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## EVALUATION OF MS IONISATION MODES (EI, PCI AND NCI) FOR THE ANALYSIS OF CHLORINATED PARAFFINS

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### Introduction

Chlorinated paraffins (CPs) are industrial formulations mainly containing polychlorinated *n*-alkanes (PCAs), with carbon chain lengths between  $C_{10}$  and  $C_{30}$  and a chlorination degree between 30 and 70 % by mass<sup>1</sup>. Short-chain chlorinated paraffins ( $C_{10}$ – $C_{13}$ , SCCPs) have been the most used mixtures in the industry, and also the most frequently detected in environmental samples. These compounds are considered toxic, persistent and liable to bioaccumulate. For instance,  $C_{12}$  SCCPs with 60 % chlorine content have been classified as *possibly carcinogenic to humans* (Group 2B), by the IARC<sup>2</sup>.

CP analysis is difficult due to the large number of individual PCA congeners that are present in technical mixtures. Capillary GC is not able to separate all individual congeners, and the chromatograms consist on a characteristic big hump corresponding to the coelution of several thousands of compounds. The determination of CPs is often carried out by GC-ECD<sup>3</sup> or GC coupled to high<sup>4</sup> or low-resolution<sup>5</sup> mass spectrometry (MS). Generally, negative chemical ionisation (NCI-MS) is frequently used due to its high selectivity and selectivity. The use of NCI with high-resolution MS at a resolving power of 12,000 makes possible to obtain the elution profiles corresponding to the different homologue groups. Nevertheless, the use of this technique in routine analysis shows some limitations, such as the difficulty of providing daily reproducible conditions and the need of qualified personnel.

In this work, three different MS ionisation modes (electron impact, EI; positive chemical ionisation, PCI and negative chemical ionisation, NCI) were evaluated for their applicability to the analysis of chlorinated paraffins. For each mode, commercially available individual PCA congeners and standard CP mixtures were used for the optimisation of the experimental conditions. In addition, characterisation of mass spectra and fragmentation pathways for individual congeners was performed. GC-NCI-MS quality parameters (repeatability, limits of detection and dynamic ranges) were established, and the proposed method was applied to the determination of SCCPs in river sediment samples.

### Methods and Materials

#### Standards and Samples

A stock standard solution of a short-chain chlorinated paraffin,  $C_{10}$ - $C_{13}$ , 63 % Cl, of 100 ng/ $\mu$ l in cyclohexane and five standard solutions of  $C_{10}$  individual PCA congeners (10 ng/ $\mu$ l in cyclohexane), were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table 1 lists the congener code, the molecular formula, the chlorine-substituted positions and the number of diastereoisomers for each individual PCA congener:

**Table 1.** List of individual PCA congeners.

Congener code	Formula	Cl-substituted positions	n° diastereoisomers
CP-1	$C_{10}H_{18}Cl_4$	2, 5, 6, 9	3

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CP-2	$C_{10}H_{18}Cl_4$	1, 2, 9, 10	1
CP-3	$C_{10}H_{17}Cl_5$	1, 2, 5, 6, 9	2
CP-4	$C_{10}H_{16}Cl_6$	1, 2, 5, 6, 9, 10	1
CP-5	$C_{10}H_{16}Cl_6$	1, 2, 5, 6, 9, 10	2

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$^{13}C_6$ -hexachlorobenzene (Dr. Eherenstorfer GmbH), was used as internal standard for quantification purposes. River sediment samples were collected from six different sampling points located at several industrial areas near of Barcelona.

### GC-MS instrumentation

The analysis of PCAs was carried out on a Trace GC 2000 gas chromatograph coupled with a GCQ/Polaris ion-trap mass spectrometer (ThermoFinnigan). The GC instrument was equipped with a DB-5 (J&W Scientific, Folsom, USA) (5 % phenyl-, 95 % methylpolysiloxane) fused-silica capillary column (30 m  $\times$  0.25 mm I.D., 0.25  $\mu$ m film thickness). The oven temperature program was 90 °C (held for 1 min) to 150 °C at 25 °C/min and to 300 °C at 8 °C/min (held for 10 min). Helium was used as carrier gas at a flow rate of 38 cm/s. Injector temperature was maintained at 250 °C and splitless injection mode (1min) was used.

The ion trap MS conditions were: ion source temperature 170 °C, transfer line temperature 275 °C and trap-offset 3 V. Lens voltages for L1, L2 and L3 were tuned at 13, 130 and 16 V, respectively. For NCI and PCI modes, methane was used as reagent gas at a pressure of  $1.2 \times 10^{-4}$  mTorr and  $1.6 \times 10^{-4}$  mTorr, respectively.

### Analytical method

The extraction, purification and clean up of river sediment samples was as follows. Briefly, 10 g of sediment were Soxhlet-extracted with *n*-hexane:dichloromethane (DCM) (1:1) for 16 h. The extract was concentrated to 1 ml and transferred to a column containing 15 g of activated Florisil. Two fractions were collected: F1 with 60 ml of *n*-hexane, where PCBs and OCPs are eluted, and F2 with 80 ml *n*-hexane:DCM (85:15) and 100 ml *n*-hexane:DCM (1:1), which contained the CPs and some of the OCPs. The second fraction was reduced over a gentle stream of nitrogen and  $^{13}C_6$ -hexachlorobenzene was added as internal standard. The extracts obtained were injected into the GC-NCI-MS system in the optimal conditions.

## Results and Discussion

### Evaluation of EI+, PCI and NCI ionisation modes

The three different MS ionisation modes were evaluated for their suitability and subsequent applicability to the analysis of chlorinated paraffins. The absence of molecular ion clusters was a common feature to all the ionisation modes studied. In EI+ mode (Figure 1a), two main fragmentation pathways were observed and can be summarised as follows: (a) successive losses of HCl and/or Cl from the molecular ion; (b) molecular ion central bond cleavage resulting in a  $C_5$  cation ( $[C_5H_8Cl_3]^+$  and/or  $[C_5H_9Cl_2]^+$ , depending on the number of chlorine atoms), which undergoes successive losses of HCl.

In PCI mode (Figure 1b), the spectra were characterised by successive losses of HCl and/or Cl from the molecular ion as indicated for EI+ ionisation mode (fragmentation pathway a). Thus, for these two ionisation modes, a high degree of fragmentation was observed.

NCI mode was also characterised by the absence of the molecular ion (Figure 1c), but the observed degree of fragmentation was remarkably lower than in EI+ or PCI. Two cluster ions at  $m/z$  70-75

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corresponding to  $[\text{Cl}_2]^-$  ( $m/z$  70, 72 and 74) and  $[\text{HCl}_2]^-$  ( $m/z$  71, 73, 75) were observed. In addition,  $[\text{M}-\text{Cl}]^-$  and  $[\text{M}-\text{HCl}]^-$  cluster ions were also present in the spectra, and the abundance of the  $[\text{M}+\text{Cl}]^-$  adduct decreased with the chlorine content of the molecule.

In view of the results obtained, NCI was chosen for the analysis of SCCPs because the lower degree of fragmentation is expected to provide high sensitivity and selectivity.

### *GC-NCI-MS analysis of SCCPs in river sediment samples*

At low-resolution MS, the  $[\text{M}-\text{Cl}]^-$ ,  $[\text{M}-\text{HCl}]^-$  and  $[\text{M}+\text{Cl}]^-$  cluster ions of each homologue group were always interfered by other PCA homologues present in the mixture. Therefore, these cluster ions did not allow to distinguish between the different PCA homologue groups. Moreover, these cluster ions showed lower responses than the  $[\text{Cl}_2]^-$  and  $[\text{HCl}_2]^-$  ions, which were always present in the mass spectra of the whole SCCP standard mixture. Therefore, the  $m/z$  70-75 range was chosen for quantification of SCCPs, and the  $m/z$  286-296 range was scanned for the internal standard  $^{13}\text{C}_6$ -hexachlorobenzene. No interferences with other organochlorine compounds (organochlorine pesticides and PCBs), were observed in the selected MS conditions. This is probably due to the fact that the NCI conditions were the optimal ones for the SCCPs and fragmentation for other chlorinated compounds did not occur.

Quality parameters were established using standards and blank sediment samples. Repeatability (%RSD,  $n=5$ ) was 5.7 % and 7.9 % for standards and samples, respectively. LODs were calculated as the amount of analyte injected that produced a signal-to-noise ratio (S/N) of 3, and was 0.20 ng for standards and 0.25 ng for sediment samples. Calibration curve (established between 1 and 80 ng of SCCP injected) was non-linear and it was adjusted to a second-degree polynomial curve.

Triplicate analysis were performed for five river sediment samples. Results obtained are summarised in Table 2. Concentrations ranged between 0.27 and 3.26  $\mu\text{g/g}$ , and the %RSD values did not exceed 10 %. As an example, Figure 2 shows GC-NCI-MS chromatogram corresponding to the S5 river sediment sample.

**Table 2.** Concentrations of short-chain chlorinated paraffins ( $\mu\text{g/g}$ ) in river sediment samples.

Sample code	Mean	%RSD
S1	<b>0.71</b>	<b>5.3</b>
S2	0.27	10.5
S3	0.42	3.2
S4	0.81	10.1
S5	1.79	7.2
S6	3.26	9.9

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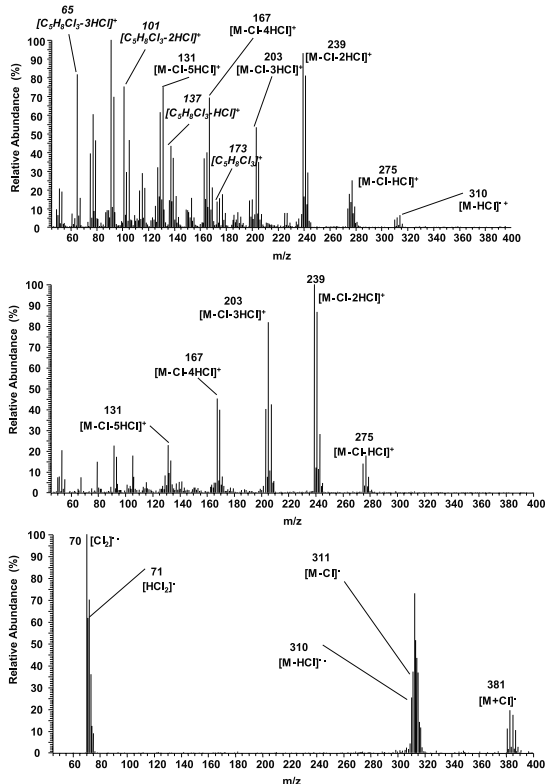


Figure 1. Mass spectra of the CP-5 individual congener for (a) EI+; (b) PCI; and (c) NCI modes.

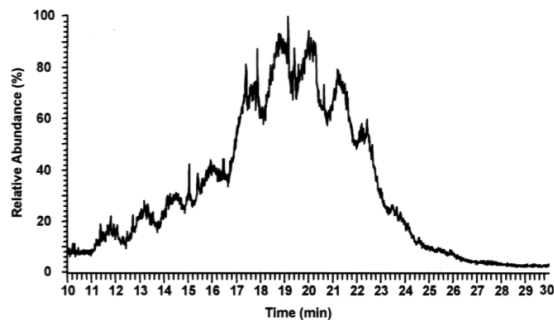


Figure 2. GC-NCI-MS chromatogram of the S5 river sediment sample.