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Solid-phase microextraction for the analysis of short-chain chlorinated paraffins in water samples

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Abstract

A novel solid-phase microextraction (SPME) method coupled to gas chromatography with electron capture detection (GC–ECD) was developed as an alternative to liquid–liquid and solid-phase extraction for the analysis of short-chain chlorinated paraffins (SCCPs) in water samples. The extraction efficiency of five different commercially available fibres was evaluated and the 100-μm polydimethylsiloxane coating was the most suitable for the absorption of the SCCPs. Optimisation of several SPME parameters, such as extraction time and temperature, ionic strength and desorption time, was performed. Quality parameters were established using Milli-Q, tap water and river water. Linearity ranged between 0.06 and 6 μg l^{-1} for spiked Milli-Q water and between 0.6 and 6 μg l^{-1} for natural waters. The precision of the SPME–GC–ECD method for the three aqueous matrices was similar and gave relative standard deviations (RSD) between 12 and 14%. The limit of detection (LOD) was 0.02 μg l^{-1} for Milli-Q water and 0.3 μg l^{-1} for both tap water and river water. The optimised SPME–GC–ECD method was successfully applied to the determination of SCCPs in river water samples.

Keywords: Water analysis; Solid-phase microextraction; Short-chain chlorinated paraffins; Paraffins

1. Introduction

Chlorinated paraffins (CPs) are complex industrial formulations of polychlorinated *n*-alkanes (PCAs) with carbon chain lengths between C_{10} and C_{30} and a chlorine content ranging from 30 to 70% by mass [1–3]. CPs are formed by direct chlorination of *n*-alkane feedstocks with molecular chlorine under forcing conditions of temperature and UV–Vis irradiation. These reactions yield complex mixtures containing several thousands of individual compounds [4,5]. Commercial CP mixtures are divided into three different categories depending on the carbon chain length: short-chain (C_{10}–C_{13}, SCCPs), medium-chain (C_{14}–C_{17}, MCCPs) and long-chain (C_{20}–C_{30}, LCCPs). CPs are used industrially because of their chemical stability and viscosity, flame resistance and low vapour pressure. CPs are used as additives in cutting fluids and lubricants for the metal working industry, and in paints and sealants as well as plasticizers and flame retardants [6]. Since their introduction in the 1930s, the world production of CPs has increased to more than 300 000 t/year [7], especially after the banning of polychlorinated biphenyls (PCBs), for which CPs are good substitutes in some applications.

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CPs are hardly soluble in water, from 22.4 to 975 $\mu g\ l^{-1}$ for SCCPs [8]. Because of these low solubilities, the octanol–water partition coefficients are large, with log K_{ow} values between 5.85 and 7.14 [9]. The non-polar nature of SCCPs is consistent with their high bioconcentration factor in mussels (4.1×10^4) [10]. On the other hand, these compounds are toxic to aquatic invertebrates, with LC_{50} values ranging from 14 to 530 $\mu g\ l^{-1}$ [11], and other effects such as reduction of growth have been observed [12]. Moreover, the International Agency for Research on Cancer (IARC) has concluded that CPs of average carbon chain length C_{12} and average degree of chlorination of ~60% are *possibly carcinogenic to humans* (Group 2B) [13]. The US Environmental Protection Agency (USEPA) [14], as well as several international organisations (OSPAR, CEPA) [15,16] have listed SCCPs as substances requiring priority actions and regulations. In particular, the European Union [17] has recently included SCCPs [18] on the list of *priority hazardous substances* in the field of water policy, amending Directive 2000/60/EC [19]. This list contains substances that are considered toxic, persistent, and liable to bioaccumulate. Therefore, development of analytical methods for the monitoring of SCCPs in water is needed.

The analysis of CPs is extremely difficult due to the large number of congeners (a minimum of several thousands) present in the technical mixtures. Even with capillary GC the chromatograms show a characteristic broad profile of unresolved peaks [20]. In addition, the presence of other halogenated compounds results in an important source of interferences in the analysis, which are generally removed by normal-phase liquid chromatography and/or gel permeation chromatography [4,7,21]. CPs are usually detected using GC–ECD or coupled to high- or low-resolution electron capture negative ion MS [4,7,22,23].

Few papers related to the analysis of the CPs in water have been published. In these studies, CPs were found in river and marine waters from industrial and remote areas at concentration levels of $ng\ l^{-1}$ [24–28]. Most of the methods used in these studies are based on separation techniques such as liquid–liquid extraction and/or solid-phase extraction (SPE). Generally, liquid–liquid extraction involves large quantities of high purity solvents, whereas solid-phase extraction may be susceptible to high baseline blanks, channelling, and sorbent bed plugging problems. After extraction, concentration steps of the extract prior to analysis are often required.

Solid-phase microextraction (SPME) is a simple, rapid and solvent-free extraction technique and it is a good alternative to the above mentioned conventional extraction techniques. After a well-defined extraction time, the compounds absorbed on the fibre coating can be thermally desorbed in the injection port of a gas chromatograph, or redissolved in an organic solvent if coupled to LC. Since its introduction in 1989, SPME has been successfully applied in a large number of fields (environmental, pharmaceutical, biological, clinical) and novel SPME coatings have been introduced [29].

To our knowledge, the application of SPME to the analysis of CPs has not yet been reported. Direct SPME is expected to be a suitable technique for the extraction of CPs from aqueous matrices due to their hydrophobic nature and low volatility. The present paper describes the development of a novel method for the analysis of SCCPs in water using SPME–GC–ECD. An evaluation of the performance of different commercially available SPME fibres for the extraction of SCCPs was studied. SPME parameters were optimised and the method has been used for the determination of SCCPs in river water samples.

2. Experimental

2.1. Standards and reagents

Two stock standard solutions of a short-chain chlorinated paraffin (SCCP, C_{10}–C_{13}, 63% Cl) in acetone and in cyclohexane of 100 $\mu g\ ml^{-1}$, were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Secondary standard solutions were prepared by dilution of the primary standard solution in acetone to give concentrations of 10 and 1 $\mu g\ ml^{-1}$.

Water standard solutions, which contained the C_{10}–C_{13}, 63% Cl SCCP at concentrations between 0.02 ng ml^{-1} and 7 ng ml^{-1}, were prepared by spiking 35 ml of Milli-Q water with appropriate volumes of the secondary standard solutions. In all cases, the volume of acetone added to the water was

lower than 50 μl (no more than 0.15% v/v of acetone content) because slight changes in the extraction yield started to be noticed when the acetone content was higher than 0.5% v/v.

For SPME extractions, the water standard solutions were placed in 40-ml screw-cap glass vials fitted with silicone-PTFE septa. Water from a Milli-Q water purification system (Millipore Corporation, Bedford, MA, USA) was used in the preparation of these standards.

On the other hand, calibration standard solutions at concentrations between 5 and 80 μg ml^{-1} were prepared by dilution of the stock standard solution in cyclohexane for the determination of the SCCP partition coefficient.

Acetone and cyclohexane of residue analysis grade were purchased from Merck (Darmstadt, Germany). All vials and sampling bottles were cleaned with AP-13 Extran alkaline soap (Merck) for 24 h, rinsed consecutively with Milli-Q water and acetone, and dried at 180 °C. Volumetric glassware was washed as described above, but was air-dried.

2.2. Chromatographic conditions

Analyses were performed with a Trace GC 2000 gas chromatograph (ThermoFinnigan, Milan, Italy), equipped with a ^{63}Ni electron-capture detector (ECD). A DB-5 (5% phenyl-, 95% methylpolysiloxane), 30 m×0.25 mm I.D., fused-silica capillary column (J&W Scientific, Folsom, USA) of 0.25 μm film thickness was used. Carrier gas was helium and flow-rate was held at 1 ml min^{-1} by electronic pressure control. Nitrogen was used as ECD make-up gas at 40 ml min^{-1}. Injector and ECD temperatures were kept at 250 and 330 °C, respectively. For studies with the 7-μm PDMS fibre, injector temperature was maintained at 280 °C. Samples were injected in the splitless injection mode (5 min). The oven temperature programme was: 90 °C (held for 5 min), to 150 °C at 30 °C min^{-1}, and to 300 °C (held for 10 min) at 8 °C min^{-1}. Chrom-Card 32-bit version 1.06 software (ThermoFinnigan) was used for data acquisition.

2.3. Solid-phase microextraction procedure

SPME experiments were performed using a manual fibre holder supplied from Supelco (Bellefonte, PA, USA). Five commercially available fibres, polydimethylsiloxane, PDMS, 100 μm; polyacrylate, PA, 85 μm; Carboxen-polydimethylsiloxane, CAR-PDMS, 75 μm; polydimethylsiloxane-divinylbenzene, PDMS–DVB, 65 μm; and polydimethylsiloxane, PDMS, 7 μm were purchased from Supelco. Before use, each fibre was conditioned in the injection port of the gas chromatograph under helium flow according to the time and temperature recommended by the manufacturer. Fibre blanks were run daily to ensure the absence of contaminants or carryover.

The SPME procedure was as follows: a 35-ml water sample was placed in a 40-ml screw-cap glass vial fitted with a silicone-PTFE septa and then it was conditioned for 10 min in a thermostatic water bath. Then the analytes were extracted at a constant agitation rate of 1000 rev./min, using a 6-mm-diameter×20-mm-long stirring bar and a magnetic stirplate. Finally, thermal desorption of the analytes was carried out by exposing the fibre in the GC injection port. The fibre was kept in the injector for an additional time of 5 min, with the injector in the split mode (purge on). Quantification of SCCPs was carried out by integration of the total area for the elution profile in each GC–ECD chromatogram.

2.4. Water samples

River and tap water samples were analysed using the proposed SPME procedure. Barcelona tap water was collected from our laboratory, after allowing the water to flow for a minimum of 10 min. River water samples were collected from the Llobregat river (Barcelona, Spain) at two different sampling zones. The first group of sampling points in the river were close to industries that are known to use CPs. A second group of samples was taken from points of the river course situated before the aforementioned industrial area. Samples were collected in 2.5-l amber glass bottles and stored in the dark at 4 °C until analysis. All 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 SPME procedure

Initially, the relative extraction efficiencies of the short-chain chlorinated paraffin (C_{10}–C_{13}, 63% Cl) from water using SPME with different stationary phases and film thickness were evaluated. For this purpose, five SPME fibres were tested. A 35-ml Milli-Q water sample spiked with the SCCP mixture at a concentration level of 1 ng ml^{-1} was analysed with the different fibres. The initial SPME conditions for the extraction process were: extraction time 30 min, and extraction temperature 22 °C (laboratory temperature), desorption time 10 min, using a conditioning time before extraction of 10 min. The 100-μm PDMS fibre showed the highest extraction efficiency, while for the rest of the fibres the yields obtained were lower (90% for the 85-μm PA coating, 53% for 75-μm CAR-PDMS, 41% for 65-μm PDMS–DVB and 31% for 7-μm PDMS, relative to the 100-μm PDMS yield). In view of these results, the 100-μm PDMS fibre was chosen for all subsequent experiments.

After selection of the fibre, the extraction and desorption steps of the SPME process were optimised. Initially, the absorption temperature was fixed to 22 °C and the extraction time profiles were then studied between 30 and 90 min. In these conditions, the extraction time required to achieve equilibrium between the aqueous phase and the fibre coating was found to be too long (more than 90 min), so the influence of the temperature on the extraction efficiency was tested. For this purpose, the effect of sample temperature on the SPME extraction yield was examined at 22, 40 and 60 °C, using extraction times of 30, 60 and 90 min. The extraction temperature profiles showed an increase of the response with the temperature, although above 40 °C only a slight improvement was achieved. Nevertheless, a high variability was observed at 60 °C and, therefore, poor repeatability should be expected at these conditions. As a compromise, 40 °C was chosen as the optimum extraction temperature.

The time required to reach the equilibrium between the SPME coating and the water samples was determined up to 120 min at 40 °C and 45 min were enough to reach equilibrium. Finally, the desorption time of the analytes from the fibre into the GC injection port (250 °C) was determined and 5 min were enough for the quantitative desorption of the SCCPs. No sample carryover or memory effect was observed at these conditions.

The effect of ionic strength up to 25% of NaCl (w/w) on the extraction efficiency was also studied. Generally, an enhancement on the extraction efficiency is expected when the ionic strength of the aqueous phase is increased. Nevertheless, in our case the addition of NaCl to the water sample did not improve the amount of SCCP extracted. In fact, a decrease on the response down to 30% was observed. For compounds with low water solubilities, the extraction efficiency is not enhanced at high ionic strength [30,31]. Moreover, the addition of large amounts of salt to the aqueous phase increases its viscosity. Therefore, the velocity of the mass transfer processes of the analytes from the aqueous matrix to the stationary phase is diminished and, consequently, the time required to reach the equilibrium increases. These facts could explain the decrease observed in the extraction yield of the SCCPs at high concentrations of salt in the aqueous phase. Therefore, no salt addition was used in further experiments.

In summary, the SPME optimal conditions for the analysis of SCCPs in water using a 100-μm PDMS fibre were: extraction time 45 min, extraction temperature 40 °C, desorption time and temperature, 5 min and 250 °C, respectively, and no salt addition.

3.2. Determination of the partition coefficient (K)

The equilibrium process in SPME can be defined in terms of the partition coefficient (K) between the fibre stationary phase and the aqueous phase:

$$n_s = \frac{KV_sV_{aq}C^0_{aq}}{KV_s + V_{aq}}$$

where n_s is the amount of analyte extracted by the fibre coating under equilibrium conditions, V_{aq} and V_s are the volumes of the aqueous and stationary phase, respectively, and C^0_{aq} is the concentration of the analyte in the aqueous phase. In our case, n_s was determined by extracting a water standard solution spiked with the SCCPs at a concentration of 1 ng ml^{-1} under the optimal conditions previously estab-

lished, where the equilibrium is achieved in 45 min. The amount extracted was estimated using an external calibration curve, obtained by direct GC injection of SCCP standards in cyclohexane at concentration levels ranging from 5 to 80 μg ml^{-1}. The water volume, V_{aq}, was 35 ml, and the concentration in the aqueous phase, C^0_{aq}, was 1 ng ml^{-1}. The volume of stationary phase, calculated from the dimensions of the 100-μm PDMS coating (O.D. = 310 μm; I.D. = 110 μm; height = 1 cm) was 6.597×10^{-4} ml. For the C_{10}–C_{13}, 63% Cl SCCP, a K value of ca. 25 000 was obtained, which agreed with values reported for other non-polar organochlorine compounds similar to SCCPs [31].

3.3. Quality parameters

Linear dynamic range, repeatability, and detection limits of the SPME–GC–ECD procedure were established using Milli-Q water, tap water, and river water samples. In order to study the linear range, aqueous samples were spiked with appropriate amounts of SCCPs over the range between 0.02 and 7 μg l^{-1}, and they were extracted with the established SPME–GC–ECD method. Good linearity ($r^2 = 0.996$) was obtained between 0.06 and 6 μg l^{-1} for spiked Milli-Q water, whereas for tap and river water samples, linearity was established between 0.6 and 6 μg l^{-1} with correlation coefficients higher than 0.991 (Table 1).

Limit of detection (LOD), defined as the concentration that produces a signal-to-noise ratio (S/N) of 3, was calculated using Milli-Q water, tap water and river water without detectable quantities of SCCPs, spiked at low levels of these compounds. In these conditions, the detection limit of the SPME–GC–ECD method for Milli-Q water was 0.02 μg l^{-1}, and for both tap and river waters was 0.3 μg l^{-1}. Similar LODs (0.1 μg l^{-1}) have been obtained for CPs detected in river water samples, using solid-phase extraction (SPE) in combination with GC coupled to negative chemical ionisation low-resolution MS [28].

Table 1
Quality parameters

Aqueous sample	Run-to-run[a] (RSD, %)	Linearity range (μg l^{-1})	LOD (μg l^{-1})
Milli-Q water	12	0.06–6 ($r^2 = 0.996$)	0.02
Tap water	15	0.6–6 ($r^2 = 0.991$)	0.3
River water	14	0.6–6 ($r^2 = 0.993$)	0.3

[a] $n = 5$.

For repeatability studies, five replicates of 35-ml spiked Milli-Q water, tap water, and river water samples (3 μg l^{-1}) were consecutively analysed by the SPME–GC–ECD method at the optimal conditions. Relative standard deviations (RSD) for the three aqueous matrices were very similar and ranged from 12 to 14% (Table 1).

3.4. Analysis of water samples

In order to examine the feasibility of the method, the SPME procedure was used to determine SCCPs in river water samples. The samples were collected from different sites of the Llobregat River (Barcelona) close to industrial effluents. Triplicate analysis of three river water samples were carried out using external calibration for quantification, assuming that the matrix did not significantly interfere with the extraction. The external calibration was performed by analysing six Milli-Q water standards spiked at concentrations within the linear range of the method. As an example, a GC–ECD chromatogram of a non-spiked river water sample (35 ml) containing SCCPs is given in Fig. 1A. Fig. 1B shows the GC–ECD chromatogram of a 35-ml Milli-Q water sample spiked at 3 μg l^{-1} of SCCP (C_{10}–C_{13}, 63% Cl). As can be seen, the GC–ECD chromatograms are characterised by a big hump corresponding to the co-elution of the polychlorinated *n*-alkanes. Taking into account the elution pattern shapes and the retention time of the SCCPs in the spiked Milli-Q water and river water samples, it can be deduced that the composition of the CPs present in the sample and the standard C_{10}–C_{13}, 63% Cl SCCP are very similar and this standard mixture is adequate for quantification purposes. From the samples analysed, the presence of SCCPs was only detected in a river water sample (Fig. 1A) at a concentration of 2.1 μg l^{-1}, whereas for the other samples, levels below the limit of detection were obtained. In order to determine the matrix effect in the extraction process, the standard addition method was also applied for quantification of the river water sample. Replicate analysis using the SPME–GC–ECD method was performed by

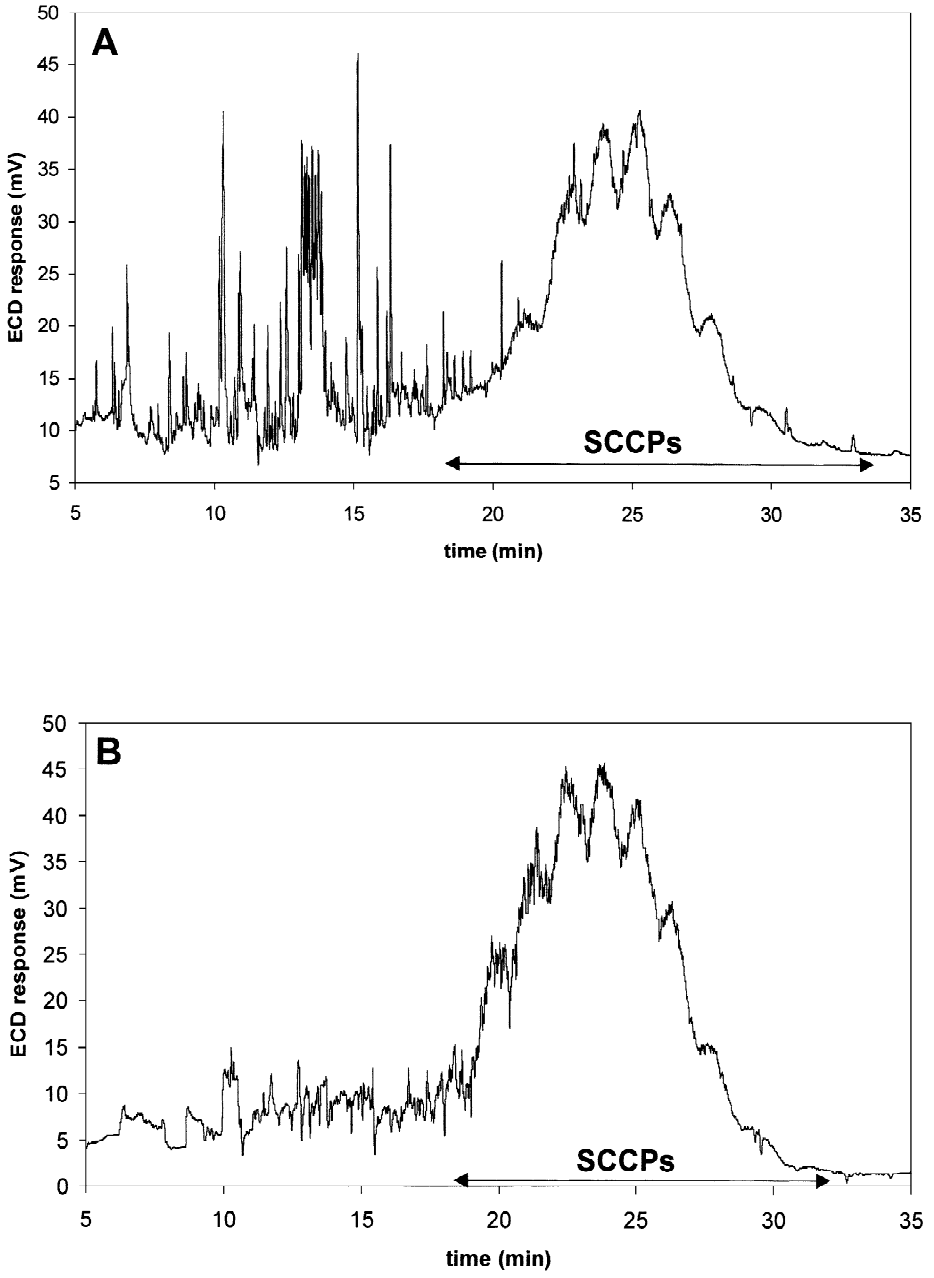

Fig. 1. SPME–GC–ECD chromatograms of (A) a water sample from the Llobregat river and (B) Milli-Q water spiked with 3 μg l^{-1} of the C_{10}–C_{13}, 63% Cl SCCP.

spiking the river water with 250, 500 and 1000 ng of SCCP (about 350%, 700% and 1400% of the native concentration in the water sample). A good linear relationship between spiked amounts and peak areas could be obtained ($r^2 = 0.997$) and SCCP concentration in the water sample was found to be 20.3±2.0 μg l^{-1}. This value was ~10-fold higher than the concentration obtained using external calibration.

This fact can be explained by taking into account the presence of organic compounds in the water matrix. These compounds could compete with the analytes for the absorption on the fibre, so the fibre extraction efficiency may be reduced. Therefore, standard addition is recommended as a quantification method to overcome matrix effects in the analysis of SCCPs in river water samples by SPME–GC–ECD, although SPME and GC injection steps have to be automated in order to reduce the analysis time and labour costs in routine analysis. Nevertheless, for clean water samples such as tap water, where the matrix does not significantly interfere, the proposed method can be applied using external calibration.

4. Conclusions

The feasibility of SPME–GC–ECD for the analysis of short-chain chlorinated paraffins in waters has been demonstrated. The 100-μm PDMS fibre was found to be the most effective coating for the extraction of CPs. Maximum responses of the analytes were obtained using 35-ml water samples, no salt addition, extraction time of 45 min at 40 °C, and a desorption time of 5 min. A partition coefficient (K) of ca. 25 000 was calculated for the short-chain chlorinated paraffin C_{10}–C_{13} (60% Cl). Direct SPME in conjunction with GC–ECD gave good repeatability values (RSDs between 12 and 14%) and low detection limits (0.02 μg l^{-1} for Milli-Q water and 0.3 μg l^{-1} for tap and river water samples). The optimised procedure has been successfully applied to the analysis of SCCPs in river water samples. Significant differences in quantification were observed between external calibration and standard addition methods. To overcome the influence of the water matrix in the extraction process, the use of standard addition is recommended. The SPME procedure developed is proposed as a novel, fast, and accurate method for the analysis of SCCPs in water at low μg l^{-1} levels instead of conventional extraction techniques.

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