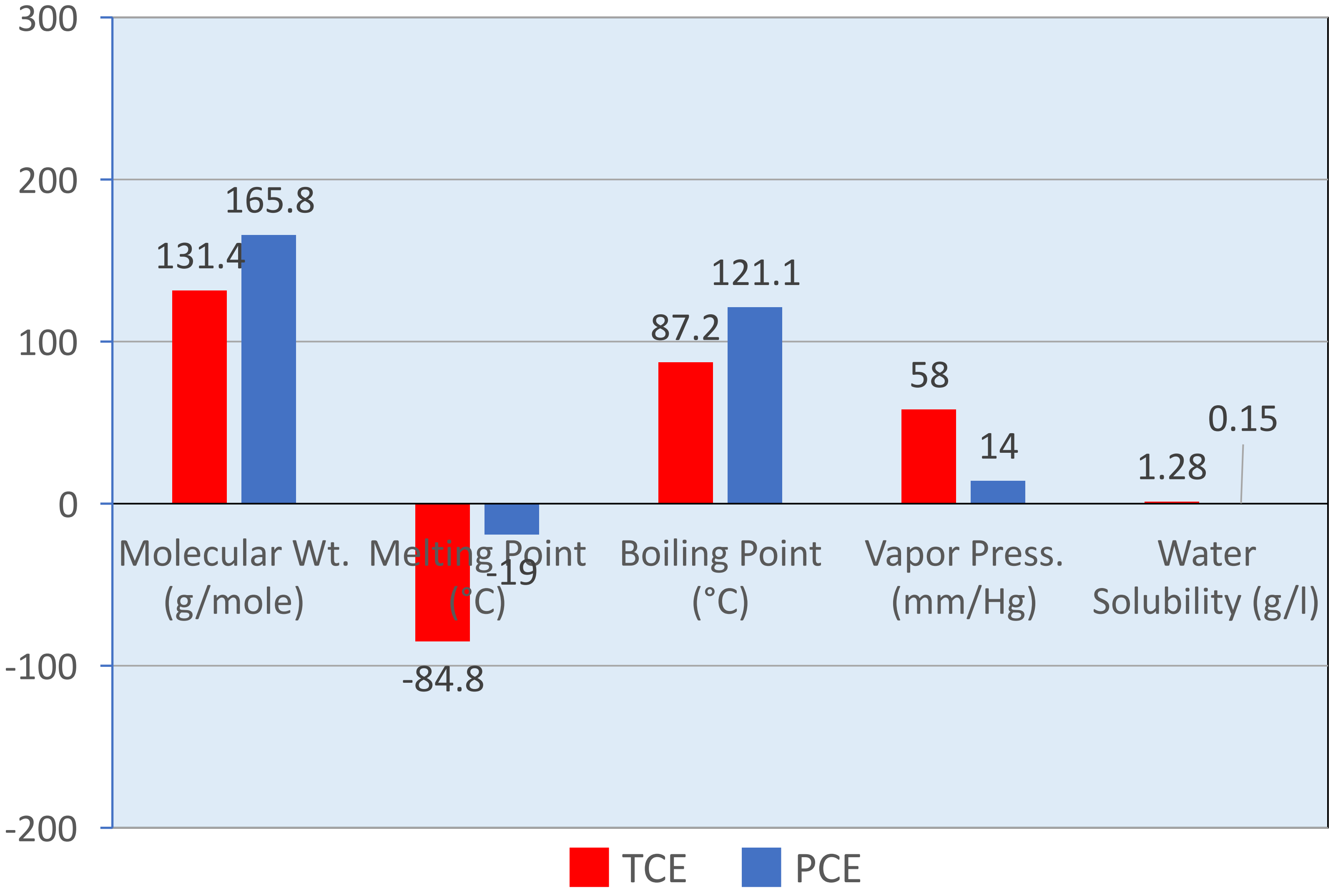
TCE & PCE

- Low boiling points
- Moderate vapor pressure
- Low water solubility
- Low molecular weight
- Low melting points

Characteristics make TCE & PCE good candidates for MIP detection.



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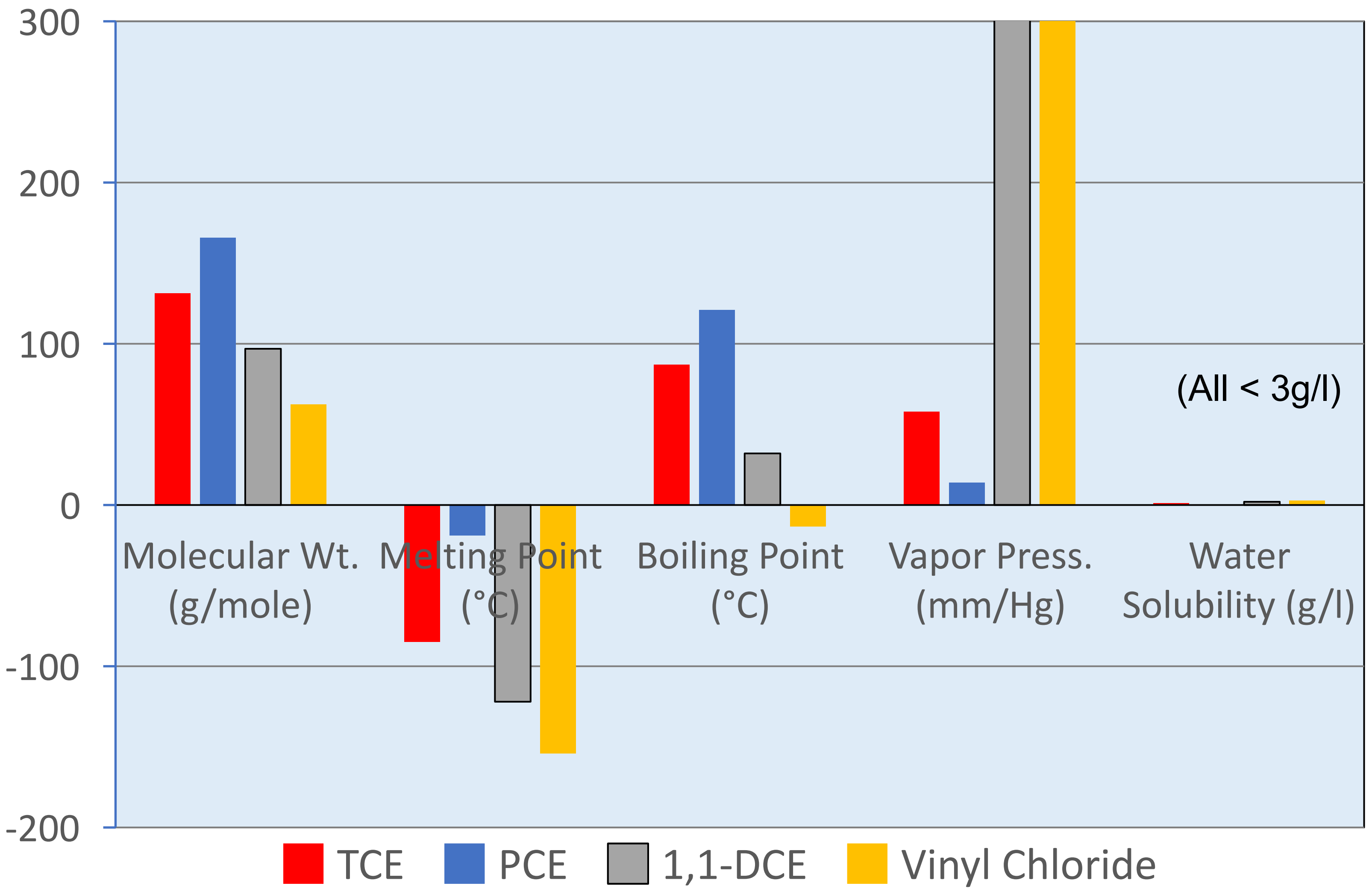
1,1-DCE & Vinyl Chloride

- Low boiling points
- Elevated vapor pressure
- Low water solubility
- Low molecular weight
- Low melting points

All these characteristics make TCE, PCE, DCE & VC good candidates for MIP detection.



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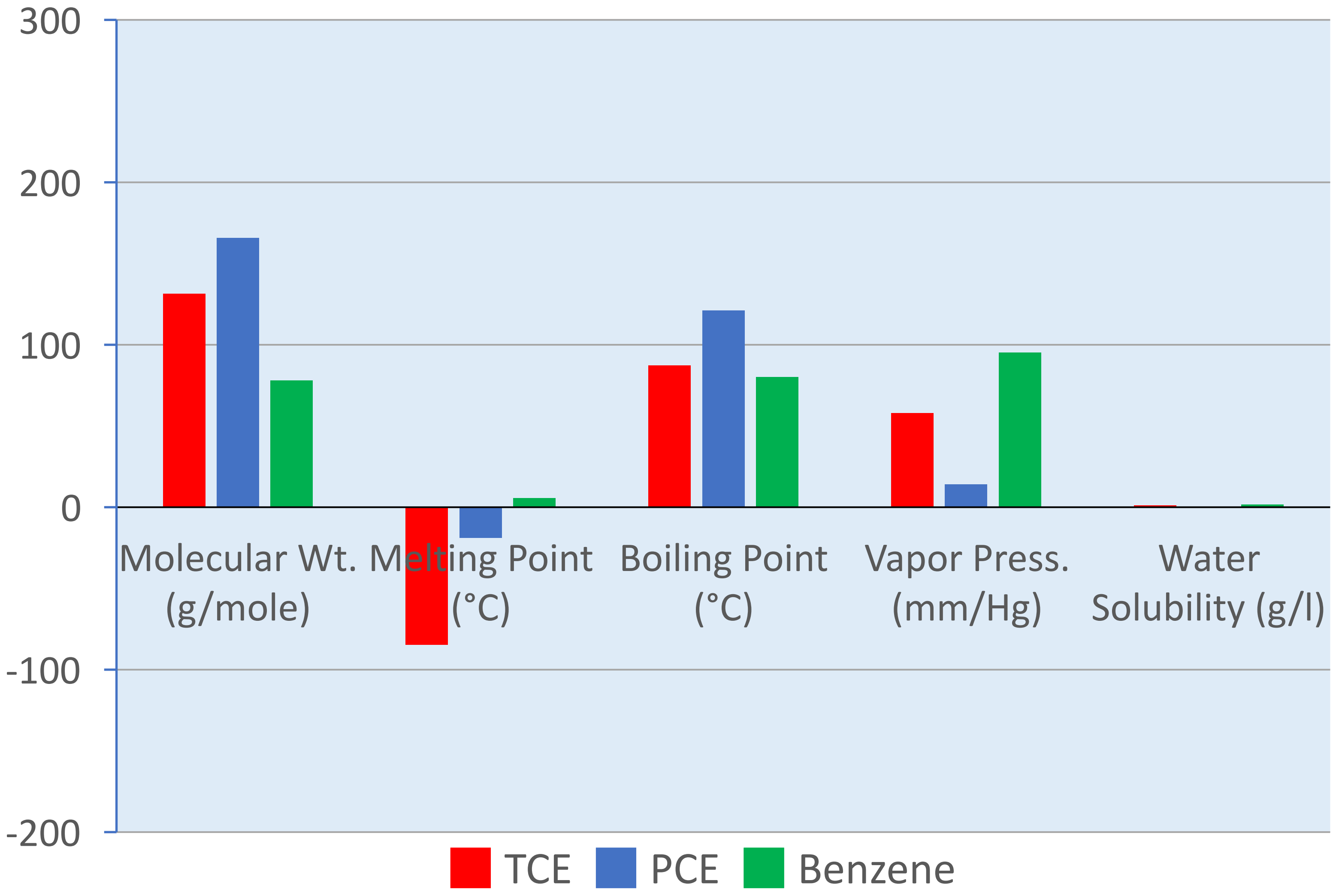
Benzene

- Low boiling points
- Elevated vapor pressure
- Low water solubility
- Low molecular weight
- Low melting points

Similar characteristics make Benzene a good candidate for MIP detection.



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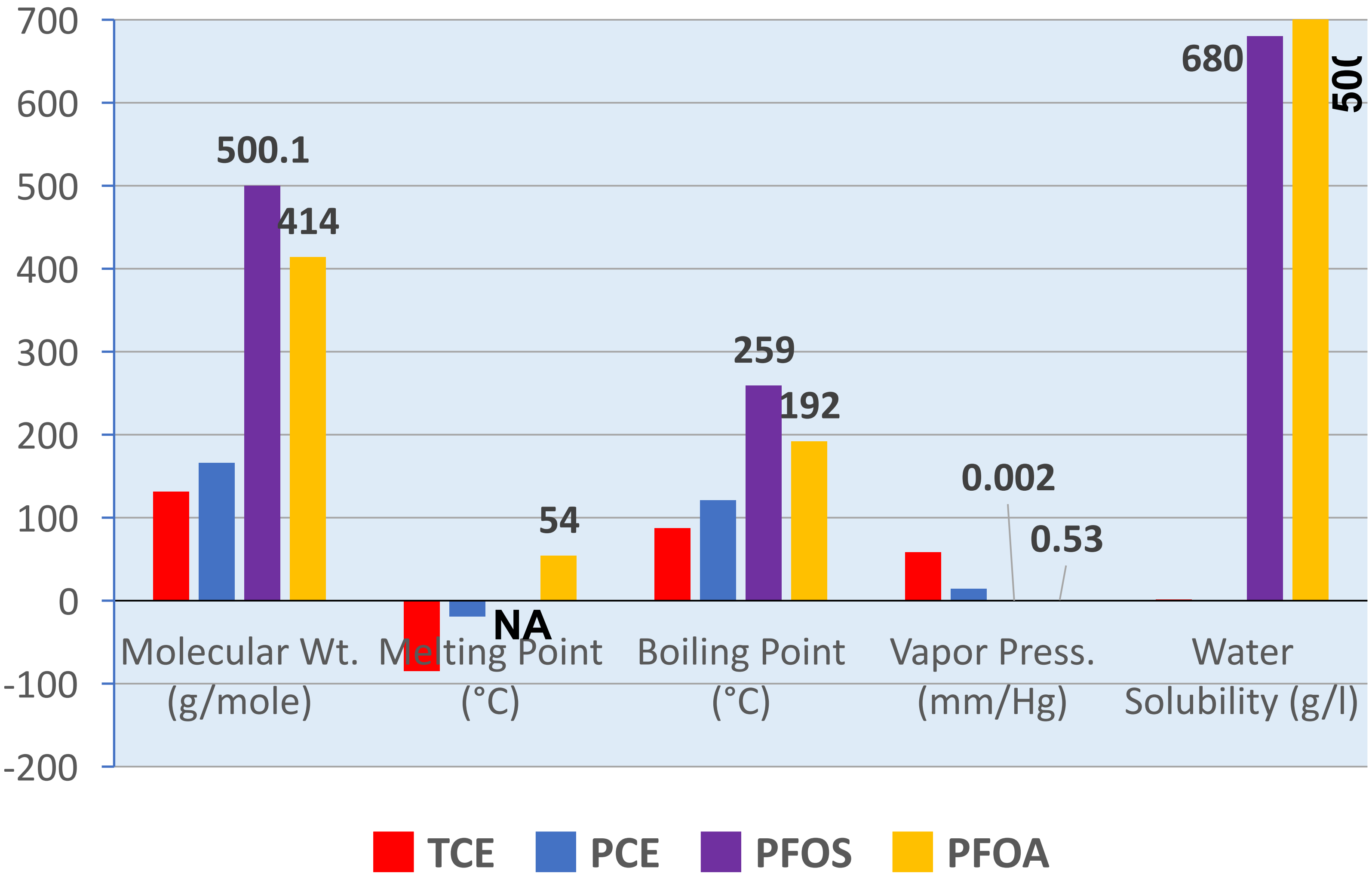
PSAS-PFOA

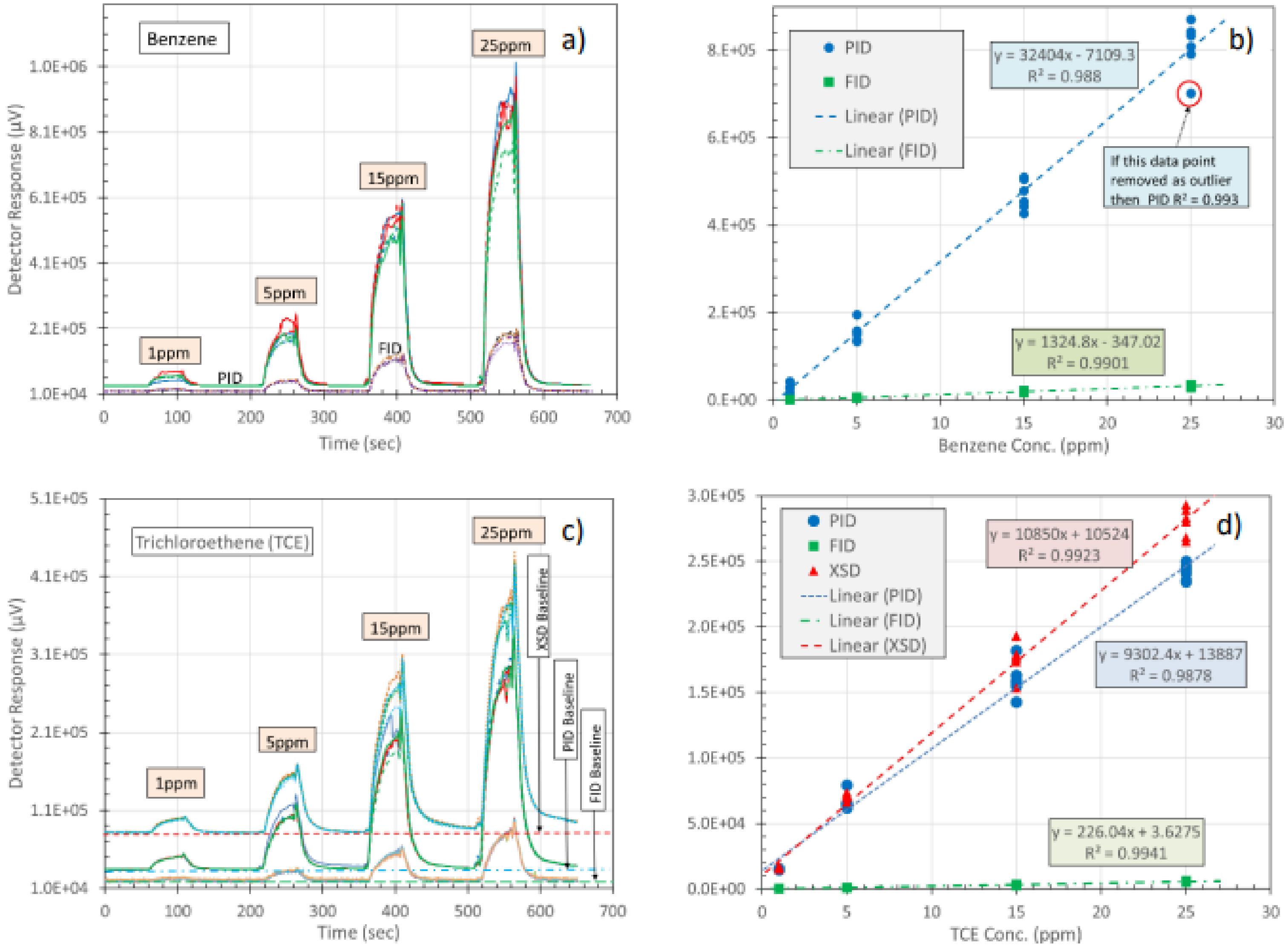
- High boiling points
- Low vapor pressure
- Water solubility
- High molecular weight
- Elevated melting points

All the characteristics of PFOS and PFOA make them a very bad candidate for detection with MIP.

PFOA 9.5g/l
PFOS 0.7g/l



MIP Chemical Response Testing

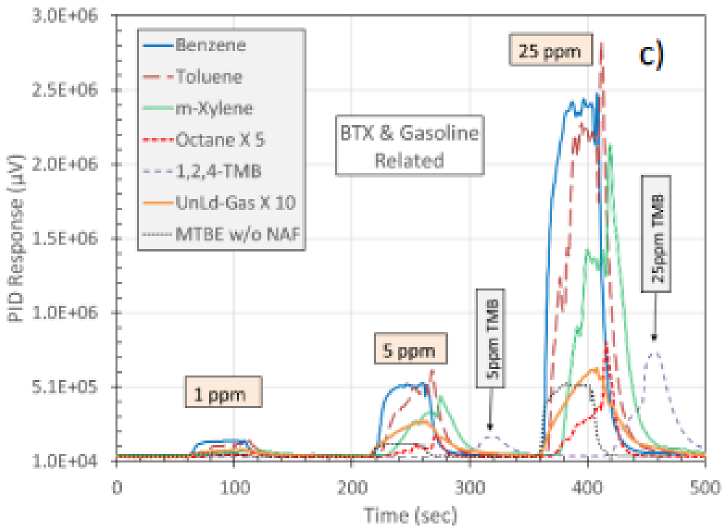


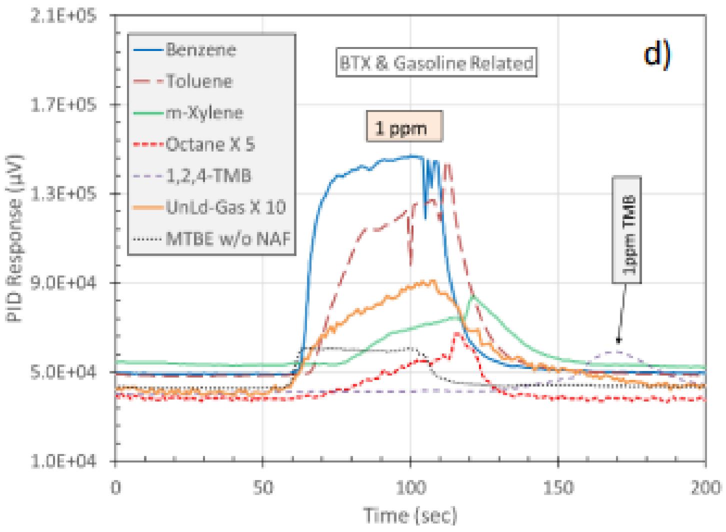
Six response tests were run with Benzene (a and b), TCE (c and d) at four concentrations to assess the repeatability and response curves of the MIP detectors for these common analytes.

No XSD response for benzene.

As the FID response was much lower for each of these analytes than the PID and/or XSD the FID responses were multiplied by ten (10 X) and then the baseline was adjusted to approximately the original level for plotting. The FID regression data is determined based on the unmodified FID results.

MIP Chemical Response Testing

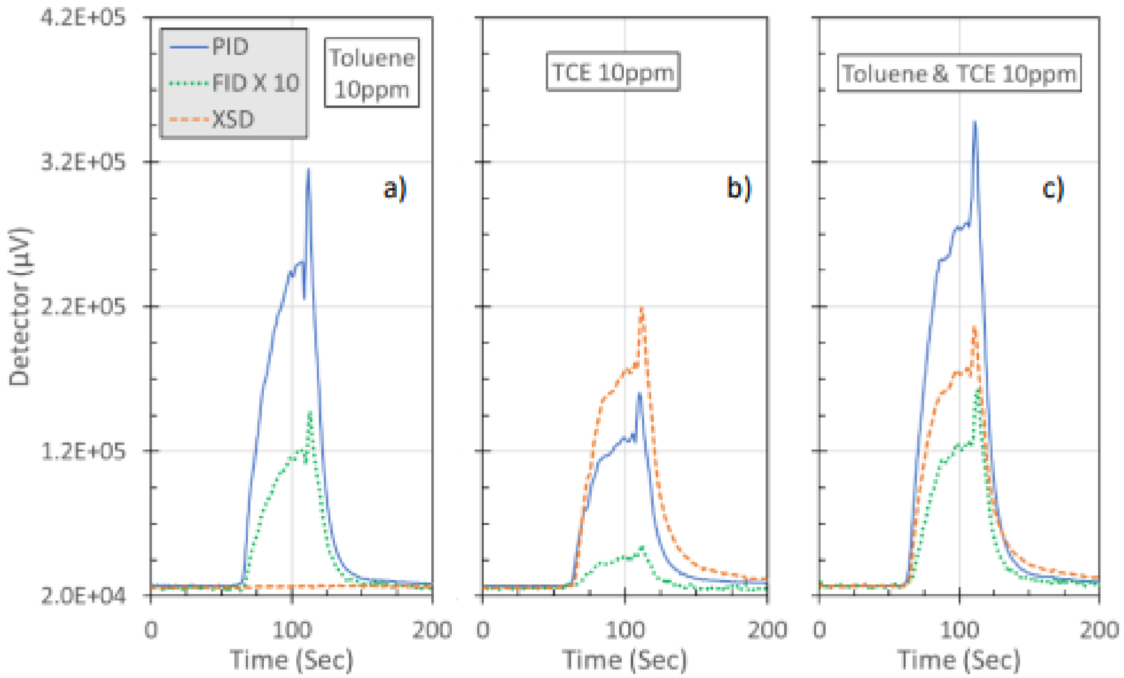




Unleaded gasoline and selected components of gasoline were run independently on the PID (c) and FID (e) to assess relative responses and trip times.

d) Enlarged view of the 1ppm standards on the PID.

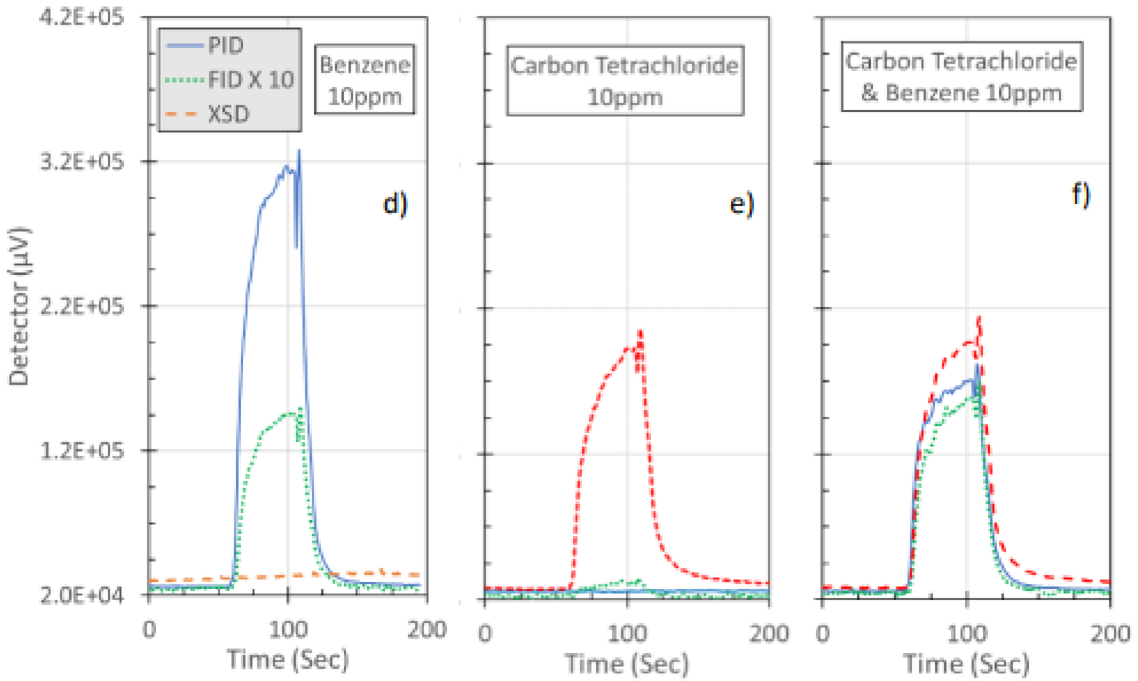
MIP Chemical Response Testing



Mixtures of halogenated and non-halogenated VOCs occur at some facilities.

Individual response tests with toluene (a) and TCE (b) are presented with a response test where toluene and TCE were combined for analysis (c). The results for the combined toluene and TCE standard are generally additive.

MIP Chemical Response Testing

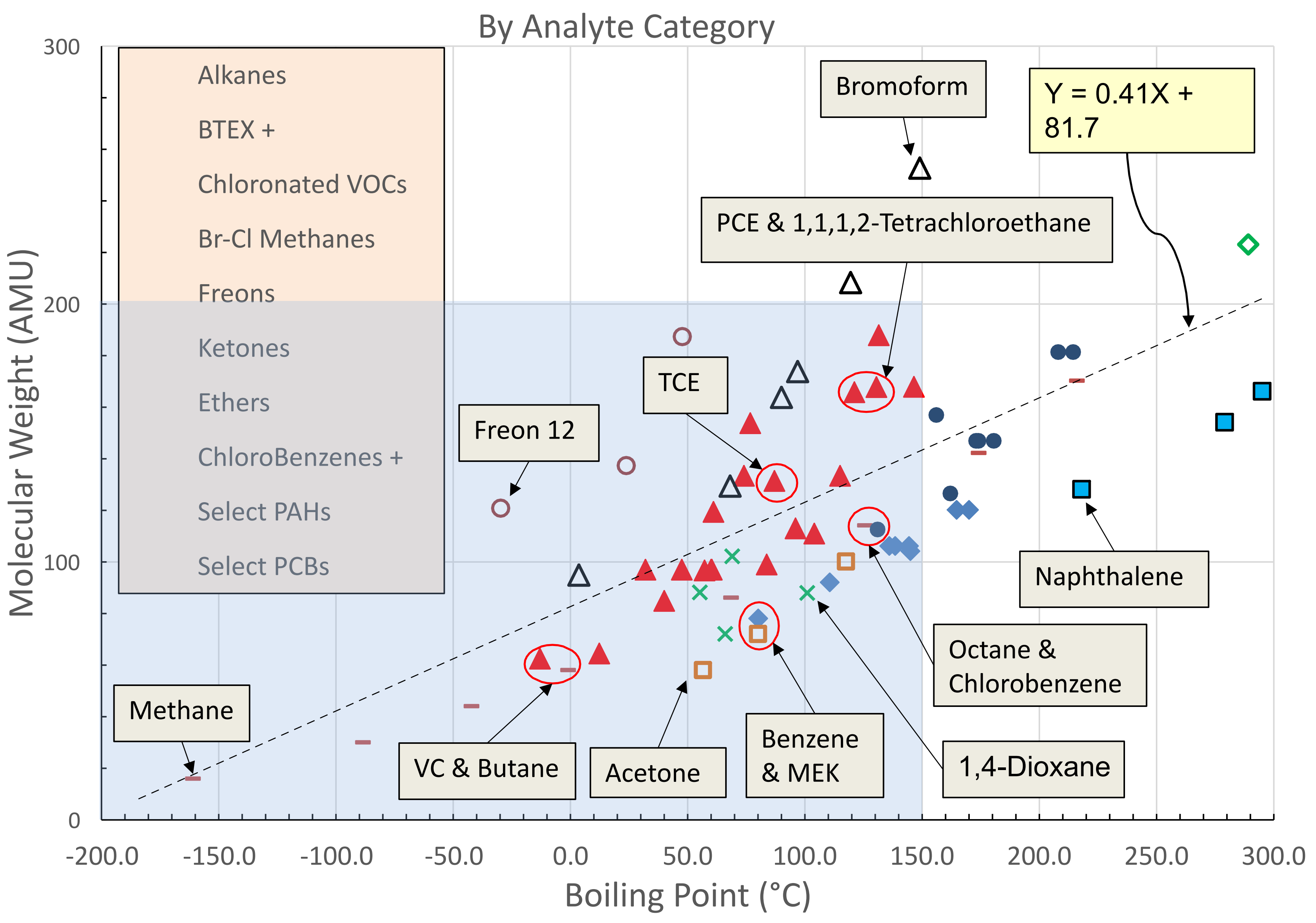


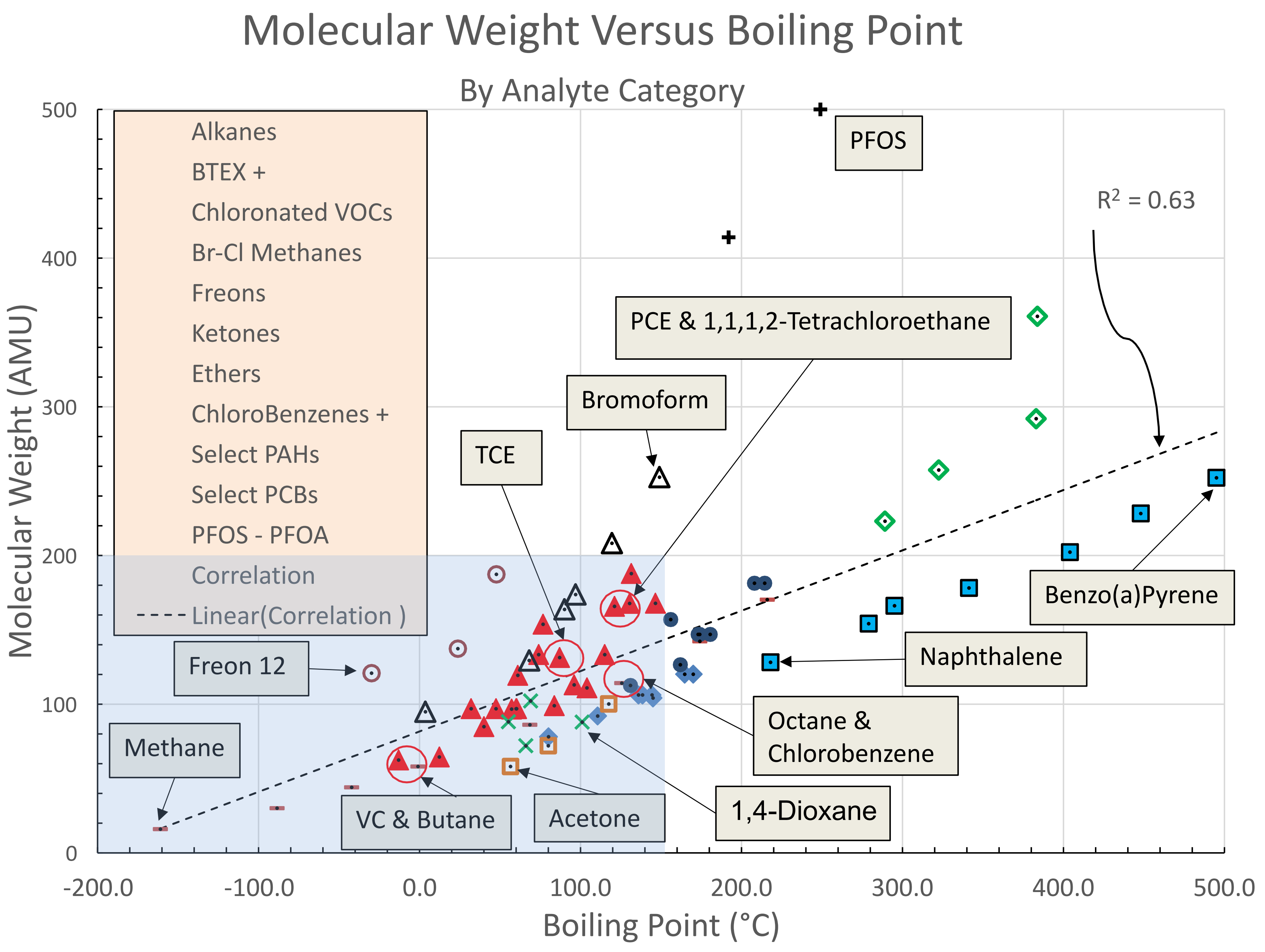
Mixtures of halogenated and non-halogenated VOCs occur at some facilities.

Individual response tests with benzene (d) and carbon tetrachloride (e) are presented beside a response test where benzene and carbon tetrachloride were combined for analysis (f). In this case the carbon tetrachloride suppressed the benzene response on the PID.

The XSD baseline is adjusted lower for easy comparison in each graph. The FID response is multiplied by 10 for better visibility in each graph.

Molecular Weight Versus Boiling Point





Molecular Weight Versus Boiling Point
By Analyte Category
Alkanes
BTEX +
Chloronated VOCs
Br-Cl Methanes
Freons
Ketones
Ethers
ChloroBenzenes +
Select PAHs
Select PCBs
PFOS - PFOA
Correlation
Linear(Correlation)
PFOS
R^2 = 0.63
PCE & 1,1,1,2-Tetrachloroethane
Bromoform
TCE
Freon 12
Methane
VC & Butane
Acetone
1,4-Dioxane
Octane &
Chlorobenzene
Naphthalene
Benzo(a)Pyrene
Molecular Weight (AMU)
Boiling Point (°C)
500
400
300
200
100
0
-200.0
-100.0
0.0
100.0
200.0
300.0
400.0
500.0

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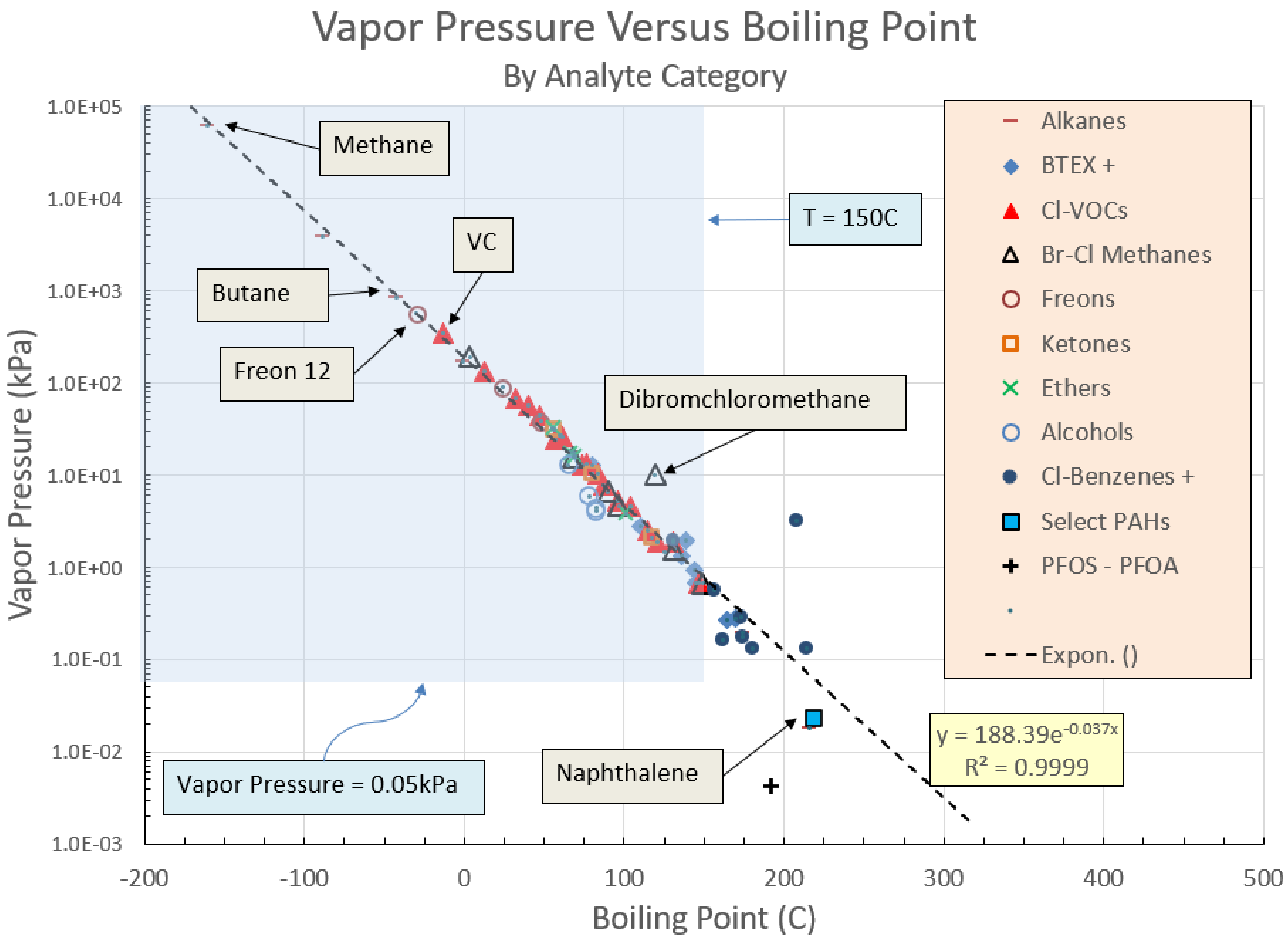
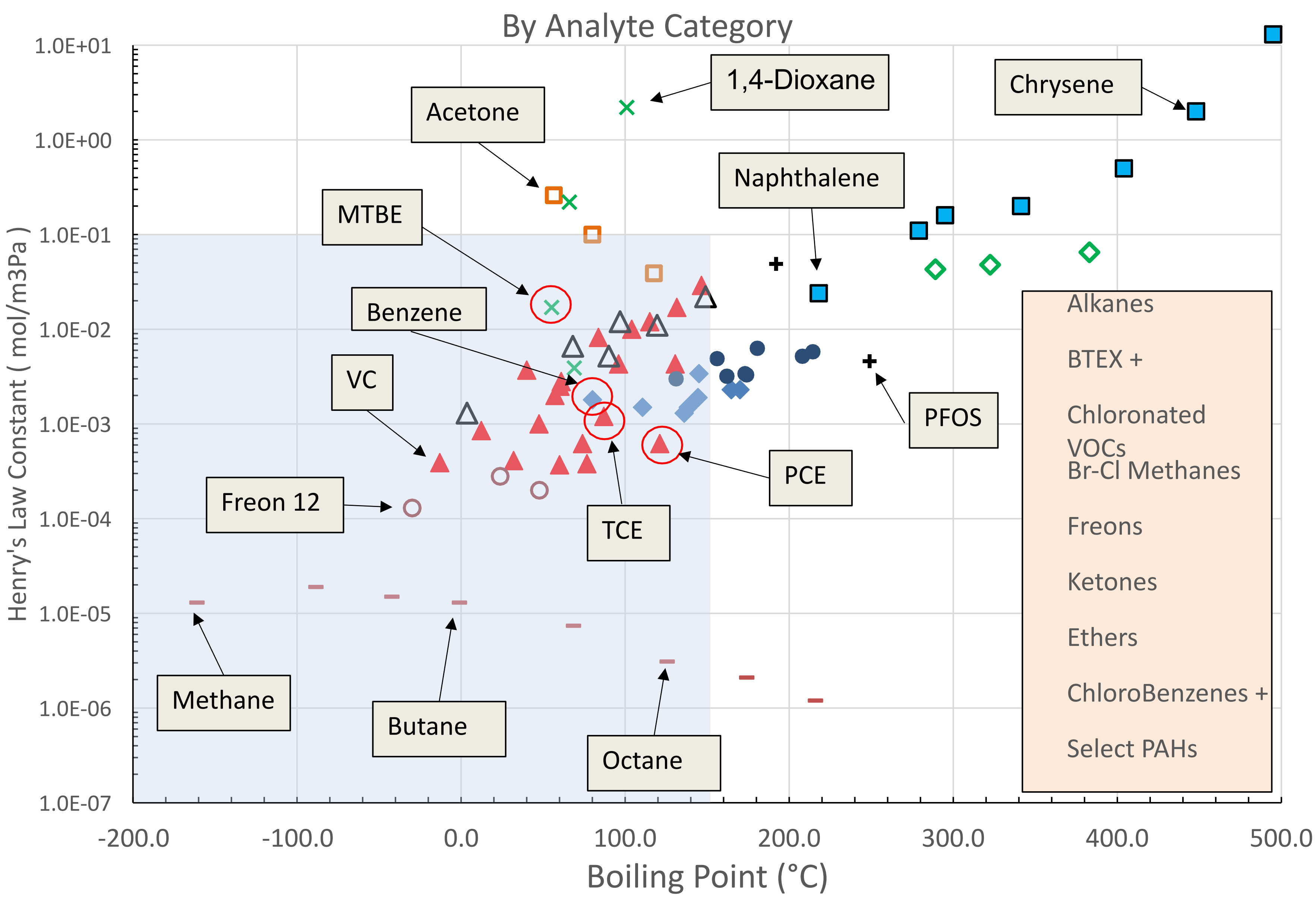

Vapor Pressure Versus Boiling Point
By Analyte Category
Vapor Pressure (kPa)
Boiling Point (C)
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
1.0E-01
1.0E-02
1.0E-03
-200
-100
0
100
200
300
400
500
Methane
VC
Butane
Freon 12
T = 150C
Dibromchloromethane
Vapor Pressure = 0.05kPa
Naphthalene
y = 188.39e^-0.037x
R² = 0.9999
Alkanes
BTEX +
Cl-VOCs
Br-Cl Methanes
Freons
Ketones
Ethers
Alcohols
Cl-Benzenes +
Select PAHs
PFOS - PFOA
Expon. ()

Henry's Law Constant Versus Boiling Point



Membrane Interface Probe

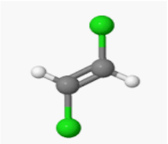
Not all gas phase detectors are created equal

XSD vs ECD

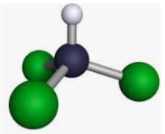
XSD provides a consistent response to varying chlorinated compounds

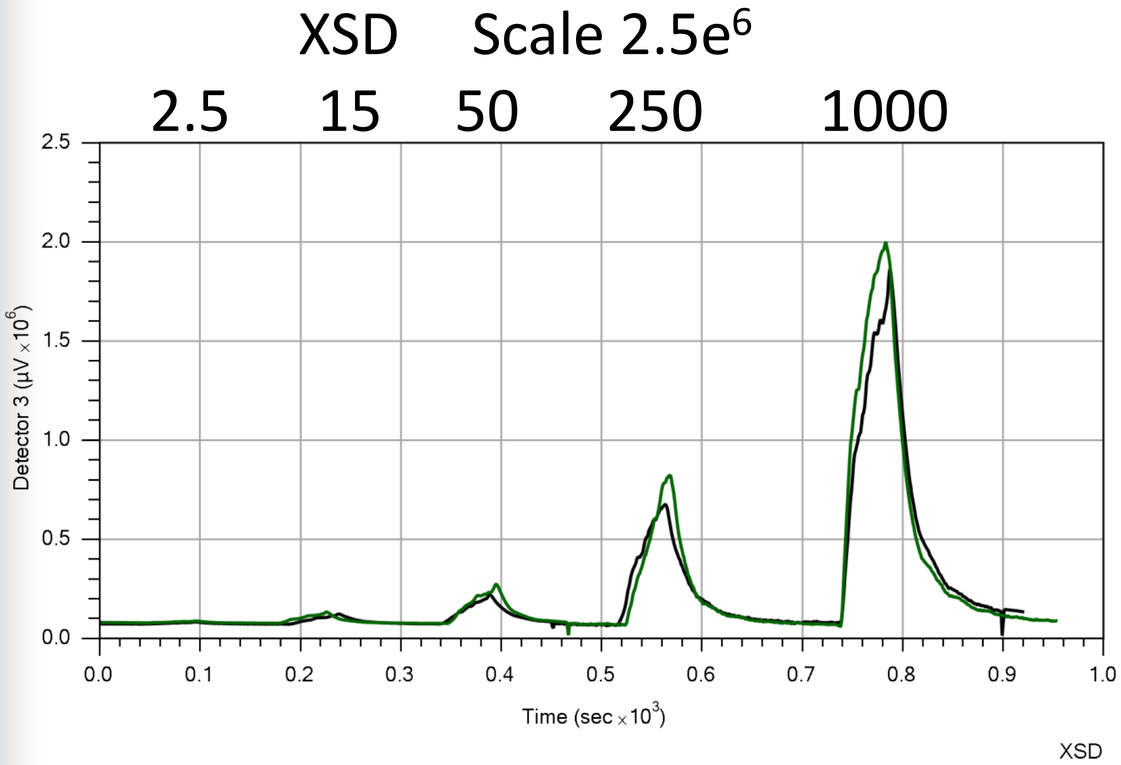
ECD responds to chemical electronegativity.
Influence greatly by # of chlorines on the molecule as well as chemical structure.
Huge range of response for compound structure ranging from 1 to 4 Chlorine.

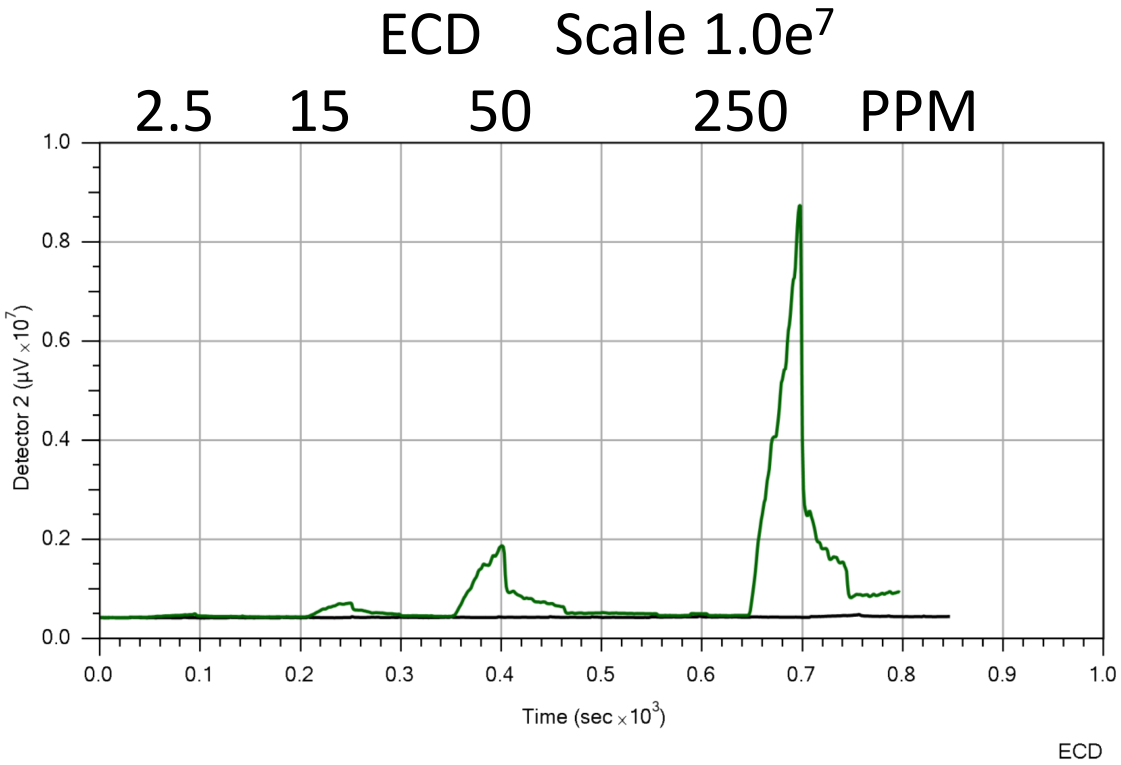
Membrane Interface Probe – XSD-ECD Comparison



cis-1,2-DCE & Chloroform







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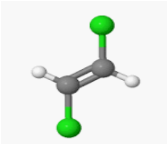
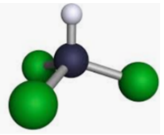
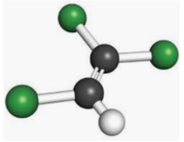
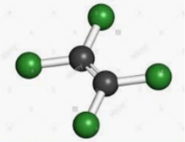
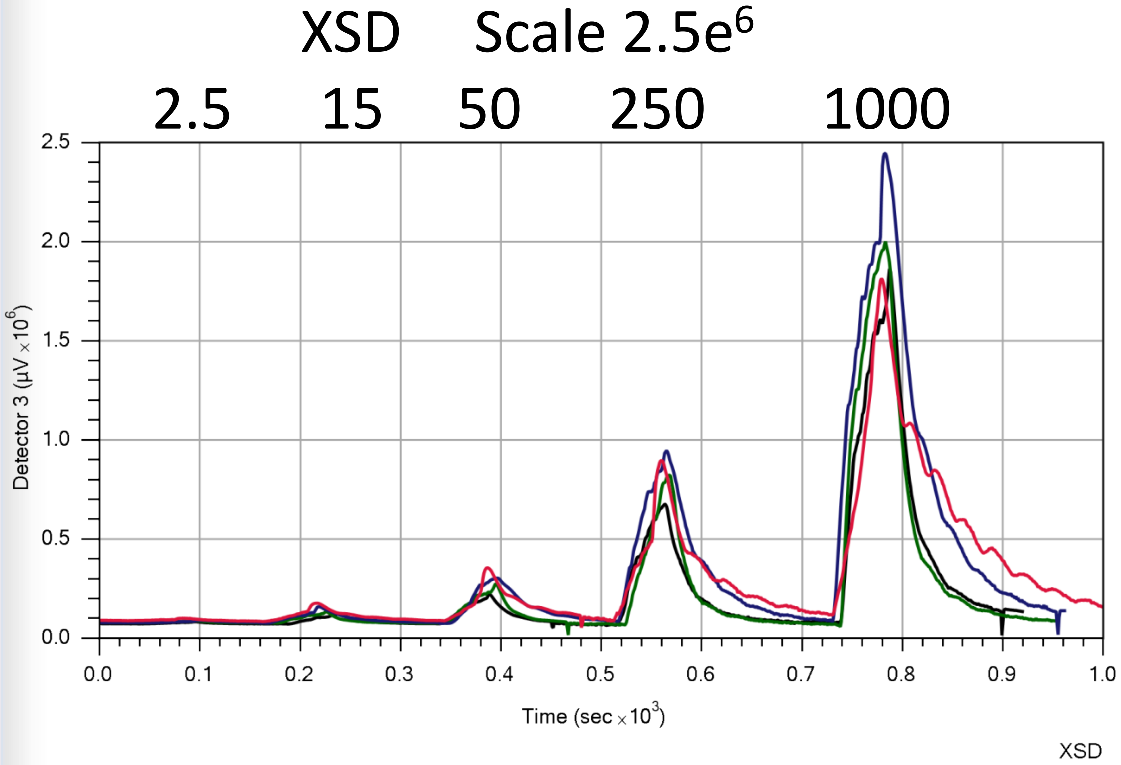
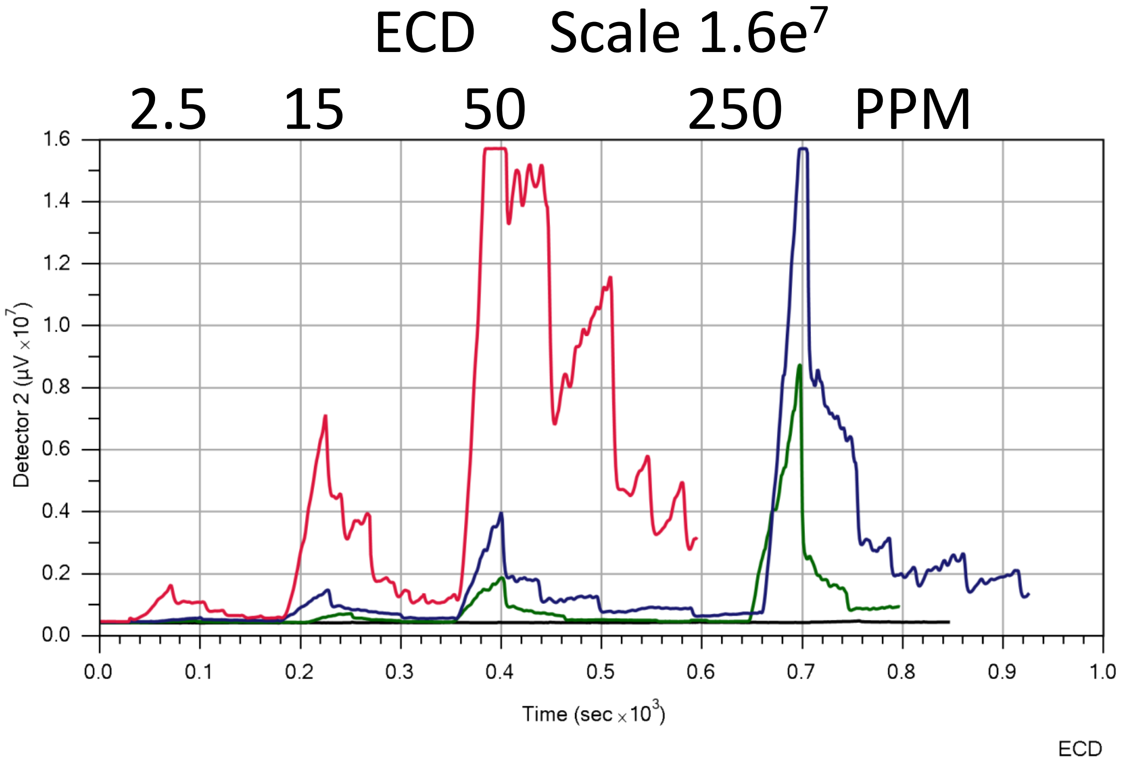


cis-1,2-DCE, Chloroform, TCE, PCE







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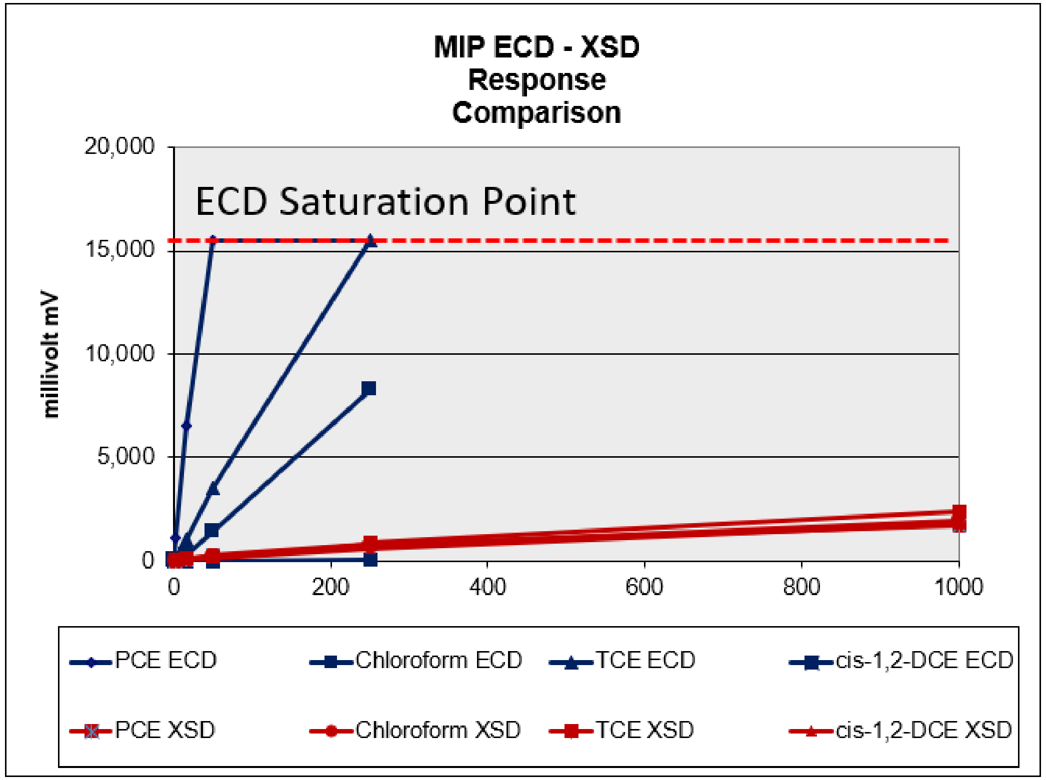
Membrane Interface Probe – XSD-ECD Comparison

cis-1,2-DCE, Chloroform, TCE, PCE



Summary

MIP analyte detection and detection limits depends upon

- Analyte chemical and physical properties
  Staying within the HLC-BP parameters

- System is outfitted with proper gas phase detectors for analytes of interest
- Comingled plumes – chemical interactions can influence response
- Wear and maintenance of detectors
- MIP Trunkline system pressures
- History of equipment

Questions?

Geoprobe Systems
1835 Wall St.
Salina, KS 67401
785-825-1842