



Parameters optimization using experimental design for headspace solid phase micro-extraction analysis of short-chain chlorinated paraffins in waters under the European water framework directive



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ABSTRACT

The water framework directives (WFD 2000/60/EC and 2013/39/EU) force European countries to monitor the quality of their aquatic environment. Among the priority hazardous substances targeted by the WFD, short chain chlorinated paraffins C₁₀–C₁₃ (SCCPs), still represent an analytical challenge, because few laboratories are nowadays able to analyze them. Moreover, an annual average quality standards as low as 0.4 μg L⁻¹ was set for SCCPs in surface water. Therefore, to test for compliance, the implementation of sensitive and reliable analysis method of SCCPs in water are required. The aim of this work was to address this issue by evaluating automated solid phase micro-extraction (SPME) combined on line with gas chromatography–electron capture negative ionization mass spectrometry (GC/ECNI–MS).

Fiber polymer, extraction mode, ionic strength, extraction temperature and time were the most significant thermodynamic and kinetic parameters studied. To determine the suitable factors working ranges, the study of the extraction conditions was first carried out by using a classical one factor-at-a-time approach. Then a mixed level factorial 3 × 2³ design was performed, in order to give rise to the most influent parameters and to estimate potential interactions effects between them. The most influent factors, i.e. extraction temperature and duration, were optimized by using a second experimental design, in order to maximize the chromatographic response.

At the close of the study, a method involving headspace SPME (HS–SPME) coupled to GC/ECNI–MS is proposed. The optimum extraction conditions were sample temperature 90 °C, extraction time 80 min, with the PDMS 100 μm fiber and desorption at 250 °C during 2 min. Linear response from 0.2 ng mL⁻¹ to 10 ng mL⁻¹ with *r*² = 0.99 and limits of detection and quantification, respectively of 4 pg mL⁻¹ and 120 pg mL⁻¹ in MilliQ water, were achieved. The method proved to be applicable in different types of waters and show key advantages, such as simplicity, automation and sensitivity, required for the monitoring programs linked to the WFD.

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1. Introduction

Chlorinated paraffins (CPs), of the general formula C_{*n*}H_{2*n*+2-*z*}Cl_{*z*}, are industrially synthesized compounds obtained by direct chlorination of the *n*-alkane feedstock. Due to the low regioselectivity of this reaction, complex mixtures of optical isomers and congeners of CPs with carbon lengths from C₁₀ to C₃₀ and chlorination degree between 30 and 70% by mass have been produced and commercialized since the 1930s. CPs are classified into three categories: short

chain (C₁₀–C₁₃ SCCPs), medium chain (C₁₄–C₁₇ MCCPs) and long chain (C_{>17} LCCPs) [1,2].

Because of their chemical stability, viscosity and their flame retardant properties, CPs found applications in many fields of industry: as lubricants and cutting fluids in the metalworking industry (71% of total use), as flame retardants in the rubber industry (10%), as paints (9%) and sealing materials (5%), and others (5% leather, textiles) [3]. They have also replaced to some extent polychlorinated biphenyls after the mid-1980s, when PCBs usage was banned. In the last decade, annual world-wide production of CPs has been estimated to 300ktons. In Europe, annual consumption varied from 100 to 200 ktons [3]. Furthermore, due to release from improper disposal of metal-working fluids and leaching from

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polymers or paints, the presence of SCCPs has been revealed in a variety of environmental matrices worldwide [3–9].

A recent risk assessment evaluation classified this group of compounds as dangerous to the environment because of their toxicity towards aquatic organisms, high potential for bioaccumulation, and persistence in the environment [10], and the United Nations Environment Program (UNEP) [11] 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 paraffin as metal-working fluids and leather finishing products (Directive 2002/45/EC [12]). SCCPs are currently listed in the black list of substances of environmental protection agencies of the USA and Canada. And the European Union has included SCCPs as hazardous priority substance into the initial list of the 33 priority substances from the Water Framework Directive (WFD 2000/60/EC [13]), which requires their regular monitoring at a river basin scale since January 2007. For these targeted priority hazardous substances, environmental quality standards (EQSs) have been recently established for inland surface waters and other surface waters [14]. Precisely, annual average and maximum acceptable concentration quality standards (AA-QS and MAC-QS, respectively) are to be used for compliance. For SCCPs, AA-QS and MAC-QS were settled to 0.4 and 1.4 $\mu\text{g L}^{-1}$, respectively [15].

Though, analytical methodology for the reliable determination of SCCPs is scarce. This is mainly due to the number of isomers (up to 7000) of which this class of compounds consists [2], and the lack of pure solutions of individual SCCPs for calibration as well as the lack of matrix reference materials. Several approaches have been attempted [1,3,16–19] and the studies mainly focused on the determination of SCCPs in sediment, sludge or biota. Due to their high hydrophobicity ($\log K_{ow}$ between 5.06 and 8.12) and their low water solubility (0.49–1260 $\mu\text{g L}^{-1}$) [1,3], SCCPs are indeed hardly detectable in water samples, even if obligatory in the track of the WFD.

The classical liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are still the most commonly used extraction techniques for preconcentration of CPs from aqueous samples [20,21]. But, LLE requires high purity solvent and tedious clean-up task and SPE often causes high baseline blanks. Currently there is a growing analytical trend towards the use of environmentally friendly extraction techniques. Following this trend, solvent-free extraction techniques such as solid phase micro-extraction (SPME) [22] and stir bar sorptive extraction (SBSE) [23] were successfully applied to SCCPs determination in waters. To bring down detection limits, both preconcentration techniques were coupled to GC/ECD analysis, which proved to be more sensitive for SCCPs detection but less specific as compared to GC/ECNI-MS.

Most of the practical work, involving SPME or SBSE optimization, use strategies based on systematic studies of one factor-at-a-time. All of the variables are held constant during test runs except the one being studied. This type of experiment reveals the effect of the chosen variable under set conditions assuming that the variables are independent and that the effect will be the same at another level of the remaining variables; it does not show what would happen if the other variables are also changed. Thus, it can lead many times to erroneous or incomplete conclusions for particular factors during the analytical process [24–26] due to the fact that interactions between factors are not being considered. Moreover, as this procedure generates many run tests, it is extremely time-consuming. To address both latter issues, an approach based on experimental design [27], is the most suitable approach. In this case, the optimal design should consider the multilevel variables and will be an asymmetric fractional factorial design considering four factors with two levels and one factor with three levels (fiber polymer).

In this contribution, the aim of this work is to evaluate automated solid phase micro-extraction (SPME) combined on line with gas chromatography-electron capture negative ionization mass spectrometry (GC/ECNI-MS). In comparison to the only one paper dealing with the water analysis of SCCPs by SPME [22], the novelty of the present work is to optimize the SPME parameters by using experimental design instead of one factor at a time methodology and to investigate the extraction in headspace mode. Fiber polymer, extraction mode, ionic strength, extraction temperature and time were the most significant thermodynamic and kinetic parameters studied [28]. Parameters were first rapidly screened following a classical one factor-at-a-time approach in order to define the proper factors variation domains to help in building the experimental design. And we have focused on conditions not investigated by the other research group [22]. Then a mixed level fractional factorial design was performed, in order to quantify the influence of parameters taking into account the possible interactions among them. Given these results, the most influent parameters were then optimized from a response surface design of experiments. In opposite to current issues supporting that SPME in direct mode is preferable for semi-volatile molecules [29], we particularly probe the extraction in headspace mode. The performance of the developed method is evaluated in terms of linearity, precision, and limits of detection. Finally, the method is applied to the analysis of different types of surface waters.

2. Materials and methods

2.1. Reagents and material

Acetone (EMSURE[®] for analysis) and sodium chloride (Normapur, 99.9%, analytical reagent) were obtained from Merck (Darmstadt, Germany) and VWR (France), respectively. SCCPs technical mixtures, Cloparin D55 (55% Cl, w/w) and Cloparin D70 (68.5% Cl, w/w), were kindly provided by Caffaro chemical S.R.L. (Italy). Stock solutions were prepared at 2 g L^{-1} in acetone and diluted to 50 $\mu\text{g L}^{-1}$ in acetone (working solutions). Stock standard solution of chloroparaffins (C_{10} – C_{13} , 63% Cl (w/w), 100 $\text{ng } \mu\text{L}^{-1}$) in acetone was provided by CIL Cluzeau (France) and diluted to 500 $\mu\text{g L}^{-1}$ in acetone (working solution).

Standard working aqueous samples were prepared weekly by appropriate dilutions of the working solutions in MilliQ water (Aquaderm). Stock and working solutions were stored at 4 °C. Experiments concerning the development of the method, i.e. preliminary investigation of the influence of SPME parameters by one-at-a-time approach and the optimization of SPME variables by experimental design, were performed with MilliQ water spiked at 10 $\mu\text{g L}^{-1}$ with the SCCPs technical mixture named Cloparin D55. Then, the tests of performance for method validation were carried out by using MilliQ water spiked at appropriate levels, with the standard mixture of chloroparaffins (C_{10} – C_{13} , 63% Cl), which is generally used for SCCPs quantification.

The SPME autosampler holder and fibers were supplied by Supelco (Supelco-Sigma-Aldrich, France). Seven commercially available coatings were tested in this work: 100 μm and 7 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 85 μm polyacrylate (PA), 75 μm carboxen-polydimethylsiloxane (CAR-PDMS), 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS), 70 μm carbowax-divinylbenzene (CW-DVB). Prior to use, the fibers were conditioned as recommended by the manufacturer.

2.2. Experimental set up

Automated SPME was carried out with a Combi-Pal autosampler (CTC Analytics). The samples were placed in 23 mL borosilicate

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