ELSEVIER

Journal of Chromatography A, 963 (2002) 159–167

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Development of a solid-phase microextraction method for the determination of short-ethoxy-chain nonylphenols and their brominated analogs in raw and treated water

Alfredo Díaz[a], Francesc Ventura[a,*], M. Teresa Galceran[b]

[a]*AGBAR, Aigües de Barcelona, Pg. Sant Joan, 39, 08009 Barcelona, Spain*

[b]*University of Barcelona, Department Analytical Chemistry, Martí i Franquès, 1–11, 08028 Barcelona, Spain*

Abstract

A direct solid-phase microextraction (SPME) procedure has been developed and applied for the simultaneous determination of nonylphenol, nonylphenol mono- and diethoxylates and their brominated derivatives in raw and treated water at low $\mu g\ l^{-1}$ concentrations. Several parameters affecting the SPME procedure, such as extraction mode (headspace or direct-SPME), selection of the SPME coating, extraction time, addition of organic modifiers such as methanol and temperature were optimized. The divinylbenzene–carboxen–polydimethylsiloxane fiber was the most appropriate one for the determination of nonylphenol ethoxylates (NPEOs) and bromononylphenol ethoxylates (BrNPEOs) by SPME–GC–MS. The optimized method was linear over the range studied (0.11–2.5 $\mu g\ l^{-1}$) and showed good precision, with RSD values between 4 and 15% and detection limits ranging from 30 to 150 $ng\ l^{-1}$ depending on the compound. The SPME procedure was compared with a solid-phase extraction–GC–MS method (C_{18} cartridge) for the analysis of NPEO and BrNPEOs in water samples. There was good agreement between the results from both methods but the SPME procedure showed some advantages such as lower detection limits, a shorter analysis time and the avoidance of organic solvents. The optimized SPME method was applied to determine nonylphenol and brominated metabolites in raw and treated water of Barcelona (NE Spain). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase microextraction; Water analysis; Nonylphenols; Ethoxylates; Organobromine compounds; Halogenated compounds

1. Introduction

Nonylphenol ethoxylates (NP*n*EO *n*=number of ethoxy units) are widely used nonionic surfactants. The biodegradation of the parent compound under aerobic conditions leads mainly to the formation of nonylphenol mono- and diethoxylate (NP1EO and NP2EO) [1,2], whereas the fully deethoxylated nonylphenol (NP) is also produced under anaerobic conditions [3]. Further oxidation of the ethoxylate chain produces carboxylated metabolites [4]. It has also been shown that these metabolites can react during chlorination in water treatment plants producing mainly brominated derivatives if bromide is present. Thus, brominated nonylphenols have been identified in wastewater [5], tap water [6], sediments [7] and sludge [8]. Fig. 1 displays the chemical structures and acronyms used.

Concerns over the toxicity of NPEOs and their biodegradation products have restricted their use in industrial applications in Europe. Recently, several

*Corresponding author. Fax: +34-93-342-3666.

E-mail address: fventura@agbar.es (F. Ventura).

0021-9673/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0021-9673(02)00542-3

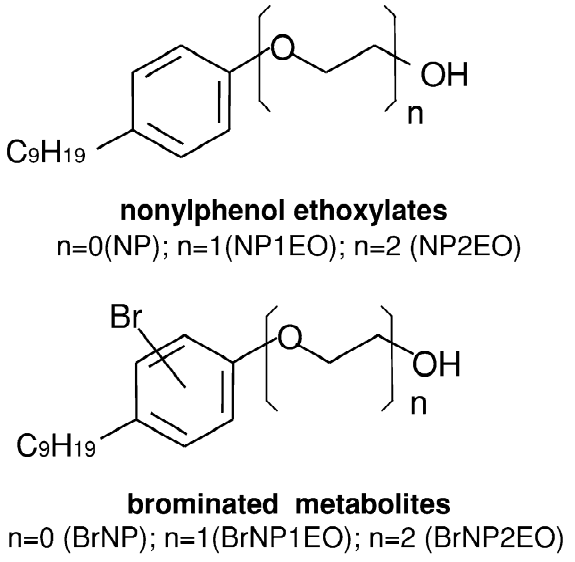

Fig. 1. Chemical structures of short ethoxy chain nonylphenols and brominated analogs.

reports have demonstrated that these metabolites affect endocrine systems in fishes, birds and mammal cells in vitro through weak estrogenic-like properties [9,10]. Brominated metabolites have shown higher acute toxicity to *Daphnia magna* than their non-brominated precursors [11]. Reviews on aquatic toxicity and bioaccumulation [12]. analytical methods [13], persistence [14], and environmental occurrence [15] of nonylphenol and nonylphenol ethoxylates have been published. The analytical approaches most employed for their determination included solvent sublation, steam distillation, liquid–liquid extraction and solid-phase extraction [13]. However, solid-phase microextraction (SPME), an increasingly popular method for the determination of organics in water, has seldom been used to analyze surfactants and related compounds. Thus, the determination of NP in water by SPME by using a polydimethylsiloxane fiber (PDMS) [16], the analysis of NP*n*EOs at the low $\mu g\ l^{-1}$ range by using a Carbowax-template resin and HPLC–UV [17] and the determination of alcohol ethoxylates by SPME–HPLC–fluorescense detection [18] are the few papers dealing with nonionic surfactants determination by SPME.

The objective of this work is to develop a method for the simultaneous determination of the estrogenic short ethoxy chain nonylphenols and their halogenated metabolites by SPME–GC–MS in raw and treated water at low $\mu g\ l^{-1}$ levels. The SPME method developed was compared to the solid-phase extraction (SPE) procedure, which is the method of choice for the determination of these compounds, in order to demonstrate the feasibility of the methodology proposed.

2. Experimental

2.1. Chemicals and materials

4-Nonylphenol (NP) technical grade was obtained from Sigma–Aldrich (Milwaukee, USA). Nonylphenolmonoethoxylate (NP1EO), nonylphenoldiethoxylate (NP2EO), bromononylphenol (BrNP), bromononylphenolmonoethoxylate (BrNP1EO) and bromononylphenoldiethoxylate (BrNP2EO) were synthesized in our laboratory according to the methods described elsewhere [5,19]. Sodium chloride and the dechlorinating agent sodium thiosulfate were obtained from Carlo Erba (Rodano, Italy) at a high purity (≥99%). 4*n*-Nonylphenol (*n*-NP) and 4*n*-nonylphenol monoethoxylate (*n*-NP1EO, 99%) used as internal standards were purchased from Lancaster Synthesis (Newgate, UK) and Dr. Ehrenstorfer (Ausburg, Germany), respectively. Methanol, ethyl acetate, isooctane and methylene chloride of residue analysis grade were supplied by J.T. Baker (Deventer, The Netherlands). Water from a Milli-Q® water purification system (Millipore, Beldford, MA, USA) was used for all analyses.

SPME experiments were performed with a manual fiber holder supplied by Supelco (Bellefonte, PA, USA). Three commercially available fibers, polyacrylate (PA) 85 μm; Carbowax–divinylbenzene (CW–DVB) 65 μm, and StableFlex divinylbenzene–carboxen– polydimethylsiloxane (DVB–CAR–PDMS) 50 and 30 μm were purchased from Supelco. Before use, each fiber was conditioned in a heated GC split/splitless injection port under helium flow according to the manufacturer's instructions. Screw-capped vials (40 ml) sealed with a PTFE-lined silicon septum and used for extraction in both HS-SPME and direct-SPME procedures, were obtained

from Wheaton (Millville, NJ, USA). The vials were cleaned by sonication with AP-13 Extran alkaline soap (Merck) for 1 h, rinsed consecutively with (i) deionized water, (ii) chromic–sulfuric acid, (iii) again with deionized water and (iv) acetone RS grade, and baked at 50 °C overnight. Volumetric glassware was washed as described above, but was air-dried. Sodium chloride was cleaned for 30 min by sonication with methylene chloride residue analysis grade, and heated at 50 °C under low pressure to remove interfering organic substances.

Stock standard solutions of each NP metabolite (1000 μg ml^{-1}) were prepared by mass in methylene chloride. Standard mixtures were prepared weekly or daily in methanol, depending on their concentration. All solutions were stored in the dark at 4 °C until use. For the evaluation of the direct-SPME procedure, water samples containing NP and BrNP (25 μg l^{-1} each) and NP1EO, BrNP1EO NP2EO and BrNP2EO (62.5 μg l^{-1} each) were prepared by adding 10 μl of a standard mixture of 100 and 250 μg ml^{-1}, respectively, into 40 ml Milli-Q water, and then sealed in a 40-ml screw capped vial. The same procedure was applied for the HS-SPME by using 33 μg l^{-1} of each NP and BrNP and 83 μg l^{-1} for the rest of compounds in 30 ml water (40-ml vial).

2.2. Sampling collection

Llobregat river water (Catalonia, NE Spain), sand filtered and final treated water from the St. Joan Despí water treatment plant (SJD WTP) and raw and treated water from the Abrera WTP (situated in the upper course of Llobregat river) were analyzed by using the direct-SPME and SPE methods. The samples were collected in 1-l amber glass bottles with PTFE-faced septa. All analyses were performed within 2 days of sampling. Sodium thiosulfate was added as a dechlorinating agent to preserve the treated water samples from free chlorine.

2.3. Synthesis of nonionic surfactants metabolites

NP1EO and NP2EO were synthesized following the method described elsewhere [19], whereas the bromination of NP and the synthesized compounds was performed following the procedure described by Reinhard et al. [5]. Briefly, 160 mg of bromine in 5 ml of glacial acetic acid was added dropwise over a solution of 400 mg of each compound (NP, NP1EO and NP2EO, respectively) in 20 ml of glacial acetic acid After an 8 h reaction, the excess of bromine was destroyed by adding 0.1 *M* sodium thiosulfate. Then, 200 ml of water were added and the solution was extracted with diethyl ether (2×100 ml). The combined extracts were dried, filtered and concentrated. The resulting red oils were purified by column chromatography (silica gel, 70–230 mesh; hexane–ethyl acetate, 20:1) affording the products expected (60% yield). The purity (>95%) of the compounds was established by means of ^{1}H-NMR and confirmed by GC–MS.

2.4. Instrumentation

A HRGC-3000C Konik Instruments (Barcelona, Spain) capillary gas chromatograph equipped with a flame ionisation detection (FID) system was used for the optimization of the SPME and SPE procedures, whereas quality parameters and quantification of samples by direct-SPME and SPE were performed with a GC Fisons 8060 capillary gas chromatograph coupled to a Fisons MD 800 GC–MS quadrupole mass spectrometer (Milan, Italy). A DB-5 MS fused-silica capillary column, 30 m×0.25 mm I.D., 0.25 μm (J&W Scientific, Folsom, CA, USA), a 0.5-m polar poly(ethyleneglycol) precolumn and helium as a carrier gas (70 kPa; 100 kPa N_2 for FID make-up) were used. The column was held at 70 °C for 3 min, then up to 160 °C at a rate of 20 °C min^{-1}, and finally up to 300 °C at 10 °C min^{-1} and held for 7 min. The desorption time and injection port temperature were set at the optimum values.

The quadrupole mass spectrometer was operated in electron ionization (EI) positive mode. For EI experiments, filament emission current and electron multiplier voltage were set at 750 μA and 450 V, respectively. The transfer line and the source temperature were maintained at 310 and 200 °C, respectively. The instrument was operated in SIR (Selected Ion Recording) mode at 0.08 s/scan and a delay time of 10 ms. For quantitation, the sum of areas of all isomers for the selected ions of each compound were monitored [6]. The following fragment ions were chosen: *m/z* 121/135 for NP, *m/z* 179/193 for NP1EO, *m/z* 223/237 for NP2EO, *m/z* 213/227 for

BrNP, *m/z* 257/271 for BrNP1EO and 301/315 for BrNP2EO. For halogenated compounds, the base peak of each group of isomers rather than the characteristic isotopic ratio of brominated compounds of one single isomer were selected in order to enhance sensitivity. For internal standards, the selected ions were *m/z* 107/220 for *n*-NP and *m/z* 107/264 for *n*-NP1EO. Different acquisition windows during each chromatographic run were applied. MASSLAB version 1.4 software was used for data acquisition.

2.5. SPME procedures

Different stationary phases were evaluated to obtain high sensitivity and selectivity for both HS-SPME and direct-SPME methods. Three polar fibers were tested: PA, 85 μm; CW–DVB, 65 μm partially crosslinked, and StableFlex DVB–CAR–PDMS, 50 and 30 μm. For the direct SPME procedure, a screwcap glass vial (40 ml) containing a 10×5 mm PTFE-coated stir bar was filled with the spiked water sample and the vial was clamped inside a water-thermostated bath and placed on a hot plate/stirrer. The fiber was introduced into the aqueous solution for 60 min at room temperature. For the HS-SPME method, 30 ml of a spiked water sample were placed in a 40-ml screwcap glass vial (10 ml headspace volume) containing a 10×5 mm PTFE-coated stir bar and 4.5 *M* of sodium chloride. The fiber was exposed to the headspace above the aqueous solution for 60 min at 65 °C. In both cases, magnetic stirring at 1200 rpm was applied during extraction and the fiber was desorbed in the injection port of the gas chromatograph for 5 min at 250 °C (splitless injection mode). Several parameters affecting direct-SPME were then studied: (i) volume of organic modifier (methanol volume between 0 and 1000 μl, (ii) extraction time (up to 90 min), (iii) stirring rate (700–1200 rpm) and (iv) extraction temperature (from room temperature to 60 °C). Other parameters affecting the direct-SPME procedure, such as desorption temperature (230–270 °C) and desorption time (up to 5 min) were also optimized. Possible carryover was prevented by keeping the fiber in the injector for an additional time with the injector in the split mode (purge on). Moreover, blanks were run periodically during the analysis to confirm the absence of contaminants. For optimization, all determinations were performed in duplicate and the average values are reported.

2.6. Solid-phase extraction procedure

Solid-phase extraction for the determination of NPEOs and BrNPEOs in river, sand filtered and treated water was performed following the procedure described by Lee Ferguson et al. [7] and Blackburn et al. [20] with minor modifications. Briefly, 500 ml spiked with NPEOs and BrNPEOs (2.5 μg l^{-1} each) and *n*-NP, *n*-NP1EO as surrogates (1 μg l^{-1} each) were passed through a reversed-phase C_{18} (C_{18} 500 mg Accubond, J&W Scientific) at a flow-rate of 10 ml min^{-1}. in a SPE workstation (Zymark, Hopkinton, MA, USA). The NPEOs and BrNPEOs residues were eluted from the cartridge with 3 ml of ethyl acetate and next with 5 ml of methylene chloride. Once the extract was concentrated to ca 1 ml by a gentle stream of nitrogen, isooctane (500 μl) was added and the extract was evaporated to a final volume of 500 μl. Finally, 1 μl of the isooctane extract was injected into the GC–MS.

3. Results and discussion

The objective of this work was to develop a SPME method for the simultaneous quantification of short ethoxy chain NPEOs and BrNPEOs from water. In order to optimize the extraction of these compounds by SPME, two approaches have been tested: HS-SPME and direct-SPME using three different fibers for each procedure.

The relative responses obtained for all studied compounds using the three different fibers are shown in Table 1. For HS-SPME, higher responses were obtained for NP and BrNP with all the fibers tested. In contrast, direct-SPME gave better results for the diethoxylated metabolites due to their low volatility. As a consequence, HS-SPME is restricted to the analysis of NP and BrNP but for the determination of all short ethoxy chain nonylphenols and brominated derivatives, the direct-SPME is proposed.

Of all the fibers evaluated, the dual coated DVB–CAR–PDMS proved to be the most effective for the extraction of the compounds from water samples

Table 1
Relative response (%) of different compounds using direct-SPME and HS-SPME procedures and three fibers (PA, CW–DVB and DVB–CAR–PDMS)

Compound	Direct-SPME 1 h at room temperature			HS-SPME 1 h at 65 °C		
	DVB–CAR–PDMS	CW–DVB	PA	DVB–CAR–PDMS	CW–DVB	PA
NP	44	25	26	100[a]	95	98
BrNP	33	18	36	76	74	79
NP1EO	90	70	77	37	63	17
BrNP1EO	65	30	35	3	10	6
NP2EO	18	8	18	3	6	4
BrNP2EO	48	15	25	0	8	5

[a] Reference value to evaluate relative response data.

when direct-SPME was used; this fiber was selected for the following experiments. Fig. 2 shows as an example the chromatographic profile of ultrapure water spiked with the studied compounds obtained by direct-SPME and the DVB–CAR–PDMS fiber selected.

3.1. Optimization of the direct-SPME procedure

3.1.1. Effect of addition of an organic modifier

The effect of the addition of an organic reagent to the sample in order to increase the response of the analytes was also studied [21]. Different amounts of methanol up to 1 ml were added to the spiked water sample and the results obtained are given in Table 2. In general, an increase in the responses was obtained with the addition of methanol, but the highest relative responses occurred when 100 μl of methanol were added and, therefore, this value was chosen as the optimum amount to be added to the water samples. When labeled compounds such as [^{13}C]*n*-NP, [^{13}C]*n*-NP1EO and [^{13}C]*n*-NP2EO were tested as internal standards, an important decrease in the

Table 2
Effect of the addition of methanol on the relative response (%); direct-SPME procedure using a DVB–CAR–PDMS fiber (1 h, room temperature)

Amount of methanol (μl)	Compound		
	NP	NP1EO	NP2EO
0	38	44	32
100	78	100[a]	70
200	60	63	42
400	58	60	49
1000	38	41	29

[a] Reference value to evaluate relative response data.

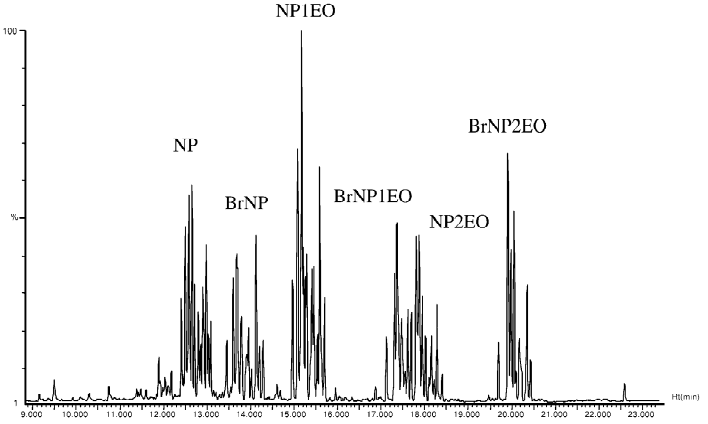

Fig. 2. Total ion current chromatogram obtained by direct-SPME GC–MS. CAR–PDMS–DVB fiber under the optimized conditions.

response close to 30% independently of the fibers was observed for all the compounds. These standards are commercially available in nonane solutions (100 ng μl^{-1}) and the presence of minor amounts of nonane (i.e. 5 μl) in the water sample can explain the decrease in the response. So methanolic solutions of *n*-NP and *n*-NP1EO were employed as internal standards instead of commercial nonane solutions of labeled compounds.

3.1.2. Extraction time, temperature and stirring rate

The extraction time profiles of NPEOs and BrNPEOs were then studied from 15 to 90 min (Fig. 3). A 40-ml volume of Milli-Q water spiked with the studied compounds was analyzed under the conditions described in the Experimental section. The adsorption time profiles for the DVB–CAR–PDMS fiber were established by plotting the GC–FID area response of each compound versus the extraction time in order to obtain the experimental equilibrium curve. The equilibrium time is reached when a further increase in the extraction time does not result in a significant increase in the detector response and it was established at 1 h working at room temperature.

The effect of the stirring rate on the responses was tested between 700 and 1200 rpm at room temperature. In terms of precision, stirring rates of 700 rpm gave significantly better RSD values than the higher ones but a decrease in the recovery of some compounds (NP1EO) was observed. To enhance extraction yield, the effect of temperature was studied. Four different temperatures from room temperature to 60 °C were tested. The profiles obtained are given in Fig. 4 and showed that the extraction efficiency for all compounds increased by increasing the temperature up to 50 °C. This effect can be due to the enhancement of mass transfer which was low at 700 rpm and room temperature. At temperatures above 50 °C the uptake decreased because the distribution constant on the fiber diminished. Therefore, 50 °C was chosen as the optimum temperature for all subsequent analyses.

3.1.3. Optimization of desorption conditions

Three desorption temperatures (230, 250 and 265 °C) within the recommended DVB–CAR–PDMS fiber operating range were evaluated for a desorption time of 5 min. Results showed that optimum temperature was 250 °C. All compounds were quantitatively desorbed from the CW–DVB fiber in 5 min at 250 °C.

In short, for optimum sampling of NPEOs and BrNPEOs from water, direct-SPME was the method of choice. Methanol as an organic modifier (100 μl) was added to 40 ml of water. The sample was maintained at 50 °C and was stirred at 700 rpm and the DVB–CAR–PDMS fiber was immersed in the water sample for 1 h. The optimum desorption conditions in the GC injection port were 250 °C and 5 min.

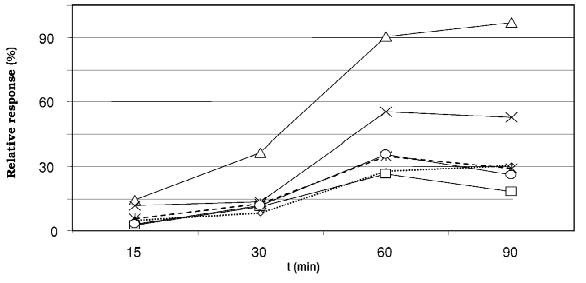

Fig. 3. Equilibration time profile for direct-SPME. Milli-Q water containing 25 $\mu g\ l^{-1}$ of NP, BrNP; 62.5 $\mu g\ l^{-1}$ of NP1EO, NP2EO, BrNP1EO and BrNP2EO; extraction at room temperature; sodium chloride, 3.6 *M*; extraction time, 60 min; stirring rate, 1200 rpm; desorption temperature, 250 °C, and desorption time, 5 min. Organic modifier: methanol (100 μl). ◊, NP; □, BrNP; △, NP1EO; ×, BrNP1EO; ★, NP2EO; ○, BrNP2EO.

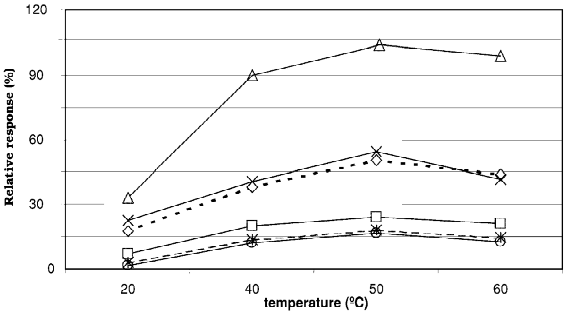

Fig. 4. Effect of temperature for the extraction of NPEOs and BrNPEOs. Stirring rate, 700 rpm. Conditions as in Fig. 3. ◊, NP; □, BrNP; △, NP1EO; ×, BrNP1EO ★, NP2EO; ○, BrNP2EO.

3.2. Linearity, precision, sensitivity and matrix effect

The quality parameters of the direct-SPME–GC–MS method were evaluated by using the optimized conditions and are given in Table 3, where the values obtained for SPE–GC–MS are also included. The RSD values for run-to-run precision were less than 9%, except for BrNP2EO (15%), and were similar to those obtained by the SPE method. The linearity of the optimized direct-SPME–GC–MS method was examined over the range 0.11–2.5 μg l^{-1}, depending on the compound expressed as the initial concentration of NPEOs and BrNPEOs in water. This range agreed with environmental levels currently found in literature for these compounds. The curves were obtained by plotting the relative area of each NPEOs and BrNPEOs to its corresponding internal standard (*n*-NP for NP and BrNP and *n*-NP1EO for the rest of compounds) (A/A_{IS}) versus the concentration of each NPEOs and BrNPEOs (Table 3). Most of them showed good linearity and correlation ($r^2 \geq 0.99$). Limits of detection (LODs), defined as the level that corresponds to an area of three times the standard deviation (3σ) of the calibration curve in the intercept value, were from 0.03 μg l^{-1} for NP to 0.15 μg l^{-1} for NP2EO, which are 2–3-fold lower than those obtained with the SPE method (Table 3).

Matrix effects were evaluated by using spiked chlorine-free treated water. The mean and RSD values of three replicates of this water sample spiked at the 0.40–0.75 μg l^{-1} range were calculated. The results given in Table 4 showed that no significant effect was observed for any of the compounds.

3.3. Analysis of water samples

Samples from river water entering the two water treatment plants [Abrera and St. Joan Despí (SJD)], situated along the Llobregat river, sand filtered water (second step in SJD-WTP) and treated water samples from the two WTPs were analyzed by using the optimized direct-SPME method and SPE. Both methods gave comparable results (Table 4) irrespective of the nature of the aqueous matrix for all the samples analyzed.

River raw water and sand filtered water samples contained all the nonbrominated metabolites at sub-μg l^{-1} levels, but only NP was found in the tap water of one WTP (Abrera). On the other hand, all brominated metabolites were formed in the SJD and Abrera WTPs during the potabilization process. As an example, sand filtered water from SJD showed sub μg l^{-1} levels of all compounds but treated water leaving the plant did not contain any compound at detectable levels, thus showing the effectiveness of the treatment. Conversely, all brominated compounds were identified in the treated water leaving the Abrera WTP. Tap water samples of different origins collected in Barcelona city were also analyzed and did not give measurable values of either halogenated

Table 3
Linear range, detection limits and precision for direct-SPME–GC–MS (in brackets for SPE–GC–MS method)

Compound	Linear range studied (μg l^{-1})	Corr. coef. (r^2)	LOD[a] (μg l^{-1})	Precision[b]	
				Run-to-run[c]	Day-to-day[d]
NP	0.11–2.0	0.9986	0.03 (0.08)	4 (5)	5 (10)
BrNP	0.18–2.0	0.9965	0.05 (0.07)	5 (10)	7 (13)
NP1EO	0.32–2.5	0.9878	0.09 (0.23)	9 (5)	11 (7)
BrNP1EO	0.15–2.5	0.9984	0.05 (0.30)	7 (9)	15 (12)
NP2EO	0.51–2.5	0.9831	0.15 (0.33)	6 (9)	12 (12)
BrNP2EO	0.30–2.5	0.9927	0.09 (0.29)	15 (9)	22 (14)

[a] The limit of detection (LOD) is defined as the level of a compound in μg l^{-1} that corresponds to an area of 3σ in the intercept value from the calibration curve.
[b] Precision expressed as RSD (%).
[c] $n=3$.
[d] $n=3$ replicates $\times 3$ days.

Table 4
Quantitation results for BrNPs in Barcelona tap water and river sources by SPME and SPE methods

Compound	Matrix effect (treated water)		River water				Sand filtered water[d]		Tap water			
			SPME ($\mu g\ l^{-1}$)[a]		SPE ($\mu g\ l^{-1}$)[a]		SPME ($\mu g\ l^{-1}$)[a]	SPE ($\mu g\ l^{-1}$)[a]	SPME ($\mu g\ l^{-1}$)[a]		SPE ($\mu g\ l^{-1}$)[a]	
	Mean (true value)	RSD (%) $n=3$	SJD	Abrera	SJD	Abrera			Abrera Treated[b]	SJD Treated[c]	Abrera Treated[b]	SJD Treated[c]
NP	0.62 (0.63)	7	1.3	1.6	1.2	1.6	0.26	0.33	0.20	<0.11	0.26	<0.24
BrNP	0.58 (0.63)	7	N.d.[e]	N.d.	N.d.	N.d.	0.41	0.36	0.32	<0.18	0.24	<0.24
NP1EO	0.57 (0.63)	13	1.4	0.56	1.7	0.83	2.3	2.0	N.d.	<0.32	N.d.	N.d.
BrNP1EO	0.68 (0.63)	5	N.d.	N.d.	N.d.	N.d.	0.78	<0.9	1.2	<0.15	1.0	<0.9
NP2EO	0.75 (0.63)	12	2.2	0.51	3.8	<1	2.9	2.4	N.d.	N.d.	N.d.	N.d.
BrNP2EO	0.52 (0.63)	15	N.d.	N.d.	N.d.	N.d.	0.41	<0.9	0.64	<0.3	<0.9	<0.9

[a] I.S., *n*-NP, *n*-NP1EO.
[b] Abrera treated, treated water leaving Abrera WTP.
[c] SJD treated, treated water leaving SJD WTP.
[d] Second step of SJD treatment plant.
[e] N.d., not detected.

or nonhalogenated nonylphenol metabolites (data not shown).

Direct-SPME–GC–MS showed some advantages over the SPE–GC–MS method, such as the avoidance of organic solvents and labor-intensive sample manipulation steps. In addition, lower detection limits were obtained with the SPME method, which allowed the identification in samples where the SPE method gave negative results.

4. Conclusions

The feasibility of direct-SPME–GC–MS for the analysis of short ethoxy chain NPEOs and BrNPEOs in water has been demonstrated. The DVB–CAR–PDMS fiber was found to be the most effective coating for the analysis of these compounds. Maximum responses were obtained by using 40-ml water samples with addition of 100 μl methanol as an organic modifier, an equilibration time of 60 min and a temperature of 50 °C. Direct-SPME–GC–MS gave good precision, it was linear over the range studied ($0.11–2.5\ \mu g\ l^{-1}$) and the detection limits were at the low $\mu g\ l^{-1}$ level. The method is suitable as an alternative to the SPE method for the analysis of short ethoxy chain NPEOs and their halogenated byproducts in aqueous matrixes containing low concentration levels, such as drinking water.

Acknowledgements

This study was supported by SANDRINE project number ENV4-CT98-0801 of the European Union. A.D. acknowledges a Ph.D. fellowship from Fundació Agbar.

References

[1] M. Ahel, W. Giger, M. Koch, Water Res. 28 (1994) 1131.
[2] M. Ahel, W. Giger, C. Schaffner, Water Res. 28 (1994) 1143.
[3] W. Giger, P.H. Brunner, C. Schaffner, Science 225 (1984) 623.

[4] M. Ahel, T. Conrad, W. Giger, Environ. Sci. Technol. 21 (1987) 697.
[5] M. Reinhard, N. Goodman, K.E. Mortelmans, Environ. Sci. Technol. 16 (1982) 351.
[6] F. Ventura, A. Figueras, J. Caixach, I. Espadaler, J. Romero, J. Guardiola, J. Rivera, Water Res. 22 (1988) 1211.
[7] P. Lee-Ferguson, C.R. Iden, B.J. Bronawell, Anal. Chem. 72 (2000) 4322.
[8] M. Petrovic, A. Díaz, F. Ventura, D. Barceló, Anal. Chem. 73 (2001) 5886.
[9] S. Jobling, J.P. Sumpter, Aquat. Toxicol. 27 (1993) 361.
[10] S. Jobling, D. Sheahan, J.A. Osborne, P. Matthiessen, J.P. Sumpter, Environ. Toxicol. Chem. 15 (1996) 194.
[11] H. Maki, H. Okamura, I. Aoyama, M. Fujita, Environ. Toxicol. Chem. 17 (1998) 650.
[12] M.R. Servos, Water Qual. Res. J. Can. 34 (1999) 123.
[13] H.B. Lee, Water Qual. Res. J. Can. 34 (1999) 3.
[14] R.J. Maguire, Water Qual. Res. J. Can. 34 (1999) 37.
[15] D.T. Bennie, Water Qual. Res. J. Can. 34 (1999) 79.
[16] K.K. Chee, M.K. Wong, H.K. Lee, J. Microl. Sep. 8 (1996) 131.
[17] A. Boyd-Boland, J. Pawliszyn, Anal. Chem. 68 (1996) 1521.
[18] R. Aranda, R.C. Burk, J. Chromatogr. A 829 (1998) 401.
[19] A. Díaz, F. Ventura, M.T. Galceran, Anal. Chem. (2002) in press.
[20] M.A. Blackburn, M.J. Waldock, Water Res. 29 (1995) 1623.
[21] J.A. Shoemaker, J.W. Munch, T.D. Beyhmer, J. Expos. Anal. Environ. Epidemiol. 9 (1999) 181.