DETERMINATION OF SHORT-CHAIN CHLORINATED PARAFFINS BY CARBON SKELETON GAS CHROMATOGRAPHY

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Introduction

Short-Chain Chlorinated Paraffins (SCCPs) are highly complex technical mixtures of polychlorinated *n*-alkanes with a chlorination degree between 50 and 70 % by mass, and a linear carbon chain length from C_{10} to $C_{13,}$ constituted by thousands of homologues, diastereomers and enantiomers. They have been used in many different applications, such as extreme pressure additives in lubricants and cutting fluids, plasticizers in PVC, and flame retardants in paints, adhesives and sealants. SCCPs are toxic towards aquatic organisms, bioaccumulative and persistent, and therefore the concern about this class of pollutants has increased in the last few years.

In 2000 the European Union has included SCCPs in the list of priority substances in the field of water policy, amending the Water Framework Directive (WFD) 2000/60/EC[1]. The implementation of the directive requires that laboratories should be able to measure such substances reliably at the level of the environmental quality standard (EQS). Unfortunately, this is not the case for SCCPs. The analytical tools currently available for the analysis of this class of compounds are scarce and no methodology has been fully validated. This is due to the complexity of their mixtures, and the lack of pure solutions for calibrations as well as matrix-matched reference materials. No routine method for monitoring purposes exists and a poor comparability of results was demonstrated.[2,3]

At present determination of SCCPs is mostly performed by mass spectrometry (MS) in the Electron Capture Negative Ionisation (ECNI) mode. The quantification relies on the monitoring of $[M\text{-}Cl]^-$ ions of specific mass to charge (*m/z)* ratio for each SCCP group according to the method developed by Tomy et al..[4] This approach is prone to interferences from other chlorinated compounds and from medium chain chlorinated paraffins, therefore a thorough clean-up of the sample and a careful selection of the ions to be detected are necessary.[5] The method is also affected by a strong dependence on the degree of chlorination of the standard used for calibration. Errors of up to 1100 % have been reported when the calibrant does not match the chlorination degree of the sample.[6]

An alternative approach for SCCPs determination is the carbon skeleton gas chromatography (GC)-MS in which chlorinated paraffins are catalytic hydrodechlorinated to the corresponding *n*-alkanes (see Figure 1).[7,8] Information on the chlorination degree is lost, but accurate quantification is possible.

In this paper the two approaches are compared, and some preliminary results in the determination of SCCPs in water samples with the carbon skeleton method are presented.

Materials and Methods

Standard solutions of SCCPs with chlorination degrees of 63 %, 55.5 % and 51 % Cl (100 mg/L) were purchased from Dr. Ehrenstorfer GmbH. Commercial mixtures of SCCPs from European and American producers with a degree of chlorination of 55 and 70 % were kindly provided by LGC Ltd. ^{13}C labelled hexachlorobenzene [$^{13}C_6$ HCB] was purchased from Cambridge Isotope Laboratory.

In the ECNI-MS experiments, the GC-MS conditions used were as follows: capillary column DB5-MS fused silica column (15 m, i.d. 0.25 mm, film thickness 0.25 μm). Temperature program: initial T 100 ºC for 2 minutes, then 16 ºC min^{-1} up to 280 ºC, 8 min at 280 ºC. Injection volume: 3 μL per sample in the splitless mode; carrier gas He at a constant flow of 1 mL min^{-1}. Methane was used as reagent gas at a pressure of 120 Pa. The ion source temperature was 200 °C, the quadrupole temperature was 100 °C, and the transfer line temperature 270 °C. Compounds were detected in the selected ion monitoring (SIM) mode at a dwell time of 100 ms per ion using m/z 331 for the internal standard, ^{13}C labelled hexachlorobenzene, and the most abundant $[M\text{-}Cl]^-$ isotope ion of each congener group of SCCPs.

In the carbon skeleton approach, a Pd-modified liner filled with palladium catalyst prepared following the instruction reported in Koh et al.[8] was used. To activate the Pd, the liner was left for at least 5 hours inside the injector at 300 ºC under a flow of hydrogen with the column disconnected and the injector closed by a blind

screw. GC-MS conditions were as follows: capillary column DB5-MS fused silica column (60 m, i.d. 0.25 mm, film thickness 0.25 μm). Temperature program: 50 ºC for 3 minutes, then 10 ºC min^{-1} up to 280 ºC, 10 min at 280 ºC. Injection volume: 1 μL per sample in the splitless mode; carrier gas H_2 at a constant flow of 2 mL min^{-1}. Injector temperature: 300 ºC. Compounds were detected in the selected ion monitoring (SIM) mode at a dwell time of 100 ms per ion using *m/z* 57 and 41 as the quantification ions for the four *n*-alkanes (C_{10}-C_{13}) and the internal standard; *m/z* 43, 71, 98, 85 and 99 were used as qualifying ions.
For the application of the carbon skeleton method to water samples, two approaches were used. In the liquid liquid extraction (LLE) experiments, water samples (1000 mL) were extracted twice with 30 mL dichloromethane (DCM) using a separatory funnel. After extraction the glass containers were rinsed with 20 mL DCM, and the rinsing solvent was added to the sample extract. The extracts were dried over sodium sulfate, concentrated using a rotary evaporator and spiked with the internal standard (cyclododecane).
In the SPE experiments, four commercially available C_{18} cartridges were used: Bond Elut C_{18} 500 mg/3 mL (Varian), ENVI-18 2000 mg/12 mL (Supelco), ENVI-18 glass tube 500 mg/6 mL (Supelco), Discovery DSC-18 2000 mg/12 mL (Supelco). Before use, cartridges were washed with 2 mL of methanol and 2 mL Milli-Q water. Water samples (1000 mL) were passed through the cartridges at a flow rate of 10 mL min^{-1} using a vacuum manifold (Alltech). Then 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^{-1}. The extract was dried over sodium sulfate, concentrated to 1 mL and spiked with the internal standard (cyclododecane). Extracts were injected into the GC-MS using a Pd-modified liner.

Results and Discussion

Comparison between GC-ECNI-MS and the carbon skeleton GC

The two approaches for SCCPs determination, on one hand the GC-ECNI-MS method described by Tomy et al.[4], and on the other hand the carbon skeleton GC-MS, were tested and their performances compared.
First of all repeatability and between days variation were compared injecting a standard solution (50 mg L^{-1}) of the mixture Chloroparaffin C_{10}-C_{13} 55.5 % Cl in 5 days, 5 replicates per day. The results were evaluated by one-way ANOVA (5 groups, 5 replicates each). The repeatability within one day ranged from 2 to 18 % for ECNI-MS depending on the group of congeners considered. The relative standard deviation between days ranged between 1 and 20 % depending on the congener. These values are higher than those obtained using the carbon skeleton method. Those ranged from 0.2 to 2 %, and from 2 to 6 % for method repeatability and between days variation, respectively.
Quantification is one of the most problematic steps in the determination of SCCPs. It is usually carried out by comparing the areas of the peaks occurring in the sample with those in technical mixtures. Unfortunately, very few standard solutions are available up to now on the market, and no one of those is certified, making the selection of the calibrant solution a very critical step in the determination of SCCPs in the ECNI-MS method. To achieve better results the pattern of the standard used for the quantification should resemble as much as possible the one of the sample, in terms of molecular weight and chlorination degree.
Solutions of commercial mixtures of SCCPs at known concentration were used to check the error in the quantification using the two procedures. Using one single calibrant the bias in the quantification of solutions of SCCPs at known concentrations ranged from -97 to +3579 %. These values are in agreement with those reported in the literature.[6,9] However, high errors were found also when chlorination degree and molecular mass of the calibrant were similar to those of the sample.
To tackle the problem of calibration, Reth et al.[10] have suggested an alternative procedure in the quantification of SCCPs. In this procedure the total response factor of the SCCPs in the sample is calculated from the linear correlation found between the total response factors for a set of SCCP standards and their chlorine content. Their approach compensates for the influence of different response factors and makes results independent from the chlorine content of the reference calibrant, nevertheless the chlorination degree of the sample should be known in advance. To test this approach, five solutions of SCCPs at different chlorination degree in the range between 51.5 and 70 % were injected in the GC-MS. The solutions used to build up the regression line were injected for five consecutive days. The day to day variation of the regression line is reported in Figure 2.

The amount of SCCPs in a sample can be calculated through the regression line by dividing the relative total area of the sample (*i.e.* the sum of the relative area of each congener group) by the total response factor (*i.e.* the response factor calculated from the equation of the regression line of the calibration).
This approach is easier than the one used by Tomy et al.[4], but the bias in quantification of solutions at known concentrations of SCCPs carried out using multiple calibrants is still very high, ranging from -143 to +980 %.
In the case of the carbon skeleton method the bias in the quantification of a solution at known concentration of SCCPs ranged from -31 to +31 %.
The comparison between the method performances using the two approaches shows that the carbon skeleton method exhibits a better performance in terms of reproducibility, between days variation and reliability of the results. In addition to that, the ECNI-MS method is difficult to apply, time-consuming, and not applicable for routine analysis. The carbon skeleton method on the other hand requires less expensive equipment, it is easier to perform and, above all, it simplifies the problems of calibration which can simply be performed with *n*-alkanes, which are commercially available as pure standards.

Application of the carbon skeleton approach to water samples
Because of the considerable advantages of the carbon skeleton GC-MS approach, we decided to investigate the performances of this method for the analysis of environmental samples, and in particular of water.
In a previous paper[11], we proposed the use of the carbon skeleton GC as a *standardised method*. This means that the quantity intended to be measured (*i.e.* the *method-defined parameter*) is defined *via* the application of a precisely described analytical procedure, which provides also the reference for the metrological traceability of the measurement results. As *method-defined parameter*, we proposed to use the sum of SCCPs corresponding to the sum of *n*-alkanes with the related carbon chain backbone as obtained from the application of the carbon skeleton GC.
This method was applied to the determination of SCCPs in water samples. Two approaches were tested, liquid-liquid extraction and solid phase extraction. Since contamination in the blanks is a well known problem when analysing SCCPs[12], a preliminary test was done to verify that the sensitivity of the method is suitable for the analysis of SCCPs content in environmental samples. The reference values to which the LOD will be compared are the EQS for SCCPs in inland surface waters or other surface waters. These values are thresholds for the concentrations of pollutants which should not be exceeded in order to protect human health and environment. EQS expressed as annual average (AA) is equal to 0.4 $\mu g\ L^{-1}$, while the EQS expressed as maximum allowable concentration (MAC) is equal to 1.4 $\mu g\ L^{-1}$. In Table 1 the levels of detection are reported for the four different types of SPE and for LLE experiments. The results show that lower detection limits can be achieved using the SPE approach. Among the different SPE tested, the glass tube cartridges are the only ones which allow the determination of SCCPs at the level of EQS. These results are encouraging because they show that the carbon skeleton method can be used as a routine method for the determination of SCCPs in water samples, providing an instrument to the environmental laboratories to comply with the requirements of the WFD.

References:

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Figure 1: Conversion of SCCPs to alkanes by H_2/Pd catalyst in the GC injector: a) chromatogram of a commercial mixture of SCCPs with a chlorination degree of 55 % obtained on a DB5-MS column by ECNI-MS; b) chromatogram of the same commercial mixtures using the same column with the carbon skeleton GC-MS approach (i.s.=internal standard).

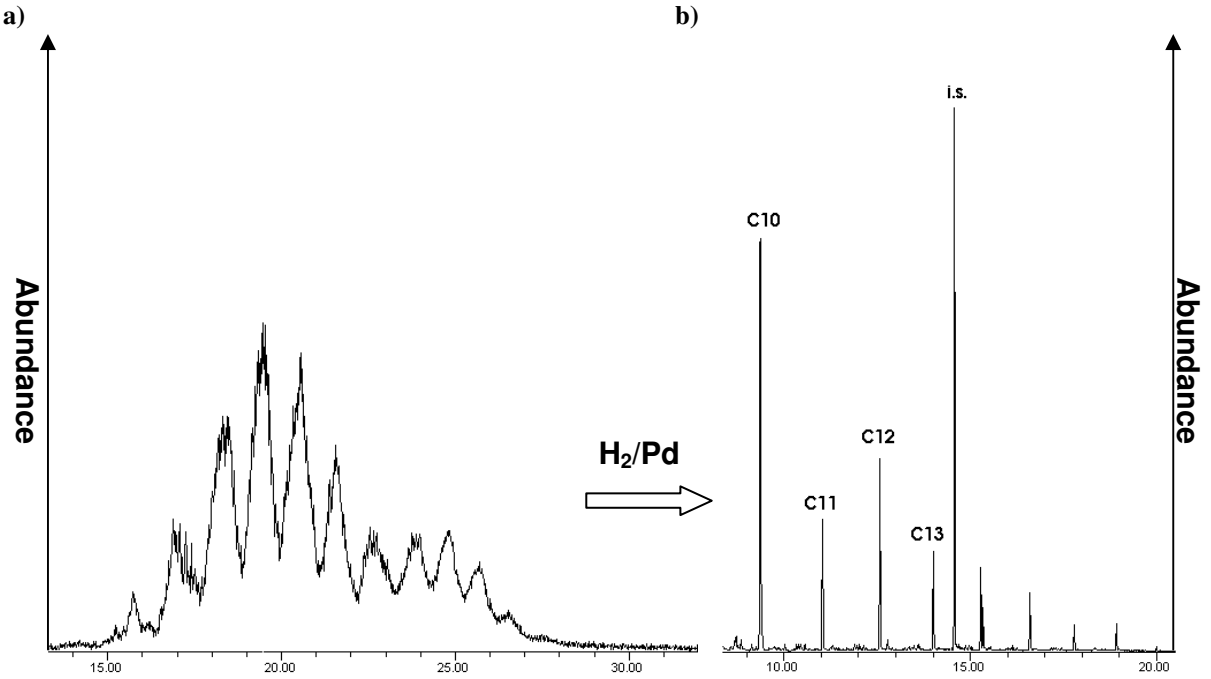

Figure 2: Day to day variation of the regression line for the calibration of SCCPs using the GC-ECNI-MS method.

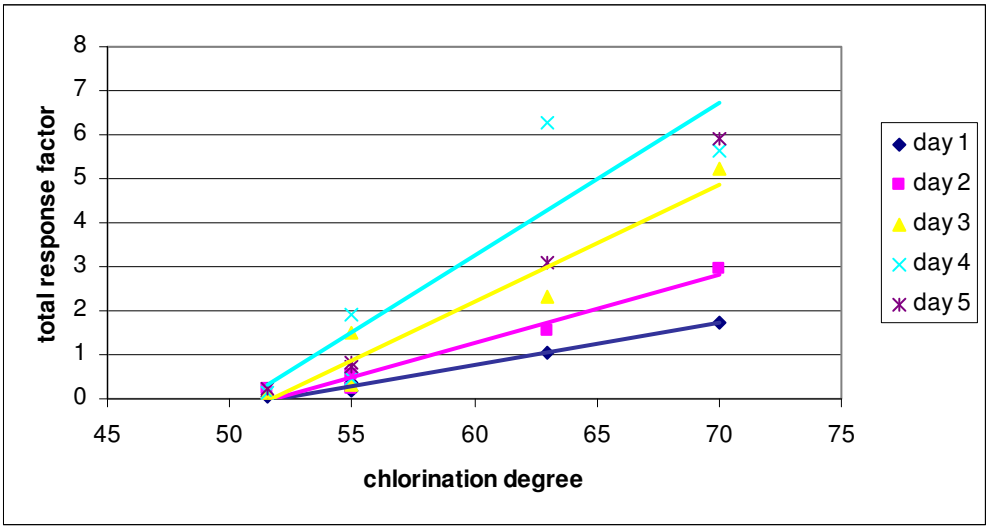

Table 1: Limit of detection expressed as µg L^{-1} for the four SPE cartridges and for the LLE approach.

	BOND ELUT C18	DISCOVERY-18	ENVI-18	ENVI-18 glass tube	LLE
LOD (µg L^{-1})	1.36	1.84	1.84	0.39	2.8