

What You Always Wanted to Know About EMPC but were Afraid to Ask

Fundamentals of Method 23

Ray Merrill

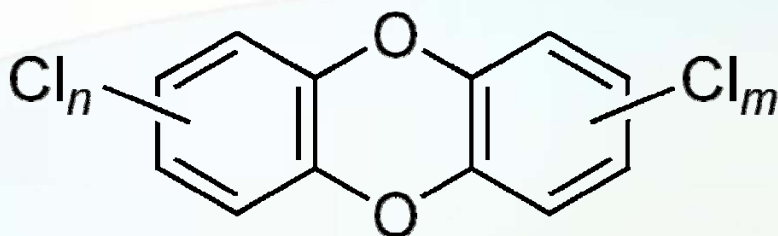
merrill.raymond@epa.gov



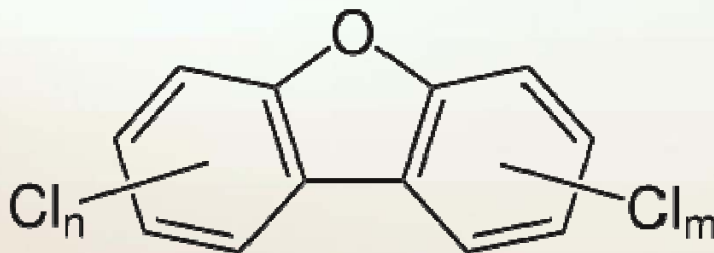
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Measurement Technology Group
Emission Measurement Center

Dioxin, Furan, PCDE Background

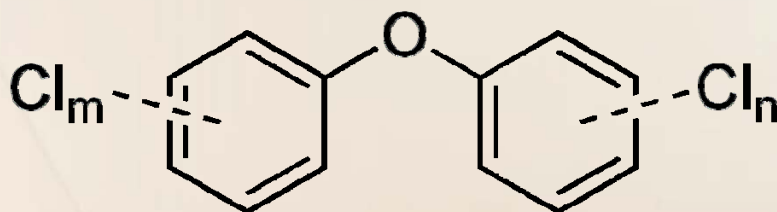
Compound Structures



Chlorinated dibenz(p)dioxin



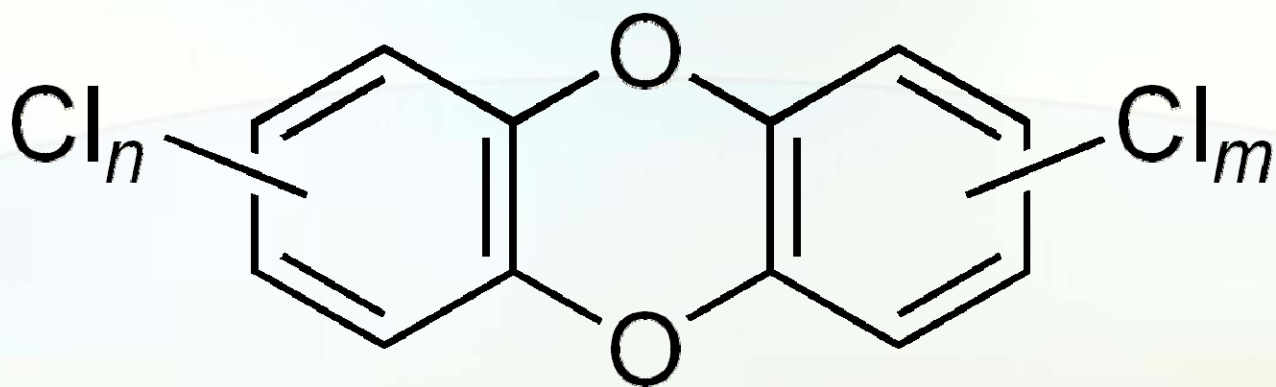
Chlorinated dibenzofuran



Chlorinated diphenyl ether



Polychlorinated dibenzo(p)Dioxin



12 carbon atoms (~12 amu)

2 oxygen atoms (~32 amu)

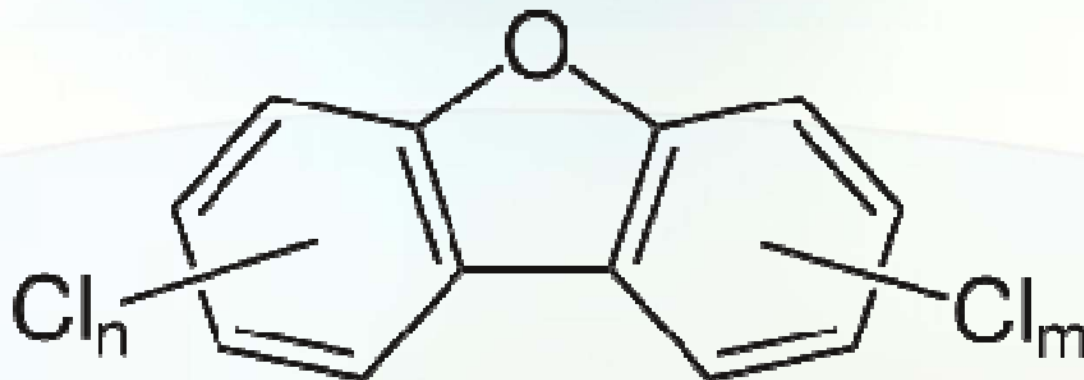
Up to 8 positions where chlorine atoms can be substituted

Base mass with no chlorine = 184 amu

Multiple chlorine atoms add mass in increments of ~35 or 37 amu



Polychlorinated dibenzofuran



12 carbon atoms (~12 amu)

1 oxygen atoms (~16 amu)

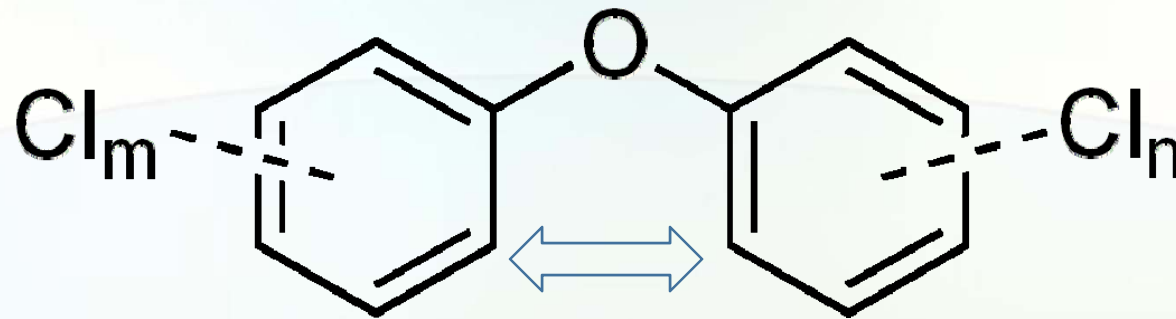
Up to 8 positions where chlorine atoms can be substituted

Base mass with no chlorine = ~168 amu

Multiple chlorine atoms add mass in increments of ~35 or 37 amu



Polychlorinated diphenyl ether



12 carbon atoms (~12 amu)

1 oxygen atoms (~16 amu)

Base mass with no chlorine = ~170 amu

Up to 10 positions where chlorine atoms can be substituted
(two more positions than Dioxins or Furans)

Multiple chlorine atoms add mass in increments of ~35 or 37 amu

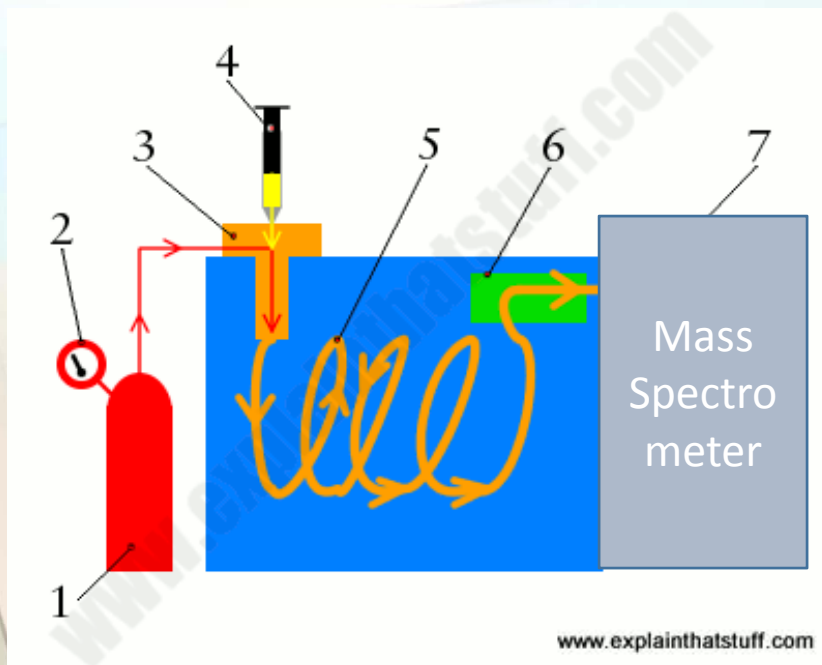


Method 23 Basics

- Sample Acquisition
(Sorbent Sampling Train)
- Target Compound Recovery
(Extraction of Filter + Sorbent)
- Target Compound Separation and Cleanup
(Liquid Chromatography of Extract)
- Target Compound Separation
(High Resolution Gas Chromatography)
- Identify and Quantify Compounds
(High Resolution Mass Spectrometry)



How does gas chromatography work?

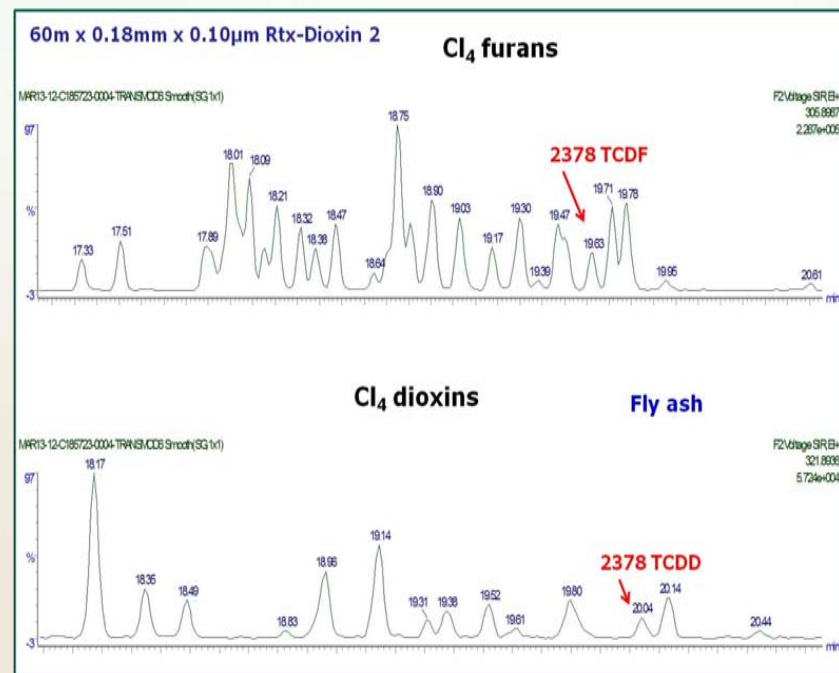


1. The carrier gas (**red**) transports the sample to the separation column.
2. The rate of flow of the carrier gas is controlled to give the separation of the components in the sample.
3. The carrier gas enters the GC through an inlet.
4. The sample is injected into the carrier gas and vaporizes.
5. The gaseous sample separates out as it moves along the column (**orange**). The temperature of the oven is be carefully controlled.
6. The sample components enter a detector that senses the time and quantity of material
7. The detector signal is recorded

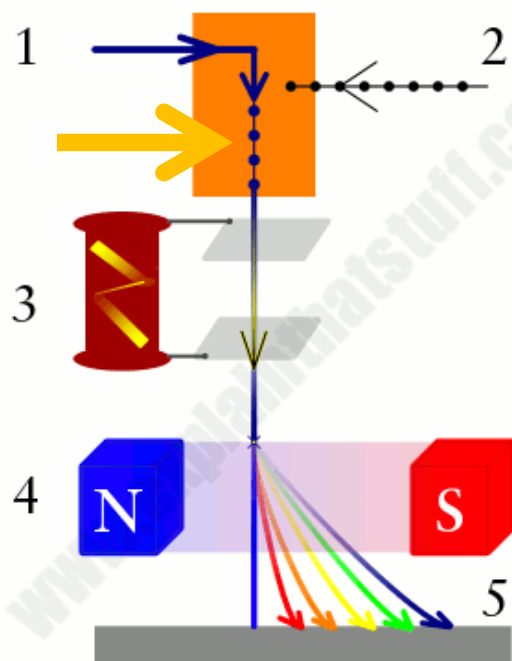


GC Identification Criteria for Target Compounds

- Compounds emerge from the GC column roughly based on their volatility.
- Identification by retention time requires:
 - Comparison to isotopically-labeled standard if present or
 - Comparison to relative retention time of calibration standards or
 - Comparison to the corresponding homologous compound retention time windows.



How does a mass spectrometer work?



www.explainthatstuff.com

1. Sample components enter a vacuum chamber in the order they emerge from the GC.

2. The components are bombarded with electrons turning them into characteristic mass fragments of the compounds (ions).

3. The ions are accelerated and

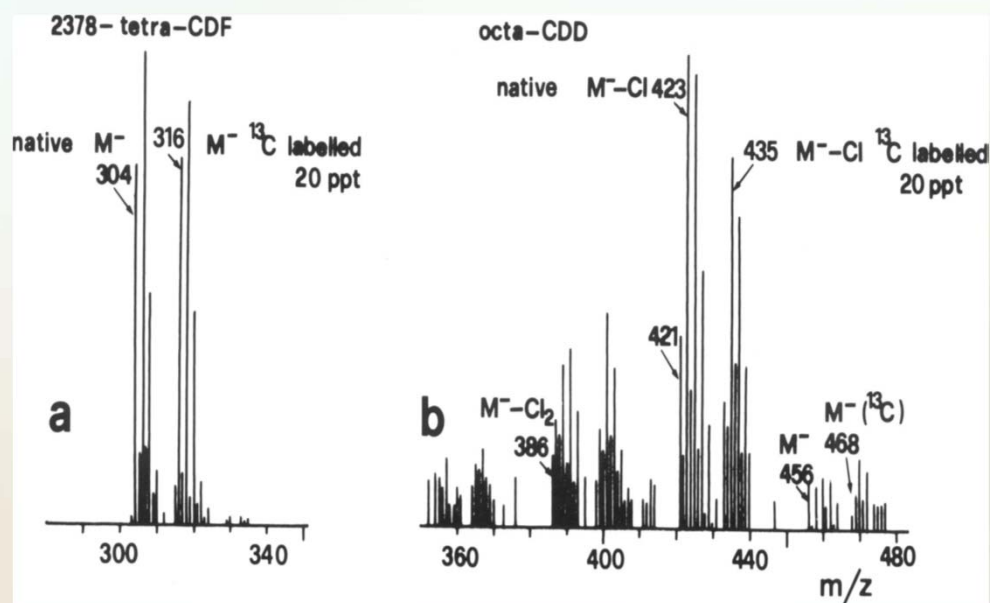
4. Separated according to the amount of charge and mass they have.

5. The ions are detected and the fragments (amount and mass) are recorded.



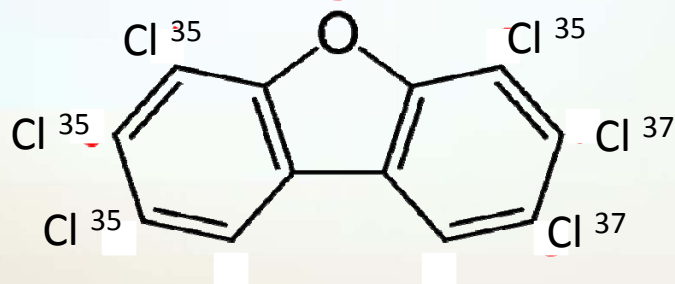
MS Identification Criteria for Target Compounds

- Mass fragment patterns (like a fingerprint) are related to the strength that holds the atoms together.
- Qualitative Identification requires
 - Characteristic Ions (2) must maximize simultaneously
 - Characteristic ion quantity (ratio of 2) must meet method specifications
 - Signal to noise ratio for ions must be ≥ 2.5
 - Polychlorinated diphenyl ether (PCDE) interference mass must be absent

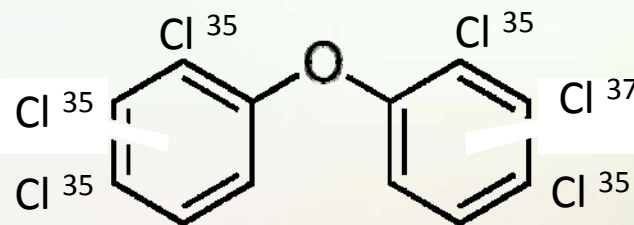


PCBE Interference Example

4-Cl³⁵, 2-Cl³⁷ Hexachlorodibenzofuran and 5-Cl³⁵, Cl³⁷ Hexachlorodiphenyl ether



C₁₂H₂³⁵Cl₄³⁷Cl₂O (HxCDFE Mass 375.82)



C₁₂H₄³⁵Cl₅³⁷ClO (HxCDE Mass 375.84)



EMPC Definition

- SW-846 Method 8290
 - An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that
 - Are above detection limit ($S/N \geq 2.5$ for both the quantitation ions) and
 - meet all of the identification criteria in the method except the ion abundance ratio criteria or when a peak representing a PCDDPE has been detected.
- An EMPC is a worst-case estimate of the concentration.
- Method 23 makes no mention of EMPC



Practical Summary of EMPC Causes and Remedies

- ***Interferences (e.g., chlorinated diphenyl ethers)***

- Typical Cause – Inadequate sample cleanup after extraction
- Potential Remedy - reprocess archive and reanalyze or retest

- ***Mass Spectrometer Setup (e.g., ion ratios)***

- Typical Cause – Incorrect or drifting instrument tuning
- Potential Remedy – Maintenance, retune, recalibrate, reprocess archive and reanalyze or retest

- ***Detection limitations***

- Typical Cause - Insufficient sample size
- Potential Remedy -- Retest collecting additional sample (more stack gas/DSCM)
- Or decide detection limit is low enough and report as zero per the method.



Summary

Dealing with EMPC Issues

- Method 23 does not address EMCP
 - We recommend requiring sources to report EMPC (according to SW-846 Method 8290).
 - We recommend including EMPC in emissions calculations.
- If EMPC results in emission non-compliance, then facilities and testers should pursue potential remedies or retest.



Questions?



Office of Air Quality Planning and Standards
Air Quality Assessment Division
Measurement Technology Group
Emission Measurement Center