Analysis of Short Chain Chlorinated Paraffins (SCCPs) by GC-Q/TOF using Complimentary and Novel Ionization

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated alkanes with alkane lengths C10 to C30 and various degrees of chlorination, typically 30 to 75%. They are classified based on carbon chain lengths as short (C10 to C13), medium (C14 to C17), and long (>C17) chained. CPs, particularly short chain CPs (SCCPs), are bio-accumulative, and persistent in the environment.[1,2] They are commonly used as a component of lubricants and coolants in metal processing and as a flame retardant in plastics and other materials such as paints, rubber formulations, adhesives, and sealants.[3]

Analysis of these compounds presents a substantial challenge due to their self-interference as well as interference with other components of complex industrial matrices, such as PCBs and toxaphenes. Therefore, it is highly recommended to use a high-resolution MS technique for their analysis.[4] In addition to a high selectivity requirement, the analytical technique for the analysis of SCCPs must also be highly sensitive.

Here we discuss the benefits of two complimentary acquisition modes of the high-resolution GC/Q-TOF, negative CI and low energy EI, for SCCP analysis.

Samples & Standards

The standard SCCP mixtures with 51%, 55.5%, and 63% chlorine content were from Dr. Ehrenstorfer GmbH (Germany). The final total concentration of SCCPs in highest concentration standard was 5 ng/µL. Isotopically labeled 1,5,5,6,6,10-hexachlorodecane ($^{13}C_{10}$) was obtained from Cambridge Isotope Laboratories (USA), and was used as an internal standard.

Individual SCCP Congeners			
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 1. List of pure congener standards. The SCCP congeners were obtained from:

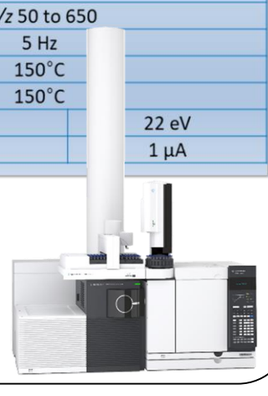
a Dr. Ehrenstorfer GmbH, Germany
b Chiron, Norway
c Cambridge Isotope Laboratories, USA

GC/MS Analysis

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

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	*m/z* 50 to 650	
Spectral Acquisition Rate	5 Hz	
Quadrupole Temperature	150°C	
Source Temperature	150°C	
Electron Energy	200 eV	22 eV
Emission Current	40 µA	1 µA

Table 2. Instrument parameters for Agilent 7890/7250 GC/Q-TOF analysis.

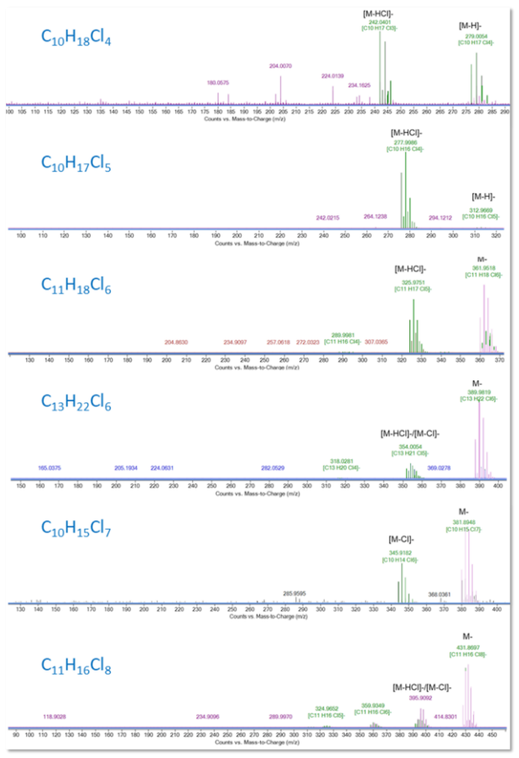


SCCP Spectra in Negative NCI

NCI spectra of SCCPs exhibited minor fragmentation. [M]–, [M-HCl]– and in a few cases, [M-H]– were predominant ions.

No significant fragmentation of the carbon backbone was observed, and other ions (such as [M-2Cl]–) were present at small proportions, if at all, in these conditions. This is different from the observations reported in a separate study using NCI Q-TOF, where predominant ions were [M-2Cl]– and [M-Cl].[5]

The fragmentation pattern was somewhat dependent on the number of chlorines, and the congeners with higher chlorine content had a tendency to have greater relative abundance of [M]–.



NCI Analysis of SCCP Mixtures

The quantitation of SCCPs in standard SCCP mixtures was performed using available pure congener standards, and was based on four calibration points (Figure 2B). A few abundant congeners identified in SCCP mixtures were not present in pure congener standards, and, therefore, their amounts were estimated using the *inherit calibration reference* feature of MassHunter Quantitative Analysis software 10, and were based on the available congener standards with equal number of chlorines and closest carbon chain length.

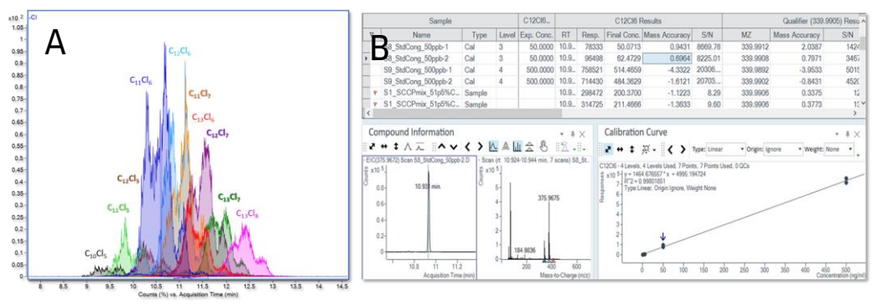


Figure 2. Analysis of SCCP mixtures in NCI. A) EIC overlay of the most abundant congeners identified in a standard SCCP mixture containing 55.5% Cl. EICs were extracted using ±20 ppm accurate mass window. The $C_{11}Cl_5$, $C_{11}Cl_7$, $C_{12}Cl_7$, and $C_{13}Cl_7$ congeners (in bold) are not present in pure congener standards. B) Example of a calibration curve based on a pure congener standard ($C_{12}Cl_6$) in NCI.

Table 3 summarizes the NCI quantitation results for the SCCP mixtures. The quantitation results based on calibrations from individual congener standards accounted for approximately 71, 93, and 78% of SCCPs in 51, 55.5, and 63% Cl SCCP mixtures, respectively.

Congener	RT range, min	Concentration, ppb			%		
		51.50%	55.50%	63%	51.50%	55.50%	63%
$C_{10}Cl_4$	8.8-9.1	115.5	193.7	23	2.3	3.9	0.5
$C_{10}Cl_5$	9-10.3	106.1	135.3	84.3	2.1	2.7	1.7
$C_{10}Cl_6$	9.6-10.8	5.9	15.3	41.7	0.1	0.3	0.8
$C_{10}Cl_7$	10.1-11.2	0.9	6.7	51.6	0.02	0.1	1
$C_{10}Cl_8$	10-11.3	2.5	4.4	38	0.05	0.1	0.8
$C_{11}Cl_4$	9.2-10	189.2	96.2	36.6	3.8	1.9	0.7
$C_{11}Cl_5$	9.5-10.5	364.6	340.7	89.4	7.3	6.8	1.8
$C_{11}Cl_6$	10-10.8	342	614.5	330.3	6.8	12.3	6.6
$C_{11}Cl_7$	10.5-11.7	70.4	353.2	825.9	1.4	7.1	16.5
$C_{11}Cl_8$	11-12.5	3.3	25.4	210.6	0.1	0.5	4.2
$C_{12}Cl_4$	9.4-10.5	290.7	129.8	11.1	5.8	2.6	0.2
$C_{12}Cl_5$	10-11.2	351.3	253.7	31.3	7.0	5.1	0.6
$C_{12}Cl_6$	10.3-11.5	205.9	240.2	46.8	4.1	4.8	0.9
$C_{12}Cl_7$	10.9-12.1	331.9	733.3	763.7	6.6	14.7	15.3
$C_{12}Cl_8$	11.4-12.6	9.5	49.3	167.3	0.2	1	3.3
$C_{13}Cl_5$	10.1-11.3	218.8	126.5	12.3	4.4	2.5	0.2
$C_{13}Cl_6$	10.8-11.8	200.9	161.9	26.1	4	3.2	0.5
$C_{13}Cl_7$	11.4-12.5	642.3	865.9	497.4	12.8	17.3	9.9
$C_{13}Cl_8$	11.9-13	84.9	287.8	628.2	1.7	5.8	12.6
Total					70.7	92.7	78.2

Table 3. NCI quantitation results for SCCP mixtures containing 51, 55.5, and 63% Cl. Highlighted in blue are estimated amounts based on congener standards with an equal number of chlorine atoms.

Low Energy EI Analysis of SCCP

To improve sensitivity of detection and accuracy of quantitation for SCCP congeners with low chlorine content, the low energy EI approach was used. Traditional 70 eV EI results in a high degree of fragmentation of SCCP molecules, and does not provide enough unique ion clusters for individual identification. Multiple low electron energy settings were evaluated and the optimum combination of spectral tilt and signal response was achieved with an energy set at 22 eV.

Low energy EI data indicated a higher degree of fragmentation of the SCCP molecules compared to negative CI (Figure 3). However, this technique allowed more sensitive detection of the SCCP species with low chlorine atom number (such as $C_{10}Cl_4$, Figure 4).

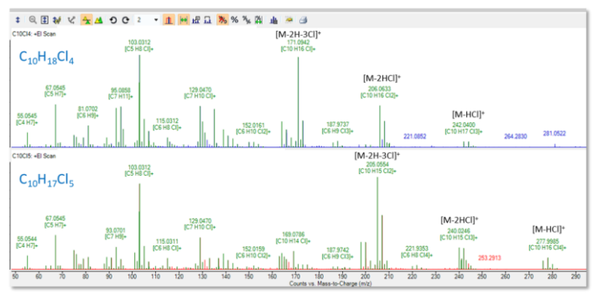
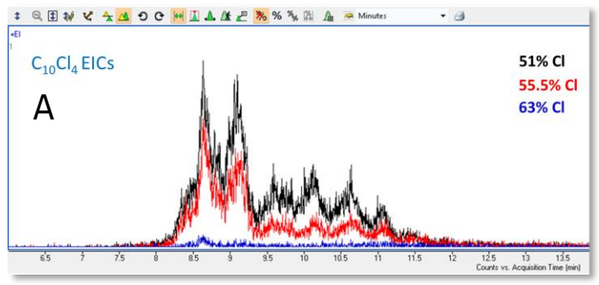


Figure 3. Examples of fragment formula annotated low energy EI spectra for the $C_{10}Cl_4$ and $C_{10}Cl_5$ congeners using 22 eV ionization.



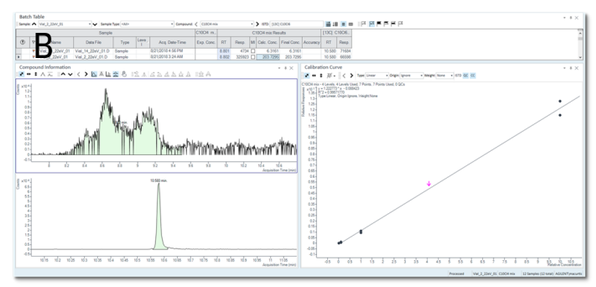


Figure 4. Analysis of SCCP using low energy EI. A) Overlaid low energy accurate-mass extracted ion chromatograms for the $C_{10}Cl_4$ congeners of different %Cl SCCP mixtures. B) Calculated concentration for the $C_{10}Cl_4$ congener in the 55.5% Cl mixture using low energy EI based on the calibration curve from pure congener standards. The estimated amount of this congener in the 55.5% Cl SCCP mixture was 4.0%, which is comparable with quantitation results obtained in NCI.

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 NCI demonstrated low degree of fragmentation that simplified the SCCP spectra, low energy EI appeared to be more sensitive for SCCP species with low Cl content indicating complimentary techniques are beneficial for comprehensive SCCP analysis.

References

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