Analysis of short-chain chlorinated paraffins: a discussion paper†

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Short-chain chlorinated paraffins are a class of organic compounds widely used in many industrial applications, extensively diffused into the environment, persistent, bioaccumulative, and toxic towards aquatic organisms. However, their study and monitoring in the environment are still limited. Because of the enormous number of positional isomers that characterise their mixtures, the analysis of this class of pollutants is very difficult to perform. Beside this, the lack of certified reference materials poses a problem for the assessment of the quality assurance/quality control of any analytical procedure. At present, the scientific community does not agree on any analytical reference method, although the monitoring of short-chain chlorinated paraffins has already started in order to comply with the Water Framework Directive of the European Union on water quality. In this paper the regulatory framework, in which chlorinated paraffins are included, and the status concerning their determination are summarized. The main analytical difficulties still existing are discussed, and the definition of a method-defined parameter as well as the development of a standardised method are suggested as a way to obtain comparable monitoring data.

Introduction

Chlorinated paraffins (CPs) are highly complex technical mixtures of polychlorinated *n*-alkanes (PCAs) with a chlorination degree between 30 and 70% by mass, and a linear carbon chain length from C_{10} to C_{30}. Three classes can be defined according to their carbon chain length: short-chain C_{10}–C_{13} (SCCPs), medium-chain C_{14}–C_{17} (MCCPs), and long-chain chlorinated paraffins $C_{>17}$ (LCCPs), each formed by thousands of homologues, diastereomers and enantiomers.[1]

CPs are viscous, colorless or yellowish dense oils or solids produced by chlorination of *n*-alkane feedstocks with molecular chlorine under high temperature and pressure and/or UV irradiation, and do not occur naturally. Due to their physical properties, such as viscosity, flame resistance, and low vapour pressure, they have been used in a wide range of applications: extreme pressure additives in lubricants and cutting fluids, plasticizers in PVC, and flame retardants in paints, adhesives and sealants. They have also been adopted as substitutes for polychlorinated biphenyls (PCBs) in some applications.

Among the CP mixtures, SCCPs have the highest potential to be released into the environment because of their higher vapour pressure and higher water solubility (10 to 100 times higher than for PCBs). Release into the environment can occur from improperly disposed metal-working fluids, leaching from polymer or loss from paints and coatings containing CPs.[2] Their presence in the environment has been ascertained in a variety of matrices (water, sediments, soils, biota and air)[3–5] worldwide, including remote areas like the Canadian Arctic.[6,7]

A recent risk assessment evaluation has classified SCCPs as dangerous to the environment because they are toxic towards aquatic organisms and may cause long-term adverse effects.[8] SCCPs show long-term toxicity to algae, aquatic invertebrates and fish at concentration as low as 19.6, 8.9 and 3.1 µg l^{-1}, respectively. The high $\log K_{ow}$ values (from 4.39 to 8.01) imply a high potential for bioaccumulation, resulting in bioconcentration factors in the range of 7 to 7155 for fish and 223 to 138 000 for mussels.[2] In addition, the International Agency for Research on Cancer[9] has concluded that there is sufficient evidence for the carcinogenicity to humans of CPs of the C_{12} carbon chain length group with an average chlorine content of 60%.

The concern for their toxicity towards terrestrial and aquatic organisms and their relevant release into the environment have induced many countries to restrict the marketing and use of chlorinated paraffins as metal working fluids and leather finishing products. 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. Similar provisions were also taken by the Environmental Protection Agencies in Canada and the United States.

Up to now, few papers have reported the analysis of SCCPs in the environment, and this is both due to the limited knowledge about their physico-chemical properties and the difficulty of analysing and quantifying CPs. No fully-validated and suitable-for-routine-analysis method is available in the literature and pure solutions for calibration as well as matrix-matched reference materials are missing.

To comply with European regulations, a proper analytical method and quality assurance tools were required since the

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beginning of 2007, but so far no major improvements have been achieved for the routine determination of SCCPs.

In this paper, the European regulatory framework in which SCCPs are included and the status of their determination are presented. Moreover, an approach to quantify CPs for harmonized environmental monitoring is discussed.

The regulatory framework

The Water Framework Directive 2000/60/EC sets the objective to prevent deterioration of the status of all Community waters and to assure achievement and maintenance of their good chemical and ecological status by 2015. The implementation of the Directive is based on the establishment of management plans at a river basin scale and includes the design of water monitoring programmes to be carried out by laboratories mandated by competent authorities of the Member States.

Chemical monitoring is focused primarily on the measurement of the so-called priority substances grouped in a list (Annex X of the WFD, Decision No. 2455/2001/EC) which currently includes thirty-three pollutants, most of which are organic compounds well-known as hazardous for environment and human health. These pollutants are classified in three groups: *priority substances, priority hazardous substances*, and *priority substances under review*. Given their toxicity and persistence in the environment, SCCPs have been classified as priority hazardous substances and were therefore included in the second group. The substances belonging to this group are subject to measures aiming at ceasing or phasing out of discharges, emissions and losses within an appropriate timetable that shall not exceed 20 years.

Article 16 of the WFD requests the Commission to present a proposal with specific measures against water pollution caused by individual compounds or groups of pollutants presenting a significant risk to, or *via*, the aquatic environment. Accordingly, the Commission was required to set environmental quality standards (EQS) and emission controls for the priority substances. This was done in the "Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending the WFD" dated July 2006 (COM (2006) 397 final).

EQS are thresholds for the concentrations of pollutants which should not be exceeded in order to protect human health and environment. In the context of the WFD, EQS define the environmental objective of "good surface water chemical status" and thereby represent criteria for assessing whether Member States are in compliance with the regulation. The establishment of EQS at Community level should ensure that implementation of the Directive is consistent with the obligations of the legal text and comparable among the Member States. In Table 1, the EQS related to SCCPs are reported as indicated in Annex I of the Commission Proposal. EQS are expressed as annual averages (AA) calculated as annual arithmetic means, and maximum allowable concentrations (MACs), and specified for inland surface waters and other surface waters.

WFD requirements for priority substances are currently focusing on establishing quality standards for the water phase.

Table 1 Environmental quality standards set by the European Union for SCCPs (expressed in $\mu g\ l^{-1}$)

	AA-EQS inland surface waters	AA-EQS other surface waters	MAC-EQS inland surface waters	MAC-EQS other surface waters
C_{10}–C_{13} chloroalkanes	0.4	0.4	1.4	1.4

However, given that Article 16(7) of the directive states the following: "The Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments and biota", it is predictable that the Commission will explore the opportunities in establishing EQS for compartments other than the water phase. Sediments and biota, in fact, are important parts of the aquatic ecosystem in strong connection with the water cycle, and many compounds tend to accumulate more in these matrices than in water. This is also the case for SCCPs, which in fact have been included in the Appendix I (Annex IV) of the AMPS draft final report,[10] among those priority substances of the WFD that are suggested for trend monitoring in sediment and biota.

Currently, there is also a Commission Decision under discussion concerning *minimum performance criteria* for analytical methods used for chemical monitoring and the quality of analytical results. It is expected that target values for the measurements uncertainty and limit of detection (LOD)/limit of quantification (LOQ) of methods will be defined as well as requirements for quality assurance in monitoring laboratories will be set.

In any case, monitoring laboratories have to be able to measure SCCPs reliably at the level of the proposed EQS. This requires validated methods capable of delivering comparable and traceable results with a fit-for-purpose measurement uncertainty as well as internal (*e.g.* reference materials) and external (*e.g.* proficiency testing) quality control tools.

Since the monitoring schemes imply routine analyses, the economic aspect also plays an important role. The measurement techniques used in the monitoring should be able to deliver reliable data at an affordable cost.

State of the art of analytical methodologies

According to Coquery *et al.*,[11] "SCCPs are the most challenging group of substances with respect to analysis and quantification". Their determination is difficult because of the complexity of the mixtures and the enormous amount of congeners characterising this class of pollutants, as well as the numerous substances that could interfere with them. The analytical methodologies tested and applied for the determination of chlorinated paraffins have recently been reviewed by Zencak and Oehme,[12] Eljarrat and Barceló,[13] Bayen *et al.*[14] and Santos *et al.*[15] Those papers provide an extensive and detailed overview on all the methodologies attempted so far and the environmental occurrence of chlorinated paraffins. In general, the determination of SCCPs comprises four steps: extraction and clean-up, separation, detection and finally

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quantification. In the following, only the main difficulties for each step of the analysis of SCCPs are highlighted. Moreover, the advantages and disadvantages of each approach are discussed using, as judgement criteria, the routine applicability (easiness to perform, cost-effectiveness and required time) of the method.

Extraction and clean-up

Extraction usually does not represent a problem, because the same procedures used for the determination of other organochlorine compounds are suitable and applicable also to the extraction of SCCPs. Well-known more or less routine applicable methodologies can be applied such as Soxhlet, accelerated solvent extraction (ASE), solid-phase micro-extraction (SPME), or solid-phase extraction (SPE).

The clean-up step can be regarded as more critical because other organic compounds, potentially co-extracted together with SCCPs (pesticides, PCBs, toxaphenes and chlordanes), might represent a problem in the following steps of the analytical process. The choice of the clean-up procedure mainly depends on the selectivity of the detection system applied: electron capture detector (ECD), low resolution mass spectrometer (LRMS) or high resolution mass spectrometer (HRMS). A strict clean-up procedure, including e.g. fractionation of the extracts and gel permeation chromatography (GPC), could be necessary. This implies long and more expensive analytical conditions. At present, the clean-up is one of the steps that makes the analysis of SCCPs so challenging.

Separation

After clean-up, the extract is injected into a gas chromatograph. At present, no gas chromatographic technique is able to separate SCCPs, partly or completely, into single isomers, even when applying lengthy and expensive clean-up procedures, and when using several stationary phases of different polarity. The chromatograms obtained have a characteristic broad profile corresponding to a large number of co-eluting peaks (see Fig. 1). The congeners present in higher concentrations give rise to the broad unresolved peaks because of co-elution, while the underlying broad hills result from the large number of congeners present at low concentrations. The
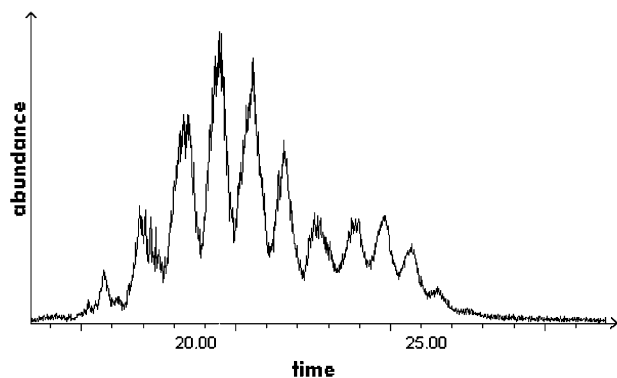

Fig. 1 Chromatogram of a commercial mixture of chlorinated paraffins with a chlorination degree of 55% obtained in our laboratory on a DB-5MS column by ECNI-MS.

chromatogram can be complicated by the presence of interfering components, such as PCBs, toxaphenes and chlordanes, if they are not properly removed in the clean-up step.

In an attempt to simplify the gas chromatographic (GC) analysis, Coelhan[16] proposed the approach of short column GC-electron capture negative ionisation (ECNI). Because separation of the mixture cannot be achieved anyway, the sample can be introduced into the MS via a very short column. SCCPs elute all in one peak, with a width of only a few seconds, increasing the sensitivity of the determination. However, in order to apply this method, the clean-up of the sample has to be very thorough.

Conversely, considerable improvements in the separation of CPs were recently obtained by Korytar et al.[17] using comprehensive two-dimensional gas chromatography (GC × GC) coupled to a rapid-scanning quadrupole mass spectrometer (qMS) with ECNI, or to electron-capture negative ionization time-of-flight mass spectrometry.[18] These findings are certainly useful to improve the characterization of the mixtures, but this type of equipment is very expensive, it needs expert operators, it requires a very long time for data processing, and therefore it is not suitable for routine analysis.

An alternative procedure for the determination of SCCPs is the use of the carbon skeleton gas chromatography.[19-21] In this method, chlorinated paraffins are reduced to the corresponding alkanes by catalytic hydrodechlorination. The reaction is achieved in a gas phase by passage of the chlorinated paraffins over a heated palladium catalyst placed in the liner of the GC injector. Conversion efficiencies around 90% to alkanes and less than 10% to cyclic alkanes were reported.[21] Any information on the chlorination degree is lost, but a good characterisation of the carbon chain is achieved. The carbon skeleton chromatography can be coupled both to a flame ionization detector (FID) or MS detectors.

Detection

For the detection of SCCPs, GC can be coupled to ECD or MS. For MS, various ionization techniques are used: ECNI, electron impact (EI), or metastable atom bombardment (MAB). The most common method of ionisation, EI, is not usually applied for the determination of SCCPs because it lacks specificity. Even EI spectra of single SCCP congeners do not present a recognizable pattern, and are characterised by extensive fragmentations with abundance of fragment ions common to the mass spectra of any chlorohydrocarbon.[22-24]

The risk of interference can be avoided by monitoring characteristic negative ions produced by ECNI-MS. This is by far the most widely used MS ionization technique for the analysis of SCCPs: the degree of fragmentation is notably lower than that with EI and positive chemical ionisation (PCI), and depending on the detection system used, high abundance of Cl_2^- and HCl_2^- [25] or of $[M–Cl–2HCl]^+$ [22] are reported.

Currently, SCCPs analysis in environmental samples is mainly performed by GC-ECNI due to its high selectivity and sensitivity, following or adapting the method developed by Tomy et al.[25] In this method, the quantification relies on the monitoring of $[M–Cl]^-$ ions for each of the groups of congeners with the same carbon chain length and number of

chlorine atoms. Nevertheless, this procedure is still hampered by some drawbacks. The results are strongly dependent on the degree of chlorination of the applied standard because compounds with a low chlorination degree have a low response factor, and *vice versa*. To avoid interferences from other chlorinated compounds, especially when working with LRMS, a very thorough clean-up of the sample is required, thus contributing to make the analytical procedure more complicated and time consuming. Another drawback of this procedure is that more injections of the same sample are required because of the large number of ions to be monitored.

The use of LRMS instead of HRMS increases the risk of errors due to interferences by other chlorinated compounds or even by different CP congeners. Reth and Oehme[26] observed that disturbances might occur in mixtures where short and medium chained chlorinated paraffins are present simultaneously. In fact, congeners with five carbon atoms more and two chlorine atoms less present ions and fragments with the same nominal mass. This can result in an overestimation of the total SCCP concentrations if signal shape and isotope ratios are not checked accurately.

To overcome the problems highlighted above, and in an attempt to provide better instrumental techniques for the determination of SCCPs, alternative methodologies have been recently developed. For instance, the addition of dichloromethane to the reagent gas in NCI increases selectivity and sensitivity in the chloride enhanced atmospheric pressure negative ion chemical ionisation mass spectrometry (CH_4/CH_2Cl_2-NICI-MS). Quite similar response factors for the studied single congeners are obtained allowing direct comparison of the CPs signals and the use of technical mixtures as standards.[27] To implement this technique, some instrumental modifications, although not complex, are necessary. Nevertheless, it is important to note that the use of dichloromethane (DCM) causes the deposition of a black residue in the ion source that can damage the instrument in the long term.

The EI-MS-MS technique[28] is not influenced by the degree of chlorination of the quantification standard, although it cannot be applied for the study of congener patterns and is unable to differentiate between short- and medium-chain CPs. Moreover, it requires quite expensive instrumentation that makes it unsuitable for routine analysis.

Another methodology recently proposed is the metastable atom bombardment (MAB) ionisation, where the base peak is $[M–Cl]^+$ and molecules with any number of chlorine atoms can be analysed contrary to ECNI.[29]

These techniques do not systematically measure the same group of compounds, which seriously hinders comparison between studies.[14]

Quantification

The quantification step is usually carried out by comparing the areas of the chromatographic peaks originating from the sample with those in technical mixtures. Unfortunately, very few standard solutions are available on the market up to now, and not one of those is certified, making the selection of the calibrant solution a very critical step in the determination of SCCPs. It has been already demonstrated that grossly biased

results can result from improper calibration,[30] undermining the accuracy of the measurement.[31] Often, the uncertainty of the calibration step is the largest contribution to the combined uncertainty of the analytical result. When the analytical data are used for compliance checks with very low legal limits, like *e.g.* the aforementioned EQS, within a stated uncertainty, the importance of reducing all the uncertainty sources becomes even more evident.

It has been ascertained in the only interlaboratory study performed so far on SCCPs that quantification in environmental matrices varies if different industrial formulations are used as external standards.[32] The presence of different impurities in commercial mixtures (isoparaffins, aromatic compounds, sulfur, metals, unreacted *n*-alkanes, organotin compounds and epoxides) has been claimed as a possible explanation of the differences.

Moreover, it has been noticed that differences in the chlorination degree of the SCCPs in the sample and in the standard can result in differences of the quantified concentration up to 1100%.[32,33] Therefore, the SCCP pattern of the standard used for the quantification should resemble as much as possible the one of the sample, in terms of molecular mass and chlorination degree, to achieve better results.

To reduce the uncertainties related to the determination of SCCPs, Tomy *et al.*[34] have proposed the synthesis of SCCP standards starting from *n*-alkanes. After isolation and purification on Florisil, the mixtures were then combined to form a mixture as similar as possible to the environmental samples to be analysed, so that it could be used as a calibrant.

This approach is time consuming because a different calibrant should be prepared for each sample. In fact, although formula group abundance profiles (congener patterns) are rarely reported in the literature, it seems that congener profiles are matrix-, and sometimes method-dependent. Differences in the formula group abundance profile were reported between matrices and also within the same matrix (for example sediment samples at different depths,[6] or fishes of different species,[35] see Fig. 2), for both the carbon chain length, and the number of chlorine atoms.

Reth *et al.*[36] have suggested an alternative procedure to tackle the problem of calibration. Their approach compensates for the influence of different response factors and makes results independent from the chlorine content of the measurement standard. In this procedure the total response factor of the CPs in the sample is calculated from the linear correlation found between the total response factors for a set of CP standards and their chlorine content. This seems an interesting approach, although the chlorination degree of the sample should be known in advance.

Designing a method defined parameter

Reviewing the existing literature indicates that the difficulties in the analysis of SCCPs have discouraged many environmental laboratories to tackle this class of pollutants. Until now, only few laboratories worldwide analyse SCCPs. Despite the considerable progress made in the past few years, the determination of SCCPs is still not reliable and far from being under control, and there is no fully validated procedure at present.
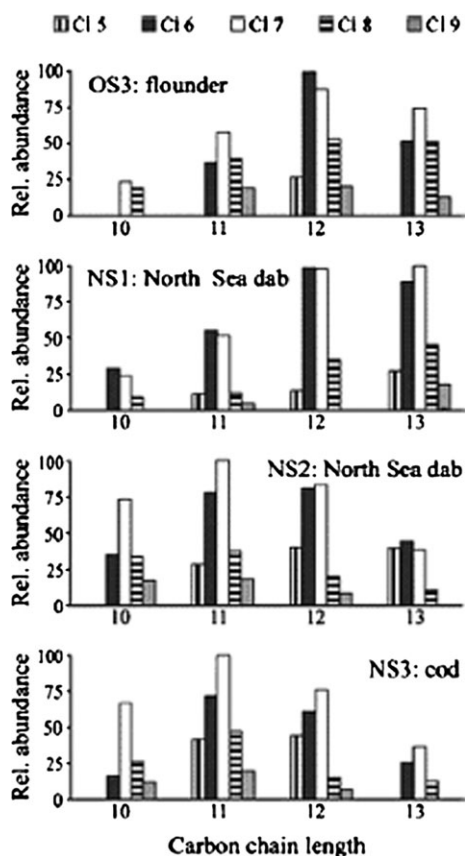
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Fig. 2 Congener pattern (C_{10}–C_{13}) found in different fish tissues [reprinted from ref. 35 with permission from Elsevier].

Not one of the methods most currently used can be applied for routine analyses. The methods require a chemical ionisation source that is not as common in the laboratories as electron impact. Moreover, the quantification procedures proposed are tedious and time consuming. There is a lack of reference materials, both calibrant solutions and matrix reference materials, which are required to ensure accuracy and traceability of the results. These problems result in poor laboratory performance and comparability.

As already mentioned, SCCPs have been included in the list of priority substances of the Annex X of the WFD. This implies that they should be included in the regular monitoring plan of the water quality of each European river basin and monitored by 2007. But, as the situation is at present, the lack of an agreed analytical reference method and the lack of a well-defined set of indicator substances will impede the environmental laboratories to meet the requirements of the WFD as regards this parameter if a solution is not found as soon as possible.

In a paper about priority substances of the WFD, Coquery et al.[11] addressed the problem of comparability of analytical results for four groups of priority substances: SCCPs, nonyl- and octylphenols, polybrominated diphenylethers and organotin compounds. The authors stated that, because it seems impossible to select indicator substances for SCCPs, the only way to gain comparability of results would be to define clearly an analytical methodology that must be used by all laboratories participating in a common monitoring program.

In their review paper, Bayen et al.[14] wonder whether there is any chance to simplify the analysis of SCCPs in order to accomplish the requirements of the WFD directive, and they question whether the method development should be directed towards the total CP concentration approach or a congener specific approach. To this regard, SCCPs are mentioned in the list of priority substances in the Annex X of the WFD as C_{10}–C_{13}, but a footnote specifies that at present, appropriate indicative parameters cannot be given. The sum of SCCPs would be, unless differently specified, the parameter to look for, without further specification of the formula group profile.

Since SCCPs are not clearly defined analytes at the molecular level, because of the huge number (more than six thousand[37]) of congeners which characterise their mixtures, the definition of a *method defined parameter* is a promising way forward. That means that the measurand ("quantity intended to be measured") is defined *via* the application of a precisely described analytical procedure, which provides also the reference for the metrological traceability of the measurement results.

Looking at the structure of SCCPs and taking into account the carbon skeleton of the molecule, a possible method defined parameter could be the sum of alkanes corresponding to the carbon chain backbone of the SCCPs. The advantages derived from the choice of such a method defined parameter are numerous. The analytes to be determined would be better defined, being reduced from more than six thousand to only four, and the chlorination degree would not be a critical information any longer. Moreover, one of the factors of major concern in the determination of SCCPs, the choice of an appropriate measurement standard for calibration purposes, would be overcome because a simple mixture of C_{10}–C_{13} *n*-alkanes would serve the purpose.

The concept of the method

In order to quantify the method defined parameter chosen, an appropriate *standardised method* should also be developed. The application of a standardised method is actually mentioned already by the legislator as a way to assure comparability of results. At paragraph 1.3.6 of Annex V, the WFD specifies that "The methods used for the monitoring . . . shall conform to international standards . . . or such other national or international standards which will ensure the provision of data of an equivalent scientific quality and comparability". The general use of a standardised method associated to the method defined parameter could indeed improve the comparability of analytical data for SCCPs.

We are currently investigating the possibility to use the carbon skeleton method as standardised method for the determination of SCCPs. It allows the accurate quantification of well separated *n*-alkanes as shown in Fig. 3. The amount of alkanes is equal to the amount of the corresponding SCCPs, when expressed as amount of substance (mol).

The carbon skeleton method, applied for the first time to the analysis of SCCPs by Cooke and Roberts[19] in 1980, has been more recently used by Koh et al.[21] for the determination of
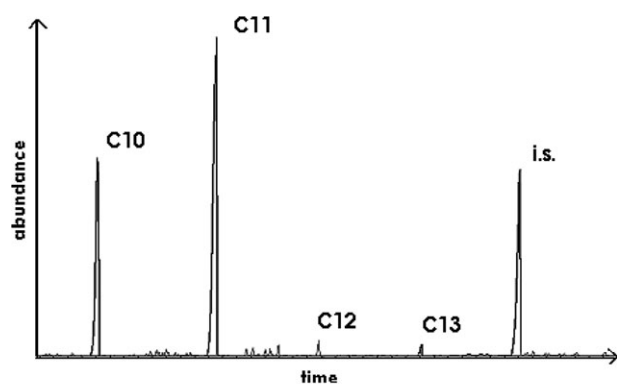
Fig. 3 GC-FID chromatogram of a commercial mixture of chlorinated paraffins with a chlorination degree of 55% obtained in our laboratory on a DB-5MS column in the presence of Pd catalyst in the liner and H_2 as carrier gas (i.s. = internal standard).

chlorinated paraffins in cutting fluids and sealing materials. So far, no applications to environmental samples have been reported, however, a first investigation in our laboratory indicates that it is feasible.

The main steps of the analytical procedure under development are: extraction with ASE, clean-up on a glass column packed with Florisil by eluting first with hexane to remove the non-chlorinated hydrocarbons, and subsequently with a mixture of *n*-hexane/DCM (1 : 1), concentration to small volume, and injection into GC-MS equipped with a Pd-modified liner. Considering that the procedure is not yet optimized, the performance parameters are already very encouraging. The method is selective, reproducible (relative standard deviation below 15%), and an LOD below 1 nmol g^{-1} was achieved. Furthermore, the bias in the quantification of solutions at known concentrations is reduced (bias found from −31% to +31%) in comparison to the huge bias obtained with the approach based on the chemical ionisation (from −143% to +980%). It seems that this method could give more reliable results also when analysing environmental samples. Furthermore, there is a very good agreement between different Pd-modified liners (relative standard deviation ranging between 1 and 18%), and the conversion efficiency of the carbon skeleton method shows to be largely independent of the chlorination degree. Therefore, only one standard with a known chlorination degree could be sufficient to check the performance of the Pd catalyst. By working on the carbon skeleton of the molecule, the knowledge of the chlorination degree is not mandatory as for the quantification by other methodologies. This is a particular advantage for analysing environmental samples with an unknown chlorination degree.

In addition, the procedure is easy to perform, relatively fast and of low cost, once a batch of Pd catalysts has been prepared. There is no necessity of highly qualified personnel, neither of expensive equipments; in fact, those already in use for the analysis of other organic compounds could be sufficient. Finally, the method could be applied and in-house validated in a short period of time. All these characteristics fulfil the requirements necessary to routinely apply the method by any environmental laboratory.

Besides these advantages, also the production of reference materials for calibration and matrix reference materials for quality control would be easier. Therefore, the method could provide all the quality assurance/quality control tools needed and the comparability of the results would be secured.

Conclusions

The scientific community did not agree so far on a method for the determination of SCCPs, although it is already mandatory to comply with the requirements of the European WFD about the monitoring of water quality. The current methodologies are hardly applicable for routine analyses and there are many problems of comparability of the results. The definition of a method defined parameter, for example the sum of alkanes related to SCCPs, and the use of a standardised method could be useful to solve some of the difficulties in the determination of SCCPs. We are investigating the possibility to use the carbon skeleton method for this purpose, in order to propose a solution to the problem and allow compliance with the directive. Currently, the applicability of the method to environmental samples is being investigated in our laboratory, followed by a full method validation. Moreover, the application of other promising techniques, *e.g.* multidimensional gas chromatography or other recent developments, should be investigated in further detail, in order to improve the knowledge on SCCP mixtures in environmental samples.

Disclaimer

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.

Abbreviations

AA: annual average; ASE: accelerated solvent extraction; CPs: chlorinated paraffins; DCM: dichloromethane; ECD: electron capture detector; ECNI: electron capture negative ionisation; EI: electronic impact; EQS: environmental quality standard; FID: flame ionization detector; GC: gas chromatography; GPC: gel permeation chromatography; HRMS: high resolution mass spectrometer; LCCPs: long-chain chlorinated paraffins; LRMS: low resolution mass spectrometer; MAB: metastable atom bombardment; MAC: maximum allowable concentration; MCCPs: medium-chain chlorinated paraffins; MS/MS: mass spectrometer/mass spectrometer; NICI: negative ion chemical ionisation; PCAs: polychlorinated alkanes; PCBs: polychlorobiphenyls; PCI: positive chemical ionisation; qMS: quadrupole mass spectrometer; SCCPs: short-chain chlorinated paraffins; SCGC: short column gas chromatography; SIM: single ion monitoring; SPE: solid phase extraction; SPME: solid phase microextraction; WFD: water framework directive.

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References

1 G. T. Tomy, A. T. Fisk, J. B. Westmore and D. C. G. Muir, *Rev. Environ. Contam. Toxicol.*, **158**, 53–128.
2 World Health Organization, Chlorinated Paraffins, Environmental Health Criteria 181, ISBN 92-4-157-181-0, World Health Organization, Geneva, Switzerland, 1996.
3 B. Jansson, R. Andersson, L. Asplund, A. Bergman, K. Litzén, K. Nylund, L. Reutergårdh, U. Sellström, U. Uvemo, C. Wahlberg and U. Wideqvist, *Anal. Bioanal. Chem. (Historical Archive)*, 1991, **340**, 439–445.
4 A. J. Peters, G. T. Tomy, G. A. Stern and K. J. Jones, *Organohalogen Compd.*, 1998, **35**, 439–442.
5 C. R. Nicholls, C. R. Allchin and R. J. Law, *Environ. Pollut.*, 2001, **114**, 415–430.
6 G. T. Tomy, G. A. Stern, W. L. Lockhart and D. C. G. Muir, *Environ. Sci. Technol.*, 1999, **33**, 2858–2863.
7 G. T. Tomy, D. C. G. Muir, G. A. Stern and J. B. Westmore, *Environ. Sci. Technol.*, 2000, **34**, 1615–1619.
8 European Commission, European Union Risk Assessment Report Alkanes, C_{10}–C_{13} Chloro-Risk assessment, European Chemicals Bureau, 1999.
9 IARC, in *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, Lyon, France, 1990, pp. 55–72.
10 AMPS, Draft final report of the expert group on analysis and monitoring of priority substances EAF(7)-06/01, 2004.
11 M. Coquery, A. Morin, A. Bécue and B. Lepot, *Trends Anal. Chem.*, 2005, **24**, 117–127.
12 Z. Zencak and M. Oehme, *Trends Anal. Chem.*, 2006, **25**, 310–317.
13 E. Eljarrat and D. Barceló, *Trends Anal. Chem.*, 2006, **25**, 421–434.
14 S. Bayen, J. P. Obbard and G. O. Thomas, *Environ. Int.*, 2006, **32**, 915–929.
15 F. J. Santos, J. Parera and M. T. Galceran, *Anal. Bioanal. Chem.*, 2006, **386**, 837–857.
16 M. Coelhan, *Anal. Chem.*, 1999, **71**, 4498–4505.
17 P. Korytár, J. Parera, P. E. G. Leonards, J. de Boer and U. A. Th. Brinkman, *J. Chromatogr., A*, 2005, **1067**, 255–264.
18 P. Korytár, J. Parera, P. E. G. Leonards, F. J. Santos, J. de Boer and U. A. Th. Brinkman, *J. Chromatogr., A*, 2005, **1086**, 61–70.
19 M. Cookes and D. J. Roberts, *Anal. Chem.*, 1980, **193**, 437–443.
20 N. Sistovaris and U. Donges, *Fresenius' J. Anal. Chem.*, 1987, **326**, 751–753.
21 I. O. Koh, W. Rotare and W. H. P. Thiemann, *Chemosphere*, 2002, **47**, 219–227.
22 P. Castells, F. J. Santos and M. T. Galceran, *Rapid Commun. Mass Spectrom.*, 2004, **18**, 529–536.
23 A. Randeggar-Vollrath, *Fresenius' J. Anal. Chem.*, 1998, **360**, 62–68.
24 S. A. Junk and H. U. Meisch, *Fresenius' J. Anal. Chem.*, 1993, **347**, 361–364.
25 G. T. Tomy, G. A. Stern, D. C. G. Muir, A. T. Fisk, C. D. Cymbalisty and J. B. Westmore, *Anal. Chem.*, 1997, **69**, 2762–2771.
26 M. Reth and M. Oehme, *Anal. Bioanal. Chem.*, 2004, **378**, 1741–1747.
27 Z. Zencak and M. Oehme, *Rapid Commun. Mass Spectrom.*, 2004, **18**, 2235–2240.
28 Z. Zencak, M. Reth and M. Oehme, *Anal. Chem.*, 2004, **76**, 1957–1962.
29 S. Moore, L. Vromet and B. Rondeau, *Chemosphere*, 2004, **54**, 453–459.
30 K. Heydorn and T. Anglov, *Accredit. Qual. Assur.*, 2002, **7**, 153–158.
31 M. Gardner and I. Taylor, *Accredit. Qual. Assur.*, 1999, **1–2**, 33–36.
32 G. T. Tomy, J. B. Westmore, G. A. Stern, D. C. G. Muir and A. T. Fisk, *Anal. Chem.*, 1999, **71**, 446–451.
33 M. Coelhan, M. Saraci and H. Parlar, *Chemopshere*, 2000, **40**, 685–689.
34 G. T. Tomy, B. Billeck and G. A. Stern, *Chemosphere*, 2000, **40**, 679–683.
35 M. Reth, M. Z. Zencak and M. Oehme, *Chemosphere*, 2005, **58**, 847–854.
36 M. Reth, Z. Zencak and M. Oehme, *J. Chromatogr., A*, 2005, **1081**, 225–231.
37 S. Shojania, *Chemosphere*, 1999, **38**, 2125–2141.