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Short Chain Chlorinated Paraffins (SCCPs) analysis using negative chemical ionization (CI) and low energy EI by high-resolution GC/Q-TOF

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Introduction

Short Chain Chlorinated Paraffins (SCCPs) are bioaccumulative and persistent in the environment, and commonly used as flame retardants in plastics and other materials, as well as in few other applications such as metal processing. Analysis of these compounds represents a substantial challenge due to their self-interference as well as interference with other components of complex industrial matrices. Thus, the analytical techniques applied not only have to be sensitive, but also very selective; this is where high-resolution MS can be very attractive, especially when combined with negative CI and low energy EI. Here, we describe the performance of high-resolution GC/Q-TOF for SCCP analysis.

Experimental

Standard SCCP mixtures as well as pure congener standards were analyzed using an Agilent 7890B GC system coupled to a high resolution 7250 GC/Q-TOF (Figure 1) equipped with a low energy capable EI source and as well as interchangeable CI source. The data were acquired in both negative CI (using methane as a reagent gas) as well as low energy EI (at 22 eV). MS parameters are listed in Table 1. Congener standards are listed in Table 2

The GC separation was done on a 30 m x 0.25 mm id x 0.25 µm film thickness DB-5MS capillary column using He as carrier gas at 1.2 mL/min. spectral data were acquired at 5 Hz and the mass range was 50-650 m/z. Methane gas at 40% was used as a reagent gas for NCI.

The data were processed using pre-released MassHunter Quantitative and Qualitative Analysis software version 10.

GC and MS Conditions:	NCI	Low energy EI
Column	DB-5MS UI, 30 m, 0.25 mm, 0.25 µm	
Injection volume	1 µL	
Injection mode	Splitless	
Inlet temperature	280°C	
Oven temperature program	40°C for 1 min; 25°C/min to 320°C, 9.8 min hold	
Carrier gas	Helium at 1.2 mL/min constant flow	
Transfer line temperature	290°C	
Mass range	50 to 650 m/z	
Spectral acquisition rate	5 Hz	
Quadrupole temperature	150°C	
Source temperature	150°C	200°C
Electron energy	200 eV	22 eV
Emission current	40 µA	1 µA

Table 1. GC/Q-TOF acquisition parameters.

Experimental

SCCP congeneres			Sample
C	H	Cl	Chlorine position
10	18	4	2,5,6,9 + 1,2,9,10[a]
10	17	5	1,2,5,6,9 (2 en) [a]
10	16	6	1,1,1,3,9,10[b] -1,5,5,6,6,10[c]- 1,2,5,6,9,10 (2 en) [a]
10	15	7	1,2,4,5,6,9,10 and 1,2,5,5,6,9,10[a]
10	14	8	2,3,4,5,6,7,8,9[a]
10	13	9	1,2,3,4,5,6,7,8,9[a]
11	20	4	1,1,1,3 + 1,2,10,11[b]
11	18	6	1,1,1,3,10,11[b]
11	16	8	1,1,1,3,9,11,11,11[b]
12	22	4	1,1,1,3 [b]
12	20	6	1,1,1,3,10,11[b]
12	18	8	1,1,1,3,10,12,12,12[c]
13	24	4	1,1,1,3[b]
13	22	6	1,1,1,3,12,13[b]
13	20	8	1,1,1,3,11,13,13,13[b]

Table 2. List of pure congeners standards.

The SCCP congeners listed in Table 2 were obtained from Dr. Ehrenstorfer, Germany (a), Chiron, Norway (b), and Cambridge Isotope Laboratories, USA (c).

Figure 1. Agilent 7250 GC/Q-TOF

Negative CI, SCCP Spectra Examples

NCI fragmentation patterns of SCCPs were evaluated for comparison using pure congeners standards. When methane was used as a reagent gas, NCI spectra of SCCPs exhibited minor fragmentation. In all cases examined, M- and (M-Cl)-/(M-HCl)- were predominant ions. No significant fragmentation of the carbon backbone was observed in these conditions (Figure 2).

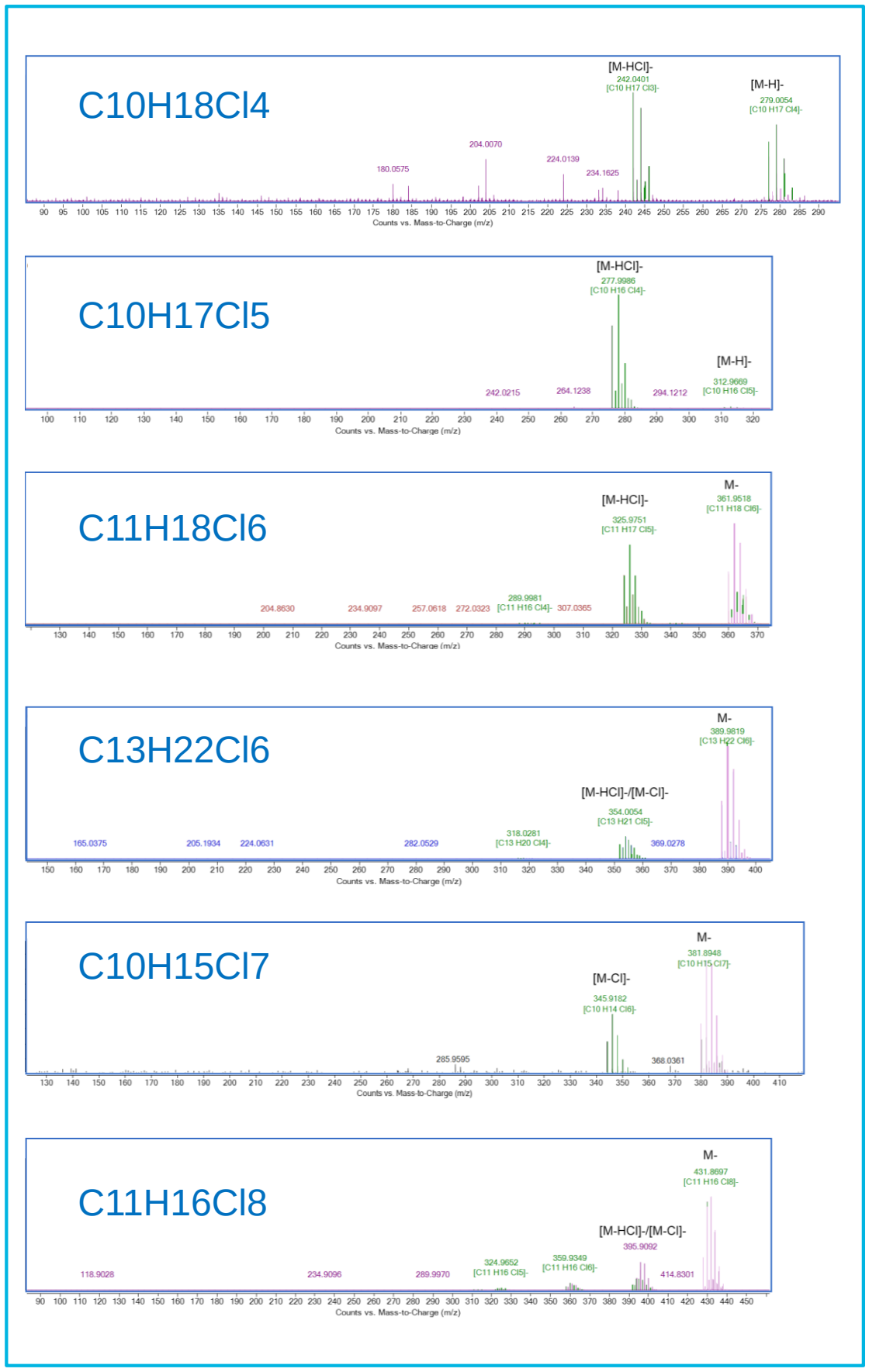

Figure 2. Examples of NCI spectra obtained for individual congener standards.

NCI Analysis of Standard SCCP Mixtures

In negative CI mode, M- and (M-Cl)- ions were found to be most selective and were preferably used for congeners quantitation.

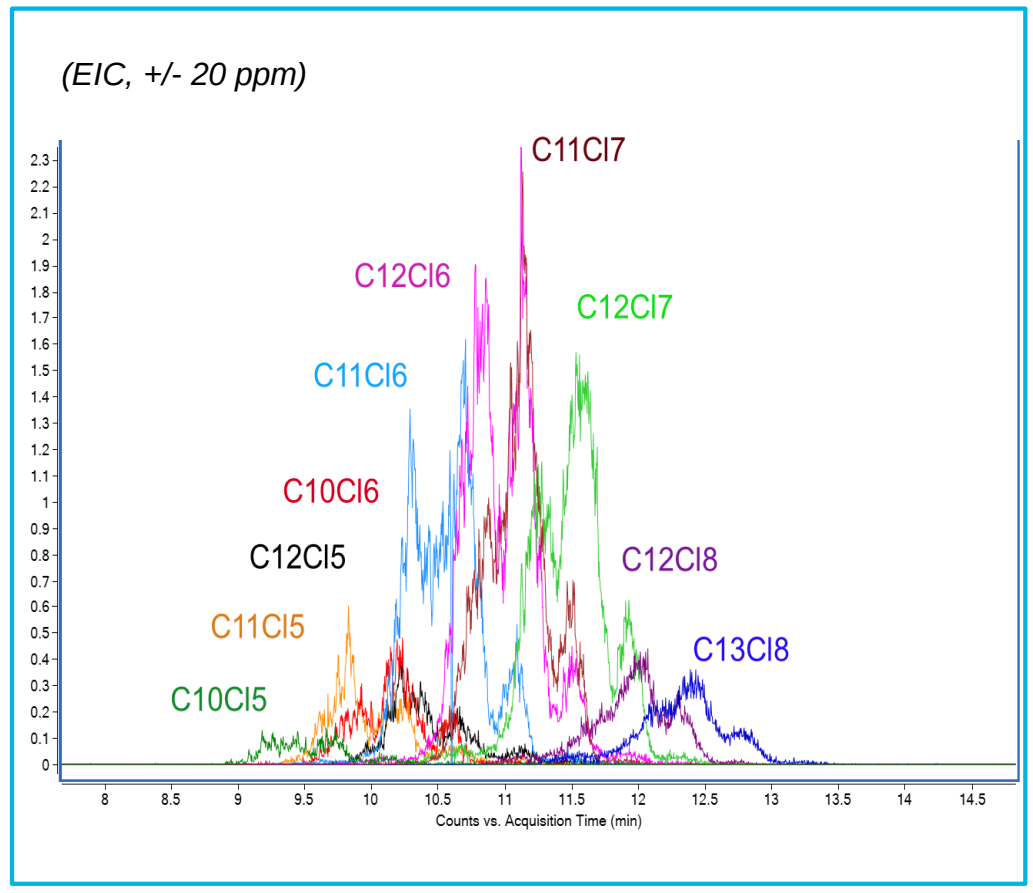

Figure 3. Example of EIC overlay for standard SCCP mixture containing 55% Cl.

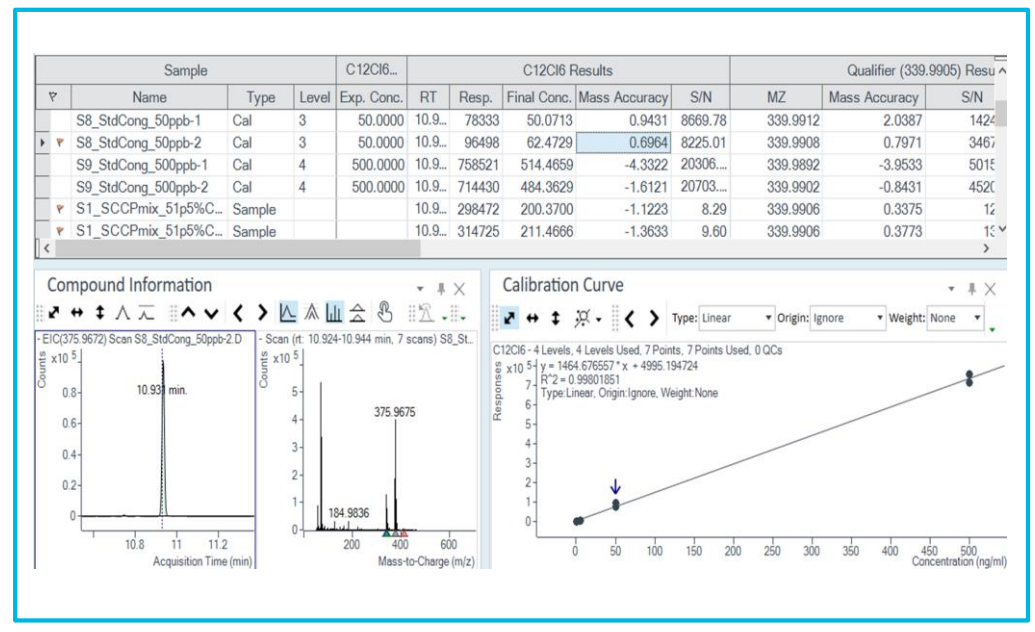

Figure 4. Example of calibration curve based on pure congener standards.

Results and Discussion

NCI Analysis of Standard SCCP Mixtures (Continued)

Congener	RT range, min	NCI, SCCP mixtures					
		Concentration, ppb			%		
		51.5%	55%	63.5%	51.5%	55%	63.5%
C10Cl4	8.8-9.1	115.5	193.7	23.0	2.3	3.9	0.5
C10Cl5	9-10.3	106.1	135.3	84.3	2.1	2.7	1.7
C10Cl6	9.6-10.8	5.9	15.3	41.7	0.1	0.3	0.8
C10Cl7	10.1-11.2	0.9	6.7	51.6	0.02	0.1	1.0
C10Cl8	10-11.3	2.5	4.4	38.0	0.05	0.1	0.8
C11Cl4	9.4-10	189.2	96.2	36.6	3.8	1.9	0.7
C11Cl6	10-10.8	342.0	614.5	330.3	6.8	12.3	6.6
C11Cl8	11-12.5	3.3	25.4	210.6	0.1	0.5	4.2
C12Cl6	10.3-11.5	205.9	240.2	46.8	4.1	4.8	0.9
C12Cl8	11.4-12.6	9.5	49.3	167.3	0.2	1.0	3.3
C13Cl6	10.8-11.8	200.9	161.9	26.1	4.0	3.2	0.5
C13Cl8	11.9-13	84.9	287.8	628.2	1.7	5.8	12.6

Table 3. NCI quantitation results for SCCP mixtures containing 51.5 %, 55 %, and 63.5% Cl.

Low Energy EI

Low energy EI data indicated a higher degree of fragmentation of the SCCPs as compared to negative CI. However, using this technique allowed more sensitive detection of the SCCP species with low Cl content (such as C10Cl4).

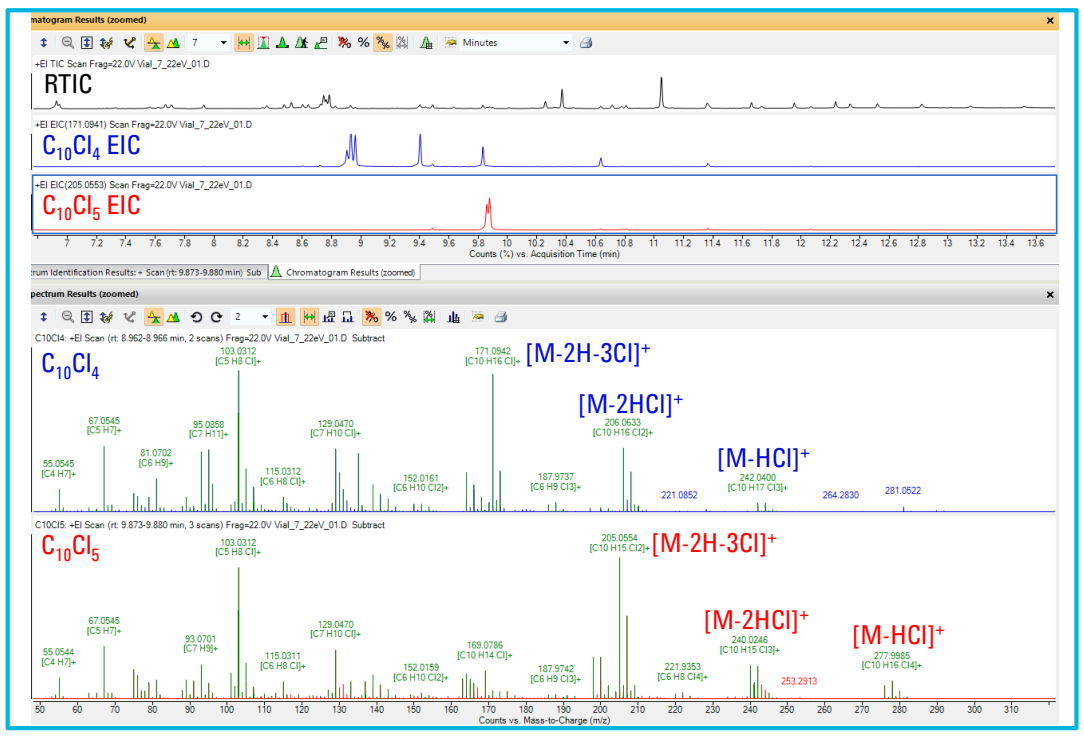

Figure 5. Annotated spectra for the $C_{10}Cl_4$ and $C_{10}Cl_5$ isomers using 22 eV ionization.

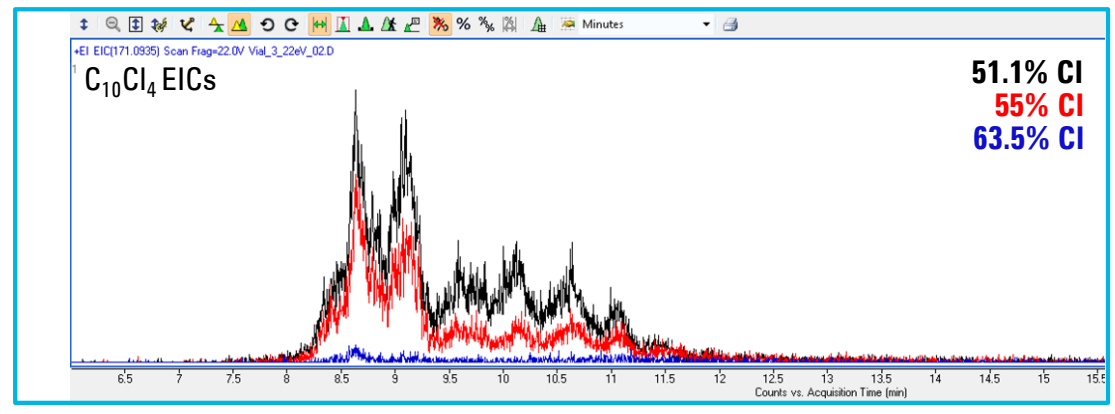

Figure 6. Overlaid exact mass extracted chromatograms of different %Cl mixtures for the $C_{10}Cl_4$ isomer.

Initially, traditional 70eV ionization was performed, but the degree of fragmentation did not provide enough unique ion clusters for individual identification. Multiple eV settings were evaluated to determine the optimal value in the range of 10 – 25eV. Due to the structure of these analytes, the optimal spectral tilt was achieved with a 22 eV ionization while optimizing the signal response. A lower eV did not further reduce fragmentation due to the immediate loss of HCl from the ion. Low energy EI provided additional information for the lower Cl content isomers for higher confidence in the identification of the specific isomer. C_{10} – C_{17} isomers were evaluated using low eV to provide orthogonal information compared to chemical ionization.

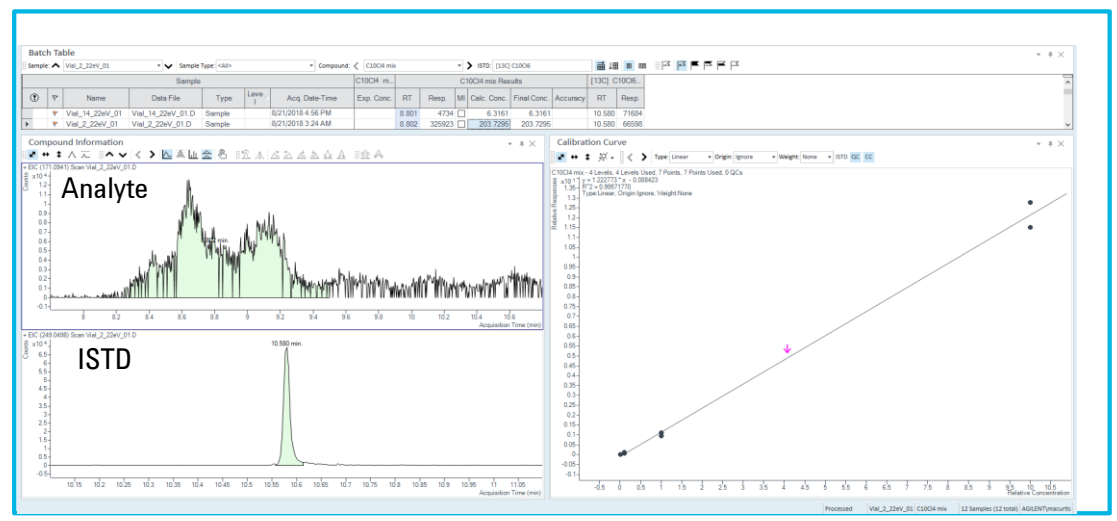

Figure 7. Calculated concentration for the $C_{10}Cl_4$ isomers in the 55% Cl mixture. This calculates to 4.0% for this isomer.

Conclusions

- 7250 GC/Q-TOF system equipped with a low energy-capable EI source as well as an interchangeable CI source was used for SCCP analysis in both negative CI and low energy EI modes.
- While negative chemical ionization technique demonstrated low degree of fragmentation that significantly simplified the SCCP spectra, low energy EI appeared to be more sensitive for SCCP species with low Cl content.

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