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PRACTITIONER'S REPORT

Validation of a method for the determination of short-chain chlorinated paraffins in soil and sediments

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Abstract An alternative approach for the reliable quantification of short-chain chlorinated paraffins (SCCPs) in sediment and soil, based on the existing method of carbon skeleton gas chromatography is presented. The method is proposed to establish an operationally defined measurand. The number of analytes to be looked at is notably reduced and the calibration problems encountered with the electron capture negative ionisation detection overcome because the conversion efficiency and the response are largely independent on the chlorine content of SCCPs. The accurate quantification is facilitated by the availability of *n*-alkanes as pure standards for calibration. To achieve the comparable results between laboratories, this method should be standardised. The first steps of this process, in-house development and full validation in sediment and soil, are presented for the first time. The limit of detection and quantification of 1.1 and 3.5 nmol g^{-1}, respectively, repeatability of 5% and relative expanded uncertainty of 12% were achieved providing a routinely applicable method for a reliable quantification of SCCPs.

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

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Introduction

Short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated *n*-alkanes with chain lengths between 10 and 13 carbon atoms and chlorine content between 49 and 70% [1]. They are synthetic compounds produced by chlorination of *n*-alkanes feed stocks mainly used in metal-working fluids, paints and sealants, as flame retardants in rubber and textiles, and in leather fat liquoring.

Their presence in the environment, due to the release from improper disposal of metal-working fluids, leaching from polymers, or loss from SCCP-enriched paints and coatings, has been ascertained in a variety of environmental matrices [2–9] worldwide. Remote areas such as the Canadian [10, 11] and European [12] Arctic have been reported to be affected by SCCP contamination showing that these pollutants have potential for long range environmental transport. A recent risk assessment evaluation classified this class of compounds as dangerous to the environment because of their toxicity towards aquatic organisms, high potential for bioaccumulation, and persistence in the environment [1], and the United Nations Environment Program (UNEP) [13] has proposed to list them in the Stockholm convention on persistent organic pollutants. In the attempt to reduce their release in the environment, the European Union has restricted the marketing and use of chlorinated paraffins as metal-working fluids and leather finishing products (Directive 2002/45/EC [14]). The European Union has included SCCPs in the list

of priority substances of the Water Framework Directive (WFD 2000/60/EC [15]) which requires their regular monitoring at a river basin scale since January 2007. Similar provisions were also taken by the environmental protection agencies of the USA and Canada.

Analytical methodology for the reliable determination of SCCPs is scarce. This is mainly due to the number of isomers (up to 6,300) of which this class of compounds consists [16], and the lack of pure solutions of individual SCCPs for calibration as well as of matrix reference materials. Many approaches have been attempted [17–20], but so far the scientific community has not agreed on which analytical methodology should be chosen.

The chromatograms of SCCP mixtures have a characteristic broad profile corresponding to a large number of coeluting compounds because the separation of the different isomers is not possible, even when using several stationary phases with different characteristics. The use of comprehensive two-dimensional gas chromatography (GC) has recently shown that an improvement in the separation of SCCPs is possible [21, 22], although neither routinely nor quantitatively applicable. In fact, data processing for this technique demands expert operators and is time consuming. The use of mass spectrometry (MS) in the electronic ionisation mode generates an extensive fragmentation of SCCPs with unspecific patterns difficult to interpret. Therefore, analysis is currently mostly performed in the electron capture negative ionisation mode. The quantification relies on the monitoring of $[M\text{-}Cl]^-$ ions of specific mass to charge (*m/z)* ratio for each group of congeners with the same chain length and number of chlorine atoms, according to the method developed by Tomy et al. [23]. A thorough clean up of the sample and a careful selection of the ions to be detected are necessary when applying this approach [24]. These precautions allow the avoidance of interferences from other chlorinated compounds, especially when using low-resolution MS, and between SCCPs and medium chain chlorinated paraffins. The method is also affected by a strong dependence on the content of chlorine of the standard used for calibration. Errors of up to 1100% can occur if the calibrant does not match the chlorine content of the sample [25]. Reth et al. [26] proposed to overcome this problem using the linear relationship between response factors and chlorine content. The chlorine content of the sample should be calculated with the measured data for this purpose. The metastable atom bombardment (MAB)-MS was recently proposed [27] as a detection mode able to analyse molecules of polychlorinated *n*-alkanes with any number of chlorine atoms and the ions abundances are not influenced by the number of chlorine atoms. Dichloromethane-enhanced electron capture negative ionisation (ECNI)-MS [28] and EI-MS/MS [29] are other techniques with a less pronounced dependency of the response factor [17] on the chlorine content, but not suitable for routine analysis due to the fast decline in sensitivity of the detector and the complexity of data evaluation, respectively.

An alternative approach for SCCP determination is based on the carbon skeleton GC [30], where SCCPs are catalytically hydrodechlorinated to the corresponding *n*-alkanes. By that the complexity of the chromatogram is enormously reduced and only four peaks of *n*-alkanes have to be quantified (see Fig. 1), which simplifies the calibration step. Information on the chlorine content is lost, but accurate quantification of the sum of SCCPs is possible. Koh et al. [31] applied this approach for the determination of chlorinated paraffins in cutting fluids and sealing materials. We have been working in applying this approach to the analysis of environmental samples. In a previous paper [32], we envisaged the development of a *standardised method* based on this technique together with the introduction of a *method-defined parameter* as a way to overcome some of the main difficulties in the analysis of SCCPs, such as data reliability and comparability, which are required in monitoring campaigns. This means that the measurand ("quantity intended to be measured" [33]) 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 measurand, 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 method.

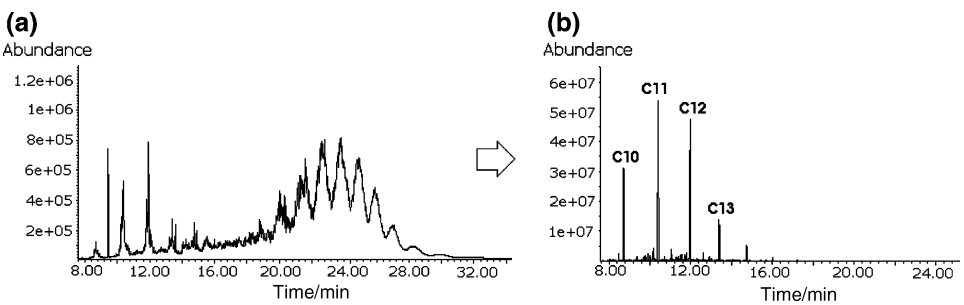

Fig. 1 Conversion of SCCPs to alkanes by H_2/Pd catalyst in the GC injector: **a** chromatogram of a technical mixture of SCCPs with a chlorine content of 55.5% obtained on a DB5-MS column by ECNI-MS, **b** chromatogram of the same commercial mixture using the same column with the carbon skeleton GC–MS approach

The use of validated methods conforming to CEN/ISO or other international standards to ensure data comparability in the monitoring of water quality is strongly recommended by the WFD, and mandatory for operationally-defined parameters. In support of the WFD, the European Commission has already given a mandate to CEN for the development or improvement of fit-for-regulatory-purpose standards. The WFD focuses on the water phase, but contains provisions that call for the monitoring of SCCPs also in other matrices such as sediments and biota [15].

In this paper, we present the detailed description of a method for the accurate determination of SCCPs in soil and sediment samples based on the carbon skeleton GC. This method could be a candidate to the standardisation procedure for a fit-for-regulatory-purposes approach for the determination of SCCPs. The optimisation of the analytical procedure and the complete in-house method validation reported in this paper constitute the first steps of this process.

Experimental

Materials and reagents

Palladium (II) chloride (59% Pd) anhydrous for synthesis was purchased from Merck (Darmstadt, Germany); sand white quartz (50/70 mesh) was purchased from Aldrich (Bornhem, Belgium); $CaCO_3$ precipitated was purchased from Merck (Darmstadt, Germany); *n*-decane (99.9% purity), *n*-undecane (99.7% purity), *n*-dodecane (99.8% purity) and *n*-tridecane (99.6% purity) were purchased as reference substances for GC from Merck (Darmstadt, Germany); stock standard solutions of individual C_{10}-SCCP congeners (10 mg L^{-1} in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany): 1,2,9,10-tetrachlorodecane (CP-2, 99.3% purity), 1,2,5,6,9,10-hexachlorodecane (CP-4, 100% purity), 1,2,5,6,9,10-hexachlorodecane (CP-5, 99.9% purity). Standard solutions of SCCPs with a chlorine content of 63, 55.5, and 51% (100 mg L^{-1} in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany); a technical mixture of SCCPs with a chlorine content of 55% was kindly provided by LGC Standards (Teddington, Great Britain); individual mixtures of SCCPs with carbon chain length of C_{10}, C_{11}, C_{12} and C_{13} were purchased by LGC Standards (Teddington, Great Britain); cyclododecane >99% was purchased from Merck (Darmstadt, Germany); lindane (99.3%) was purchased from Campro (Veenendaal, The Netherlands); aldrin (98.1%) and α-endosulfan (99.6%) were purchased from Riedel de Haen (Seelze, Germany); hexachlorobenzene (99.8%), α-HCH (99.7%), β-HCH (99.0%), γ-HCH (99.7%) were purchased from IOIC (Warsaw, Poland); individual congeners of polychlorinated biphenyls (PCBs) (CB28, CB52, CB101, CB105, CB118, CB138, CB153, CB156, CB170, and CB180) were purchased from Campro (Veenendaal, The Netherlands); cyclohexane for trace analysis was purchased from Merck (Darmstadt, Germany); *n*-hexane and dichloromethane (DCM) SupraSolv grade were purchased from Merck (Darmstadt, Germany); Florisil for column chromatography (0.150–250 mm) was purchased from Merck (Darmstadt, Germany); aluminium oxide activated basic was purchased from Aldrich (Bornhem, Belgium); Cu powder, Na_2SO_4 anhydrous, p.a., and acetic acid (96%) were purchased from Merck (Darmstadt, Germany); ammonia solution (25%) was purchased from Riedel-de Haën (Seelze, Germany).

Samples

A range of different types of soil and sediment reference materials obtained from the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) were screened for the presence of SCCPs: BCR-481 (industrial soil certified for eight PCBs), BCR-524 (industrial soil certified for organic pollutants), BCR-142R (light sandy soil certified for elements), BCR-320R (channel sediment certified for elements), BCR-701 (lake sediment certified for elements), BCR-462 (coastal sediment certified for elements), BCR-536 (freshwater harbour sediment certified for organic pollutants). Method development and validation were performed using BCR-481 and BCR-142R for the matrix soil, and BCR-320 and BCR-701 for the matrix sediment. The procedure was tested also on three natural samples: a calcareous loam soil collected in an undisturbed grass field near Brussels (Belgium), an undisturbed soil collected near IRMM, and an industrial sediment collected from a channel inside the industrial area of Porto Marghera in Venice (Italy). All the three natural materials were air-dried for a week and sieved to a particle size <125 μm before analysis.

Analytical procedure

The determination of SCCPs with the carbon skeleton GC is based on their catalytic hydrodechlorination to the corresponding *n*-alkanes. The reaction is achieved in a hydrogen gas atmosphere by the passage of the chlorinated paraffins over a heated palladium catalyst placed in the GC injector. The procedure includes the following steps: extraction from the soil or sediment, clean up and fractionation, and quantification by GC–MS (see Fig. 2).

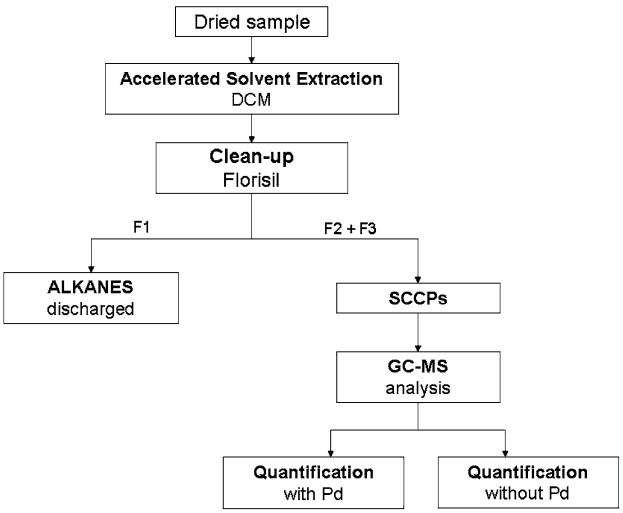

Fig. 2 Flow chart of the analytical procedure for the determination of SCCPs in soil and sediment using the carbon skeleton GC–MS (*F1* first fraction *n*-hexane, *F2* second fraction *n*-hexane/DCM, *F3* third fraction DCM)

Extraction and sulphur removal

Soil and sediment samples were extracted using an accelerated solvent extractor (ASE) (ASE-200 Dionex, Sunnyvale, USA). Approximately, 2 g of Al_2O_3 were placed on the bottom of an ASE cartridge, and then an amount between 0.8 and 1.2 g of dry sample mixed with 5 g of a 1:3 mixture of Cu powder/Na_2SO_4 (w/w) were introduced in the same thimble that was filled up with Na_2SO_4 powder. The extraction was performed using DCM at a temperature of 100 °C and at a pressure of 13.8 MPa for 10 min (two static cycles of 5 min each). Following the extraction, 1 mL of *n*-hexane was added to the extract, which was evaporated to 1 mL using a rotary evaporator (Laborota 4001, Heidolph, Kelheim, Germany).

Clean up and fractionation

After volume reduction, the extract was placed onto a chromatographic glass column (1.5 cm i.d., 20 cm length, equipped with a glass frit and a Teflon stopcock) manually packed with 5 g of Florisil, and 1 cm of anhydrous sodium sulphate placed on the top of it. The column was packed and conditioned using around 40 mL of *n*-hexane. The extract was fractionated using the following elution sequence at a flow rate of about 1 mL min^{-1}: the first fraction (F1), containing *n*-alkanes and *n*-alkenes, was eluted with 20 mL of *n*-hexane, the second fraction (F2) containing SCCPs was eluted with 40 mL of a mixture *n*-hexane/DCM 1:1 (v/v), and, to allow the complete elution of all SCCPs from the column, a third fraction (F3) of 10 mL of DCM was eluted and combined with F2. F1 was discarded, while, immediately after elution, the combined fraction F2 + F3 was reduced to a volume of about 1 mL using a rotary evaporator, and spiked with the internal standard cyclododecane.

Instrumentation and analytical conditions

Preparation of the Pd catalyst

The Pd catalyst used for the reduction of chlorinated paraffins to *n*-alkanes was prepared following the procedure described by Koh et al. [31]. In brief, 0.08 g of $PdCl_2$ was dissolved in 10 mL hot 5% acetic acid in a reagent vial (under stirring). The solution was transferred to a flat glass dish, mixed with 19 g of sand white quartz (50/70 mesh) and dried under stirring in a steam bath for 10 min. The residue was taken up in distilled water, and dried over steam bath after the pH was adjusted to pH 9 by drop wise addition of ammonia solution (25%). Finally, the catalyst material was washed with 50 mL of cyclohexane in a sintered glass funnel, and air-dried under a fume hood before use.

Preparation of the liner

A new single tapered liner (i.d. 4 mm, HP Part number 5181-3316) was packed from bottom to top by insertion in the order of 0.5 cm glass wool, 0.2 cm of calcium carbonate, 1.6 cm of Pd catalyst, 0.5 cm glass wool. Before packing the liner, the glass wool, calcium carbonate, and the Pd catalyst were baked at 300 °C for 3 h in a muffle furnace to remove all possible organic contaminants. To activate the Pd, the liner was left for at least 5 h inside the injector at 300 °C under a flow of hydrogen with the column disconnected and the injector outlet closed by a blind screw.

GC–MS conditions

A Hewlett-Packard GC (HP 5890 Serie II) equipped with an HP 7673 Automatic Sampler and coupled to a MS (HP 5972) was used. The chromatographic conditions were as follows: capillary column DB5-MS fused silica column, length 60 m (or shorter), i.d. 0.25 mm, film thickness 0.25 μm. Temperature program: 50 °C for 3 min, then 10 °C min^{-1} up to 280 °C, 10 min at 280 °C. 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 °C. The liner was packed with the Pd catalyst as described in the previous paragraph. In the type of instrument used, only the transfer line temperature could be manually set at 280 °C, whereas it was not possible to control the temperature of ion source and quadrupole.

Compounds were detected in the selected ion monitoring (SIM) mode at a dwell time of 100 ms per ion using the most abundant ions characteristics for the fragmentation of *n*-alkanes: *m/z* 57 and 41 were chosen as the quantification ions for the four *n*-alkanes (C_{10}–C_{13}) and the internal standard, respectively, while *m/z* 43, 71, 85, 98 and 99 were used as qualifying ions.

Calibration

Calibration of the instrument response was accomplished using an internal standard multipoint calibration at six levels ranging from 0.04 to 18 mg L^{-1}. Calibration solutions were prepared gravimetrically by dilution of a stock solution prepared with the four pure *n*-alkanes (C_{10}–C_{13}) in cyclohexane. Cyclododecane was used as internal standard and kept for each level of calibrant concentration at around 15 mg L^{-1}.

Quality assurance and control measurements

Measures to reduce contamination

Contamination by SCCPs from other sources has been mentioned as one of the main problems when performing the analysis of SCCPs. Thermal treatment of glassware and adsorbents in a wide range of temperature has been reported (250–650 °C). Nevertheless, according to Reth et al. [26], heating glassware up to 270 °C is not sufficient to remove the contamination. Zencak and Oehme [17] suggested heating the glassware at least at 450 °C overnight as a good laboratory practice and as an effective measure when analysing SCCPs.

In order to avoid the contamination by hydrocarbons and by chlorinated paraffins, all glassware to be used was heated overnight at 450 °C in a muffle oven. Florisil and Na_2SO_4 were baked for 4 h at 600 °C in a muffle oven before use. In addition to that, since one of the main applications of SCCPs is in the rubber industry, every contact with rubber or plastic during sample preparation was avoided, PTFE/silicone caps for the auto sampler vials, and low-bleed septa in the GC were used.

Measuring sequence

In order to check for complete absence of interfering *n*-alkanes in the extracts not originating from the conversion, the sample was injected twice into the GC-MS, with and without the Pd-modified liner. The measuring sequence applied in presence of the catalyst always comprised the injection of solvent, the set of calibration standards, followed by three replicates injections of the control sample to check the conversion efficiency (according to the instructions reported below), the procedural blank, and the samples. After that, the modified liner was replaced by a normal liner and procedural blank and samples were run again.

Determination of conversion efficiency

To quantify the efficiency of the Pd catalyst in converting SCCPs to the corresponding *n*-alkanes and checking the performance over time, a solution with a known composition and chlorine content was used. Three single decane isomers with a different chlorine content, 1,2,9,10-tetrachlorodecane (CP-2), 1,2,5,6,9,10-hexachlorodecane (CP-4), 1,2,5,6,9,10-hexachlorodecane (CP-5), were mixed with the internal standard to obtain the control sample at a chlorine content of 57%, very close to the average chlorine content of SCCPs. This solution was injected in triplicate for each sequence in the GC–MS.

The conversion efficiency E_{CP} of the Pd catalyst is calculated as the ratio of the amount of substance of *n*-alkanes experimentally found ($^{ex}n_{alkane}$) with respect to the amount of *n*-alkanes theoretically expected ($^{th}n_{alkane}$) when injecting the control sample:

$$E_{CP} = \frac{^{ex}n_{alkane}}{^{th}n_{alkane}}.$$

The conversion efficiency value was then used as a multiplier in the quantification procedure. The Pd-modified liner was replaced with a new one when either the average conversion efficiency calculated using the control sample was below the threshold value of 50%, or the relative standard deviation (RSD) of the three replicate injections was above 5%, or both performance criteria were not fulfilled.

Quantification and expression of the results

The parameter defined as measurand by the analytical procedure described in this paper is $\sum_{x=10}^{13} n_{SCCP,C_x}$ where n_{SCCP,C_x} is the amount of substance of SCCPs with a defined carbon chain length x ($x = 10$–13). The amount of substance of *n*-alkanes quantified after the conversion process using the Pd-modified liner is equal to the amount of SCCPs with a corresponding skeleton of x carbon atoms. This amount is calculated by subtracting the amount of SCCPs quantified in a procedural blank from the amount of SCCPs measured in a sample. Both values are calculated as the difference between the moles of *n*-alkanes quantified with and without the Pd catalyst, respectively, applying the conversion factor to account for the conversion efficiency of the liner (see

above). The detailed quantification of the amount of SCCPs in a sample is reported below.

The response factors $R_{f_{C_x}}$ of each *n*-alkane C_x with a carbon chain length x ($x = 10$–13) are calculated for all calibration levels according to the following equation:

$$R_{f_{C_x}} = \frac{A_{\text{alkane},C_x} m_{\text{i.s.}}}{A_{\text{i.s.}} m_{\text{alkane},C_x}},$$

where A_{alkane,C_x} chromatographic peak area of the individual *n*-alkane, $m_{\text{i.s.}}$ mass of the internal standard, $A_{\text{i.s.}}$ chromatographic peak area of the internal standard, m_{alkane,C_x} mass of the individual *n*-alkane.

The mass of the individual *n*-alkanes C_x formed by the conversion process in an unknown sample $m_{\text{alkane},C_{x_{Pd}}}$ is calculated using the internal standard method as:

$$m_{\text{alkane},C_{x_{Pd}}} = \frac{A_{\text{alkane},C_x} m_{\text{i.s.}}}{A_{\text{i.s.}} R_{f_{C_x}}}$$

where $R_{f_{C_x}}$ is the response factor for the individual *n*-alkane at the level of calibration at which the ratio $A_{\text{alkane},C_x}/A_{\text{i.s.}}$ is the closest to the ratio in the sample (approximate matching calibration).

The amount of substance content of SCCPs with carbon chain length x ($x = 10$–13) in a sediment/soil sample, κ_{SCCP,C_x}, is given by the following formula:

$$\kappa_{\text{SCCP},C_x} = \frac{n_{\text{SCCP},C_x}}{m_{\text{sample}}} = \left(\left(\frac{m_{\text{alkane},C_{x_{Pd}}} - m_{\text{alkane},C_x}}{M_{\text{alkane},C_x}} \cdot \frac{1}{E_{CP}} \right) - n_{\text{SCCP},C_x\text{blank}} \right) \Big/ m_{\text{sample}}$$

where M_{alkane,C_x} molar mass of the corresponding individual *n*-alkane, E_{CP} conversion efficiency of the Pd catalyst, $n_{\text{SCCP},C_x\text{blank}}$ amount of substance of SCCPs with x carbon atoms per molecule in the procedural blank, m_{sample} mass of sediment or soil sample.

The amount of SCCPs found in the procedural blank $n_{\text{SCCP},C_x\text{blank}}$ obtained by applying the same approach as used for a sample, is given by the following formula:

$$n_{\text{SCCP},C_x\text{blank}} = \frac{m_{\text{alkane},C_{x_{\text{Pd}}}} - m_{\text{alkane},C_x}}{M_{\text{alkane},C_x}} \cdot \frac{1}{E_{\text{CP}}}$$

where $m_{\text{alkane},C_{x_{Pd}}}$ mass of individual *n*-alkane quantified in the injection with Pd for the procedural blank, m_{alkane,C_x} mass of individual *n*-alkane quantified in the injection without Pd for the procedural blank.

Method validation

To evaluate the method performance a complete method validation was performed following EURACHEM [35] and IUPAC [36] guidelines. Linearity and working range were assessed through injection of six calibration solutions. Limit of detection (LOD) and quantification (LOQ) were estimated as three and ten times, respectively, the standard deviation of 10 independent procedural blanks (5 samples analysed per day). Trueness was estimated as recovery by standard addition experiments. BCR-320, BCR-701, BCR-142R and the calcareous loam soil, all with a SCCPs concentration below LOD, were spiked at two different levels (approximately 50 and 100 nmol g^{-1} respectively) in triplicate using the commercial mixtures from the company Dr. Ehrenstorfer with chlorine content of 51.5 and 55.5%, and immediately extracted. Repeatability and intermediate precision of the methodology were estimated by applying one-way analysis of variance (ANOVA) to the analysis of three replicates of BCR-481 during 5 days. A 2^2 two-level full factorial design was performed to investigate the robustness of the method with regard to sample intake and duration of the extraction cycles in ASE. The stability of the extract was evaluated by comparing the results obtained analysing the extracts of the soil BCR-142 spiked with SCCPs after storage at −20 °C for 1 and 2 weeks.

Results and Discussion

Performance of the Pd catalyst

Some preliminary experiments were performed to check the selectivity of the conversion operated in the Pd-modified liner, as described in the electronic supplementary material. The presence of other chlorinated or non-chlorinated compounds in environmental samples could lead to an overestimation of the amount of SCCPs if they would be converted to C_{10}–C_{13} *n*-alkanes by the Pd catalyst. When injecting standard solutions of organochlorine pesticides and PCBs, no peaks of C_{10}–C_{13} *n*-alkanes significantly different from the solvent blank were found. This proves that there is no risk of overestimating the amount of SCCPs because the conversion on the Pd catalyst is insensitive to the presence of other chlorinated compounds, such as organochlorinated pesticides and PCBs, frequently found in the environment.

Some other experiments aimed at checking the independence on chlorine content and carbon chain length of the catalytic conversion of SCCPs to *n*-alkanes.

The first aspect was investigated injecting commercial mixtures of SCCPs with three different chlorine contents. In Fig. 3, the average carbon chain length patterns of three commercial mixtures of SCCPs with chlorine content of 51.5, 55.5 and 63% are reported. The patterns obtained with the carbon skeleton GC–MS method are in very good agreement with the patterns reported for the same mixtures by Zencak et al. [34] and INERIS [37], respectively, using

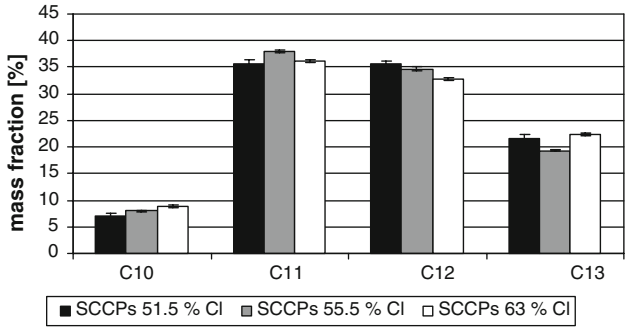

Fig. 3 Average carbon chain length patterns of three commercial mixtures of SCCPs with a chlorine content of 51.5, 55.5 and 63% obtained by carbon skeleton GC–MS (5 replicates)

the GC–ECNI–MS method. This is a first confirmation that the conversion on the catalyst does not induce any modification of the carbon chain length pattern. Moreover, in the range of 55.5–63% chlorine, which covers the average chlorine content of SCCPs, the difference in the conversion efficiency was smaller than 4%, indicating that the chlorine content has only little effect on the conversion yield.

The fact that the method is largely independent of the chlorine level is very important considering that this information is not available when analysing unknown samples, and allows the omission of this parameter from the calculation. This is a considerable advantage of the analytical procedure proposed here in comparison with other methodologies, such as those based on ECNI, where the knowledge of the chlorine content is crucial.

In Table 1, the results obtained from the experiments performed to check the dependency of the catalytic conversion on the chain length of SCCPs are reported. It can be seen that the conversion efficiency is slightly decreasing along with the increase in the chain length, with a maximum difference between the conversion efficiencies of C_{10} and C_{13} of 4%. This small variation could be attributed to

Table 1 Conversion efficiencies and their standard deviations obtained injecting twice three independent replicates of LGC mixtures of the four groups of homologues C_{10}, C_{11}, C_{12}, C_{13} in the ratio 1:1:1:1 at a concentration of about 20 mg L^{-1} each

	Chlorine content (%)	Conversion efficiency ±SD (%)
SCCP,C_{10}	59.3	102 ± 1
SCCP,C_{11}	58.0	102 ± 1
SCCP,C_{12}	56.4	99 ± 1
SCCP,C_{13}	53.0	98 ± 2
Sum of SCCPs,$C_{10–13}$	**56.7**	**100 ± 1**

Values of chlorine content for each group are calculated as a weighted average of the chlorine content of the isomers present in the mixtures according to the composition reported by LGC standards

The values reported for the sum of SCCPs correspond to the average of the results for the four homologues

the difference in the chlorine content of the group of homologues rather than to a real dependence on the chain length. This difference in conversion efficiency is in fact comparable to the one observed injecting SCCP mixtures from Dr. Ehrenstorfer with comparable chlorine levels. The two factors, chlorine content and chain length are strictly interrelated and cannot be easily distinguished. A contribution of uncertainty related to the lack of knowledge of these two factors in an unknown sample will be introduced in the uncertainty budget of the final result, as discussed later in the paper.

The choice of a proper standard to evaluate the performance of the catalyst was hindered by some difficulties. Unfortunately, well-characterised standards of SCCPs are not commercially available at present. Commercial mixtures of SCCPs are characterised by the presence of impurities [38, 39], such as isoparaffins, aromatic compounds, sulphur, metals, unreacted *n*-alkanes, organotin compounds and epoxides which affect the correct calculation of the conversion efficiency in case these solutions would be used in assessing the catalyst performance. Differences in the behaviour of commercial mixtures provided by the same producer with different lot numbers have been noticed in our laboratory, and may be due to these impurities. To reduce the uncertainty in the calculation of the final result, mixtures composed of single isomers of SCCPs with specified chlorine content and a certain carbon chain length were used in our laboratory. A mixture of C_{10} congeners with chlorine content close to the average chlorine content of SCCPs was chosen, as reported in the "Determination of conversion efficiency". Other mixtures of SCCPs with single congeners at different carbon chain length, but with the same chlorine content, could be used for the same purpose. The conversion efficiency obtained when injecting this C_{10} control sample is then applied also to the other homologue groups. This assumption is justified by the large independence of the catalytic conversion on the chain length in the investigated range.

A further step, which is currently under investigation in our laboratory, is to find a calibrant of suitable purity to be used as standard fit for the purpose to calculate the conversion efficiency of the Pd catalyst. Preliminary experiments on purity assessment of a commercially available single isomer of SCCPs indicate that the purity might be much lower than stated by the producer. Further experiments to confirm the actual purity of this candidate calibrant are ongoing.

Another aspect that had to be considered during method optimisation was the lifetime of the catalyst material and the exchangeability amongst different liners. Koh et al. [31] reported a lifetime of 20 injections for the Pd-modified liner, after which the catalyst material should be replaced. In our experience, even when injecting SCCP-enriched

environmental extracts, the lifetime of the catalyst is much longer. For up to 200 injections, the performance criteria for replacing the liner (mentioned in "Determination of conversion efficiency") were still met. In any case, even when different liners are used over time, the method allows obtaining comparable results. Good agreement was found in the performance of Pd-modified liners, independently prepared from the same batch of catalyst material with a relative standard deviation of conversion efficiency of 11% for three commercial mixtures with chlorine contents of 51.5, 55.5 and 63%. The relative standard deviation of the results when using three different liners varies from 2 to 11% for the different group of congeners. The average relative standard deviation between two sets of three replicates obtained using three different liners is 4% for the C_{10} group of homologues, 5% for C_{11}, 6% for C_{12} and 16% for C_{13}, respectively, and 5% for the sum of SCCPs. The relative standard deviation of the conversion efficiency using different liners has been introduced as a contribution of reproducibility to the uncertainty budget.

Extraction and clean up

Different procedures were tested to perform the clean up and fractionation of the sample. Special care was taken to achieve a complete separation of SCCPs from *n*-alkanes and *n*-alkenes as these compounds would result in an overestimation of SCCPs when using the carbon skeleton GC.

An attempt to separate a mixture of SCCPs and *n*-alkanes using an automated GPC system was not successful, as no separation between the two classes of compounds was achieved.

Despite the shorter time of analysis, none of the SPE cartridges tested proved to be suitable because the procedural blanks ($\sum_{x=10}^{13} n_{\mathrm{SCCP,C}_x} = 11\,\mathrm{nmol}$) were consistently higher than those obtained using the manually packed glass column ($\sum_{x=10}^{13} n_{\mathrm{SCCP,C}_x} = 1.1\,\mathrm{nmol}$) thus significantly increasing LOD and LOQ to unacceptable values. Heating of the SPE glass tube in the oven at 120 °C did not bring any improvement.

Therefore, column chromatography was chosen as clean up step and further optimised through elution of solutions of SCCPs, mixtures of SCCPs with *n*-alkanes, solutions of *n*-alkenes and chlorinated *n*-alkenes. The final procedure described above was tested on extracts of BCR-481. The elution volumes of the three fractions were optimised using the results obtained on a 5 g Florisil chromatography column with the above-mentioned certified material. Elution of 20-mL *n*-hexane enabled selective and complete elution of *n*-alkanes and *n*-alkenes from the column. More than 99% of the two families of *n*-hydrocarbons were found in the first fraction. A 40 mL of DCM/*n*-hexane 1:1 (v/v) was used to elute SCCPs almost quantitatively with recoveries ranging from 79 to 90%. A 10 mL of DCM was then used to ensure complete elution of SCCPs from the column. In case the extract would contain high amounts of *n*-alkanes or *n*-alkenes, which cannot be excluded in unknown environmental samples, there could be the risk that elution of those interferents from the column is continued in the second fraction. To ensure the accuracy of the measurement results and to avoid overestimation of the amount of SCCPs because of interfering compounds, injection without the Pd catalyst has been introduced in the analytical protocol to allow the subtraction of interferences.

BCR-481 was also used to test different types of extraction procedures. The comparison of the extraction efficiencies by three different techniques showed that the recoveries obtained by ASE ($\sum_{x=10}^{13} n_{\mathrm{SCCP,C}_x} = (88 \pm 10)\,\mathrm{nmol\,g^{-1}}$, 14 replicates), and microwave-assisted extraction ($\sum_{x=10}^{13} n_{\mathrm{SCCP,C}_x} = (80 \pm 5)\,\mathrm{nmol\,g^{-1}}$, 2 replicates) were higher with respect to those obtained by Soxhlet extraction ($\sum_{x=10}^{13} n_{\mathrm{SCCP,C}_x} = (64 \pm 1)\,\mathrm{nmol\,g^{-1}}$, 2 replicates). No reference value for the content of SCCPs in BCR-481 is available, therefore only a qualitative evaluation of recoveries is possible. Aiming at routine applicability of this method, ASE was chosen as the extraction procedure. Out of several solvents and mixtures of solvents tested in the extraction step, DCM was preferred because of better defined peaks in the chromatogram.

The internal standard proposed in our procedure, cyclododecane, is added after the clean up of the extract and, therefore, does not compensate for incomplete extraction as well as for losses during clean up. Further experiments using deuterated alkanes are currently running in our laboratories with the aim to find a more suitable internal standard.

Method performance characteristics

Once the analytical protocol was developed, the performance of the whole analytical procedure was investigated through a complete in-house method validation according to EURACHEM [35] and IUPAC [36] guidelines. The resulting method performance characteristics are reported below.

Linearity and working range

The linear range of calibration using *n*-alkanes covered concentrations from 0.04 to 18 mg L^{-1}. Coefficients of determination (R^2) were higher than 0.99 for all the groups of SCCPs.

Limit of detection and limit of quantification

The amounts of alkanes and of SCCPs found in the blanks using our procedure are reported in Table 2. Because the concentration of SCCPs in blank samples is not negligible, the amount of SCCPs quantified in blank samples has been subtracted from the total amount in the environmental sample. LOD and LOQ values for the four groups of congeners and the total sum of SCCPs are reported in Table 3 related to the sample in weight and expressed as nmol g^{-1}. The highest values are obtained for C_{13} and the lowest for C_{11}. Until environmental quality standards (EQS) will be established for the sediment/soil phase, the suitability of the LOD and LOQ obtained with this method can only be evaluated by comparison with existing ecotoxicological data. The LOD and LOQ values are below the predicted no-effect concentration (PNEC) (i.e. the concentration below which exposure to a substance is not expected to cause adverse effects) established for soil (0.80 mg kg^{-1} wet mass) and sediments (0.88 mg kg^{-1} wet mass) [40]. Therefore, it can be concluded that the LOD and LOQ of the method are adequate to analyse environmentally relevant concentrations of SCCPs in soil and sediment samples.

Table 2 Mass of n-alkanes (ng) (a) and amount of SCCPs (nmol) (b) with carbon chain length x ($x = 10$–13) found in the blanks and their standard deviations (10 replicates)

(a)	$M_{alkane} \pm$ SD (ng)
Alkane,C_{10}	14 ± 6
Alkane,C_{11}	26 ± 3
Alkane,C_{12}	39 ± 20
Alkane,C_{13}	22 ± 14
Sum of alkanes,$C_{10\text{-}13}$	**101 ± 30**
(b)	$n_{SCCP} \pm$ SD (nmol)
SCCP,C_{10}	0.34 ± 0.07
SCCP,C_{11}	0.18 ± 0.08
SCCP,C_{12}	0.6 ± 0.1
SCCP,C_{13}	0.8 ± 0.2
Sum of SCCPs,$C_{10\text{-}13}$	**1.9 ± 0.4**

Table 3 LOD and LOQ (nmol g^{-1}) for the four groups of homologues and for the sum of SCCPs estimated as three and ten times, respectively, the standard deviation of ten independent procedural blanks

	LOD (nmol g^{-1})	LOQ (nmol g^{-1})
SCCP,C_{10}	0.2	0.7
SCCP,C_{11}	0.1	0.5
SCCP,C_{12}	0.4	1.3
SCCP,C_{13}	0.7	2.2
Sum of SCCPs,$C_{10\text{–}13}$	**1.1**	**3.5**

Selectivity

As demonstrated with the experiments reported in "Performance of the Pd catalyst", the procedure is selective towards the determination of SCCPs, and is able to discriminate from interfering compounds. The catalytic conversion of SCCPs by Pd is selective and other common chlorinated compounds are not converted to *n*-alkanes. The selectivity of the entire procedure is also ensured by removing undesired interferences, such as *n*-alkanes and *n*-alkenes, using column chromatography clean up. The injection without Pd catalyst is a further precautionary measure to ensure complete selectivity and to avoid overestimation of the amount of SCCPs.

Repeatability and day-to-day variation

Repeatability and between day variation are reported in Table 4 for each group of congeners and for the sum of SCCPs, expressed as coefficient of variation and calculated applying ANOVA. Method repeatability varies between 4 and 12% depending on the group of congeners considered. A trend can be seen in the data: the shorter the chain length of the SCCP group, the better the repeatability. The between day standard deviation was always smaller than method repeatability and varied between 0.7 and 3%. When considering the sum of SCCPs, the coefficients of variation of repeatability and between day variation are 5.2 and 2.5%, respectively.

Recovery

Because no reference material certified for its SCCP content is available, trueness was estimated as recovery by standard addition experiments on two soils and two sediments. The recoveries obtained from the spiking experiments on the four materials are reported in Table 5. It can be seen that the recoveries are similar and constant for the four materials with an average value of (55 ± 3)% for the sum of SCCPs. Considering that the method is intended to be proposed as a standard method, the absolute trueness is not crucial. It is instead important that the recovery is consistent and reproducible in the different matrices, and this is confirmed by the data reported in Table 5.

Nevertheless, the reason of such a low recovery was further investigated. The results showed that there is no matrix suppression effect because the recovery of SCCPs in extracts spiked with single congeners of SCCPs was 87%. The recovery within spiking experiments in soil was also

Table 4 Repeatability and between day standard deviation expressed as coefficient of variation (%) and calculated applying one-way ANOVA to the analysis of three replicates of BCR-481 (approximately 88 nmol g^{-1}) during 5 days

	Repeatability (%)	Between day standard deviation (%)
SCCP,C_{10}	3.8	2.8
SCCP,C_{11}	6.5	2.1
SCCP,C_{12}	9.9	0.7
SCCP,C_{13}	12.4	0.9
Sum of SCCPs,$C_{10–13}$	**5.2**	**2.5**

Table 5 Recoveries (%) and their standard deviations (%) obtained in the spiking experiments for four materials with a content of SCCPs below LOD at two levels (approximately 50 and 100 nmol g^{-1} respectively) in triplicates

	Recovery (%) ± SD (%)			
	BCR-320	BCR-142R	BCR-701	Calcareous loam soil
SCCP,C_{10}	53 ± 9	47 ± 9	66 ± 6	64 ± 8
SCCP,C_{11}	52 ± 2	63 ± 3	57 ± 4	63 ± 9
SCCP,C_{12}	54 ± 3	59 ± 4	51 ± 3	55 ± 7
SCCP,C_{13}	49 ± 5	49 ± 1	40 ± 5	47 ± 11
Sum of SCCPs,$C_{10–13}$	**52 ± 3**	**57 ± 2**	**52 ± 4**	**57 ± 6**

The values reported for the sum of SCCPs correspond to the average of the results for the four homologues

improved from an average of 55% (see Table 5) to 77%. Possibly, the observed low recovery of SCCPs in standard addition experiments could be, at least partially, attributed to an undefined purity of the commercial mixtures of SCCPs used for spiking. This underlines once more how important it is to rely on standards of known purity to reduce the uncertainty of measurement results and to improve the accuracy.

Robustness

Sample intake and duration of the static cycles in ASE were the critical factors of the procedure when tested for robustness. All the other parameters in the analytical protocol could be well controlled and thus did not require robustness assessment. The effect for each factor was compared on the analytical response and a *t* test was performed for significance. No statistical significance for the two parameters in the range investigated was found, thus indicating robustness of the method under the studied conditions.

Stability of extracts

Measurements on extracts of the soil BCR-142 spiked with SCCPs and stored at −20 °C showed that the extracts are stable for 1 week within the uncertainty of the method. After 2 weeks of storage, the concentration of SCCPs found was about 20% lower than the original value. Therefore, it is advisable to proceed with the analysis of the extract within maximum 1 week after sample preparation.

Uncertainty budget

The expanded uncertainty U of the measurement result can be calculated using the data from the validation study according to the following formula [41]:

$$U = k\overline{\kappa}\sqrt{u(c_{\mathrm{st}})^2 + \frac{u_r^2}{p_1} + u_R^2 + \frac{\mathrm{CV}^2}{p_2} + u_{\mathrm{ceff}}^2}$$

where k coverage factor ($k = 2$) resulting in a confidence level of approximately 95%, $\overline{\kappa}$ average amount content of the analyte, $u(c_{\mathrm{st}})$ relative uncertainty of the concentration of the calibration standards used, including contributions arising from purity and gravimetric preparation (%), u_{r} relative uncertainty of repeatability (%), p_1 total number of repeatability samples, u_{R} relative uncertainty of reproducibility (%), CV coefficient of variation of recovery estimation (%), p_2 number of independent samples in the recovery experiments, u_{ceff} relative uncertainty of the catalytic conversion efficiency (%).

In Table 6, the calculated contributions to the uncertainty budget and the combined expanded uncertainty for the four groups of congeners and for the sum of SCCPs are reported when the uncertainty estimation is applied to the analysis of BCR-481. For $u(c_{\mathrm{st}})$ the contribution to the uncertainty of the sum of SCCPs is the quadratic sum of the contribution of the single congeners. For u_{r} the contributions to the uncertainty budget of the sum of SCCPs are obtained from the ANOVA calculations for the sum of SCCPs. The same statistical elaboration of the results gives in addition an uncertainty of the standard deviation between days. This contribution ranges from 0.7 to 2.8% depending on the congener, and is equal to 2.5% for the sum of SCCPs. However, to apply a more conservative approach, this contribution is replaced by a higher contribution of reproducibility u_{R} obtained from the relative standard deviation of the injection of the same extracts in different liners.

The contribution related to the recovery CV is obtained for the group of homologues as well as for the sum of SCCPs from the coefficient of variation of the recovery experiments. The average relative standard deviation of the recoveries on two spiked levels of only one of the four

materials tested for spiking (see Table 4) was used. The recovery results for the calcareous loam soil have been chosen because they represent a worst case scenario.

No contributions related to the conversion efficiency itself have been introduced in the uncertainty budget because the results are already corrected for this value as explained in "Quantification and expression of the results". Nevertheless, as previously discussed, a contribution related to the catalytic conversion has been introduced in terms of variability of the catalytic conversion (chlorine content and chain length dependence) and the uncertainty linked to the estimation of the chlorine content in an unknown sample. This contribution u_{ceff} is estimated as 4% for the sum of SCCPs, as discussed in "Performance of the Pd catalyst", while the contribution for each group of isomers is mathematically deduced considering that the quadratic sum of the individual contributions is equal to 4%.

Values for the relative expanded uncertainty (coverage factor $k = 2$) for the groups of homologues range from 12 to 25%, while for the sum of SCCPs it is estimated to be 12%. The highest contributions are given by the uncertainty on the repeatability, and the uncertainty of the reproducibility. The lowest comes from the uncertainty of the preparation of the standards, due to the use of pure standards of individual *n*-alkanes more easily available than SCCP standards. The use of solutions of commercial mixtures of SCCPs of lower purity would, in fact, notably increase this contribution. The expanded uncertainty value proves that the method can be used to obtain a sufficiently precise quantification of SCCPs in sediment and soil samples. The concentration values reported in Table 6 with their expanded uncertainties, estimated from an extensive method validation, can be regarded as indicative values for the SCCP content in BCR-481 as determined by the carbon skeleton method.

Natural environmental samples

Besides the reference materials used in the experiments for method validation, natural environmental samples of sediment and soil were analysed using this methodology. A sediment sample was collected in the industrial area of Porto Marghera (Venice, Italy). This is a polluted industrial area in Italy, where many petrochemical activities, including the production of plastics, are conducted, and where probably chlorinated paraffins have been used in some of the processes. The amount of SCCPs found in this sample was just above the LOQ ($\sum_{x=10}^{13} \kappa_{\text{SCCP,C}_x} = (4.2 \pm 0.2)\,\text{nmol g}^{-1}$). The amounts of SCCPs found in an undisturbed soil collected near IRMM (Geel, Belgium), and in a calcareous loam soil collected in a grass field near Brussels (Belgium) were below the LOQ.

Conclusions

The analytical procedure described in this paper, based on the carbon skeleton GC, allows the precise quantification of SCCPs in sediment and soil samples on a routine basis. The use of this procedure as a potential standard method coupled to the definition of a method-defined parameter can overcome some of the main difficulties encountered so far in the analysis of SCCPs. The analytes to be measured are better defined and the chromatograms are much simplified facilitating the quantification. The quality of the analytical result, based on a comprehensive method validation, is furthermore ensured by two factors. On the one hand, calibration is easily accomplished with *n*-alkanes, which are commercially available as high purity standards. On the other hand, the measurement results are largely independent of the chlorine content of the SCCPs present in the sample. This feature is a considerable advantage compared with the approach using ECNI detection.

In this paper, a complete method validation is reported for the first time for the determination of SCCPs in soil and sediment samples. The uncertainty budget estimations show that the expanded uncertainty is reduced to acceptable values. Assurance of trueness, an open issue in the determination of SCCPs, could be overcome by the use of a standardised method as described here and using the sum of SCCPs as a method-defined parameter. This would at least allow the comparability of SCCP data provided by the laboratories in charge of environmental monitoring. Therefore, after in-house validation of the analytical procedure, the next step will be to propose the protocol to a

Table 6 Contributions to the uncertainty budget, combined expanded uncertainty (U) and relative expanded uncertainty (U_{rel}) for measurements on BCR-481 using a coverage factor $k = 2$

	$\overline{\kappa}$ (nmol g^{-1})	$u(c_{\text{st}})$ (%)	u_{r} (%)	u_{R} (%)	CV (%)	u_{ceff} (%)	U (nmol g^{-1})	U_{rel} (%)
SCCP,C_{10}	57.5	0.25	3.8	3.9	5.1	2.0	6.8	12
SCCP,C_{11}	13.2	0.30	6.5	4.5	4.8	2.0	1.5	12
SCCP,C_{12}	12.5	0.26	9.9	6.4	5.2	2.0	1.7	14
SCCP,C_{13}	4.9	0.31	12.4	16.2	9.5	2.0	1.2	25
Sum of SCCPs,$C_{10–13}$	**88.0**	**0.57**	**5.2**	**5.0**	**4.0**	**4.0**	**11.0**	**12**

standardisation body. If the standardisation process will be successful, the compliance check with the threshold values laid down in national and European legislation (expressed in mass fraction) could be achieved by applying a uniformly prescribed conversion factor to the results obtained as amount of substance content. Such approach would not be fundamentally different, but more harmonised compared with the current situation, where de facto various artificial conversions are used in the calibration of the measurement signals of mixtures of partially non-identified individual compounds with unknown response behaviour.

The method could also be applied and extended with the necessary modifications to other environmental matrices such as water, sewage sludge and biota. Moreover, the method could be used for the characterisation of potential reference materials.

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