

Short Chain Chlorinated Paraffins (SCCP) Analysis Using Negative Chemical Ionization (CI) and Low Energy EI by High-Resolution 7250 GC/Q-TOF

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Abstract

The Agilent 7250 Series high-resolution accurate mass GC/Q-TOF was used to analyze one of the most challenging group of compounds, short chain chlorinated paraffins (SCCPs), using a comprehensive approach including both negative chemical ionization (NCI) as well as low energy electron ionization (LE-EI).

The current study focuses on evaluating the suitability of the LE-EI and NCI modes of the Agilent GC/Q-TOF for the SCCP analysis, and reveals the advantages of each technique.

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. This is where the Agilent high-resolution GC/Q-TOF becomes a useful tool for the analysis of this challenging compound class, especially for the ability to combine both ionization techniques: CI and low energy EI.

This Application Note demonstrates the benefits of two complimentary acquisition modes of the Agilent GC/Q-TOF, negative CI and low energy EI, for SCCP analysis.

Experimental

Samples

The pure SCCP congeners were obtained from Dr. Ehrenstorfer GmbH (Germany), Chiron (Norway), and Cambridge Isotope Laboratories (USA), and are listed in Table 1. The standard SCCP mixtures with 51%, 55.5%,

Table 1. List of pure congener standards.

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

The SCCP congeners were obtained from:

^a Dr. Ehrenstorfer GmbH, Germany

^b Chiron, Norway

^c Cambridge Isotope Laboratories, USA

Table 2. Agilent GC/Q-TOF acquisition parameters.

GC and MS Conditions	NCI	Low energy EI
Column	Agilent 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 minute; 25 °C/min to 320 °C; 9.8 minutes 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

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 (¹³C₁₀) was obtained from Cambridge Isotope Laboratories (USA), and was used as an internal standard.

Data acquisition and processing

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 (at 22 eV). Table 2 lists the GC/Q-TOF acquisition parameters.

The GC separation was performed on an Agilent 30 m × 0.25 mm, 0.25 μm film thickness DB-5ms capillary column using helium as carrier gas at 1.2 mL/min. Full spectrum acquisition data were acquired at 5 Hz, and the mass range was 50 to 650 m/z. Methane gas at 40% was used as a reagent gas for NCI.

The data were processed using Agilent MassHunter Quantitative and Qualitative Analysis software version 10.

Results and discussion

SCCP spectra in negative CI with methane as a reagent gas

NCl fragmentation patterns of SCCPs were evaluated using pure congener standards. Using the HES-compatible CI source and methane as a reagent gas, NCl spectra of SCCPs exhibited minor fragmentation. $[M]^-$, $[M-HCl]^-$, and in a few cases, $[M-H]^-$ were predominant ions (Figure 1). 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 $[M]^-$. The presence of a predominant molecular ion for most SCCP congeners is a great advantage since it permits the use of a more specific ion for qualitative and quantitative analysis.

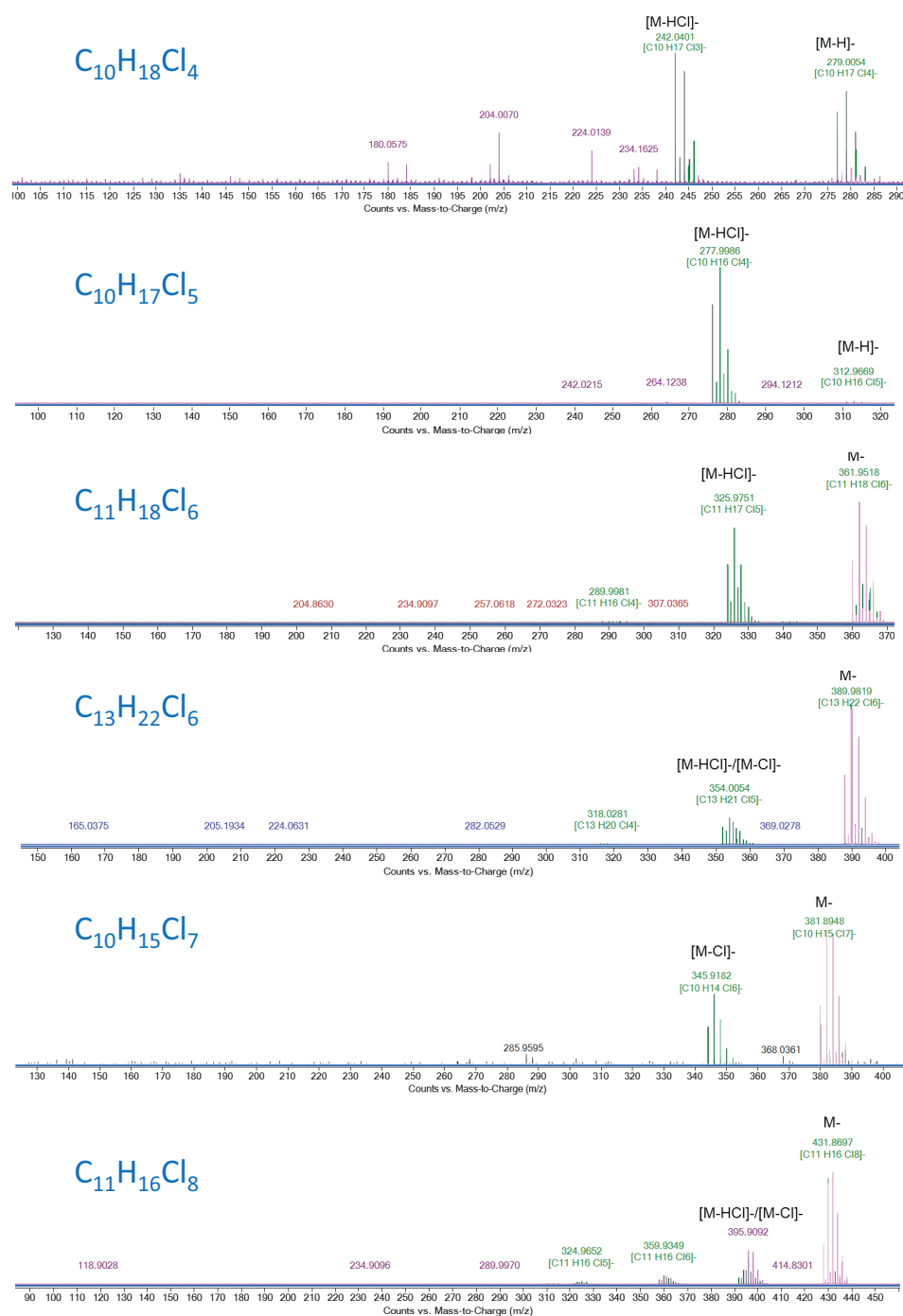


Figure 1. Examples of NCl spectra obtained for individual congener standards.

NCI analysis of standard SCCP mixtures

After spectra evaluation with pure congener standards, complex SCCP mixtures with chlorine contents of 51, 55.5, and 63% were analyzed.

Figure 2 shows an example of the accurate mass extracted ion chromatograms (EICs) for the SCCP mixture containing 55.5% chlorine. Congeners with carbon chain length ranging from C_{10} to C_{13} with five to eight chlorine atoms can easily be seen. Only the most abundant species are displayed for simplification. The response was dependent to a great extent on the number of chlorines, and less so on the carbon chain length.

The quantitation of SCCPs in standard SCCP mixtures was performed using available pure congener standards, and was based on four calibration points (Figure 3). A few abundant congeners identified in SCCP mixtures were not present in pure congener standards (Figure 2, Table 1), 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.

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.

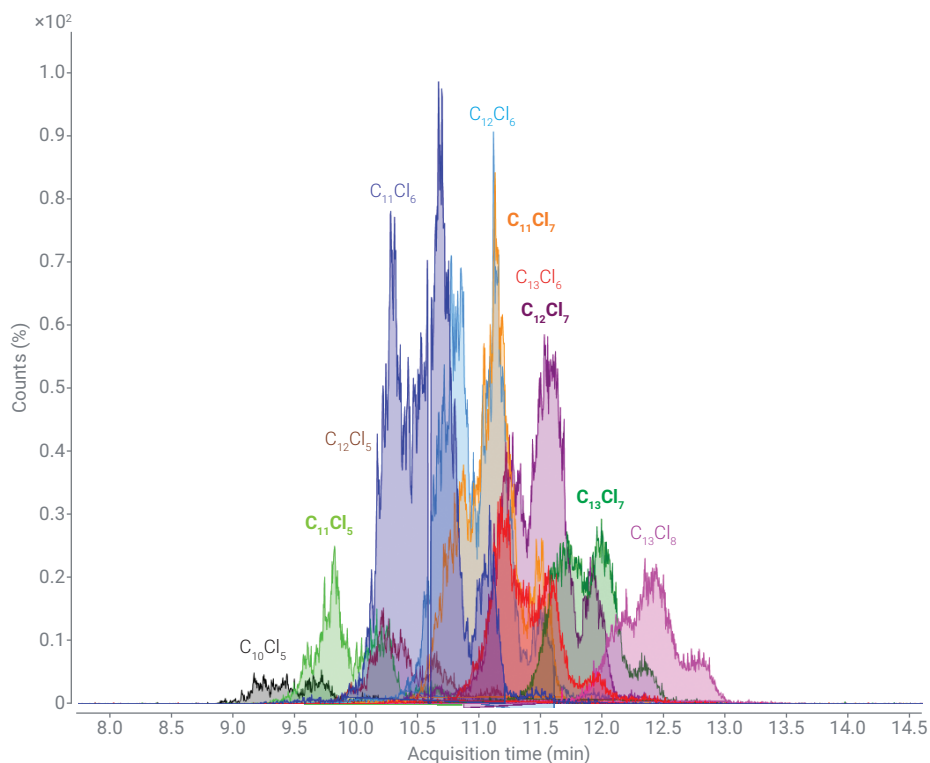


Figure 2. EIC overlay of the most abundant congeners identified in a standard SCCP mixture containing 55.5% Cl. EICs were extracted using ± 20 ppm accurate mass window. The $C_{11}Cl_6$, $C_{11}Cl_7$, $C_{12}Cl_7$, and $C_{13}Cl_7$ congeners (in bold) are not present in pure congener standards.

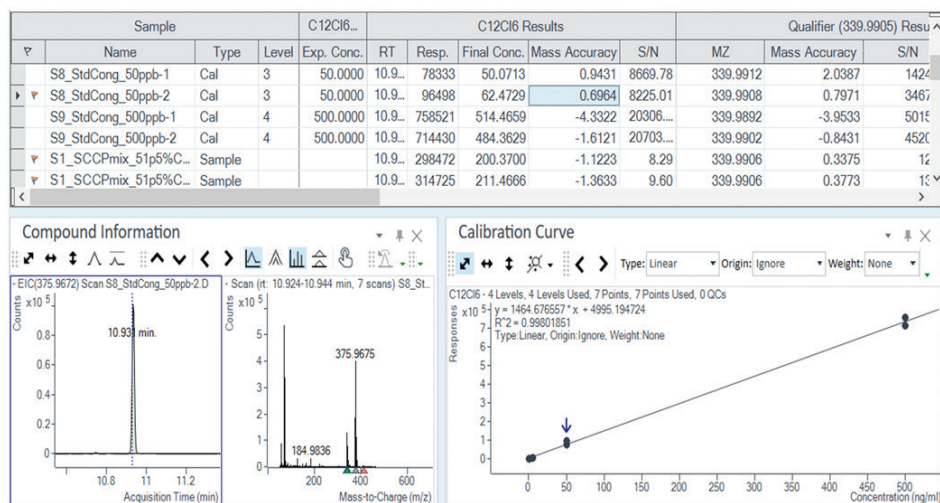


Figure 3. Example of a calibration curve based on a pure congener standard ($C_{12}Cl_6$) in NCI.

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 to determine the optimal value in the range of 10 to 25 eV. Due to the structure of these analytes, the optimum combination of spectral tilt and signal response was achieved with an electron energy set at 22 eV.

Low energy EI data indicated a higher degree of fragmentation of the SCCP molecules compared to negative CI (Figure 4). However, this technique allowed more sensitive detection of the SCCP species with low chlorine content (particularly, for congeners containing less than five chlorine atoms, for example, $C_{10}Cl_4$, Figure 5).

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.

Congener	RT range (min)	Concentration, ppb			%		
		51%	55.5%	63%	51%	55.5%	63%
$C_{10}Cl_4$	8.8 to 9.1	115.5	193.7	23	2.3	3.9	0.5
$C_{10}Cl_5$	9 to 10.3	106.1	135.3	84.3	2.1	2.7	1.7
$C_{10}Cl_6$	9.6 to 10.8	5.9	15.3	41.7	0.1	0.3	0.8
$C_{10}Cl_7$	10.1 to 11.2	0.9	6.7	51.6	0.02	0.1	1
$C_{10}Cl_8$	10 to 11.3	2.5	4.4	38	0.05	0.1	0.8
$C_{11}Cl_4$	9.2 to 10	189.2	96.2	36.6	3.8	1.9	0.7
$C_{11}Cl_5$	9.5 to 10.5	364.6	340.7	89.4	7.3	6.8	1.8
$C_{11}Cl_6$	10 to 10.8	342	614.5	330.3	6.8	12.3	6.6
$C_{11}Cl_7$	10.5 to 11.7	70.4	353.2	825.9	1.4	7.1	16.5
$C_{11}Cl_8$	11 to 12.5	3.3	25.4	210.6	0.1	0.5	4.2
$C_{12}Cl_4$	9.4 to 10.5	290.7	129.8	11.1	5.8	2.6	0.2
$C_{12}Cl_5$	10 to 11.2	351.3	253.7	31.3	7.0	5.1	0.6
$C_{12}Cl_6$	10.3 to 11.5	205.9	240.2	46.8	4.1	4.8	0.9
$C_{12}Cl_7$	10.9 to 12.1	331.9	733.3	763.7	6.6	14.7	15.3
$C_{12}Cl_8$	11.4 to 12.6	9.5	49.3	167.3	0.2	1	3.3
$C_{13}Cl_5$	10.1 to 11.3	218.8	126.5	12.3	4.4	2.5	0.2
$C_{13}Cl_6$	10.8 to 11.8	200.9	161.9	26.1	4	3.2	0.5
$C_{13}Cl_7$	11.4 to 12.5	642.3	865.9	497.4	12.8	17.3	9.9
$C_{13}Cl_8$	11.9 to 13	84.9	287.8	628.2	1.7	5.8	12.6
Total				70.7	92.7	78.2	

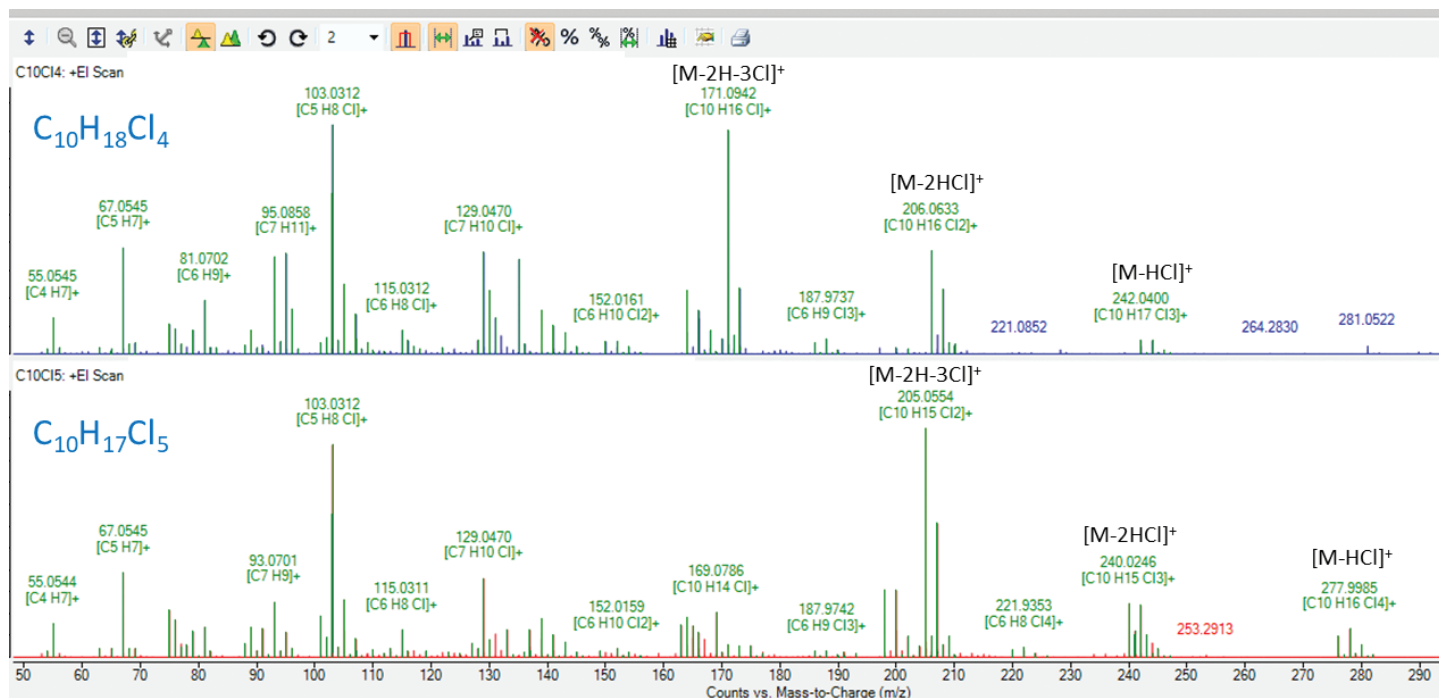


Figure 4. Examples of fragment formula annotated low energy EI spectra for the $C_{10}Cl_4$ and $C_{10}Cl_5$ congeners using 22 eV ionization.

Figure 6 shows quantitation of the $C_{10}Cl_4$ congener in the 55.5% CI SCCP mixture using low energy EI mode. The estimated amount of this congener in the 55.5% CI SCCP mixture was 4.0%, which is comparable with quantitation results obtained in NCI.

Using lower values of electron energy did not further reduce fragmentation due to the immediate loss of HCl. However, low energy EI assisted the identification and quantitation of SCCP species with lower chlorine content with higher confidence.

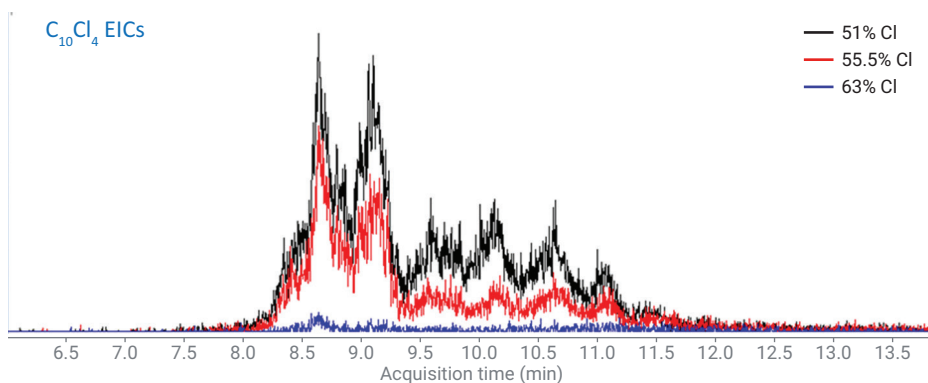


Figure 5. Overlaid low energy accurate-mass extracted ion chromatograms for the $C_{10}Cl_4$ congeners of different %CI SCCP mixtures.

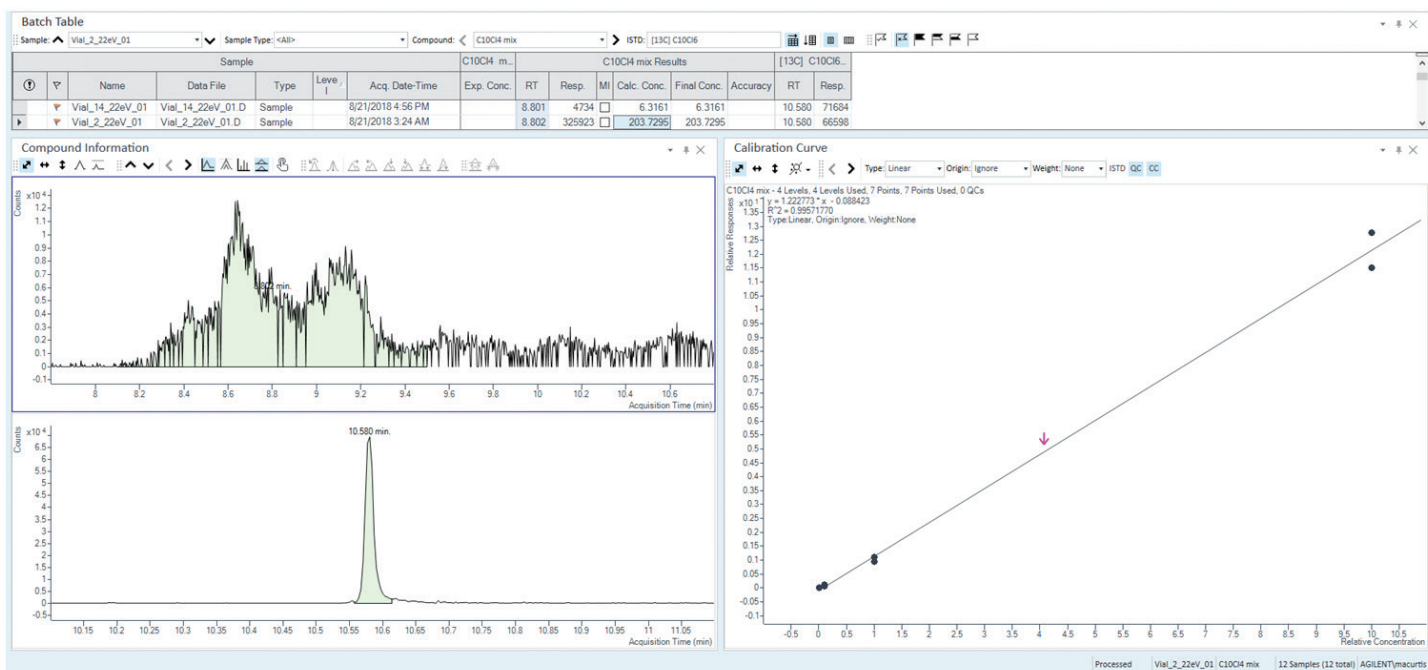


Figure 6. Calculated concentration for the $C_{10}Cl_4$ congener in the 55.5% CI mixture using low energy EI based on the calibration curve from pure congener standards.

Conclusion

The Agilent 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 to ensure high selectivity and sensitivity across SCCP congeners with various degrees of chlorination.

While the negative chemical ionization technique demonstrated a low degree of fragmentation that significantly simplified the SCCP spectra, low energy EI appeared to be more sensitive for SCCP species with low chlorine content.

References

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