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Solid-phase extraction versus solid-phase microextraction for the determination of chlorinated paraffins in water using gas chromatography–negative chemical ionisation mass spectrometry

P. Castells, F.J. Santos, M.T. Galceran*

Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, Barcelona 08028, Spain

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Abstract

Solid-phase extraction (SPE) and solid-phase microextraction (SPME) were evaluated for the analysis of short-chain chlorinated paraffins (SCCPs) in water samples using gas chromatography coupled to negative chemical ionisation mass spectrometry (GC-NCI-MS). For SPE optimisation, four commercially available SPE cartridges were tested and several SPE parameters, such as the elution solvent, elution volume and breakthrough volume were studied. The best results were obtained with Varian Bond Elut-C_{18}. In order to achieve a high selectivity in the determination of SCCPs, GC-NCI-MS was used. Quality parameters of the optimised SPE and SPME procedures were determined, and the best results were obtained for the SPE/GC-NCI-MS method with LODs of 5 and 20 ng l^{-1} for tap and river water, respectively. This method was successfully applied to the analysis of SCCPs in river water samples at concentrations below the $\mu g\,l^{-1}$ level.

Keywords: Water analysis; Solid-phase extraction; Solid-phase microextraction; Paraffins, chlorinated

1. Introduction

Chlorinated paraffins (CPs) are complex mixtures 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 [1–3]. These formulations contain a huge number of isomers and homologues [4]. CPs are mainly used as extreme pressure additives in industrial cutting fluids and as flame retardants in plastics, rubber, paints and sealants [5]. Short-chain (C_{10}–C_{13}) chlorinated paraffins (SCCPs) have been the most extensively used CP mixtures in the industry and they are considered toxic for aquatic invertebrates, persistent and bioaccumulative [6–8]. In consequence, several organisations and environmental agencies have imposed regulations on uses and/or environmental releases of SCCPs [9–12]. The presence of CPs has been reported in various environmental matrices [13], such as biota [14–16], sediments [14,17], air [18] and water [19–24]. In particular, the analysis and monitoring of SCCPs in water has a high level of concern since the European Union [25] included these substances [26] on the list of *priority hazardous substances* in the field of water policy, amending Directive 2000/60/EC [27]. CPs have been detected in river and marine waters at low concentrations (below the $\mu g\,l^{-1}$ level) except for industrial areas, where the concentrations reported are in the $\mu g\,l^{-1}$ level. Therefore, the establishment of selective and sensitive methods for the determination of SCCPs in water is needed. Unfortunately, until now few papers dealing with the analysis of CPs in water can be found in the literature.

The analysis of CPs is very difficult because of the complexity of the mixtures (>10,000 congeners) and only semi-quantitative determination can be performed. CP chromatograms are characterised by a big hump with a co-elution of the congeners. Single-capillary GC column is insufficient to resolve all the compounds of interest as individual peaks. Comprehensive gas chromatography (GC × GC), which has emerged as an extremely powerful separation technique [28], would, potentially, help to improve the separation of these compounds. Most of the methods used for the determination of CPs are based in gas chromatography with electron capture detection (GC-ECD) or GC coupled

* Corresponding author. Tel.: +34-93-402-1100; fax: +34-93-402-1233.
E-mail address: galceran@apolo.qui.ub.es (M.T. Galceran).

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to negative chemical ionisation mass spectrometry [29–31]. Liquid-liquid extraction (LLE) or solid-phase extraction (SPE) are the most commonly used extraction techniques for preconcentration of CPs from aqueous samples, although solid-phase microextraction (SPME) using gas chromatography with electron capture detection has also been recently reported [24]. This approach permits the fast analysis of SCCPs in waters at the low $\mu g\,l^{-1}$ level with reasonable selectivity. Techniques such as SPE or LLE can provide a high capacity of preconcentration, enough to allow the analysis of these compounds in water samples at the $ng\,l^{-1}$ level. Unfortunately, when these two extraction techniques are used with electron capture detection (ECD), a purification step is often necessary to remove the co-extracted interferent compounds that would not let to achieve the required selectivity and detection limits. On the other hand, gas chromatography coupled with negative chemical ionisation mass spectrometry (GC-NCI-MS) has been used for the analysis of these compounds [15,23,32–34] providing a high selectivity.

This paper will focus on the development of a selective and sensitive method for the analysis of SCCPs in water samples using GC-NCI-MS. For this purpose, two methods based on SPE and SPME were studied and evaluated. Quality parameters for both methods were established and compared, and the selected method was used for the determination of SCCPs in river water samples.

2. Experimental

2.1. Standards and reagents

Two stock standard solutions of short-chain chlorinated paraffin (SCCP, C_{10}–C_{13}, 63% Cl, $100\,\mu g\,ml^{-1}$) in acetone and in cyclohexane were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Calibration standard solutions were prepared by dilution of the stock standard solution in cyclohexane. SCCP concentrations of the standards ranged between 1 and $40\,\mu g\,ml^{-1}$. A standard solution of $^{13}C_6$-hexachlorobenzene at $1\,\mu g\,ml^{-1}$ (Dr. Ehrenstorfer GmbH) was used as the internal standard for quantification purposes. For optimisation of GC-NCI-MS method and selecting the suitable ions for quantification, a standard solution containing a mixture of five C_{10}-PCA congeners at $2\,\mu g\,ml^{-1}$ was prepared by dilution of the corresponding individual stock standard solutions (Dr. Ehrenstorfer GmbH) at $10\,\mu g\,ml^{-1}$ in cyclohexane. Chlorinated biphenyl PCB 30 (Dr. Ehrenstorfer GmbH) was used as internal standard for quantification purposes using GC-ECD.

Cyclohexane, dichloromethane and methanol of residue analysis grade were supplied from Merck (Darmstadt, Germany). Water was purified using an Elix 3 coupled to a Milli-Q system (Millipore, Bedford, MA, USA). All glass materials were cleaned with AP-13 Extran alkaline soap (Merck, Darmstadt, Germany) for 24 h, rinsed consecutively with Milli-Q water and acetone, and dried overnight.

2.2. GC-ECD and GC–MS conditions

Preliminary SPE studies were carried out on a Trace GC 2000 gas chromatograph (ThermoFinnigan, Milan, Italy) equipped with a ^{63}Ni electron-capture detector (ECD) using nitrogen as make-up gas at $40\,ml\,min^{-1}$. A DB-5MS (5% phenyl-, 95% methylpolysiloxane), $30\,m \times 0.25\,mm$ i.d., fused-silica capillary column (J&W Scientific, Folsom, USA) of $0.25\,\mu m$ film thickness was used. Carrier gas was helium at a constant flow-rate of $1\,ml\,min^{-1}$ held by electronic pressure control. Injector and ECD temperatures were 250 and 330 °C, respectively, and the splitless injection mode (1 min) was used. The oven temperature programme 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). For the quantification purposes, the integration of the total area below of the SCCP elution profile was used.

For GC-NCI-MS experiments, a Trace GC 2000 gas chromatograph coupled to a GCQ/Polaris ion-trap mass spectrometer (ThermoFinnigan, Austin, TX, USA) was used. The column and the chromatographic conditions were the same as described above for GC-ECD experiments. Xcalibur version 1.2 software was used for control, general operation and acquisition of the mass spectra.

The MS operating conditions were the following: ion source and transfer line temperatures 250 and 275 °C, respectively. The instrument was tuned in EI positive mode using perfluorotributylamine (FC-43) according to the recommendations of the manufacturer in order to achieve the best sensivity. Parameters such as automatic gain control (AGC) and multiplier voltage (1225 V, 10^5 gain) were set by automatic tune. The electron energy was 70 eV and the emission current 250 μA. The mass spectrometer was operated in the negative chemical ionisation (NCI) mode using methane as reagent gas at a pressure of 1.2×10^{-4} mTorr (reading on the ion gauge). Voltages for lenses L1, L2 (gate lens) and L3 were also tuned at 13, 130 and 16 V, respectively. Moreover, the effect of trap-offset voltage on response was studied from 3 to 10 V, and the lowest value (3 V) was selected in order to achieve the maximum sensitivity. NCI full-scan data acquisition was made over the range *m/z* 45–650. After selection of the appropriate ions for the quantification of SCCPs, the MS acquisition method was programmed in two segments. In the first segment, the internal standard $^{13}C_6$-hexachlorobenzene was detected by monitoring the range *m/z* 286–296 at 0.64 s per scan (10 μscans per scan), whereas SCCPs were monitored in the second segment by scanning the $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ cluster ions present in the 70–75 *m/z* region, at an scan rate of 0.63 s per scan (10 μscans per scan). Quantification was performed as sum of all SCCP congeners considering the area of the elution profile of SCCPs obtained in the second monitoring segment.

2.3. Solid-phase extraction procedure

For solid-phase extraction (SPE) studies, four commercially available C_{18} cartridges (500 mg/3 ml) were used: Bond Elut-C_{18} from Varian (Harbor City, CA, USA), Supelclean ENVI-18, Discovery DSC-18 and Discovery DSC-18LT from Supelco, (Bellefonte, PA, USA). Before use, all C_{18} cartridges were sequentially washed using 2 ml of methanol and 2 ml of Milli-Q water. Volumes of 1000 ml of water were passed through the cartridges at a flow-rate of 10 ml min^{-1} using a Visiprep System (Supelco). After that, the cartridges were dried using a nitrogen stream for 10 min. Chlorinated paraffins were eluted from the cartridges using 3 ml of cyclohexane at a flow-rate of 2 ml/min. The extracts obtained were dried over sodium sulphate and concentrated to ca. 1 ml. using a rotary evaporator. The extract was then transferred to a 2 ml conical vial and was concentrated under a gentle stream of nitrogen. The final volume of the extract was adjusted to 20 μl with cyclohexane after addition of the internal standard ($^{13}C_6$-hexachlorobenzene).

2.4. Solid-phase microextraction procedure

SPME experiments were performed with a manual fibre holder and a 100 μm polydimethylsiloxane fibre (PDMS 100 μm) supplied by Supelco. Before use, the fibre was conditioned in a heated GC split/splitless injection port under helium flow according to the manufacturer's instructions. The SPME procedure used in this study was optimised in a previous paper [24]. Briefly, a 35 ml water sample was placed in a 40 ml screw-cap glass vial fitted with a silicone-PTFE septa and conditioned for 10 min in a thermostatic water bath at 40 °C. Then the 100 μm PDMS fibre was immersed in the sample for 40 min at a constant magnetic stirring rate of 1000 rpm. Thermal desorption of the analytes from the fibre was performed in the gas chromatograph injection port at 250 °C for 5 min. Quantification of SCCPs was performed using the standard addition method by spiking the water samples with appropriate amounts of the standard SCCP, C_{10}–C_{13} (63% Cl), at four concentration levels. SCCP concentration were calculated from the linear relationship obtained between spiked amount and total peak area.

2.5. Water samples

River and tap water samples were analysed using the proposed SPE and SPME procedures in combination with GC-NCI-MS. Barcelona tap water was collected from our laboratory, after allowing the water to flow for at least 10 min. River water samples were collected on February 2003 at seven sampling points from the Llobregat river basin and Riera del Tenes river (Barcelona, NE Spain). Four water samples were taken at the input or the output of waste water treatment plants (WWTP). Samples were collected in amber glass bottles (2.5 l) fitted with teflon screw caps and stored in the dark at 4 °C before analysis. River water samples were filtered through a glass microfibre filter (Whatman, UK) and a 0.45 μm membrane filter (MSI, Westboro, MA, USA) in order to remove particulate matter prior to analysis.

3. Results and discussion

3.1. Optimisation of the SPE procedure

Among the different SPE sorbents commercially available, C_{18} was chosen because it is expected to be suitable for the retention of very large hydrophobic molecules such as SCCPs. Therefore, four C_{18} SPE cartridges frequently used in environmental analysis were selected for SPE optimisation. Recovery data were obtained for each cartridge by spiking Milli-Q water and tap water at a concentration level of 1 μg l^{-1} with a C_{10}–C_{13}, 63% Cl SCCP standard solution in acetone. Volumes of 400 ml of water were analysed following the SPE procedure described in Section 2. The complete elution of SCCPs from the cartridges was ensured by using 10 ml of dichloromethane. Triplicate analysis of water samples for each cartridge were performed using GC-ECD, and the results obtained for spiked Milli-Q water are shown in Table 1. As can be seen, SCCP recoveries were higher than 90% for all the cartridges except for Discovery DSC-18LT, which was 64%. These results can be explained taking into account that Discovery DSC-18LT has a lower carbon load (11% C) than the other three cartridges (17–18% C), which are expected to provide higher retention capabilities. The highest recoveries and the best baseline blanks were obtained with Varian Bond Elut-C_{18}, and therefore this cartridge was chosen for all subsequent SPE experiments. No significant differences were found in the recoveries when tap water was employed instead of Milli-Q water to study matrix effects.

In order to optimise the elution step for the selected SPE cartridge, cyclohexane and dichloromethane were tested as solvents. Volumes between 1 and 10 ml were used for each solvent and 3 ml were enough for the complete elution of the analytes. Since cyclohexane provided cleaner extracts, it was selected for all subsequent SPE experiments.

In order to study the breakthrough volume, the method described by Hennion et al. [35] was applied. For this purpose, increasing volumes of Milli-Q water (50–1500 ml) were spiked with a constant amount of the C_{10}–C_{13}, 63% Cl

Table 1
Recoveries of C_{10}–C_{13}, 63% Cl SCCP in Milli-Q water spiked at a concentration of 1 μg l^{-1}

SPE cartridge	Mean (%)	RSD[a] (%)
Bond Elut-C_{18}	96	5
Discovery DSC-18	93	6
Supelclean ENVI-18	90	6
Discovery DSC-18LT	64	8

[a] $n = 3$.

SCCP (400 ng) and spiked water samples at decreasing concentration levels (8.0–0.26 $\mu g\,l^{-1}$) were obtained. The SPE procedure previously optimised was used and the extracts were injected into the GC-ECD system. Quantification of the extracts was performed using different SCCP calibration standard solutions using PCB 30 as internal standard and the recoveries were calculated comparing the spiked amount of SCCP standard mixture and the amount of analyte found. Under these conditions, the breakthrough volume was not achieved and high and practically constant recoveries were obtained up to 1500 ml. Sample volumes higher than 1500 ml were not studied because the analysis time would have been too long. In view of these results, 1000 ml of water were chosen for all subsequent analyses, as a compromise to achieve low detection limits and a reasonable analysis time.

3.2. GC-NCI-MS analysis

After optimisation of the SPE procedure, GC-ECD analysis of river water samples was performed using both the SPE and the SPME procedures and the results obtained were compared. As expected, although SPE can provide a higher preconcentration than SPME, the selectivity of SPE/GC-ECD was notably lower and the chromatograms were strongly interfered due to the large number co-extracted compounds from the water matrix, preventing the SCCP determination. Moreover, the SPME-GC-ECD method allowed their detection but not their quantification because the signal obtained was comprised between the limit of detection (0.33 $\mu g\,l^{-1}$) and quantification (1 $\mu g\,l^{-1}$) [24]. Since GC-NCI-MS can provide higher selectivity than ECD, a method based on this technique was developed in order to quantify these compounds in river water.

For GC-NCI-MS, selection of the appropriate ions for quantification of SCCPs in the NCI mode was performed using the information provided by the NCI mass spectra of individual tetra-, penta- and hexachlorodecanes [36]. For these compounds, the $[M-Cl]^-$, $[M+Cl]^-$ and $[M-HCl]^{-\bullet}$ cluster ions were observed at high *m/z* values, whereas $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ were present in the low *m/z* region. The $[M-Cl]^-$, $[M+Cl]^-$ and $[M-HCl]^{-\bullet}$ cluster ions were not suitable for quantification of the SCCPs, because these ions were interfered by those corresponding to other polychlorinated *n*-alkanes in the SCCP mixture. In contrast, the $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ cluster ions were always present in the mass spectra of the whole SCCP mixture. For these reasons, these ions were selected for quantification of SCCPs, thus minimising possible internal interferences. The $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ ions were monitored by scanning the 70–75 *m/z* region.

3.3. Quality parameters for the SPE and the SPME procedures

The SPE and the SPME procedures were evaluated using the GC-NCI-MS method for the analysis of SCCPs. For this purpose, quality parameters for both methods were established and compared. Run-to-run precision and detection limits were studied using spiked Milli-Q water, tap water and blank river water, and the results obtained are given in Table 2. The limit of detection (LOD), based on a signal-to-noise ratio (S/N) of 3:1, was determined for the SPE/GC-NCI-MS method after passing through the cartridge 1000 ml of water spiked at low concentrations of the C_{10}–C_{13}, 63% Cl SCCP, while for the SPME-GC-NCI-MS method, 35-ml water samples spiked at low levels of these compounds were used. In these conditions, the LODs obtained for the SPE/GC-NCI-MS method for both Milli-Q and tap water were 0.005 $\mu g\,l^{-1}$, whereas for river water the LOD was 0.02 $\mu g\,l^{-1}$. The SPME-GC-NCI-MS method showed higher LODs, which were 0.1 $\mu g\,l^{-1}$ for both Milli-Q and tap water and 0.5 $\mu g\,l^{-1}$ for river water. On the other hand, the LODs for the SPE/GC-NCI-MS method were better than those obtained for the SPME-GC-ECD method previously published [24], which were 0.02 $\mu g\,l^{-1}$ for Milli-Q water and 0.3 $\mu g\,l^{-1}$ for both river and tap water.

Table 2
Quality parameters of the SPE- and the SPME-GC-NCI-MS methods

Aqueous sample	Run-to-run[a] (%RSD)		LOD ($\mu g\,l^{-1}$)	
	SPE	SPME	SPE	SPME
Milli-Q water	8	19	0.005	0.1
Tap water	8	18	0.005	0.1
River water	9	21	0.02	0.5

[a] $n = 5$.

For run-to-run precision, five replicate analyses of Milli-Q, tap and river water samples spiked at 1 and 3 $\mu g\,l^{-1}$ and were performed using the SPE and the SPME methods, respectively. The relative standard deviations (%RSD) obtained for the SPME-GC-NCI-MS method were significantly high and ranged from 18 to 21% (see Table 2). These values were higher than those obtained in a previous paper [24] using SPME-GC-ECD (RSD%, 12–15%), showing the effect of NCI-MS on the total variability of the method. On the other hand, run-to-run precision obtained for the SPE/GC-NCI-MS (%RSD, 8–9%) was remarkably better than that found for SPME-GC-NCI-MS (%RSD, 18–21%. Therefore, SPE was selected and applied to the analysis of river water samples.

3.4. SPE/GC-NCI-MS analysis of water samples

In order to study the applicability of the SPE/GC-NCI-MS method for the determination of SCCPs in waters, seven river water samples collected from the Llobregat river basin and Riera del Tenes river (Barcelona, NE Spain) were analysed. Triplicate analysis of water samples was carried out using external SCCP calibration standards for quantification. SCCP concentrations and standard deviations obtained for the samples analysed are given in Table 3. The presence of SCCPs was detected in five samples and ranged from 0.30

Table 3
River water analysis

Sample code	Sample location	Concentration[a] ($\mu g\,l^{-1}$)
S1	WWTP Manresa (input)	0.62 ± 0.05
S2	WWTP Martorell (output)	n.d.
S3	WWTP Abrera (input)	0.31 ± 0.03
S4	WWTP Manresa (output)	n.d.
S5	Anoia river	0.41 ± 0.03
S6	Riera de Rubí river	0.30 ± 0.03
S7	Riera del Tenes river	1.10 ± 0.08

n.d.: not determined (below the limit of detection, LOD = $0.02\,\mu g\,l^{-1}$).
[a] $n = 3$.

to $1.10\,\mu g\,l^{-1}$, while for the samples collected at the output of water treatment plants the concentrations were below the limit of detection. As an example, the GC-NCI-MS chromatogram of a river water sample (S3) and that corresponding to a $5\,\mu g\,ml^{-1}$ standard solution of the C_{10}–C_{13}, 63% Cl SCCP are given in Fig. 1. As can be observed in the chromatograms, the elution of the SCCP is characterised by a broad chromatographic profile, due to the coelution of several thousands of individual polychlorinated *n*-alkanes. The elution patterns of the standard SCCP and the samples were very similar, showing a moderate and relatively uniform contamination by short-chain CPs. The proposed SPE/GC-NCI-MS method allows the accurate determination of SCCPs at concentrations below the $\mu g\,l^{-1}$ level, whereas SPME-GC-ECD [24] can be used for the fast analysis of SCCPs in waters at the $\mu g\,l^{-1}$ level. Moreover, the SPE procedure could be automated for routine analysis, thus reducing the total analysis time.

4. Conclusions

Two methods based on solid-phase extraction (SPE) and solid-phase microextraction (SPME) have been evaluated for the analysis of short-chain chlorinated paraffins (SCCPs) in river water samples by GC-NCI-MS. For the SPE method, among the sorbents tested, Varian Bond Elut-C_{18} cartridges gave the best results with high recoveries (96%) and a breakthrough volume higher than 1500 ml. For NCI-MS determination of SCCPs the $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ ions have been used for quantification. Quality parameters for the SPE and the SPME methods combined with GC-NCI-MS have been established. The SPE method showed better LODs than the SPME method, being respectively 0.02 and $0.5\,\mu g\,l^{-1}$ for river water. In addition, better run-to-run precisions were obtained with the SPE method (9% RSD). Moreover, the LODs obtained with SPE/GC-NCI-MS were between 4- and 15-fold lower than those reported using SPME-GC-ECD. In summary, the combination of SPE with GC-NCI-MS provided a selective and sensitive method for the analysis of SCCPs in river waters at concentrations below the $\mu g\,l^{-1}$ level.

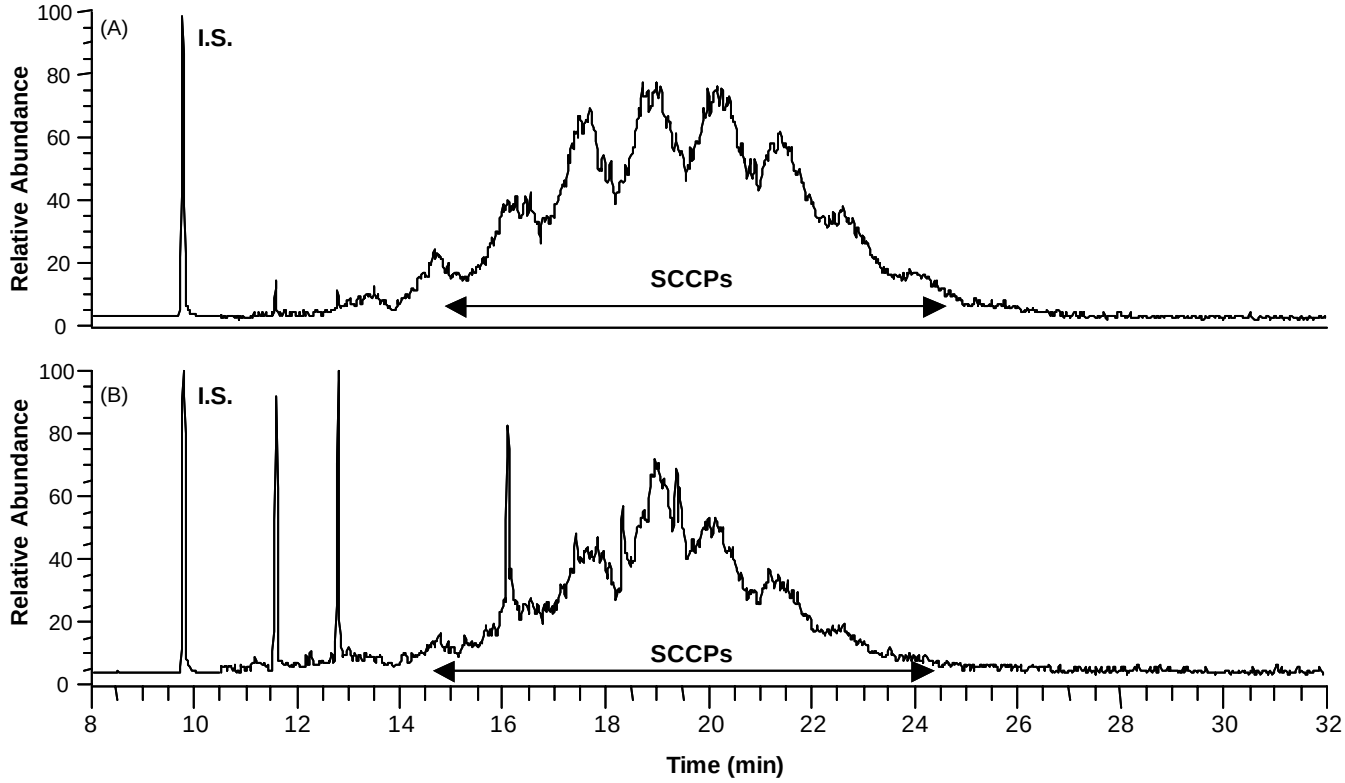

Fig. 1. SPE/GC-NCI-MS chromatograms of (A) a $5\,\mu g\,ml^{-1}$ standard solution of the C_{10}–C_{13}, 63% Cl SCCP and (B) sample S3. For each chromatogram, detection of the internal standard (I.S., $^{13}C_6$-hexachlorobenzene, *m/z* 286–296) and the SCCP (*m/z* 70–75) is showed.

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