Non-Targeted Screening of Halogenated Organics In Wastewater

SEARCHING FOR THE MISSING LINK IN TOTAL ORGANIC HALIDE (TOX) RESULTS FROM SAMPLES TAKEN AT THE STRINGFELLOW, CA SUPERFUND SITE

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Outline

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- Problem – A commercial lab experience from October 2015
- Gaps/Limitations
- Project Goals
- Data Acquisition/Processing Approach
- Data Presentation
- Conclusions/Summary
- Supplementary Figures

Problem

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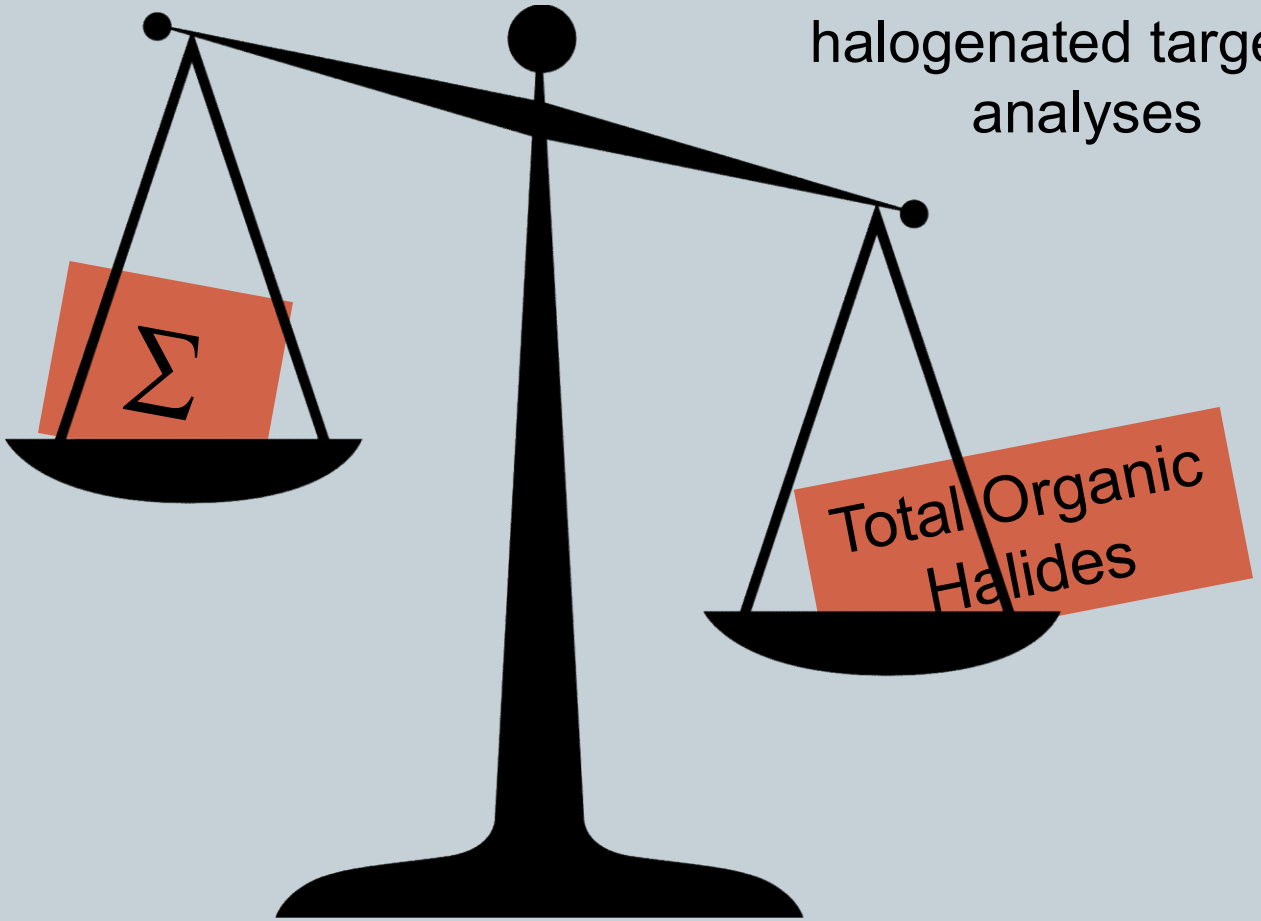
TOX >> Sum of all halogenated targeted analyses



Initial Approach

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- Let's Take a Look – Run samples full scan on a triple quad

Gaps/Limitations

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- Quantitation conundrum – ESI response dependent on:
  - ESI desolvation/temps
  - LC mobile phase and flow rate
  - Analyte functional groups (PA and GPB)
- Identity conundrum – All unknowns still putative/tentative and may have more than one identity.

Gaps/Limitations

- Isobaric interference - hundreds/thousands of candidates; limit scope to halogenated
- Liquid Chromatography matters more - coelution=ion suppression; run in RP (Biphenyl) and mixed mode anion exchange
- Convoluted data - both during acquisition and data processing
- Special case - not applicable for all types of samples/analytes

Project Goals

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- Tentatively detect, identify, and quantify highly polar unknown halogenated organics in an aqueous matrix; specifically Br and Cl.
- Highly Polar: ionic at practical pH levels (2-14).
- Use direct injection with multiple LC-MS scan modes; full scan, product scan, precursor scan, neutral loss as appropriate.

Approach: Data Acquisition

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Full scan ESI +/−
(0.2m/z FWHM)

Molecular Ion

Peak Picking, Adducts

Product Scan

237.8 > 50–800

Precursor Scan[1]
(SO_3 80)

Neutral Loss[6]
(SO_2 64)

Approach: Data Processing

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- Export Data, and partition mz ranges
- Feature (peak) detection - detecting characteristic halogen isotopic clusters specifically
- Deconvolute adducts – agglomeration of clusters. Associate isotopic clusters to a chemical; at minimum know # of Cl,Br for TOX calculation
- "Whole Mass" Quantitation – All ions associated with a target in full scan were summed and compared to p-CBSA already present.

Approach: Data Processing Tools

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- ReAdW.exe exports ThermoSci raw data files to mzXML
- Raw data imported as ASCII into Matlab, Scilab, and R.
- R has packages available for HR-MS peak picking, agglomeration, etc. Mostly from metabolomics field but some environmental focused packages. (EnviPick, Martin Loos)

Data (full-scan)

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...Not too interesting

Data (full-scan)

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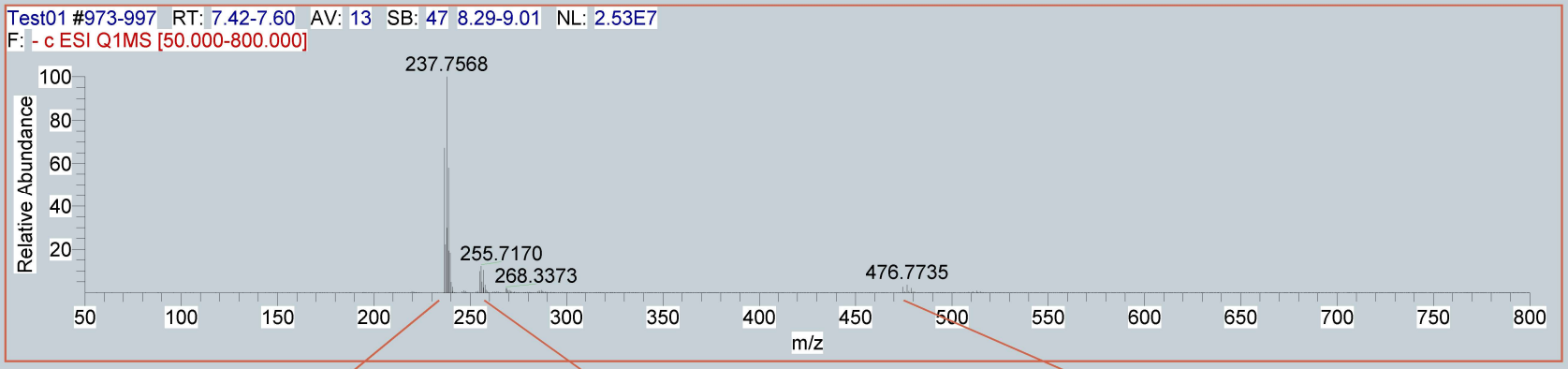

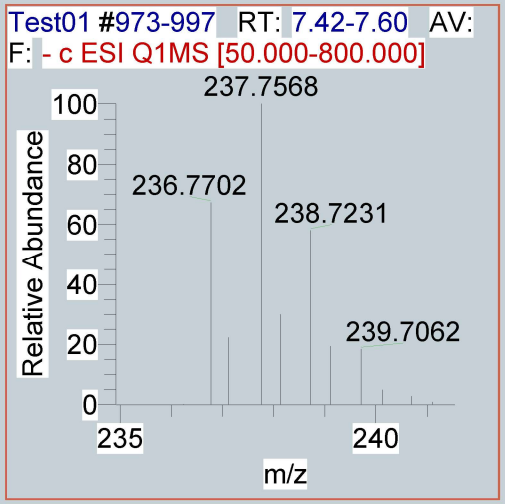

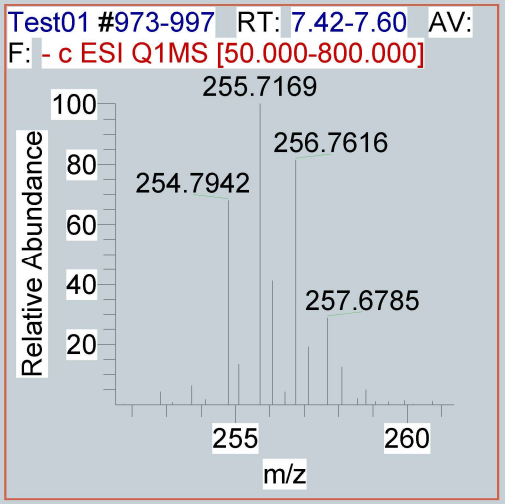

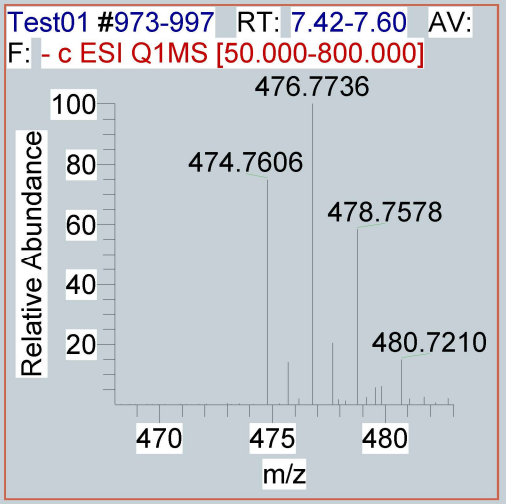

$[M-2H]^{2-}$ $[M+2H_2O-2H]^{2-}$ $[M-H]^{1-}$

Data (full-scan)

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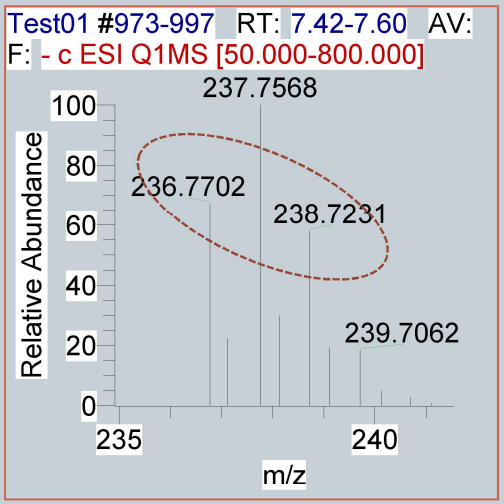
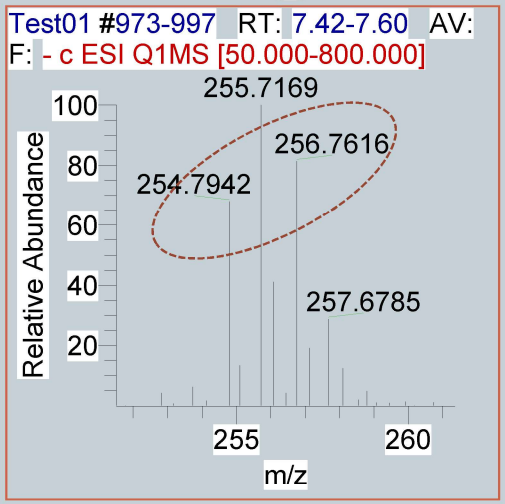
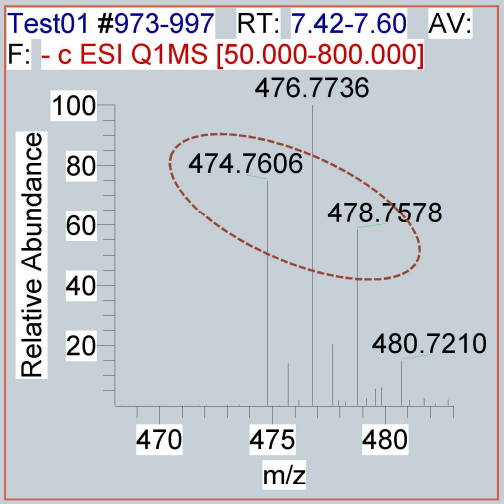
Sample

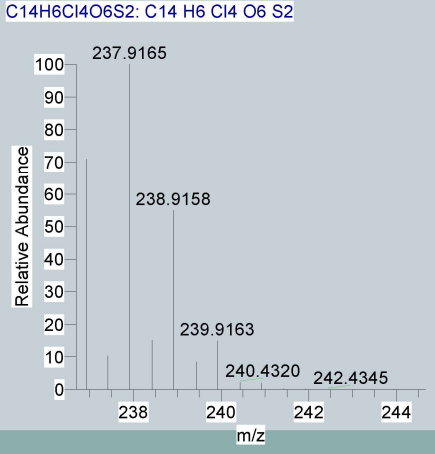


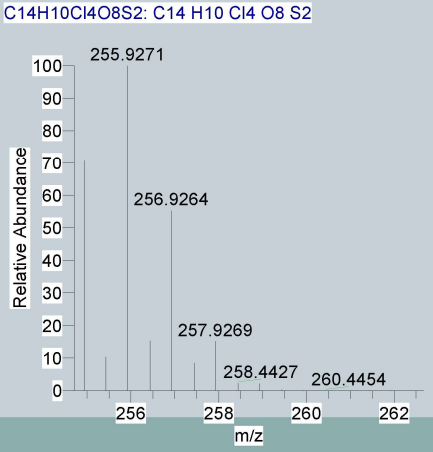


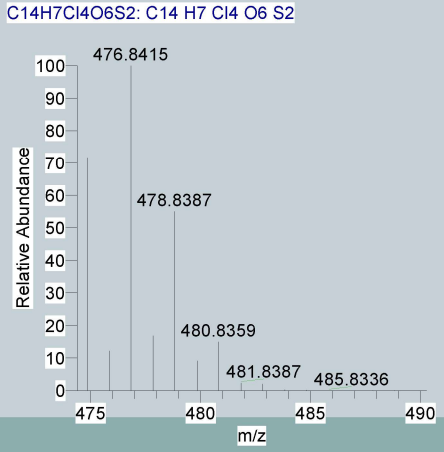


$[M-2H]^{2-}$ | ?? $[M+2H_2O-2H]^{2-}$ | $[M-H]^{1-}$

Reference







Data (full-scan)

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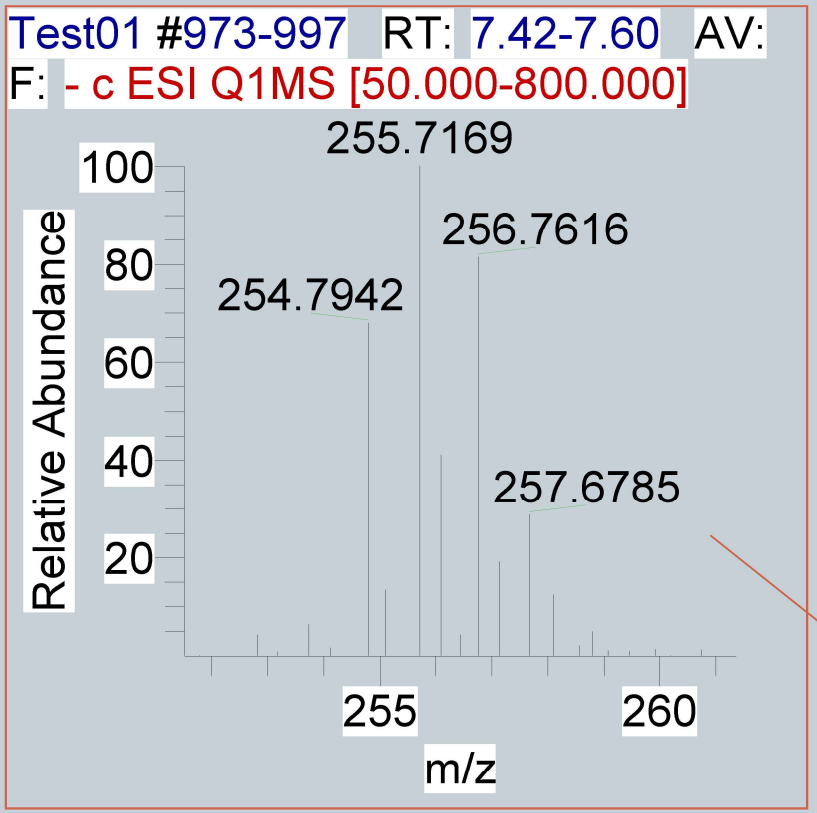
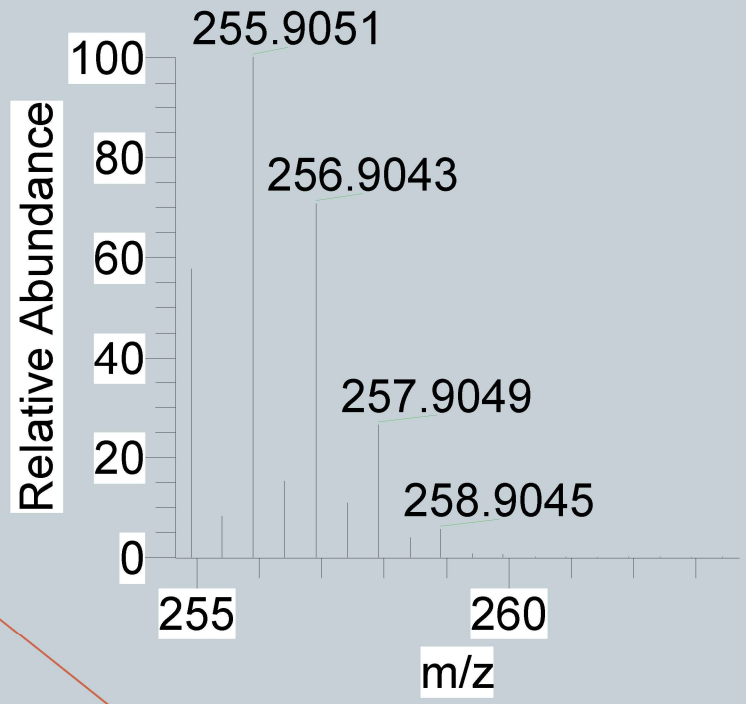


5 chlorine isocluster

C14H7Cl5O6S2: C14 H7 Cl5 O6 S2



$[M+HCl-2H]^{2-}$

Data(product-scan)

discovering z = -2

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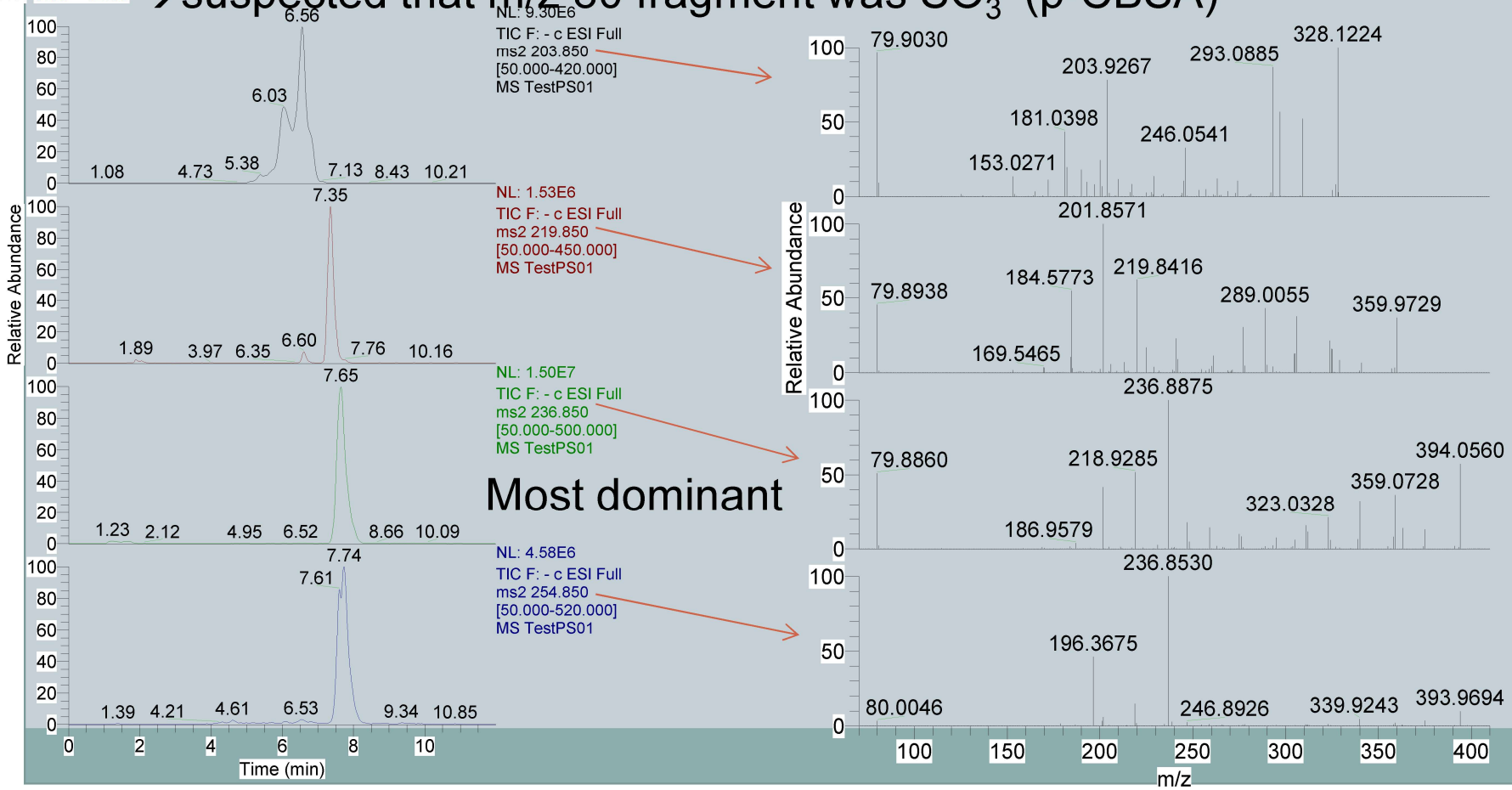
Product scan of monoisotopic precursor 236.85 showed m/z values <u>greater</u> than 236.85 which confirmed doubly charged ion
→suspected that m/z 80 fragment was SO_3^- (p-CBSA)



Data (cluster product-scan)

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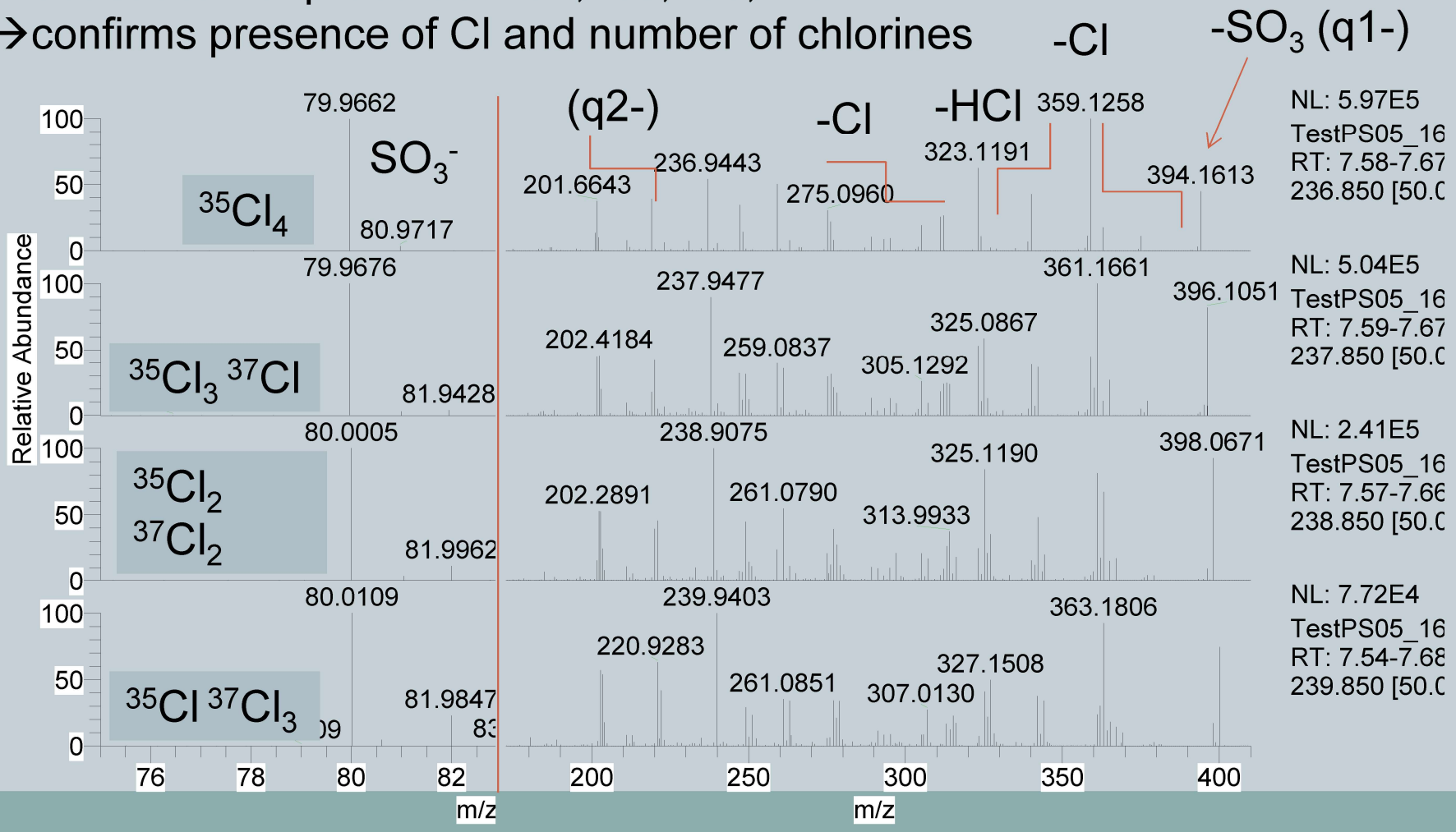
Product scan of precursor 237,238,239,240
→confirms presence of Cl and number of chlorines



Summary

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- Found 9 major chlorinated unknowns; 8 were sulfonates; 4 were disulfonates
- Accounted for missing TOX balance
- Added unknowns to Chemspider. One unknown was in PubChem DB but hidden (U.S. Patent)
- Quantitation estimate using p-CBSA already in samples was not far off

Synthesis of Unknown

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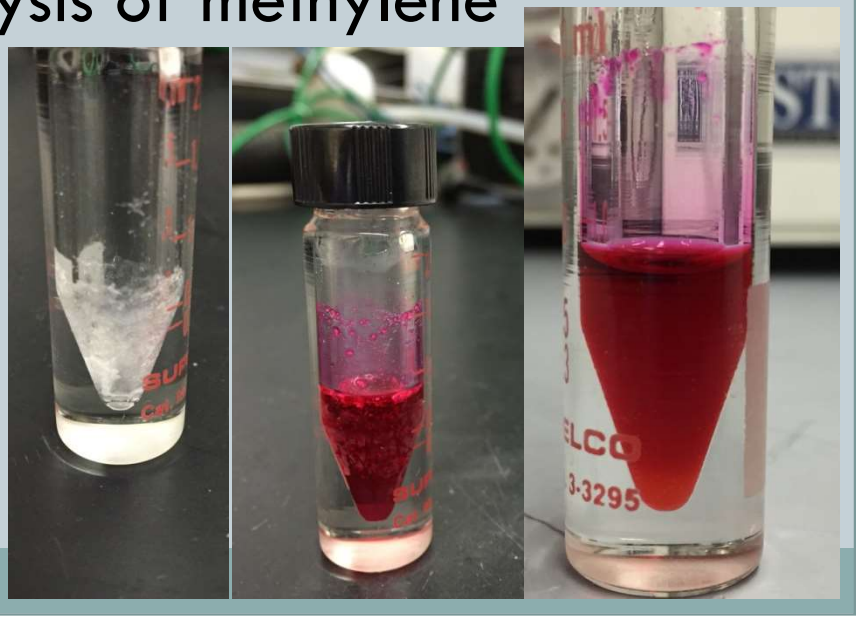
- Synthesis performed using 4,4'-DDE as starting material.
- Purity evaluated at 99.1% based on total impurities.
- Impurity analysis performed by both LC-MS direct injection and GC-MS analysis of methylene chloride micro-extraction



Conclusions

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- Low-res instruments can play a role in non-targeted analysis for both known-unknowns and specific analyte classes based on specific MS fragment rules.
- Proceed with caution, especially when using non-high resolution, non-accurate mass. Know the limitations of YOUR instrument.
- Supervise data processing to make sure unknowns are not missed
- Non-targets may not even be in the largest of databases
- Quantitate against compound with same ESI functionality in absence of standard

Figure1: Data partitioning

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Figure2:Exceedence Map

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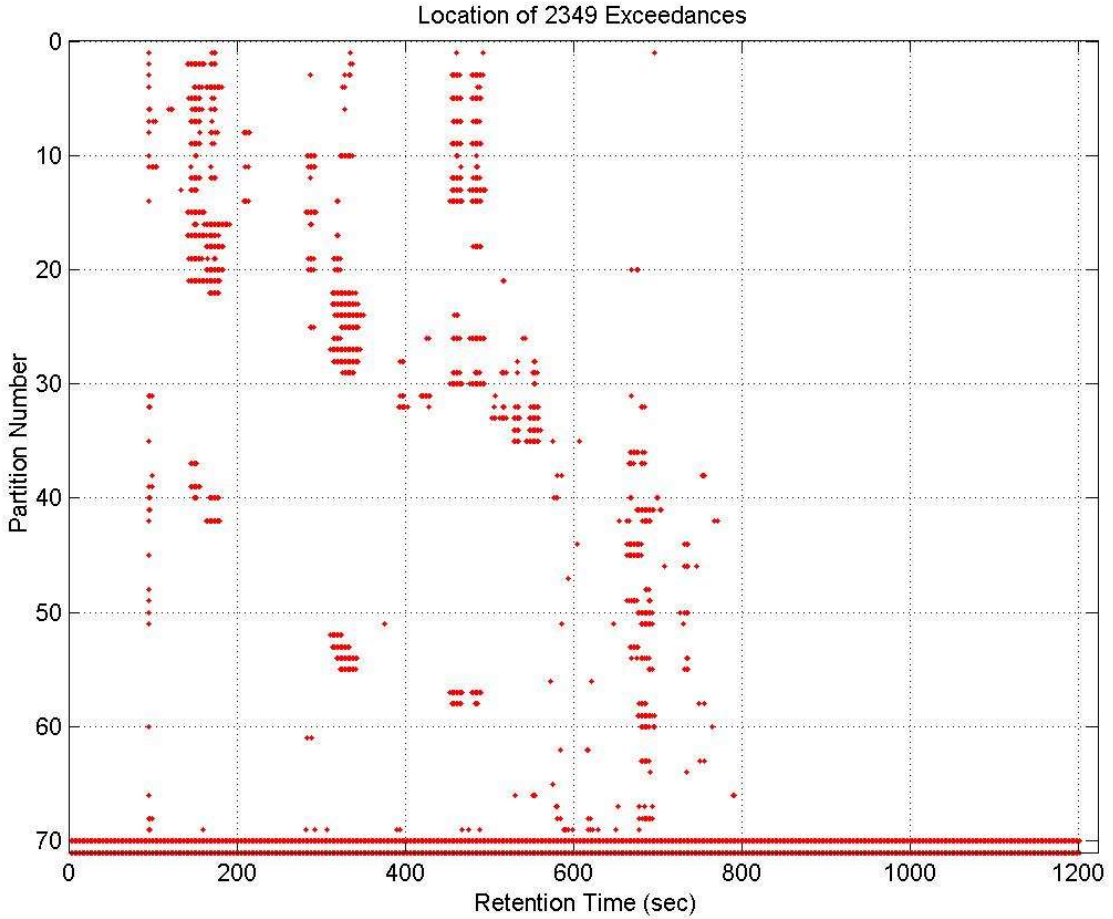

Figure3: Chemical Structures

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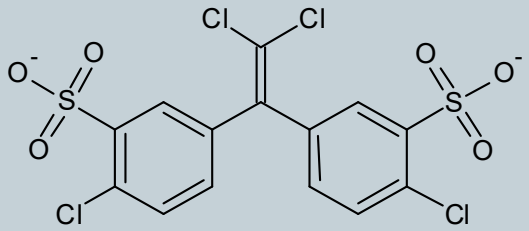
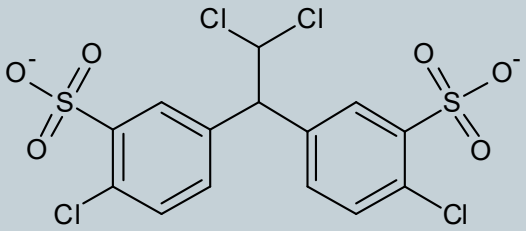
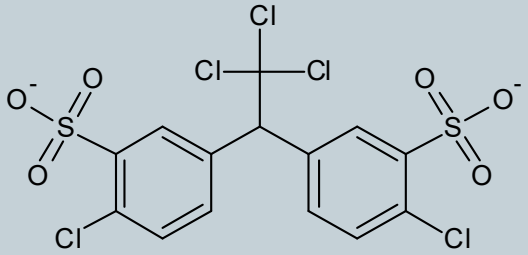
DDE Disulfonate



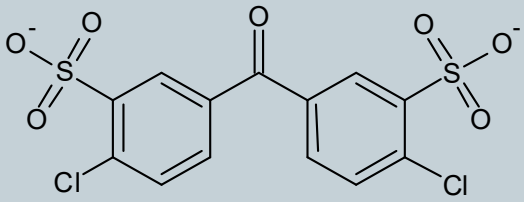
DDD Disulfonate



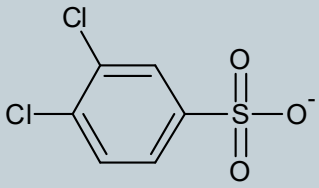
DDT Disulfonate



Dichlorobenzophenone Disulfonate



DCBSA



*Aromatic sulfonic acids dissociate in water (very low pKa)

Acknowledgements

- Laszlo Saska, P.E. | DTSC
  - Permission to present data.
- Dr. Samia Estassi | Babcock Labs
  - Advice on synthesis of DDE disulfonate
- Larry Chrystal | Babcock Labs
  - Performed TOX results/equivalents for comparison
- Klaus Schiessel, physicist | Northrop Grumman, retired
  - Signal processing algorithms

References

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