Multidimensional Characterization of Short Chain Chlorinated Paraffins (SCCPs) with GC-APCI and Cyclic Ion Mobility

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Introduction

Chlorinated paraffins (CPs) are a class of industrial chemicals that have generated attention as an environmental contaminant and are included in the Stockholm Convention list of persistent organic pollutants (POPs).[1] CPs are polychlorinated-n-alkanes with carbon lengths that range from C10 to C30 and chlorine contents of 30-70% by mass. They are categorized into three subclasses: short chain (SCCPs, C10-C13), medium chain (MCCPs, C14-C17), and long chain (LCCPs, C>18). Analysis of CPs is challenging due to their chemical complexity and large number of possible congeners. There is no consensus standard method for the analysis of SCCPs, but they have been analyzed with GC-EI, GC-NCI, and LC-APCI.[2-4] This study evaluates the suitability of GC-APCI with ion mobility and HRMS for the analysis of SCCPs.

Samples

Very few authentic standards are available for chlorinated paraffins. To optimize the ionization of SCCPs, two reference standards of a single congener, C10Cl6, were purchased: 1,5,5,6,6,10-hexachlorodecane from Cambridge Isotope Labs (Tewksbury, MA) and 1,2,5,6,9,10-hexachlorodecane from Crescent Chemical (Islandia, NY). Additionally, three SCCP technical mixtures of C10-C13 with varying degrees of chlorination (51.5%, 55%, and 63%) were tested (Cresent Chemical).

Experimental Parameters

GC Parameters

GC: Modified Agilent 8890

Column: Rxi-5SilMS 30m x 0.25mm ID, 0.25 µm film thickness

Carrier gas flow: 1.4 mL/min (He)

Make-up gas: 350 mL/min (N_2)

Transfer Line Temp: 290ºC

Injection Port Temperature: 280°C

Injection Volume: 1µL pulsed splitless

Temperature Program:

Ramp (ºC/min)	Temp (C)	Hold Time
Init	60	1
30	220	0
10	300	10

Figure 1. *The SELECT SERIES Cyclic IMS fitted with the APGC™ source.*

MS Parameters

MS: SELECT SERIES™ Cyclic™ IMS

Ionization: APCI

Corona Current: 2 µA

Cone gas: 250 L/hr

Aux Gas: 200 L/hr

Mass Range: *m/z* 50-1200

MS Analyzer Mode: V mode (Resolution ~60,000 FWHM)

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Ionization of SCCPs with GC-APCI

Positive Ion Charge Transfer Ionization

APGC offers different modes of ionization dictated by the gas flow and composition in the source region. Using 'dry' source conditions, charge transfer (Fig 2) is the expected ionization mechanism.[5] When utilized with SCCPs, the compounds fragmented extensively (Fig 3).

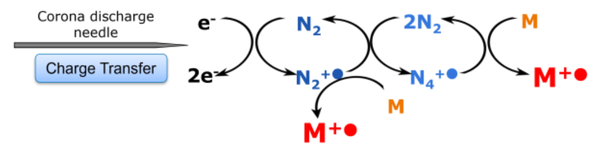

Figure 2. *Expected ionization mechanism in APGC+ charge transfer mode.*

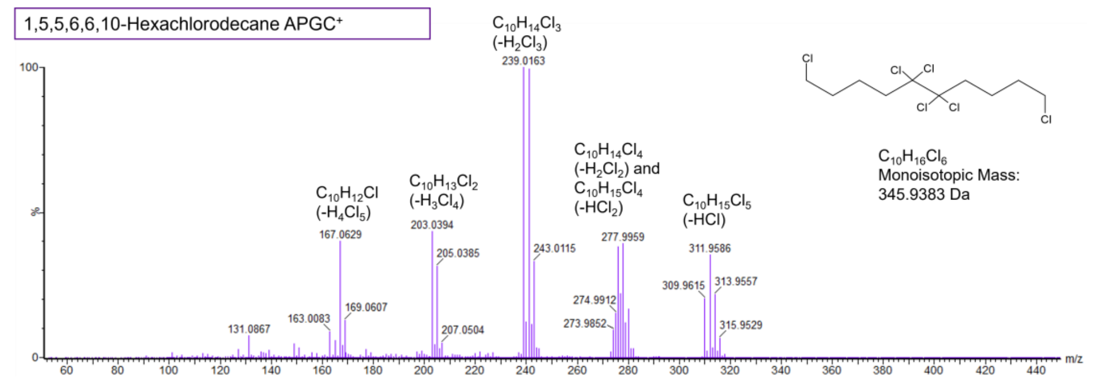

Figure 3. *MS spectrum of 1,5,5,6,6,10-hexachlorodecane collected with APGC+ mode. The compound undergoes significant fragmentation and no molecular ion is detected.*

Negative Ion Adduct Formation

The ionization in APGC can be changed by adding modifiers (Fig 4) and changing gas flows. For this study, chloroform ($CHCl_3$) was introduced to form $[M+Cl]^-$ adducts.

The MS spectra for the C10Cl6 congeners are dominated by the molecular ion (Fig 5). A molecular ion is a great advantage for qualitative and quantitative analysis of SCCPs.

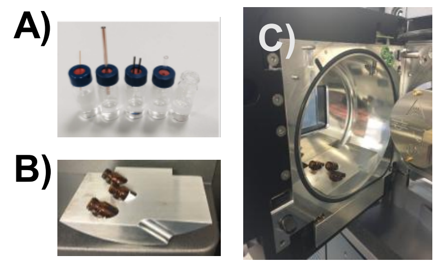

Figure 4. *How modifiers are introduced in the APGC source: A) vials of the modifier with different levels of restriction, B) holder tray for the vials, and C) image of the vial holder in the source door.*

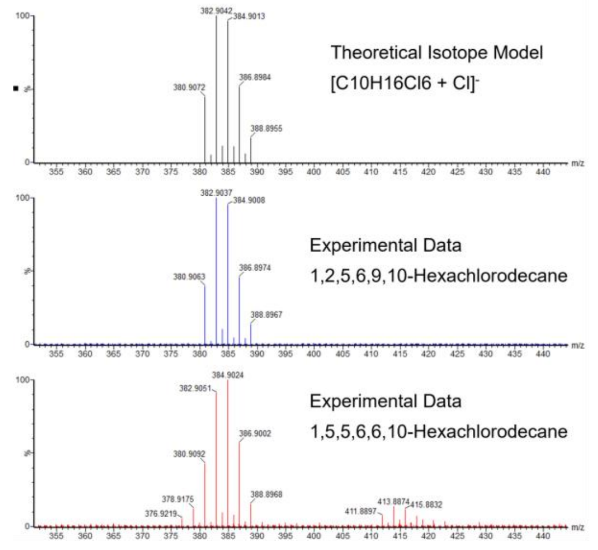

Figure 5. *MS spectra of C10Cl6 congeners in APGC- mode with chloroform in the source to form Cl adducts. Top: theoretical isotope model for the Cl adduct formation for C10H16Cl6. Middle (blue): experimental spectrum for 1,2,5,6,9,10-hexachlorodecane Bottom (red): experimental spectrum for 1,5,5,6,6,10-hexachlorodecane*

Analysis of SCCP Technical Mixtures

A big challenge with the analysis of SCCPs is the complexity of the standard technical mixes that contain several homologues with varying degrees of chlorination. The GC-APCI⁻-HRMS analysis allowed for the selective detection of homologues based on carbon atoms and chlorine atoms (as $[M+Cl]^-$ ions). There is a high degree of overlap in the elution profiles of the different CP homologues (Fig 6).

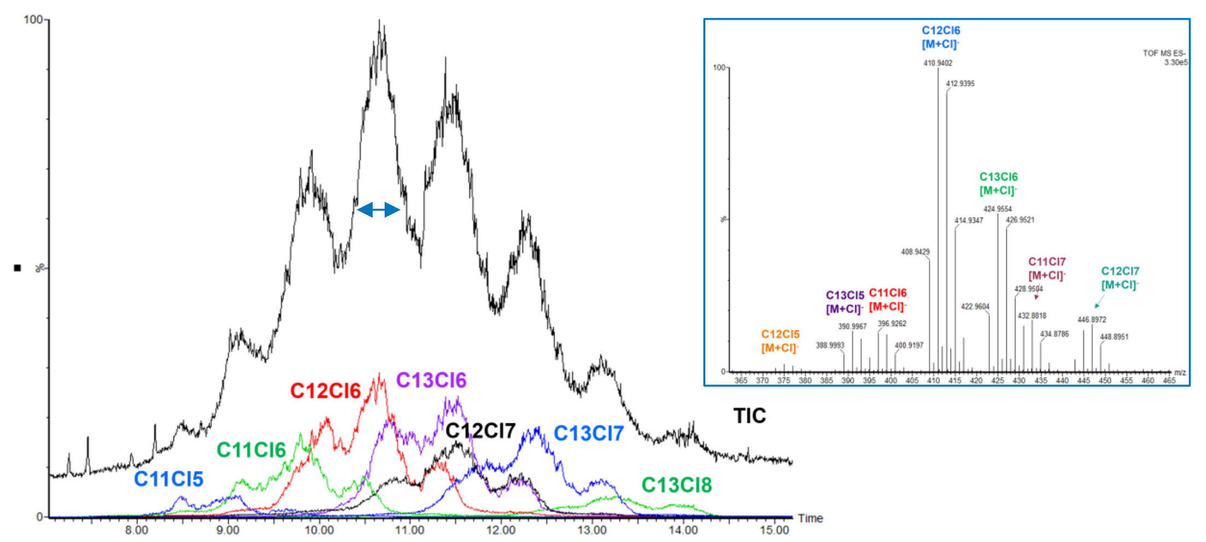

Figure 6. *Total ion chromatogram (TIC, black) for the 51.5% Cl technical mixture of C10-C13 chlorinated paraffins with extracted ion chromatograms of select homologues with varying degrees of chlorination. The inset is the mass spectrum at 10.6 min demonstrating the complexity of the sample with co-eluting CP homologues.*

Ion Mobility Separation of SCCP Technical Mixtures

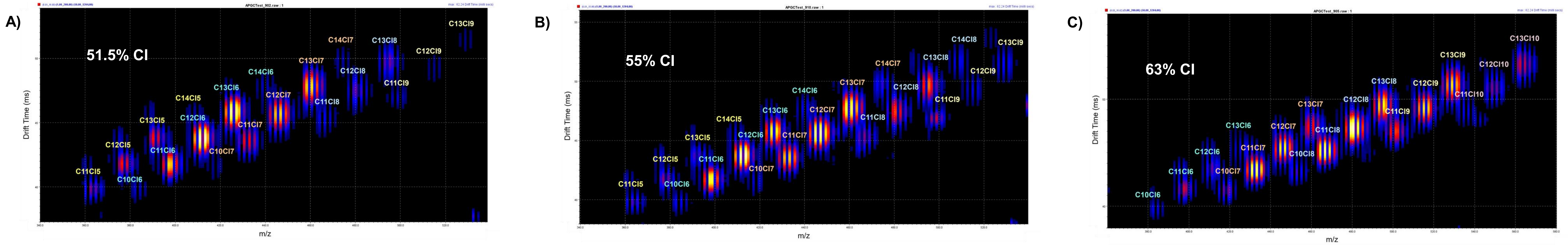

Figure 7. *Visualization of the ion mobility separation of CP homologues. Heat map plots of observed drift time vs m/z of the 51.5% Cl (A), 55% Cl (B) and 63% Cl (C) C10-C13 SCCP technical mixes. The individual homologues are annotated in the plots by C and Cl numbers.*

Utilizing ion mobility in combination with GC-HRMS gave an extra dimension to characterize SCCP technical mixures (drift time). This extra separation yielded more insight into the individual carbon chain homologue groups. Utilizing 'top and tail' ion mobility selection on the SELECT SERIES Cyclic IMS, the IMS acquisition was done with the SCCPs traveling 2 passes in the cyclic ion mobility cell. In the plots of drift time versus *m/z,* distinct trendlines were observed for the homologues that shared the same degree of chlorination (Fig 7). The trendlines could be isolated in Driftcope software and the extracted drift traces for the 55% Cl technical mix are shown in Figure 8. The peak shape in the drift time dimension for the homologues was easy to integrate and the relative percent of each homologue in the technical mixes is presented in Figure 9.

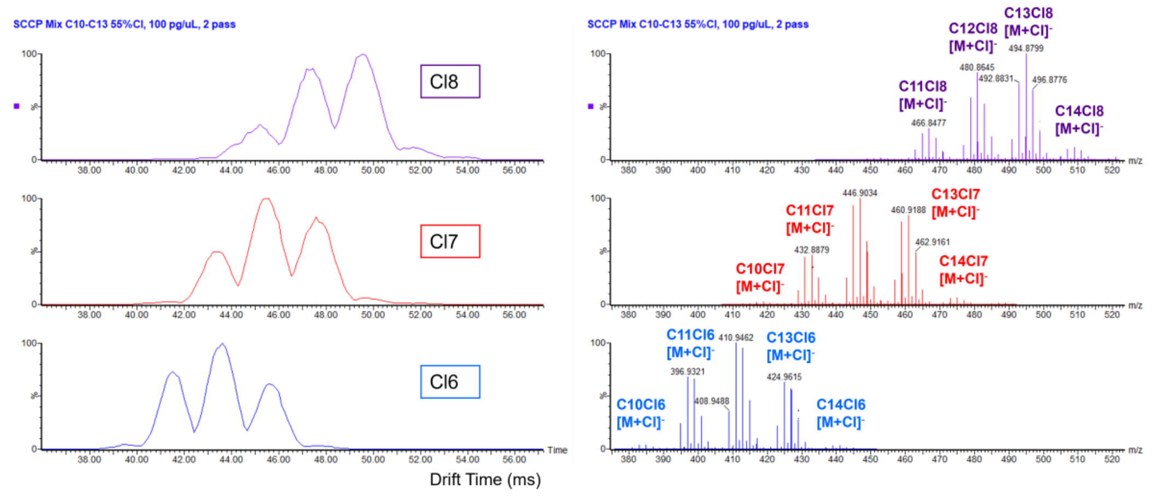

Figure 8. *Extracted drift traces (left) and MS spectra for homologue groups with the same number of chlorines (left) that could be isolated from the trendlines observed in the drift v m/z plots in the 55% Cl technical mix.*

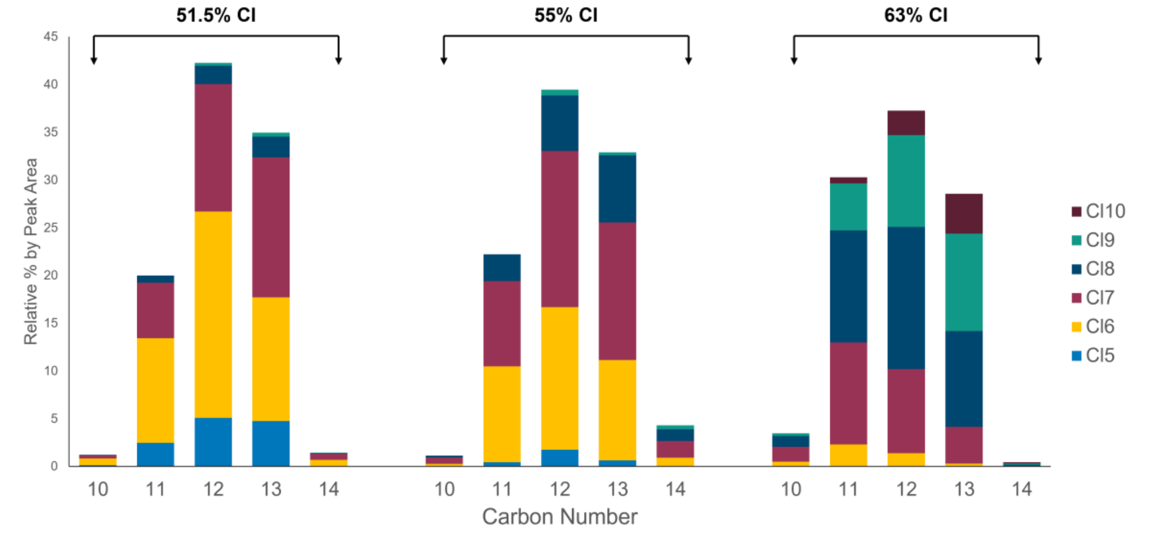

Figure 9. *Chart of the relative percent of each SCCP homologue in the three technical mixes. Percentages were calculated by dividing the peak area of the homologue in the drift dimension by the total peak area of SCCPs in the sample.*

Ion Mobility Separation of Individual Congeners with Multi-Pass IMS

Each SCCP homologue could be composed of several hundred congeners. With the SELECT SERIES Cyclic IMS, ion mobility resolution can be increased with multiple passes in the circular ion mobility path (Figure 10). Additional experiments performed with 6 or 8 passes in the cyclic ion mobility cell examined the profiles of individual congeners C11Cl6 and C12Cl7 in the technical mixtures (Figure 11). While individual congeners could not be completely separated, differences in the ion mobility space could be observed for early versus late eluting congeners in the technical mixtures.

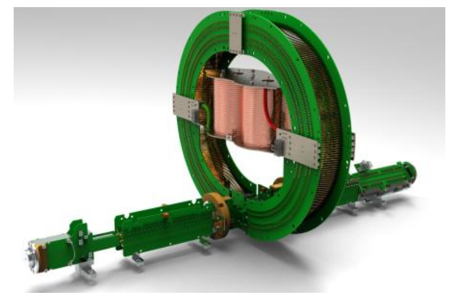

Figure 10. *The cyclic Ion mobility optics in the SELECT SERIES Cyclic IMS.*

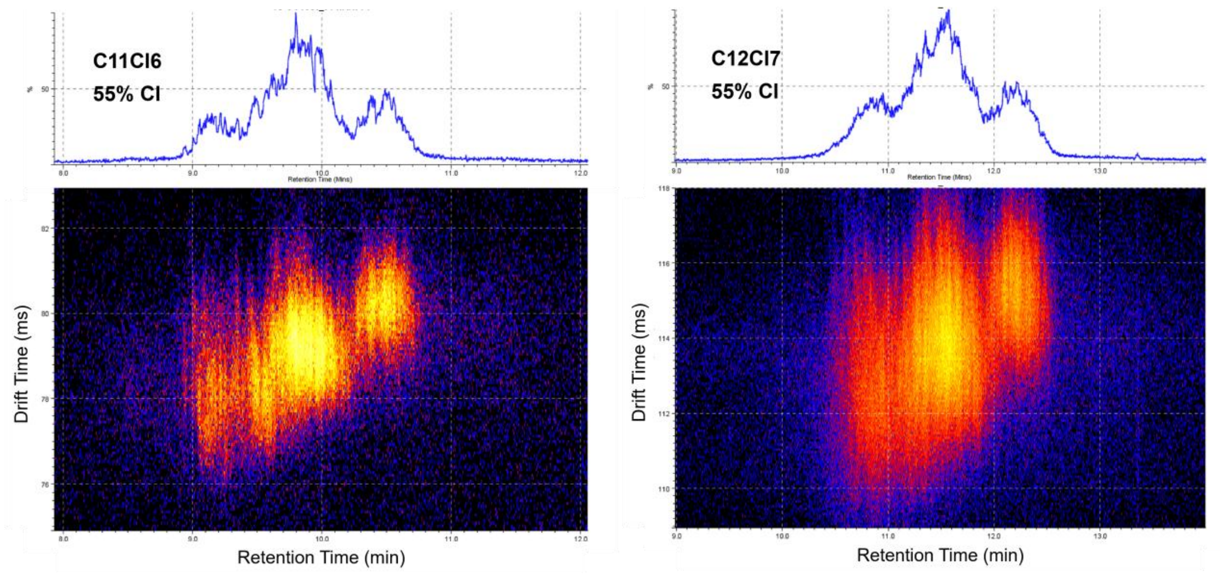

Figure 11. *Multi-pass ion mobility separation of the SCCP congeners in the 55% Cl technical mix C11Cl6 (left) and C12Cl7 (right). For C11Cl6, the quadrupole was set for* m/z *394.9 and the ions traveled 6 passes in the IMS cell (Resolution ~ 159 Ω/ΔΩ). For C12Cl7, the quadrupole was set for* m/z ***444.8*** *and the ions traveled 8 passes in the IMS cell (Resolution ~ 184 Ω/ΔΩ). The top trace is the XIC and the heat map shows the separation in drift time versus retention time for the entire isotopic envelope.*

Conclusions

- SCCPs were analyzed using APGC with a chloroform modifier, producing characteristic, homologue-specific $[M+Cl]^-$ ions.
- The addition of IMS enabled a fuller characterization of SCCP mixes. Distinct trendlines were observed in the drift time dimension for the homologues that shared the same degree of chlorination.
- Complete identification of individual congeners within a homologue may not be achievable, but adding high-resolution IMS separations gives more insight into compositional differences between samples.

References

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Conflict of Interest Disclosure: Sarah Dowd, Lindsay Hatch, and Douglas Stevens are employees of Waters Corporation and presenting the poster on behalf of the company.

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