Leveraging Cl-H Mass Defect Plots for the Identification of Halogenated Organic Contaminants

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Introduction

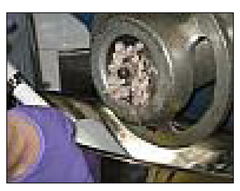
- Time-of-flight mass spectrometry (TOFMS) is unsurpassed for non-target analysis because full range mass spectra are acquired simultaneously with minimal mass bias at acquisition rates suitable for narrow gas chromatographic peaks. This provides a number of advantages, including the possibility of deconvolving chromatographic interferences using modern software, further enhancing the ability to isolate and identify a greater number of compounds.
- Mass defect is the difference between the nominal and exact masses of a compound or its fragments[1].
- Halogenated compounds have characteristic mass defects and isotope patterns that make them readily distinguishable from most other compound classes[2,3].
- Mass defect (Cl-H) can be calculated according to the following equations, where the IUPAC mass is the observed mass and the scaling factor for chlorine substituted for hydrogen equals 34/33.960479:

Cl-H Scaled Mass = IUPAC Mass × Scaling Factor

Cl-H Mass Defect = Cl-H Scaled Mass – Nominal Cl-H Scaled Mass

In this study we used non-target analysis in the form of Cl-H mass defect plots, to identify halogenated contaminants in eels (*Anguillia rostrata*) from Lake Ontario, Canada.

Methods



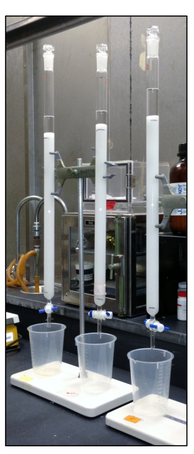
Homogenization

Extraction

Methylene chloride (DCM)

Clean-up

1:1 DCM:Hexane (v/v)
Gel Permeation Chromatography



Analysis

LECO Pegasus® GC-HRT

- A total of 10 large freshwater eels were collected from eastern Lake Ontario, Canada in 2008.
- Sample extracts were pooled for instrumental analysis on a LECO Pegasus GC-HRT, high resolution TOFMS.
- Extracts were injected (1 µL) using an Agilent 7693 autosampler attached to a 7890 GC fitted with a multi-mode inlet operated in solvent vent mode.
- A Restek Rxi-guard column (5 m x 0.25 mm) with a Rxi-5MS (30 m x 0.25 mm x 0.25 µm) was used for chromatographic separation.
- The oven program was initially 90°C (held for 2.4 min) then ramped to 320°C at 8.5°C/min (held for 15 min).
- The HRT was operated in EI mode with filament energy of 36 eV, a mass range from m/z 35 to 850, and an acquisition rate of 6 spectra/s.
- Data were processed using ChromaTOF-HRT® software, which included peak finding with mass spectral deconvolution.

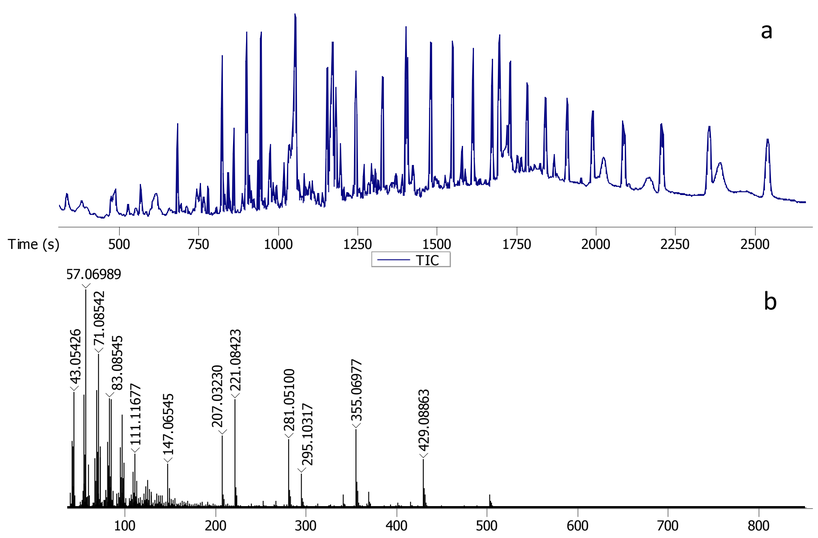


Figure 1: (a) Total ion chromatogram and (b) combined mass spectrum of a pooled eel sample from Lake Ontario, Canada. The combined mass spectrum was generated by expanding the caliper over the entire chromatographic run, which was dominated by ions corresponding to siloxanes and hydrocarbons. More than 900 peaks were identified using high resolution deconvolution in the ChromaTOF-HRT software.

Results

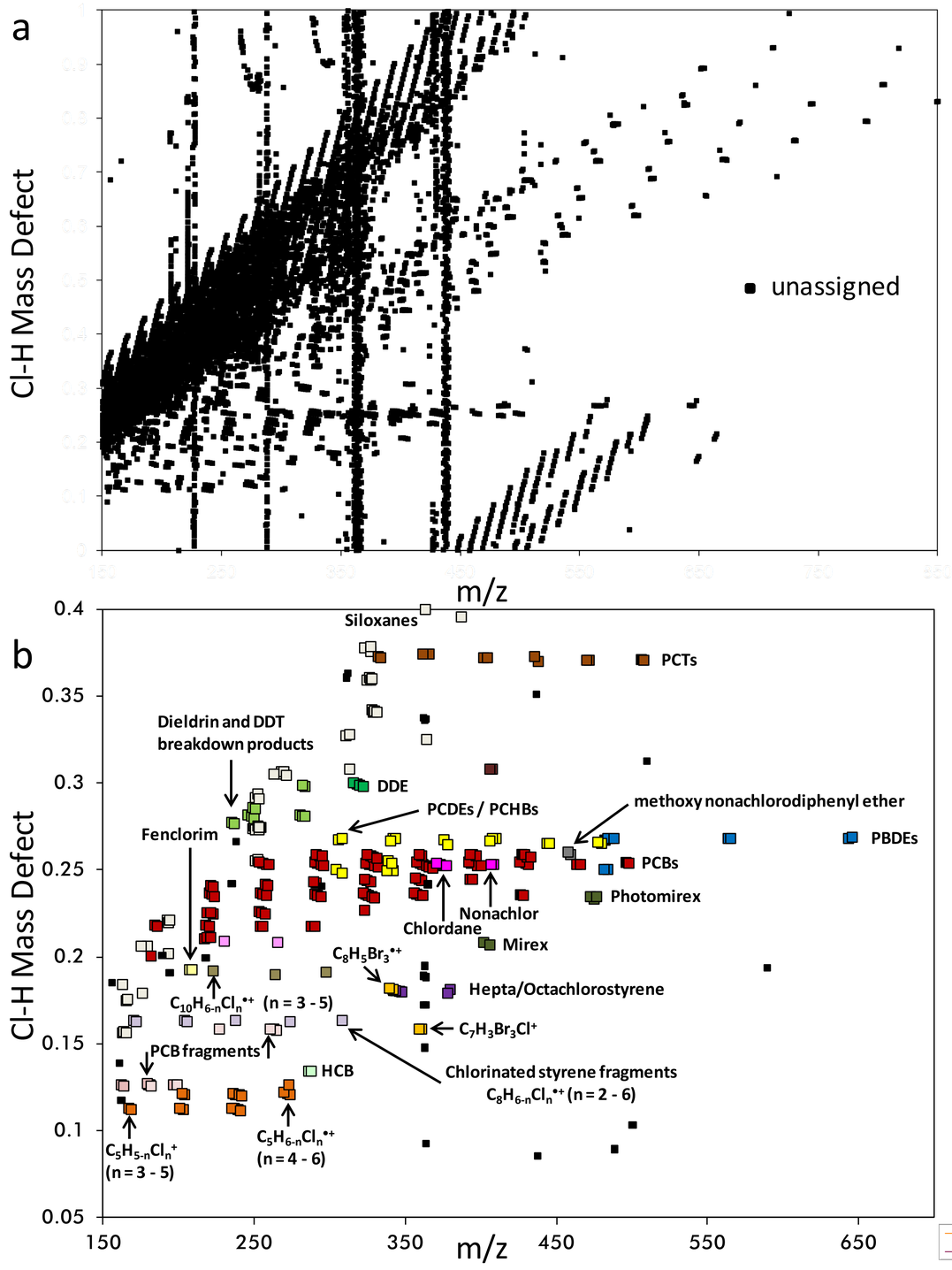


Figure 2: (a) Cl-H mass defect plot of the raw mass spectral data for a pooled Lake Ontario eel sample. (b) A zoomed-in view of the Cl-H mass defect plot highlighting the region containing halogenated species. The colored points represent m/z values with elemental compositions including Cl and/or Br calculated with a mass accuracy <2 ppm. The masses displayed in *b* were filtered from *a* by mass defect, and also required at least two masses to occur within 1.9965 ±0.0005 Da or 1.9974 ±0.0005 Da, corresponding to the mass difference between ^{37}Cl -^{35}Cl and ^{81}Br -^{79}Br, respectively.

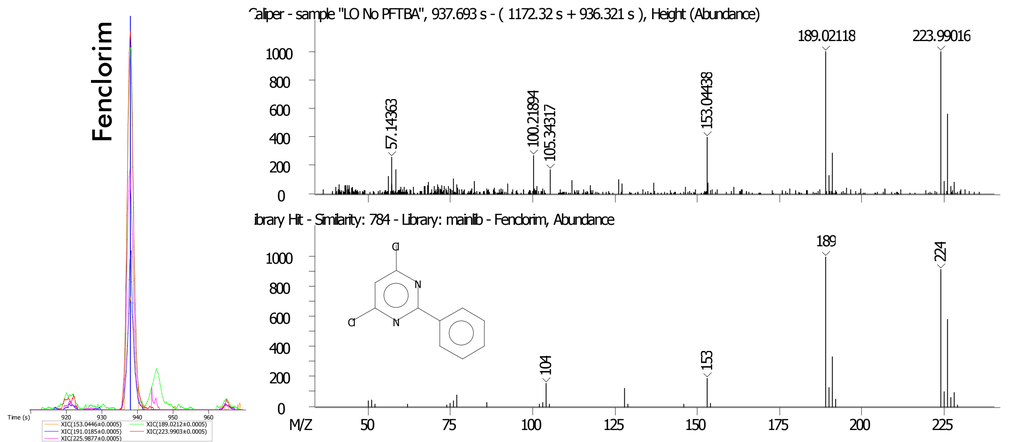


Figure 3: Extracted ion chromatograms, mass spectrum, and library spectrum of fenclorim, a herbicide safener used to protect crops against damage caused by pretilachlor. It is typically used on rice, so its occurrence in Lake Ontario fish was unexpected.

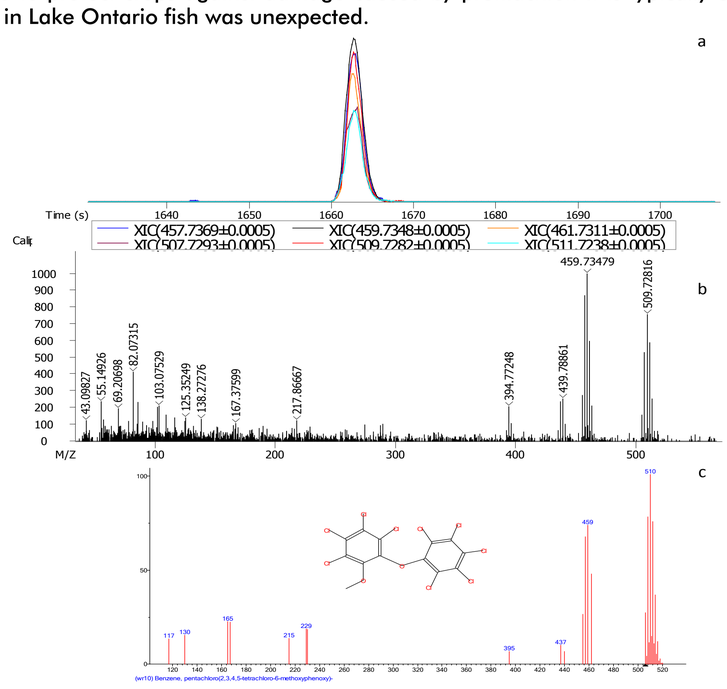


Figure 4: (a) Extracted ion chromatograms (XIC) for the six most abundant ions, as well as (b) the mass spectrum of a peak discovered from points on the mass defect plot, and (c) Wiley 10 library mass spectrum of 6-methoxy-nonachlorodiphenyl ether. The accurate mass data and the library hit suggest that the unknown compound is a methoxynonachlorodiphenyl ether.

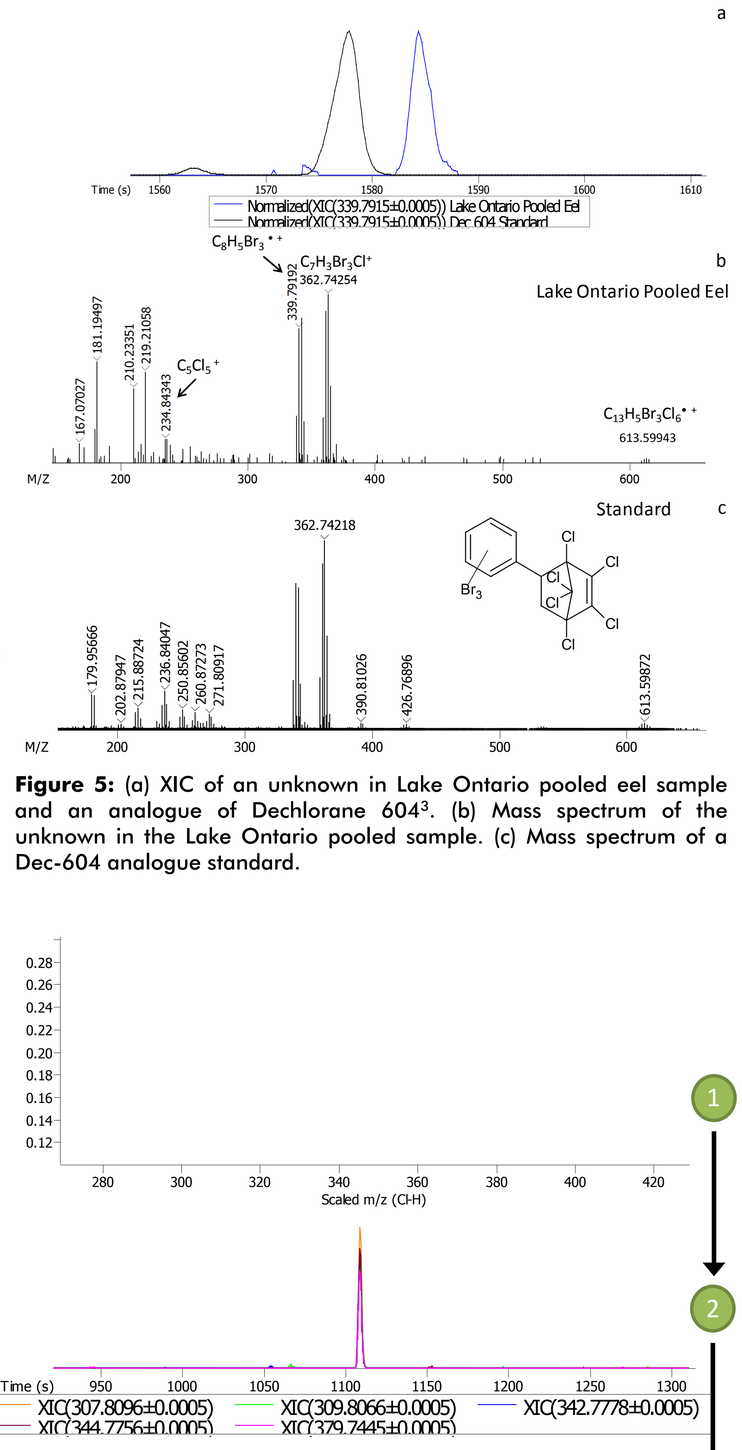
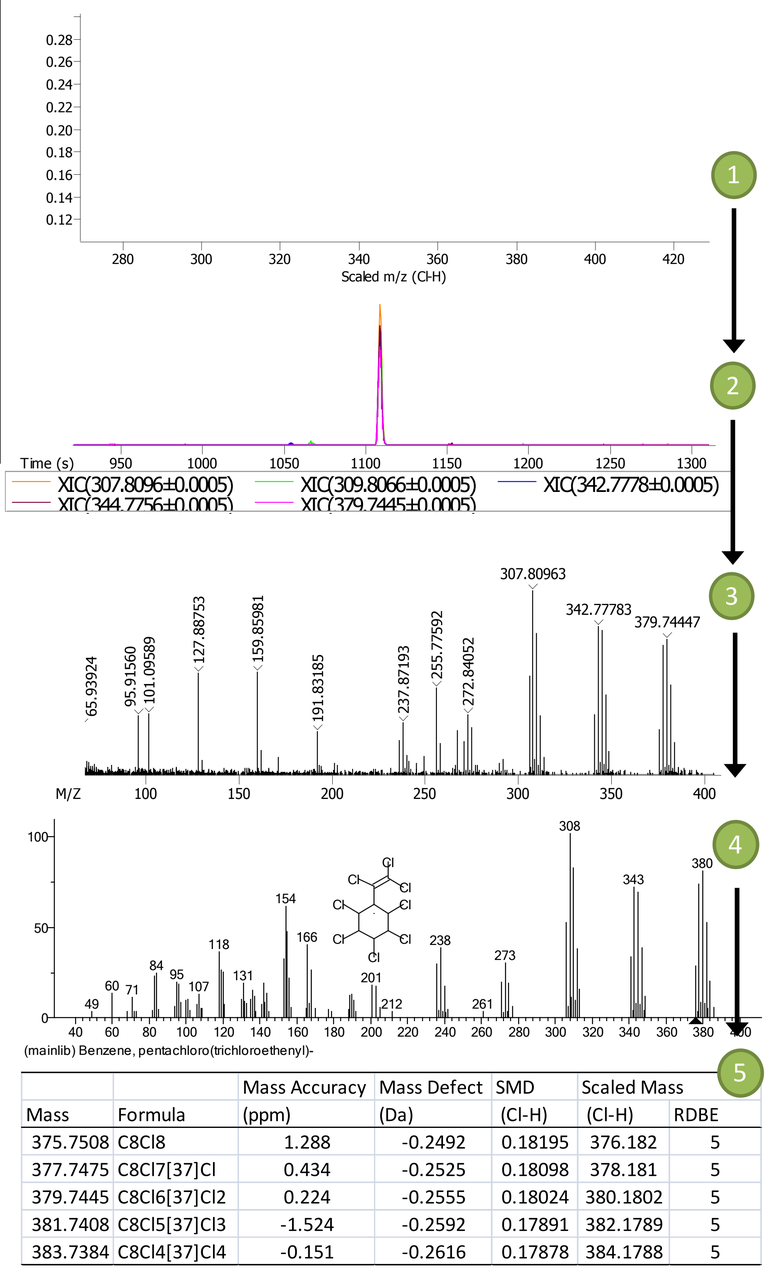


Figure 5: (a) XIC of an unknown in Lake Ontario pooled eel sample and an analogue of Dechlorane 604[3]. (b) Mass spectrum of the unknown in the Lake Ontario pooled sample. (c) Mass spectrum of a Dec-604 analogue standard.



		Mass Accuracy	Mass Defect	SMD	Scaled Mass	
Mass	Formula	(ppm)	(Da)	(Cl-H)	(Cl-H)	RDBE
375.7508	C8Cl8	1.288	-0.2492	0.18195	376.182	5
377.7475	C8Cl7[37]Cl	0.434	-0.2525	0.18098	378.181	5
379.7445	C8Cl6[37]Cl2	0.224	-0.2555	0.18024	380.1802	5
381.7408	C8Cl5[37]Cl3	-1.524	-0.2592	0.17891	382.1789	5
383.7384	C8Cl4[37]Cl4	-0.151	-0.2616	0.17878	384.1788	5

Figure 6: Workflow for the identification of compounds using Cl-H mass defect plot. (1) Select and display masses of interest on chromatogram; (2) select peak; (3) deconvoluted mass spectrum; (4) compare to NIST or other library database; (5) verify correct chemical formula with accurate mass data.

Conclusions

- A number of legacy contaminants such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated diphenyl ethers (PCDEs), dieldrin, mirex, hexachlorobenzene (HCB) and other pesticides, as well as a number of previously unknown compounds were tentively identified in the pooled sample.
- Many breakdown products and metabolites were also detected such as DDD, DDE, and methoxy nonachlorodiphenyl ether.
- Cl-H mass defect plots are a useful tool for filtering through complex data for the identification of halogenated contaminants.
- This technique functions as a screening tool for the identification of unknowns, and in the future, may be used as a form of fingerprinting to compare samples.

References

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