

# ANALYSIS OF CHLORINATED PARAFFINS BY CHLORIDE ENHANCED APCI-MS

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## Introduction

Polychlorinated *n*-alkanes, also called chlorinated paraffins (CPs), are complex technical mixtures with a degree of chlorination between 30 and 70% and a linear chain length of C<sub>10</sub>-C<sub>13</sub> (short chain, SCCPs), C<sub>14</sub>-C<sub>17</sub> (medium chain, MCCPs) or >C<sub>17</sub> (long chain, LCCPs)<sup>1</sup>. Due to their physical properties, CPs are applied as fire retardants, plasticizers in PVC, adhesives, and as extreme pressure additives in lubricants and cutting oils<sup>1</sup>. Due to their persistence in the environment<sup>2</sup> and unrestricted use, CPs can be found in aquatic and terrestrial food webs in rural and remote areas<sup>1</sup>.

Nowadays, the most applied method for the determination of CPs is high resolution gas chromatography combined with electron capture negative ionization (ECNI) mass spectrometry in the low or high resolution mode. Recently, our group showed that the use of a CH<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> reagent gas mixture for negative ion chemical ionization (NICI) enhances the formation of chloride adduct ions for CPs<sup>3</sup>. Major benefits are suppression of the ionization of other interfering chlorinated compounds and response factors independent from the degree of chlorination.

This work presents the use of chloride enhanced atmospheric pressure chemical ionization (Cl-APCI) combined with ion trap mass spectrometry for the detection of these compounds. It allowed to detect CPs after pre-separation by high performance liquid chromatography or gel permeation chromatography. This combination allows to overcome some limitations of gas chromatography such as possible discriminations in the detectability of highly chlorinated and low volatile CPs (e.g. LCCPs).

## Methods and Materials

**Chemicals and CP standards.** Single CP congeners (2,5,6,9-tetrachlorodecane, 1,2,9,10-tetrachlorodecane, 1,2,5,6,9-pentachlorodecane and 1,2,5,6,9,10-hexachlorodecane) as well as several technical SCCP mixtures (51.0%, 55.5% and 63.0% Cl content), MCCP mixtures (42.0%, 52% and 57% Cl content) and LCCP mixtures (36.0%, and 49.0% Cl content) dissolved in cyclohexane were purchased from Ehrenstorfer (Augsburg, Germany). Other chemicals used for

this work were: Dichloromethane (99.8%, Scharlau, Spain), chloroform (99.8%, J.T. Becker, The Netherlands) and cyclohexane (99.8%, Scharlau, Spain).

**Instrumentation.** Separations were performed on a column of 250 mm length and 4.6 mm i.d. packed with Nucleosil Silicagel (5  $\mu\text{m}$  particles, 100  $\text{\AA}$  pore size; Macherey-Nagel, Germany). Samples were injected with a PAL autosampler (CTC Analytics, Switzerland) overfilling twice an external loop of 20  $\mu\text{l}$  and using dichloromethane as rinsing solution. Several eluent compositions were employed (e.g. *n*-heptane,  $\text{CH}_2\text{Cl}_2$ , *n*-heptane/ $\text{CHCl}_3$  7+3, cyclohexane/ $\text{CHCl}_3$  7+3). If not present in the eluent,  $\text{CHCl}_3$  (or  $\text{CH}_2\text{Cl}_2$ ) was added post-column using a T-connection. The application of  $\text{CHCl}_3$  as mobile phase at a flow rate of 1 ml/min was the simplest and gave the best results. A Rheos 2000 pump (Flux Instruments, Switzerland) was used for all experiments.

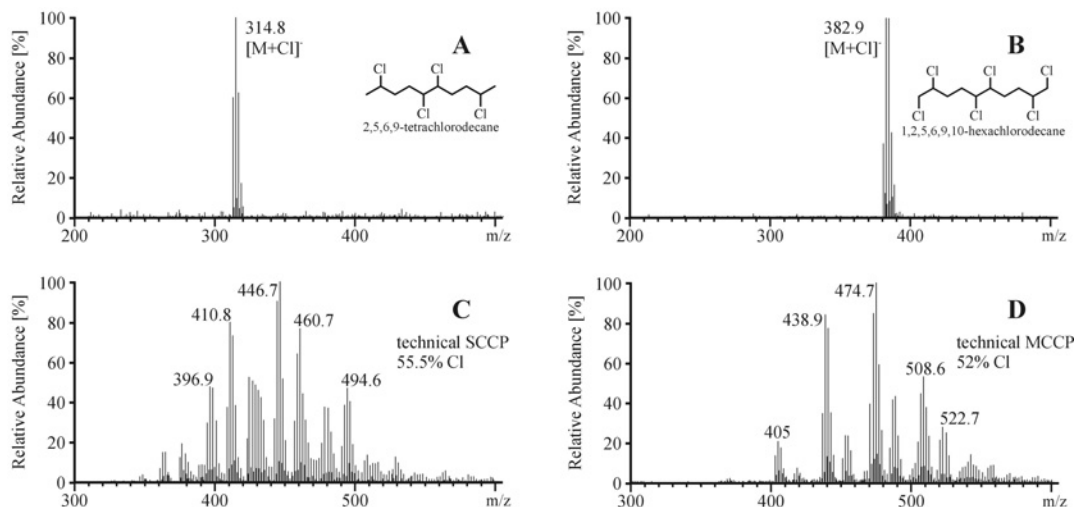
An ion trap mass spectrometer (LCQ; Thermo Finnigan, USA) was employed in the APCI negative ion mode. The instrument was tuned for maximal yield of the most abundant isotope signals of the chloride adduct ion of  $\text{C}_{13}\text{H}_{22}\text{Cl}_6$  ( $m/z$  424.9) in the SCCP mixture with 51% Cl content. The following source parameters were applied: Nitrogen sheath gas flow, 50 arbitrary units (12.5 l/min), auxiliary gas flow, 10 arbitrary units (3.5 l/min); ionization current of the corona discharge, -5  $\mu\text{A}$ , heater temperature 200  $^\circ\text{C}$ , and heated capillary at 150  $^\circ\text{C}$  and -5 V. The scan range was set to  $m/z$  200-800.

## Results and Discussion

**Selection of Cl source.** Previous studies using  $\text{CH}_2\text{Cl}_2$  as reagent gas for NICI demonstrated that the ability of CPs to form  $[\text{M}+\text{Cl}]^-$  ions can be used for quantification, if an excess of chloride anions is present in the reagent gas mixture<sup>3</sup>. Generally, the ionization processes of APCI are similar to those of classical chemical ionization (CI)<sup>4</sup>. Therefore, the chloride adduct formation observed in CI should also take place under APCI conditions. Tests with both  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  confirmed this. The latter was preferred, since it is more suited for normal phase chromatography.

**Ionization of single congeners.** In contrast to conventional ECNI forming  $[\text{M}+\text{Cl}]^-$ ,  $[\text{M}-\text{Cl}]^-$  and  $[\text{M}-\text{HCl}]^-$ ,  $\text{CHCl}_3$ -APCI yielded exclusively  $[\text{M}+\text{Cl}]^-$  adduct ions (see Figure 1 for examples). This resulted in an increased selectivity and strongly reduced mass interferences between different CP congeners. The response factors of different single congeners such as 2,5,6,9-tetrachlorodecane, 1,2,9,10-tetrachlorodecane, 1,2,5,6,9-pentachlorodecane and 1,2,5,6,9,10-hexachlorodecane varied by a factor of 5 compared to >20 for ECNI and 2.4 for  $\text{CH}_2\text{Cl}_2$ -NICI.

**Analysis of technical mixtures.** The response factors of technical mixtures were also less dependent on the degree of chlorination than for conventional ECNI ionization. They varied by a factor <3 between SCCP mixtures of 51, 55.5 and 63% chlorine content compared to 9 for conventional ECNI and 1.4 for  $\text{CH}_2\text{Cl}_2$ -NICI. Figure 2 shows the congener pattern obtained for a SCCP, a MCCP and a LCCP mixture (average of 5 measurements). In contrast to ECNI,  $\text{CHCl}_3$ -APCI was also able to detect lower chlorinated congeners ( $\text{Cl}_5$ ). A relative distribution of the homologue groups ( $\text{C}_{14}$ ,  $\text{C}_{15}$ , etc.) similar to ECNI was obtained for MCCP mixtures. However, SCCP mixtures showed a higher abundance of longer chained homologues. At the moment it is not possible to say, if this is caused by increased response factors for these homologues.

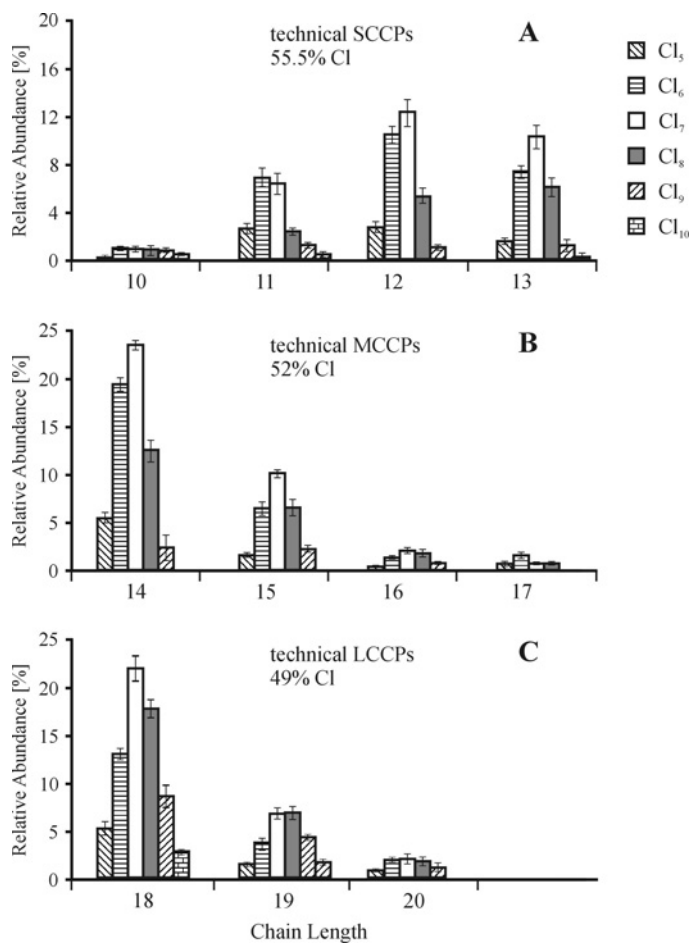


**Figure 1:**  $\text{CHCl}_3$ -APCI(-) mass spectra of two SCCP congeners (A: 2,5,6,9-tetrachlorodecane, B: 1,2,5,6,9,10-hexachlorodecane) and a SCCP mixture with 55% Cl content (C) and a MCCP mixture with 52% CP content (D).

**Linearity and detection limits.** Limits of detection were in the range 1-2 ng/ $\mu\text{l}$  for SCCP, MCCP and LCCP mixtures. The linearity of the new ionization method was good between 2 and 100 ng of technical SCCP or MCCP mixture detecting the main congeners of each homologue group ( $R^2 > 0.99$ , 7 concentrations).

**Open challenges.** Some SCCP congeners form ions with the same nominal mass-to-charge ratio as MCCP congeners (e.g.  $\text{C}_{12}\text{H}_{18}\text{Cl}_8$  and  $\text{C}_{17}\text{H}_{30}\text{Cl}_6$ )<sup>5</sup>. Therefore, a chromatographic separation is necessary, if low resolution mass spectrometry is applied and a chlorination specific identification is desired. Normal phase chromatography is not suited. A possible alternative could be gel permeation chromatography. This option is currently evaluated. Moreover, quantitative analysis by Cl-APCI-MS is currently investigated and validated. Data will also be compared to other techniques currently in use.

## SPECIAL INSTRUMENTAL TECHNIQUES AND PATTERN RECOGNITION



**Figure 2:** Congener and homologue patterns obtained by chloride enhanced APCI-MS for a SCCP (A, 55.5% Cl), a MCCP (B, 52% Cl) and a LCCP mixture (C, 49% Cl). Error bars and the average of 5 measurements are given.

### Acknowledgements

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