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Simultaneous determination of cyanogen chloride and cyanogen bromide in treated water at sub-μg/L levels by a new solid-phase microextraction–gas chromatographic–electron-capture detection method

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Abstract

A headspace solid-phase microextraction (HS-SPME) procedure has been developed and applied for the determination of cyanogen halides in treated water samples at μg/L concentrations. Several SPME coatings were tested, the divinylbenzene–Carboxen–polydimethylsiloxane fiber being the most appropriate coating. GC–electron-capture detection was used for separation and quantitation. Experimental parameters such as sample volume, addition of a salt, extraction time and desorption conditions were studied. The optimized method has an acceptable linearity, good precision, with RSD values <10% for both compounds, and it is sufficiently sensitive to detect ng/L levels. HS-SPME was compared with liquid–liquid microextraction (US Environmental Protection Agency Method 551.1) for the analysis of spiked ultrapure and granular activated carbon filtered water samples. There was good agreement between the results from both methods. Finally, the optimized procedure was applied to determine both compounds at the Barcelona water treatment plant (N.E. Spain). Cyanogen chloride in treated water was <1.0 μg/L and cyanogen bromide ranged from 3.2 to 6.4 μg/L. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Solid-phase microextraction; Headspace analysis; Cyanogen chloride; Cyanogen bromide; Halides

1. Introduction

The addition of oxidants such as chlorine, chloramines, ozone and chlorine dioxide for drinking water disinfection leads to the formation of disinfection by-products (DBPs) due to reaction with natural organic matter. Chloramines are widely used because they provide a stable residual in the distribution system and form fewer DBPs than chlorine. Cyanogen chloride (CNCl) and cyanogen bromide (CNBr) have been identified mainly as chloramination by-products. They are potential health risks; CNCl is rapidly metabolized to cyanide in the body. For this reason, CNCl was listed in the United States Environmental Protection Agency (EPA)'s 1991 Drinking Water Priority List and it is a possible candidate for USA regulation in the future [1]. The

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World Health Organization (WHO) proposes CNCl as a chemical of health significance and it has established a guideline value of 70 μg/L as the sum of all cyanide species, which includes cyanogens, for drinking water [2].

CNCl was first reported by Krasner et al. [3] in a nationwide survey of 35 water utilities in the United States. The mean value for CNCl in finished water at utilities that used only free chlorine was 0.4 μg/L; this value increased to 2.2 μg/L in those utilities where pre-chlorinated and post-ammoniated processes were used. Jacangelo et al. [4] also studied the influence of the final disinfectant on CNCl formation; their results showed that CNCl levels were eight to 15 times higher when chloramines were used as the final disinfectant rather than chlorine. The same conclusion was reported by Miltner et al. [5] and Stevens et al. [6].

CNBr was detected by West et al. [7] as an ozonation DBP in waters containing high bromide concentrations, at levels between 5 and 13 μg/L. It has also been identified as a chloramination by-product. The formation of CNBr can be postulated to be similar to that proposed for the formation of CNCl by Hirose et al. [8], who hypothesized that chlorination of aliphatic amino acids in the presence of ammonium ion leads to CNCl.

The standard method for the analysis of CNCl is EPA Method 524.2, which uses purge and trap (P&T) followed by GC–MS. Nevertheless, the analysis of CNBr using heated P&T–GC–MS is extremely difficult due to its low vapor pressure and high water solubility [9]. Alternative methods to determine CNCl and CNBr simultaneously have been proposed by Xie and Reckhow [10], who developed a headspace (HS)–GC–electron-capture detection (ECD) method; and by Sclimenti et al. [11], who elaborated a simplified liquid–liquid extraction (LLE) GC–ECD method with methyl *tert*.-butyl ether (MtBE) as organic solvent.

In recent years, solid-phase microextraction (SPME), developed by Pawliszyn and co-workers [12–15], has become popular for the analysis of organic compounds in water because it combines sampling and preconcentration in one step. It is a simple, solvent-free, reliable and flexible tool that provides good results over a wide range of analyte concentrations. The SPME technique coupled with GC has been applied to the analysis of a wide range of organic compounds. Recently, SPME has been applied for the determination of DBPs such as trihalomethanes and halogenated solvents [16,17], iodinated trihalomethanes [18], carbonyl compounds by derivatization–SPME and GC analysis [19]; and also for compounds causing taste and odor in water supplies such as geosmin and 2-methylisoborneol [20].

The objective of this work was to develop a simple HS-SPME–GC–ECD method for the determination of cyanogen halides in drinking waters. HS-SPME sampling was used due to the higher diffusion of the analytes in air than in water [21], which gives shorter equilibrium times, a cleaner background and a longer fiber life. Experimental parameters of the method such as selection of SPME coating, sample volume, addition of salt and also extraction time and desorption conditions were optimized. Limits of detection, linearity and precision were determined. In order to evaluate the suitability of the developed method, HS-SPME was compared with LLE (following the experimental protocol described in EPA Method 551.1) [22] for different water matrices such as spiked ultrapure water and granular activated carbon filtered water. Finally, the HS-SPME procedure was used to determine CNCl and CNBr levels formed at successive stages of the Barcelona treatment plant (N.E. Spain), where Llobregat river water is treated.

2. Experimental

2.1. Chemicals and materials

Cyanogen chloride (solution of 2000 μg/L in acetone) was purchased from Protocol Analytical Supplies Inc. (USA). Cyanogen bromide (99%) was purchased from Fluka (Switzerland). The chemical reagents bromochloromethane and 1,2-dibromopropane (used as internal standards) and L-ascorbic acid (used as a quenching agent for chlorine) were purchased from Sigma–Aldrich (USA). Other reagents were methanol *purge and trap grade* from Sigma–Aldrich; MtBE *Suprasolv grade* from Merck (Germany), sulfuric acid, sodium sulfate *ACS-ISO for analysis* and sodium chloride *ACS-ISO for*

analysis from Carlo Erba (Italy). Ultrapure water was from a Milli-Q water purification system (Millipore, USA). For extraction, water samples were placed in 40-mL EPA vials (Wheaton, USA) equipped with stir bars and sealed with PTFE-faced silicone septa.

2.2. Standard solutions

Stock standard solutions of cyanogen bromide were prepared in methanol, separately, by weighing approximately 0.1 g of analyte into a 10-mL volumetric flask and diluting to volume. A mixed secondary standard solution was prepared by dilution in methanol of the primary individual standards to give concentrations of 50 mg/L. When cyanogen halides were injected directly into the column, the last dilution was made using MtBE as solvent. Ultrapure water solutions were prepared by spiking with different amounts of the secondary standard and used for recovery studies and calibration.

2.3. SPME coatings

Seven types of coated fiber, 7 and 100 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), 75 μm Carboxen–polydimethylsiloxane (CAR–PDMS), 65 μm Carbowax–divinylbenzene (CW–DVB), 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 2 cm 50/30 μm divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS), were evaluated to determine cyanogen halides in water samples. The commercially available SPME device and the fibers were purchased from Supelco (Bellefonte, PA, USA). Fibers were initially conditioned at 320°C for 7-μm PDMS (5 h); at 250°C for 100-μm PDMS (3 h); at 300°C for 85-μm PA (2 h); at 280°C for 75-μm CAR–PDMS (2 h); at 250°C for 65-μm CW–DVB (1 h); at 260°C for 65-μm PDMS–DVB (1 h); and at 270°C for 2 cm 50/30-μm DVB–CAR–PDMS (5 h), according to the manufacturer's instructions in order to remove contaminants and to stabilize the phase. Conditioning was carried out in an extra split/splitless port (split open) with helium carrier gas prior to each extraction. This procedure prevents the passive extraction of interfering analytes from ambient air.

2.4. Procedure

2.4.1. Sample collection

Water samples from successive stages of the Barcelona treatment plant were collected in 100-mL glass bottles with PTFE-faced septa and polypropylene screw caps. A volume of 0.3 mL of sulfuric acid 1 *M* was added to each bottle prior to sampling. The sulfuric acid reduces the sample pH to 2–3 to avoid the hydrolysis of CNCl which forms cyanate ion at pH >8.5, and the base-catalyzed hydrolysis of CNBr at pH >5.0 [23]. When spiked ultrapure water samples were analyzed, a smaller volume of acid solution (0.1 mL) was sufficient. A volume of 0.1 mL of ascorbic acid solution 0.1 *M* was added to each bottle (100 mL) prior to analysis. The ascorbic acid eliminates free chlorine, thus preventing the production of further DBPs.

2.4.2. HS-SPME

Acidified water samples (30 mL, pH between 2 and 3) were placed in a 40 mL glass sample vial. To each sample, bromochloromethane as an internal standard (2 μL of a methanolic solution of 30 mg/L) and 7.5 g of sodium chloride were added. The vial was sealed with a Teflon-faced septum cap. The SPME fiber was exposed to the headspace. The sample was agitated with a magnetic stirring bar at 1100 rpm at room temperature (22°C) for 15 min. Magnetic stirring of the sample during the extraction process reduced the equilibration time. When the process was finished, the fiber was immediately inserted into the GC injector port for thermal desorption of the extracted analytes.

2.4.3. LLE

Water samples (35 mL, pH between 2 and 3) were placed in 40 mL EPA glass vials (Wheaton). To each sample, 1,2-dibromopropane as a surrogate standard (5 μL of a methanolic solution of 70 mg/L), 10 g of anhydrous sodium sulfate and 2 mL of glass-doubled distilled MtBE were added. The vials were then sealed with PTFE septa, shaken for 2 min, placed upright and left to stand for 3 min. Five hundred μL of the organic layer was transferred to a 2 mL vial containing bromochloromethane as an internal standard (5 μL of a methanolic solution of 10 mg/L).

2.5. Instruments

Gas chromatography was carried out with a Fisons Top 8000 gas chromatograph equipped with an electron-capture detector. A DB-1701 fused-silica column (J&W Scientific) with a 1.0 μm film thickness, 30 m×320 μm I.D., was used. The GC temperature program was 30 to 35°C (8 min) at 5°C/min, then up to 220°C (10 min) at a rate of 10°C/min. Carrier gas was helium (88 kPa) and nitrogen (33 mL/min) as make-up. Detector temperature was 300°C.

DB-1 and DB-624 capillary columns, routinely used in our laboratory for determining other DBPs (trihalomethanes, haloacetic acids, haloacetonitriles, halopropanones, chloral hydrate and cloropicrin), were tested. In the DB-1 column (J&W Scientific, 30 m×250 μm and a 1.0 μm film thickness), no signal was obtained for CNCl, whereas CNBr eluted close to the solvent and its signal was irreproducible. When a DB-624 column (J&W Scientific, 30 m×320 μm and a 1.8 μm film thickness) was used, CNBr was not found even when a new column was employed.

3. Results and discussion

3.1. Optimization of the HS-SPME procedure

The HS-SPME method development involves the selection of the SPME coating and the optimization of several parameters such as the effect of salt addition, the headspace volume and extraction time and desorption conditions.

3.1.1. Selection of SPME coating — extraction efficiencies

The selection of an appropriate coating is essential for the establishment of a HS-SPME method. The suitability of a fiber depends on the molecular weight and the polarity of the analytes to be extracted. In this study, seven SPME coatings, from the classical polydimethylsiloxane to the recent carbon-coated fibers, were evaluated to determine the most effective for the extraction of cyanogen halides from water.

A spiked aqueous sample (30 mL spiked at 15 μg/L for both CNCl and CNBr) was analyzed three times with each fiber. To increase the efficiency, sodium chloride (7.5 g) was added before the extraction. The extraction time was 15 min at room temperature for all fibers. Desorption times were the following: 30 s (split mode 1/15) at 250°C for the 100-μm PDMS, PA, CW–DVB, PDMS–DVB and DVB–CAR–PDMS; and at 300°C for the 7-μm PDMS and CAR–PDMS.

The results obtained for each compound using GC–ECD showed that non-polar fibers (PDMS) and also polyacrylate (PA) were not suitable to determine cyanogen halides because no chromatographic response was registered. Different mixed phase coatings (CAR–PDMS, CW–DVB, PDMS–DVB and DVB–CAR–PDMS) were also used. With these coatings, the interaction is practically determined by adsorption on the synthetic materials. For the mixed CAR–PDMS fiber, a phase specially designed for volatile compounds, the porous carbon adsorbent (Carboxen, CAR), increased the extraction efficiency. However, the background obtained using this fiber at the beginning of the chromatogram led to a poor profile. The mixed phases CW–DVB and PDMS–DVB contain microspheres of the DVB polymer, which are immobilized in the fiber by using Carbowax or PDMS, which increases the surface area of the fiber. For the extraction of cyanogen halides the CW–DVB coating, relatively non-polar, was also unsuitable, while the PDMS–DVB fiber, recommended for polar compounds, gave moderate efficiency for the extraction of these two compounds. For the all fibers evaluated, the DVB–CAR–PDMS proved to be the most effective for the extraction of CNCl and CNBr from water samples, since the fiber coating is composed of two adsorbents, DVB (a porous solid) and Carboxen (a porous carbon), which increase the available surface area and enhance the extraction efficiency of analytes. The results obtained show that this fiber generates ECD area counts 10 (for CNCl) and five (for CNBr) times larger than those obtained with the PDMS–DVB fiber. For the following experiments, the DVB–CAR–PDMS fiber was used.

3.1.2. Effect of salt addition

In order to evaluate the effect of the addition of a salt on the extraction process, a fortified aqueous

sample (30 mL spiked at 15 μg/L of each cyanogen halide) was analyzed three times with and without the addition of different amounts of NaCl. The extraction and desorptions conditions were as before.

The addition of salt provided a *salting-out* effect on the analytes favoring diffusion into the headspace. For a better comparison, the amount extracted by the fiber DVB–CAR–PDMS without salt was set at 100%. This resulted in a significant influence on the adsorption response of the cyanogen halides by HS-SPME. An increase of 100% in the response was obtained for CNCl, whereas for CNBr the area increased even more. The addition of 25% NaCl to the water samples was used for the remainder of this work.

3.1.3. Effect of the headspace volume

Headspace volume was optimized. The experiment was performed using EPA 40 mL vials and the volume of water was increased from 10 to 30 mL. A salted aqueous sample, spiked at 15 μg/L of each cyanogen halide, was analyzed three times with the DVB–CAR–PDMS fiber. The other conditions were as described in the Experimental section.

HS-SPME is a multiple equilibrium process in which analytes of the aqueous sample are transported through the water sample to the headspace to the fiber. The amount adsorbed on the fiber, n, can be expressed by $n = (K_{fh}K_{hs}V_fV_sC_0)/(K_{fh}K_{hs}V_f + K_{hs}V_h + V_s)$, where C_0 is the initial concentration of the analyte in the matrix, V_s, V_h and V_f are the volume of the sample matrix, the headspace and the coating, respectively, and K_{fh} and K_{hs} are defined as the equilibrium partition constants for the analyte between the headspace and the polymer film and between the condensed phase and its headspace, respectively. In this experiment, K_{fh}, K_{hs}, V_f and C_0 were kept constant and V_s and V_h were modified. The combination of K_{fh} and K_{hs} for a given compound determines the effect of sample volume on the amount extracted in the adsorption. For compounds with high K_{fh} values, an increase in the sample volume (thus, a decrease in the headspace volume) contributes significantly to the amount extracted; headspace should be minimized to obtain the highest sensitivity. However, no effect is produced for compounds with low K_{fh} values because the amount of analyte adsorbed onto the fiber is small relative to the amount contained in the headspace. No increase in the peak area was registered when headspace volume decreased from 30 to 10 mL. Therefore, further experiments were performed using 30 mL of acidified water.

3.1.4. Adsorption and desorption time profiles

The extraction of cyanogen halides with the DVB–CAR–PDMS fiber using HS-SPME is an adsorption process due to the presence of the DVB and CAR sorbents in the fiber. The adsorption time profiles for the DVB–CAR–PDMS fiber were established by plotting the ECD response versus the extraction time for each cyanogen halide (Fig. 1) in order to obtain the experimental equilibrium curve. The equilibrium time is reached when a further increase of the extraction time does not result in a significant increase in the detector response. A duplicate water sample spiked at 15 μg/L for each compound was analyzed under the experimental conditions described in the HS-SPME procedure. Extraction time profiles indicated that there were no significant differences in analyte extraction between 15 or 20 min, so a sampling time of 15 min was used in further experiments.

The GC injector temperature was optimized to ensure that cyanogen halides are completely desorbed from the fiber and to avoid carryover. For the DVB–CAR–PDMS fiber, three temperatures (230, 250 and 270°C) were tested. As can be seen in Fig. 2, desorption at 250°C gave the best response for both compounds. For a better comparison, the

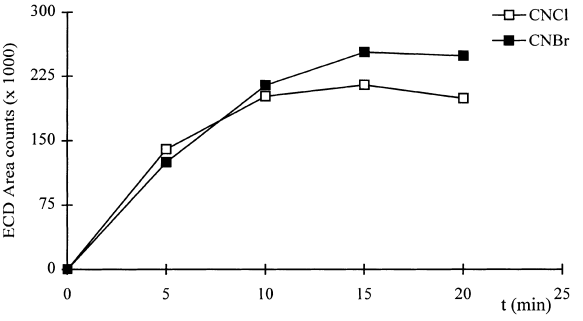

Fig. 1. Adsorption time profiles for CNXs by HS-SPME using DVB–CAR–PDMS. Water samples (30 mL) contained CNXs (15 μg/L of each compound). Key: (□) CNCl, (■) CNBr.

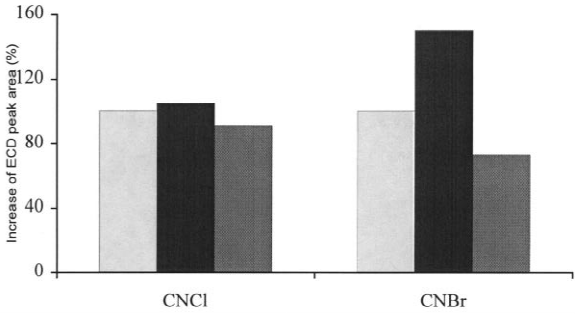

Fig. 2. Effect of GC injector temperature in the CNXs analysis by HS-SPME using the DVB–CAR–PDMS fiber. Water samples (30 mL) contained CNXs (15 μg/L of each compound). Key: (□) 230°C, (■) 250°C, (▨) 270°C.

amount desorbed at the lower temperature was also set at 100%. Desorption profiles of CNCl and CNBr were obtained by plotting the ECD response versus four different desorption times (10, 20, 30 and 45 s). As no significant differences for the times evaluated were obtained, a desorption time of 30 s was used for further experiments. Split mode (1/15) was used because the splitless mode gave a chromatographic profile with an important tail for CNCl.

Carryover on SPME fibers due to incomplete desorption of analytes during the desorption process was attributed to strong adsorption in the coating. Carryover was determined by performing a second desorption step and no peaks were obtained.

3.2. Linear range, limits of detection and precision

The linearity of the method was established by plotting the relative areas to the internal standard, bromochloromethane (A/A_{is}), versus the concentration of the analyte (C_i). Standard water samples at concentrations ranging from 0.5 to 50 μg/L were used. Acceptable linearity was obtained for both compounds with a correlation coefficient >0.99 (Table 1). The limits of detection (LODs), defined as the concentration of analytes in the sample which causes a peak with a signal-to-noise ratio of 3, were also determined. In order to calculate them, water samples containing cyanogen halides spiked at low concentrations (0.5 μg/L) were used. Under these conditions, LODs of the method were in the ng/L range (Table 1). The repeatability and reproducibility of the HS-SPME procedure were calculated by analyzing five replicates of ultrapure water, spiked at approximately 15 μg/L for each compound, on the same day and a total of nine replicates on three consecutive days under the optimized conditions. Table 2 gives the mean and the relative standard deviation (RSD), which was 6% for both compounds. The RSD values for reproducibility ranged from 8.5 to 12.5%.

3.3. Comparison of HS-SPME with LLE

The optimized HS-SPME–GC–ECD method was compared with the LLE–GC–ECD method for the simultaneous determination of cyanogen chloride and cyanogen bromide by spiking samples of ultrapure and granular activated carbon (GAC) filtered waters to study matrix effects. Ascorbic acid solutions were added to GAC filtered waters to prevent any free chlorine residual. Triplicate samples of each type of water, both spiked at two concentrations (5 and 10 μg/L), were analyzed. These values were one-tenth of the guideline values proposed by the World Health Organization. Results obtained for both methods are given in Table 2. Standard deviations and mean values of both methods were compared using the *F* Fischer test (95% probability) and the Student *t*-test

Table 1
Linear dynamic ranges, correlation coefficients (r^2), limits of detection (LODs), repeatability and reproducibility of the optimized HS-SPME method using the DVB–CAR–PDMS fiber

Compound	Linearity range (μg/L)	Slope	Correlation coefficient (r^2)	LOD[a] (ng/L)	Repeatability		Reproducibility	
					Mean[a] (μg/L)	RSD (%)	Mean[b] (μg/L)	RSD (%)
CNCl	0.6–40	0.0142	0.9989	77	13.3	6.0	13.3	8.5
CNBr	2.5–20	0.0032	0.9999	41	12.8	6.0	12.8	12.5

[a] Mean of five determinations.
[b] Mean of nine determinations.

Table 2
Estimated concentrations and standard deviations of CNXs in ultrapure spiked water and GAC filtered water determined by HS-SPME (DVB–CAR–PDMS fiber) and LLE (EPA Method 551.1) methods[a]

	Ultrapure water (5 μg/L)				Ultrapure water (10 μg/L)				GAC water (5 μg/L)				GAC water (10 μg/L)			
	HS-SPME		LLE		HS-SPME		LLE		HS-SPME		LLE		HS-SPME		LLE	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
CNCl	4.8	0.2	5.2	0.7	10.1	0.1	9.9	0.7	5.1	0.1	5.5	0.1	10.6	0.2	9.9	0.9
CNBr	5.2	0.6	5.0	0.2	9.9	0.5	9.9	1.3	5.3	0.3	5.3	0.1	11.4	0.4	10.5	0.3

[a] Mean of three determinations.

(95% probability and two sides), respectively, to ensure that they give results without significant differences [24] as observed in Table 2. On the other hand, both techniques gave the same results independent of the nature of the aqueous matrix. As a consequence, for the analysis of water samples, the HS-SPME method provides additional advantages over LLE: (i) it does not require the use of organic solvents; (ii) the analysis is simpler because sampling and preconcentration are combined in one step.

3.4. Cyanogen halide levels at the Barcelona water plant

The proposed HS-SPME method was used to monitor cyanogen chloride and cyanogen bromide at the Barcelona water treatment plant. Salt mines located in the upper course of the river are responsible for the high bromide concentration in raw water. The plant carries out conventional treatment, consisting of prechlorination (to break-point), flocculation (settling), sand filtration, ozonization, GAC filtration and final chlorination with a lower dosage of chlorine, to guarantee a 0.5–1 mg/L concentration in the distribution water system. Cyanogen halide concentrations were determined simultaneously at all stages of treatment. Calibration curves were plotted to quantify them. Sand-filtered and ozonated waters required dilution since the CNBr concentration was outside the linearity range. The results are shown in Table 3. Fig. 3 shows the chromatograms obtained by HS-SPME for the analysis of an ozonated (a) and treated (b) water sample. CNXs were initially formed at the prechlorination step, the concentration of CNCl being higher than that of CNBr at this stage. Total CNX (TCNX) concentration obtained at the prechlorination stage was lower than those obtained after sand filtration and ozonization. This can be explained because water from the prechlorination stage was sampled several minutes after the addition of chlorine, whereas CNX generation continued for 3 h, approximately, until the water reached the sand filters. Average concentrations of CNCl and CNBr in sand filtered water were respectively 2.4 and 3.6 times higher than the values obtained in the prechlorination stage. The CNCl concentration remained constant after ozonization; however, a significant increase of 100% was observed for CNBr. Both CNXs were completely removed after passing the water through the GAC filters. Nevertheless, CNXs were formed again by the final chlorination, but at lower concentrations, with values ranging between

Table 3
Average, maximum and minimum CNX levels (μg/L) in Barcelona's water treatment plant (March, April 1999)

Compound	Raw water	Prechlorination	Sand filters	Ozone	GAC filters	Treated water
CNCl	–[a]	9.0 (5.0–16)	23 (14–35)	22 (13 – 32)	–	0.4 (0–0.9)
CNBr	–	6.9 (4.1–9.1)	27 (14–39)	40 (33–53)	–	4.0 (2.6–6.4)
Total CNXs	–	15.9	50	62	–	4.4

[a] –, below LOD ($n = 6$, performed by HS-SPME–GC–ECD with a DVB–CAR–PDMS fiber in a DB-1701 column). Average raw water quality characteristics (March and April 1999): volume, 2.5 m^3/s; pH, 8.2; temperature, 14.3°C; conductivity, 2124 μS/cm; total organic carbon, 8.2 mg C/L; NH_3, 1.3 mg/L; bromide, 1.0 mg/L; break-point, 6.0 mg Cl_2/L.

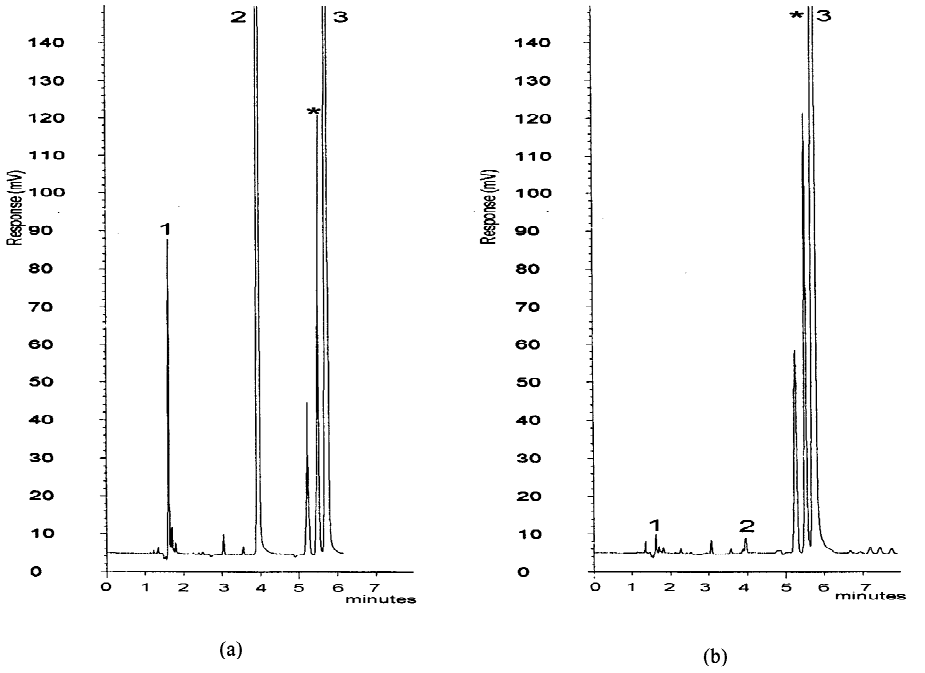

Fig. 3. GC–ECD chromatograms of an ozonated (a) and treated (b) water sample (30 mL). Extraction was performed by HS-SPME with a DVB–CAR–PDMS fiber at the optimized conditions. Peaks: 1=CNCl, 2=CNBr, 3=$CHCl_3$, ★=internal standard (chromatographic conditions as described in the Experimental section).

2.6 and 6.4 μg/L for CNBr, whereas CNCl was determined at a maximum level of 0.9 μg/L.

4. Conclusions

HS-SPME–GC–ECD is a fast, inexpensive and solvent-free procedure that has been demonstrated to be adequate for monitoring cyanogen halides in treated water samples. The divinylbenzene–Carboxen–polydimethylsiloxane fiber was found to be the most effective for extracting CNCl and CNBr simultaneously from water samples. Equilibration took place at room temperature and the sensitivity was improved by the addition of salt (25%, w/v). The optimized HS-SPME–GC–ECD analytical procedure had an acceptable linearity in the range of concentrations studied and good precision and it allowed the detection of cyanogen halides at low concentrations (40 to 75 ng/L). The method, which avoids the use of organic solvents and intensive manipulation compared with the standard LLE method, has been successfully applied for the determination of CNXs in Barcelona treatment water plant. The CNX levels found in the final treated water were lower than 1.0 μg/L for CNCl and between 2.6 and 6.4 μg/L for CNBr. These results are consistent with the values found in the literature for water with relatively high bromide levels [7,25].

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