Comprehensive Analysis of Short-Chained Chlorinated Paraffins and other POPs in Environmental Samples by GCxGC-HR-TOFMS with a Novel Ion Source

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Overview

A prototype of a novel ion source for use in GCxGC-HR-TOFMS based on the Folded Flight Path® (FFP®) mass analyzers has been developed. The preliminary results from evaluating its capabilities for analysis of short-chained chlorinated paraffins and other POPs are presented.

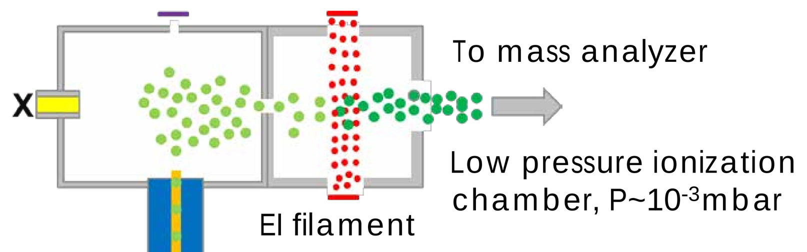
Introduction

Commercial chlorinated paraffins are derived from the free radical chlorination of n-alkane mixtures.[1] These resultant mixtures are categorized into three groups: Short-Chain Chlorinated Paraffins (SCCPs)–C_{10} to C_{13}; Medium-Chain Chlorinated Paraffins (MCCPs)–C_{14} to C_{17}; Long-Chain Chlorinated Paraffins (LCCPs)–C_{18} to C_{30}.

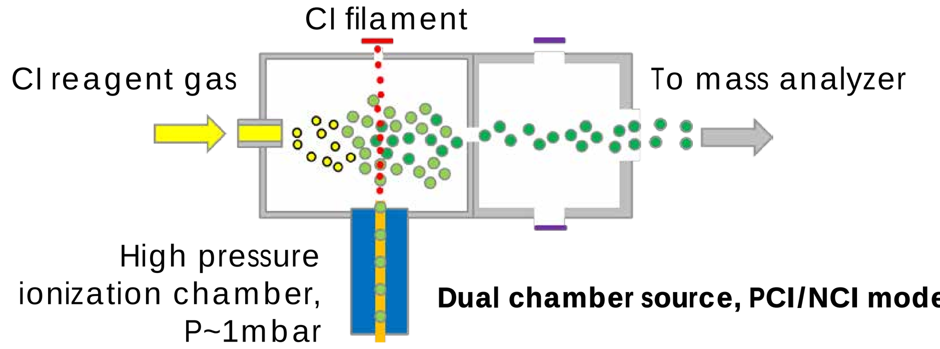
This study focuses on short-chain chlorinated paraffins (SCCPs). Due to their high electron affinity, the analysis of chlorinated paraffins is typically performed by mass spectrometry with an Electron Capture Negative Ionization (ECNI) source. High numbers of SCCP isomers requires high capacity chromatographic separation. High resolution mass spectrometry provides enhanced selectivity when analyzing complex environmental samples. We analyzed the SCCP-containing samples using a high resolution TOF mass spectrometer equipped with a novel multi-mode ionization ion source and coupled with comprehensive two-dimensional gas chromatography (GCxGC).

Ion Source

A new, dual chamber ion source was developed to operate in any of three ionization modes (electron ionization, positive chemical ionization, and electron capture negative ionization) without replacing any hardware parts. The source is intended for use in LECO's GCxGC-HR-TOFMS systems, which achieve the full mass range resolving power of 25,000 or higher with better than 1 ppm mass accuracy.



Dual chamber source, EI mode



Dual chamber source, PCI/NCI mode

LECO Pegasus® GC-HRT+ 4D

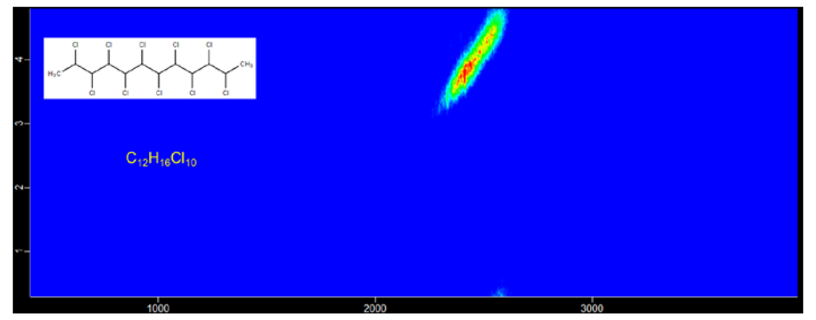
Methods

The GCxGC system is comprised of the LECO quad-jet liquid nitrogen-cooled thermal modulator in a 7890B GC. The high resolution mass spectrometer was a LECO *Pegasus* GC-HRT+ 4D research prototype. The GC method and the mass spectrometer settings were as follows.

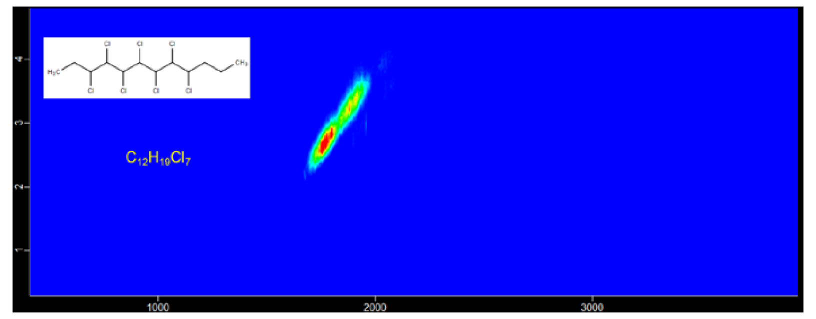
Gas Chromatograph	LECO GCxGC (Dual Stage Quad Jet Modulator) in 7890B GC
Injection	1µL Splitless, 270 °C
Carrier Gas	He @ 1.0 mL/min, Corrected Constant Flow
Column 1	Rxi-1ms, 30 m x 0.25 mm ID x 0.25 µm
Column 2	DB-XLB, 1.2 m x 0.1 mm ID x 0.1 µm film
Temperature Program	Primary Oven: 100 °C (0.2 min) to 190 °C @ 10 °C/min (0.0 min) to 300 °C @ 3 °C/min (2.0 min) Secondary Oven: 105°C (0.2 min) to 159°C @ 6 °C/min (0.0 min) to 305 °C @ 3 °C/min (7.0 min)
Modulation	4.5 s with temperature maintained +15 °C relative to the secondary oven
Mass Spectrometer	**LECO *Pegasus* GC-HRT+ 4D**
Transfer Line	300 °C
Ion Source Temperature	130 °C (ECNI Mode); 250 °C (EI Mode)
Acquisition Mode	High Resolution, R ≥ 25,000 for m/z 219, Mass Accuracy ≤ 1 ppm
Ionization Mode	ECNI (Moderation Gas: CH_4) and EI
Mass Range (m/z)	ECNI: 25–1,000; EI: 15–1,000
Acquisition Rate	200 spectra/s

Short-Chain Chlorinated Paraffin Standards—Analytical Method Development

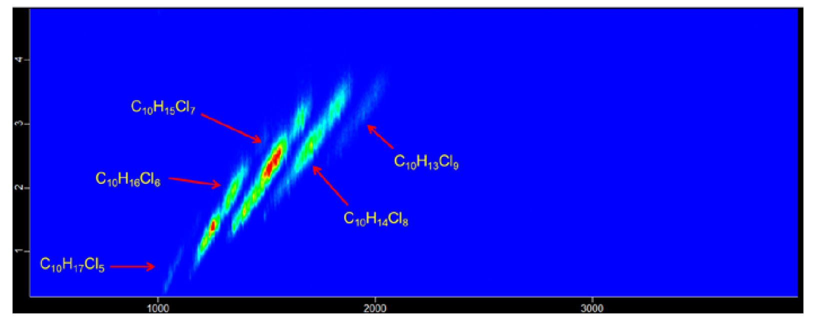
$C_{12}H_{16}Cl_{10}$ Displaying Masses for $(M\text{-}Cl)^-$ and $(M\text{-}HCl)^-$



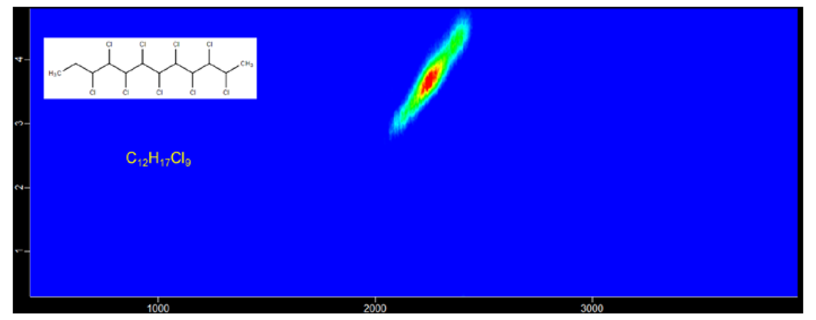
$C_{12}H_{19}Cl_7$ Displaying Masses for $(M\text{-}Cl)^-$ and $(M\text{-}HCl)^-$



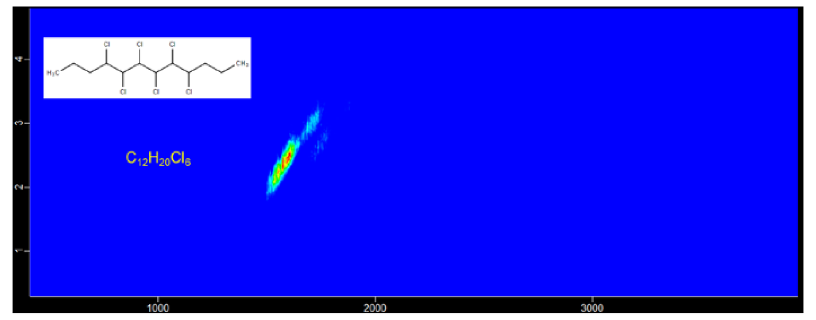
SCCP 63% Cl - $C_{10}H_{17}Cl_5$, $C_{10}H_{16}Cl_6$, $C_{10}H_{15}Cl_7$, $C_{10}H_{14}Cl_8$, and $C_{10}H_{13}Cl_9$



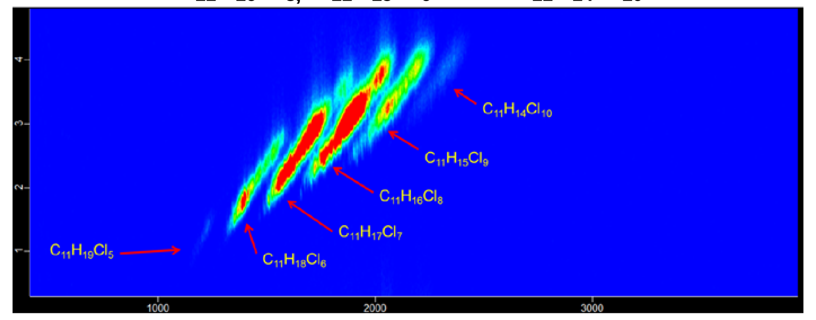
$C_{12}H_{17}Cl_9$ Displaying Masses for $(M\text{-}Cl)^-$ and $(M\text{-}HCl)^-$



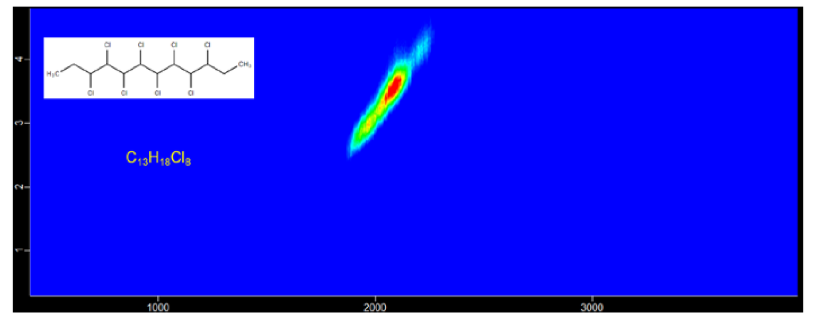
$C_{12}H_{20}Cl_6$ Displaying Masses for $(M\text{-}Cl)^-$ and $(M\text{-}HCl)^-$



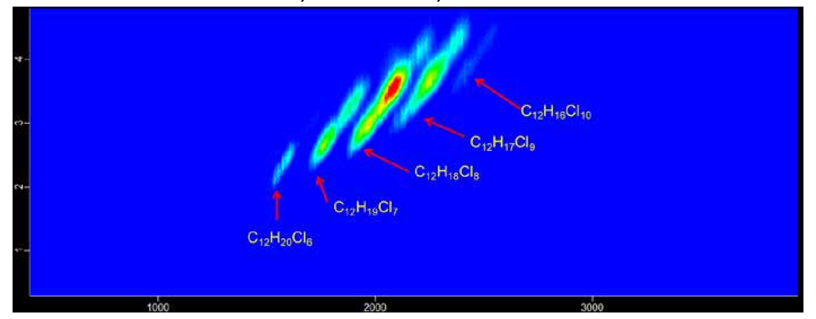
SCCP 63% Cl - $C_{11}H_{19}Cl_5$, $C_{11}H_{18}Cl_6$, $C_{11}H_{17}Cl_7$, $C_{11}H_{16}Cl_8$, $C_{11}H_{15}Cl_9$, and $C_{11}H_{14}Cl_{10}$



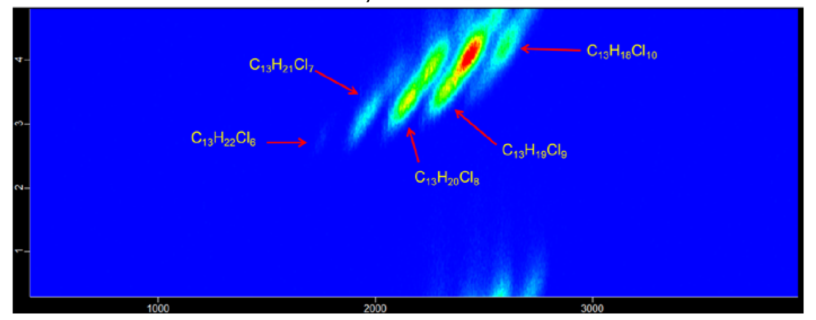
$C_{12}H_{18}Cl_8$ Displaying Masses for $(M\text{-}Cl)^-$ and $(M\text{-}HCl)^-$



SCCP 63% Cl - $C_{12}H_{20}Cl_6$, $C_{12}H_{19}Cl_7$, $C_{12}H_{18}Cl_8$, $C_{12}H_{17}Cl_9$, and $C_{12}H_{16}Cl_{10}$

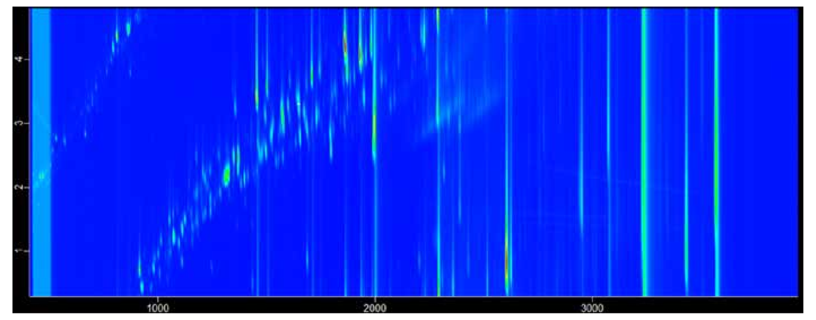


SCCP 63% Cl - $C_{13}H_{22}Cl_6$, $C_{13}H_{21}Cl_7$, $C_{13}H_{20}Cl_8$, $C_{13}H_{19}Cl_9$, and $C_{13}H_{18}Cl_{10}$

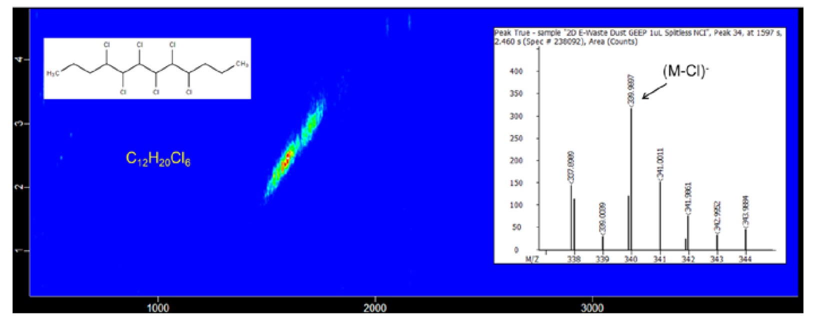


E-Waste Dust Sample SCCPs

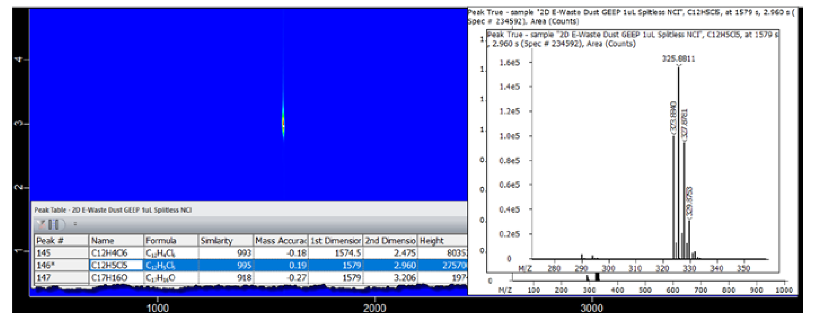
E-Waste Dust Sample TIC



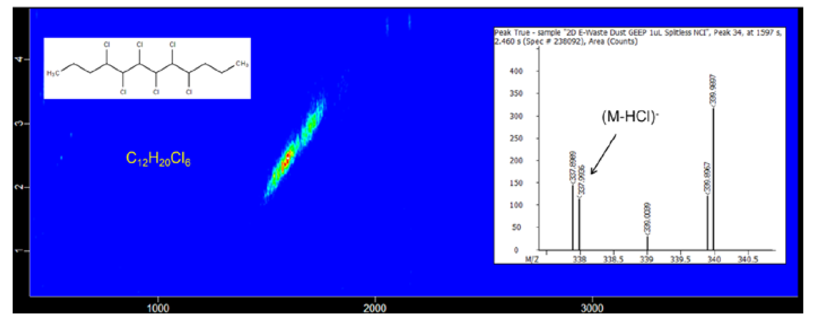
E-Waste Dust Sample $C_{12}H_{20}Cl_6$ $(M\text{-}Cl)^-$

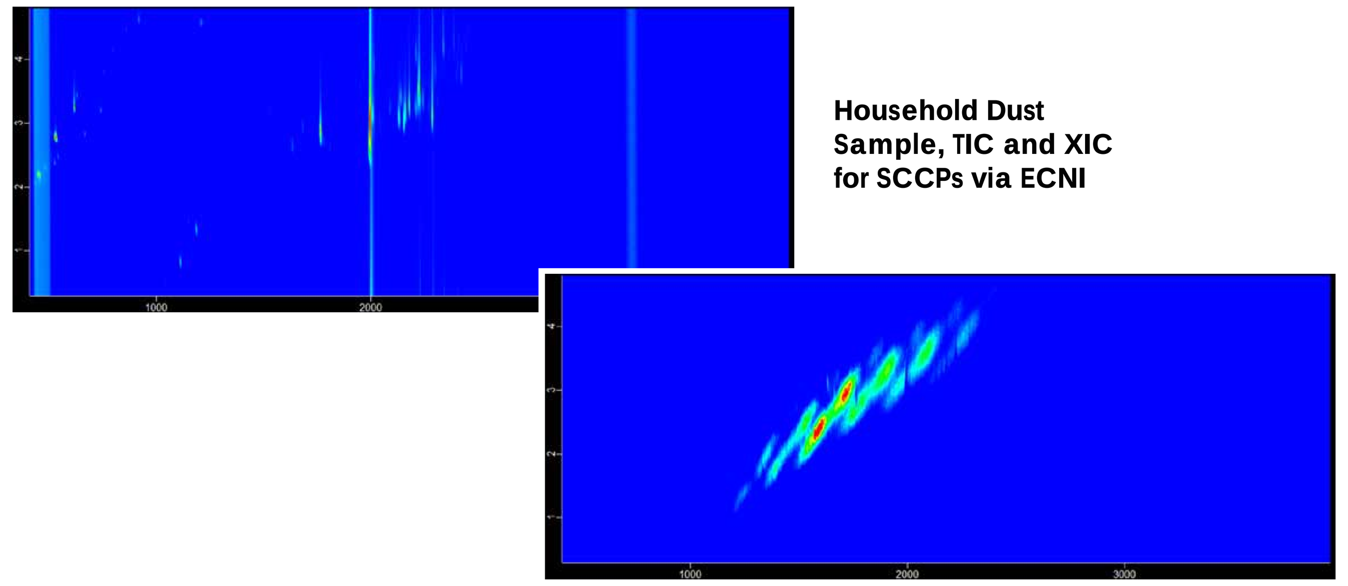


E-Waste Dust Sample, PCB Detected in Negative Ion Mode

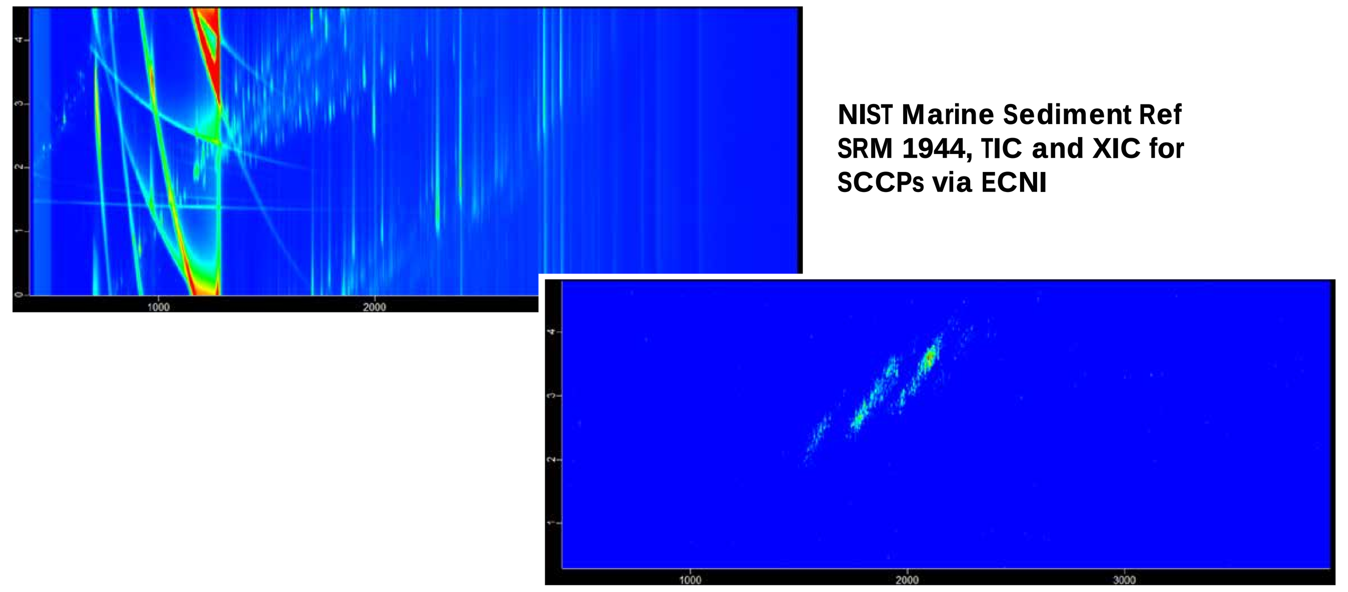


E-Waste Dust Sample $C_{12}H_{20}Cl_6$ $(M\text{-}HCl)^-$

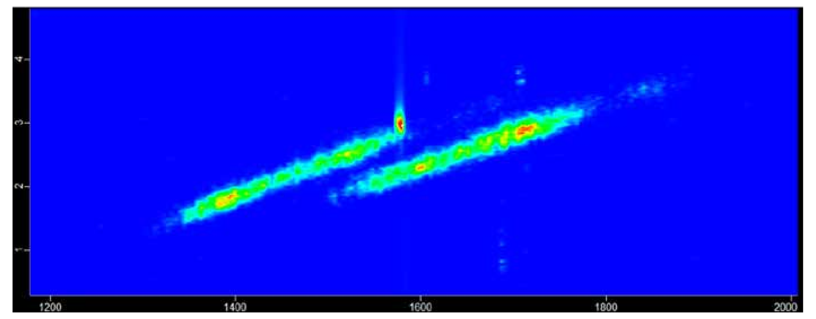




Household Dust Sample, TIC and XIC for SCCPs via ECNI



NIST Marine Sediment Ref SRM 1944, TIC and XIC for SCCPs via ECNI



ECNI XIC for E-Waste Dust Sample $C_{11}H_{18}Cl_6$, $C_{11}H_{17}Cl_7$ and $C_{12}H_5Cl_5$

Summary

- Three different short-chain chlorinated paraffin (SCCP) standards with various percentages of chlorination were analyzed using a prototype novel ionization source coupled with high resolution TOF mass spectrometry and comprehensive two-dimensional gas chromatography.
- The chromatographic patterns of multiple constituents within the chlorinated paraffin standards were characterized.
- Various dust samples were then qualitatively screened for SCCPs to evaluate the ability of the novel source coupled with the HRMS to distinguish between the various SCCP constituents within the samples.
- The use of comprehensive two-dimensional gas chromatography coupled with HR-TOFMS and the ECNI source for the analysis of SCCPs is crucial for the resolution of multiple SCCPs and other halogenated contaminates regularly found in persistent organic samples.

References

[1] Tomy, G.T. (2010). *Analysis of Chlorinated Paraffins in Environmental Matrices: The Ultimate Challenge for the Analytical Chemist*. J. de Boer (Ed.), The Handbook of Environmental Chemistry: Chlorinated Paraffins VOL 10 (pp. 83-106). London, New York: Springer Heidelberg Dordrecht

Acknowledgments

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