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Comparative study of a solid-phase extraction system coupled to capillary electrophoresis in the determination of haloacetic compounds in tap water

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Abstract

This study compares four different commercial sorbents, LC-SAX (a quaternary ammonium anion exchanger), LiChrolut EN (a highly crosslinked styrene–divinylbenzene), Envi-Carb (a graphitized carbon black) and Oasis HLB [a macroporous poly(divinylbenzene–co-N-vinylpyrrolidone) copolymer], for the solid-phase extraction (SPE) of various haloacetic compounds from aqueous samples. The recoveries with the different sorbents were studied by coupling an off-line SPE system to capillary electrophoresis with indirect photometric detection. The recoveries were highest when LiChrolut EN was used. The limits of detection for the compounds are in the low microgram per litre range and the recovery values are over 80% for dichloroacetic acid and trichloroacetic acid, two of the most habitual haloacetic acids in chlorinated water, when 500 ml of standard solution was preconcentrated using this sorbent. Finally, the performance of the method with different water samples, the effect of chlorination in a treatment plant and the evolution of the haloacetic acids in the water distribution system were tested and the results were compared with those obtained using liquid–liquid extraction and gas chromatography–mass spectrometry.

Keywords: Solid-phase extraction; Extraction methods; Water analysis; Organochlorine compounds; Haloacetic acids

1. Introduction

One of the most important sources of organohalogen compounds is water disinfection by chlorination [1–3]. Hypochlorous acid is one of the most common agent used in disinfection processes; it is formed by the disproportionation reaction that takes place when chlorine dissolves in water. During chlorination, humic and fulvic compounds are converted into toxic organohalogen compounds. The kind and amount of compounds formed depend mainly on the composition of the water and on the dose of chlorine.

The US Environmental Protection Agency (EPA) has promulgated regulations to control disinfection by-products (DBPs) [4]. The largest group of compounds formed during this process are trihalomethanes (THMs: trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane), followed by haloacetic acids (HAAs). Organobromide compounds are formed when the water being chlorinated contains large amounts of bromide [5]. The HAAs selected for control include monochloroacetic acid (MCAA), monobromoacetic

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acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (BCAA) and trichloroacetic acid (TCAA). Toxicological studies indicate that DCAA and TCAA are animal carcinogens [6].

The EPA has proposed the disinfectants/disinfection by-products (D/DBPs) rule, the first stage of which establishes maximum contaminant levels (MCLs) of 60 $\mu g\,l^{-1}$ for the sum of the five regulated HAAs [4,7]. Chromatographic methods are most commonly used to determine these compounds in water samples, in particular gas chromatography (GC) [8] and reversed-phase ion pair chromatography (RP-IPC) [9]. If HAAs are to be analysed by GC, a prior derivatization step is required because of their low volatility and high polarity. However, with RP-IPC this step is not necessary although limits of detection are higher.

Capillary electrophoresis (CE), including capillary zone electrophoresis (CZE), has been used to separate charged analytes [10,11]. In fact, in the determination of haloacetic compounds it can be a good alternative to chromatographic methods because it does not require the tedious derivatization step and analysis times can be reduced if the most appropriate CE mode is used [12].

Unfortunately, these techniques do not enable the detection limits required by legislation to be reached and so the sample needs to be enriched before to the analysis. Liquid–liquid extraction (LLE) has been the most frequently used technique for the determination of HAA compounds [8,13,14]. In this case, methyl *tert.*-butyl ether (MTBE) is used as the organic phase and an acidic pH is required to extract the nondissociated acidic compounds of the sample.

Nowadays, solid-phase extraction (SPE) is becoming the most frequently used extraction technique for environmental samples, and overcomes some of the problems of LLE (the large amounts of generally toxic and inflammable organic solvents or the greater cost and duration of the concentration step) [15]. Furthermore, SPE can adjust the selectivity, affinity and/or capacity as new materials are developed [16]. However, before a sorbent is selected for SPE, some physicochemical considerations such as the functional groups of the analytes, the nature of the bonded phase and the interactions between the sorbent and the components of the sample matrix must be taken into account [17].

In this paper, four different sorbents, a quaternary ammonium anion exchanger (LC-SAX), a highly crosslinked polymer of styrene–divinylbenzene (LiChrolut EN), a graphitized carbon black (Envi-Carb) and a macroporous poly(divinylbenzene–co-N-vinylpyrrolidone) copolymer (Oasis HLB), are compared for SPE followed by CZE with indirect ultraviolet detection of HAAs from tap water. Strong anion exchangers (SAX) have been chosen because they were used for the extraction of anionic species in tap water and river water [18]. Likewise, LiChrolut EN, Envi-Carb and Oasis HLB have been chosen because they have been used to determine highly polar species from aqueous samples [19–22].

Finally, the proposed method was applied to analyse these compounds before and after the chlorination step in a water treatment plant, and at different points in the mains water supply in order to study their evolution. The results were compared with those obtained by the LLE–GC–MS method [23] where a previous derivatization step was necessary.

2. Experimental

2.1. Instrumentation

Measurements were made on a Hewlett-Packard model ^{3D}CE instrument (HP, Waldbronn, Germany) equipped with a diode array detector. Data were collected with the HP Chemstation version A.04.01 chromatographic data system. The separations were carried out using uncoated fused-silica capillary tubing (64.5 cm×75 μm I.D.) supplied by Supelco (Bellefonte, PA, USA). A detection window was prepared by burning off the polyimide coating 56 cm from the capillary inlet. When a new capillary was used, the capillary was washed for 60 min with hydroxide solution (0.1 *M*), followed by 60 min with deionized water and, finally, 30 min with the running buffer. Samples were introduced by hydrodynamic injection, the detection was set at 235 nm in the indirect mode and the temperature was kept constant at 25°C.

2.2. Chemicals

The haloacetic acids studied were: (1) monochloroacetic acid (MCAA), (2) monobromoacetic

acid (MBAA), (3) dichloroacetic acid (DCAA), (4) dibromoacetic acid (DBAA) and (5) trichloroacetic acid (TCAA). Standards were obtained from Merck (Darmstadt, Germany) and an individual standard solution of 2000 mg l^{-1} of each compound was prepared with water which had been purified by a Milli-Q system (Millipore, Bedford, MA, USA). Standard working solutions were prepared weekly or daily, depending on their concentration. All solutions were stored at 4°C in the refrigerator.

2,6-Naphthalenedicarboxylic acid dipotassium (NDC) was suplied by from Aldrich (Milwaukee, WI, USA) and it was used as the electrolyte system. Hexadecyltrimethylammonium bromide (CTAB; Sigma, St. Louis, MO, USA) was used as the electroosmotic flow (EOF) modifier. Sodium hydroxide (Aldrich) was used to adjust the electrolyte pH.

2.3. Electrophoretic conditions and system operation

The NDC electrolyte was prepared daily from the stock solution which contained 20 m*M* NDC and the haloacetic acids were separated using 4 m*M* NDC and 0.5 m*M* CTAB with a pH of 7.5 as electrolyte solution [12].

Separations were carried out by rinsing the capillary for 3 min with a background electrolyte immediately before the injection. At the beginning of each experimental day, the capillary was washed with 0.1 *M* NaOH for 15 min and then rinsed with deionized water (10 min) and the electrolyte (5 min).

The detector was set at 235 nm (indirect UV detection) and the capillary temperature was kept constant at 25°C. The injection was made hydrodynamically at a pressure of 40 mbar for 20 s. The separation voltage used was −20 kV for 4.5 min and then a linear gradient to −15 kV in 0.5 min and finally at the same potential for a further 3 min because an increase of the sharp shape of TCAA was observed [12].

2.4. Off-line trace enrichment

Off-line trace enrichment was carried out using four different commercial SPE cartridges: a quaternary ammonium strong anion exchanger, LC-SAX (100 mg, Supelco), a highly crosslinked polymer of styrene divinylbezene, LiChrolut EN (200 mg, Merck), a graphitized carbon black, Envi-Carb (250 mg, Supelco) and a macroporous poly(divinylbenzene–co-N-vinylpyrrolidone) copolymer, Oasis HLB (60 mg, Waters, Milford, MA, USA).

In order to prevent the analytes from taking their ionic form, all the water samples were acidified to pH 0.5 with concentrated sulphuric acid. The only exception to this was when LC-SAX was used as a sorbent, because in this case the ionic form was required. The extractions were carried out using the Bond Elut/Vac Elut system (Varian, Harbor City, CA, USA). Before extracting the samples, all cartridges were rinsed using 5 ml of methanol followed by 5 ml of Milli-Q water adjusted to pH 0.5 using sulphuric acid, except for LC-SAX for which Milli-Q water alone was used. The samples were passed through the cartridges at a flow-rate of approximately 15 ml min^{-1}. A clean-up step was made using 0.5 ml of Milli-Q water when LiChrolut EN cartridge was used. Finally, 2 ml of methanol–water (50:50, v/v) at a low flow-rate was used as solution to elute the retained compounds in all cases, except for LC-SAX for which 2 ml of Milli-Q water adjusted to pH 0.5 with sulphuric acid was used.

All samples and electrolyte systems were filtered through a 0.45 μm membrane filter (MSI, Westboro, MA, USA) before being preconcentrated.

Real samples were also analysed by LLE–GC. In the LLE process, 30 ml of sample was adjusted to pH 0.5 with concentrated sulphuric acid, before the extraction step in order to be able to extract the nondissociated acidic compounds and MTBE (Merck) was used as the organic phase. Finally, the compounds were methylated with diazomethane to produce methylester derivates [23].

3. Results and discussion

The electrophoretic separation of the haloacetic acids studied in this paper has been investigated in a previous work [12], which focused on the electrolyte concentration, pH and various EOF modifiers. In optimum conditions (see Section 2) these compounds were separated in less than 8 min.

Linearity of response by hydrodynamic injection (40 mbar for 20 s), using standards prepared in methanol–water (50:50, v/v), was found to be good

between 1 and 30 mg l^{-1} for MCAA and between 2 and 30 mg l^{-1} for the rest of haloacetic acids, with good regression coefficients (r^2>0.99). The limits of detection (LODs) were calculated using a signal-to-noise ratio of 3 and they were between 0.4 mg l^{-1} for MCAA and 0.7 mg l^{-1} for DBAA.

3.1. Comparison of sorbents

Haloacetic acids are anionic species at the typical pH of water samples. This means that a strong anionic exchanger (SAX) can be used as SPE sorbent to preconcentrate these compounds. For this reason, a commercial quaternary ammonium ionic exchanger cartridge (LC-SAX 100 mg) was used as sorbent. When the sample was passed through the cartridge, the compounds retained were eluted using Milli-Q water adjusted to pH 0.5 with sulphuric acid, so that they would change to their nonionic form and be eluted from the anionic exchanger sorbent. However, the eluted solution could not be injected directly into the CE system since the injection of solutions with pH values below 2 is not recommended by the supplier because they can affect the stability of the fused-silica capillary.

In order to overcome this problem, several attempts were made to increase the pH of the eluted sample. At first, concentrated NaOH was added to this solution. However, the current developed in the separation step of the CE method was high and unstable because of the high ionic strength of the injected sample. Subsequently, in order to separate the haloacetic acids from the rest of the ionic forms of the sample, the solution eluted from the LC-SAX cartridge was passed through a highly crosslinked polymer, LiChrolut EN (200 mg). Finally, the analytes were eluted from this cartridge using a methanol–water (50:50, v/v) mixture. The solution obtained could be injected without problems since its pH was approximately 6.

This process was checked by passing 2 ml of a standard solution of 10 mg l^{-1} of the haloacetic compounds through the LC-SAX cartridge and eluting them with 2 ml of Milli-Q water adjusted at pH 0.5. Then, this solution was passed through the LiChrolut EN cartridge and then a clean-up step was made using 0.5 ml of Milli-Q water in order to decrease the initial peak that was sulfate from the initial acidification step. Finally, the analytes retained were eluted with 2 ml of methanol–water (50:50, v/v). This solution was injected hydrodynamically (40 mbar for 20 s) into the capillary and separated using a negative voltage. As can be see in Fig. 1, the resolution between peaks was good and there were no broad peaks in the electropherogram when this procedure was used.

Different sample volumes (10, 25, 50 and 100 ml) of standard solutions were preconcentrated with this SPE process. Table 1 shows the recoveries of all analytes. As can be seen, the sample volume has a considerable influence. Recoveries were lower than 30% for all compounds when 100 ml of a standard at the 0.2 mg l^{-1} levels were analysed using this process.

The same sample volumes (10, 25, 50 and 100 ml) were also studied using only the LiChrolut EN cartridge as sorbent in the SPE step. In these cases, the standard solutions were adjusted to pH 0.5 because the HAAs had to be nonionic in order to be retained. This sorbent has a higher degree of cross-linking, and so has an open structure (high-porosity material), which increases its specific surface area and allows greater π–π interactions between analytes and the sorbent [24]. As can be seen in Table 1, when 100 ml of standard solution was analysed,

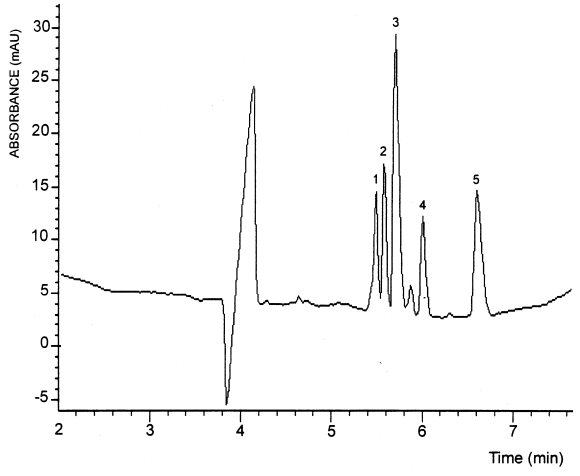

Fig. 1. Electropherogram obtained by passing 2 ml of a standard solution of 10 mg l^{-1} of haloacetic compounds through LC-SAX and LiChrolut EN cartridges, for more explanation see text. Peak assignations: 1=MCAA, 2=MBAA, 3=DCAA, 4=DBAA and 5=TCAA. For electrophoretic conditions, see Section 2.

Table 1
Recovery values obtained preconcentrating different sample volumes with the four commercial sorbents ($n=4$)

Compound	Recovery (%)												
	SAX-LiChrolut EN[a]			LiChrolut EN[a]					Envi-Carb[a]	Oasis-HLB[a]			LLE[b]
	25 ml	50 ml	100 ml	25 ml	50 ml	100 ml	250 ml	500 ml	25 ml	25 ml	50 ml	100 ml	30 ml
MCAA	52	44	28	91	76	65	56	37	14	22	11	6	66
MBAA	27	20	11	65	64	53	45	30	3	60	32	16	60
DCAA	56	35	20	104	102	94	92	82	2	95	80	65	70
DBAA	39	26	17	85	82	78	73	66	6	94	93	80	70
TCAA	59	39	20	101	100	95	92	85	5	87	82	78	80

[a] Percentage R.S.D.s are lower than 12 in all instances ($n=4$).
[b] See [12] for more details.

recoveries were higher than those obtained using LC-SAX followed by LiChrolut EN cartridges, mainly for DCAA (94%) and TCAA (95%), two of the most common haloacetic acids in chlorinated waters [1,25].

The results obtained using a polymeric sorbent such as LiChrolut EN, suggested that other types of sorbent could be used to preconcentrate these compounds, (e.g., a graphitized carbon black sorbent, Envi-Carb, or a new copolymer sorbent, Oasis HLB). Envi-Carb (250 mg) was used to retain HAAs from aqueous samples because it has been used in the analysis of different polar organic compounds [26]. In our case, the pH of the sample was adjusted to 0.5 using sulphuric acid. However, recoveries were low for all the HAAs (<15%) when 25 ml of a standard solution of 0.8 mg l^{-1} was studied. These results are in contrast to those obtained by others for polar species using this sorbent [26]. Higher sample volumes were not tested because of these recoveries.

Another new polymeric sorbent, Oasis HLB (60 mg), was studied to preconcentrate HAAs. This sorbent is formed by a poly(divinylbenzene–co-N-vinylpyrrolidone) copolymer and is water wettable due to the hydrophilic N-vinylpyrrolidone. So it is more flexible at processing samples since it can dry out during the extraction procedures without diminishing its ability to retain analytes. This is an important advantage that the previously mentioned sorbents do not have. When 100 ml of a standard solution of 0.2 mg l^{-1} was analysed, the recovery values were between 6% for MCAA and 80% for DBAA (see Table 1).

From the results obtained, the LiChrolut EN sorbent seems to be suitable for determining the HAAs studied. Nevertheless, when sample volumes of 250 and 500 ml were tested with this sorbent, the recoveries for all the compounds studied decreased. For 500 ml of a standard solution at a level of 40 $\mu g\, l^{-1}$, the recoveries were between 30% for MBAA and 85% for TCAA. It should be mentioned, though, that for DCAA and TCAA recoveries were over 80%. It should also be pointed out that in this study the four sorbents have been used as they are commercially available and their different masses have not been taken into account. In comparison with the LLE [12] process, the SPE process using LiChrolut EN gave better results for DCAA and TCAA (see Table 1), two of the most habitual HAAs in chlorinated waters. For this reason, 500 ml of sample and the LiChrolut EN sorbent were selected for further analyses.

The relative standard deviations (R.S.D.s) of six analyses of 500 ml of standard solutions at a level of 40 $\mu g\, l^{-1}$ were between 9.8% for MCAA and 5.5% for DCAA. Fig. 2a shows the electropherogram obtained when 500 ml of a standard solution of 25 $\mu g\, l^{-1}$ was analysed and there are no interfering peaks.

The linearity of the response for the total analytical system, including the preconcentration step using LiChrolut EN for 500 ml of standard solutions, was also studied. The results obtained for the linearity range and the detection limits are shown in Table 2.

The feasibility of the method was tested on tap water samples using LiChrolut EN as the sorbent. When 500 ml of the sample was analysed, it was

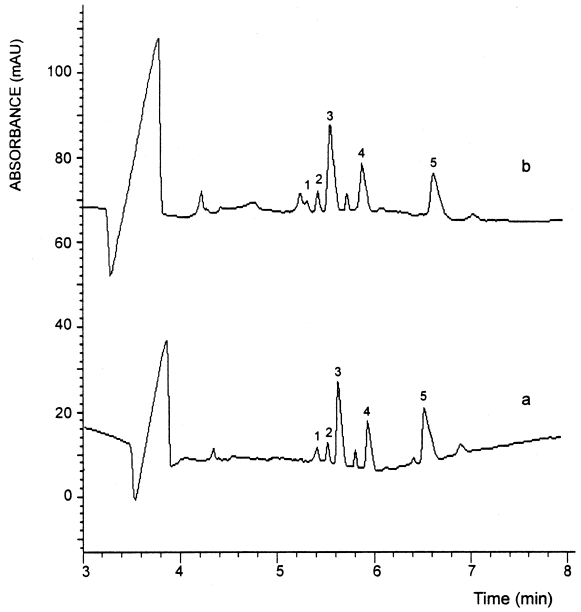

Fig. 2. Electropherogram obtained by passing (a) 500 ml of a standard solution of 25 $\mu g\,l^{-1}$ of haloacetic compounds and (b) 500 ml of tap water spiked at 25 $\mu g\,l^{-1}$ level, through LiChrolut EN cartridge. For peaks, see Fig. 1.

observed that a peak from the matrix had a migration time that was near to that for MCAA. This peak could be due to different compounds that show similar electrophoretic behaviour to HAAs, such as other organic acids. This meant that this haloacetic acetic was determined with less precision in these samples. Fig. 2b shows the electropherogram obtained for 500 ml of tap water sample spiked at 25 $\mu g\,l^{-1}$.

A study was made of HAA recoveries using 500 ml of tap water spiked at 40 $\mu g\,l^{-1}$ and it was seen that these recovery values were similar to those obtained for standard solutions.

The linearity of the response, for a volume of 500 ml of tap water spiked at different concentrations, was also studied and no significant differences were observed from the results for standard solutions.

According to the EPA regulations concerning the levels of these compounds in drinking waters (60 $\mu g\,l^{-1}$), the proposed method seems to be suitable for analysing haloacetic acids in these samples.

3.2. Applications

On the basis of the above results, the inlet and outlet water from the water treatment plant of L'Ampolla (Tarragona, Spain) was studied. In these samples, the influence of the chlorination disinfection process, could be seen. Fig. 3a shows the electropherogram obtained from analysing the water before the chlorination step and Fig. 3b shows the electropherogram after the chlorination step. Several peaks appeared at migration times similar to the haloacetic acids in this latter electropherogram. Some of these compounds, (DCAA, DBAA and TCAA) were tentatively identified by comparing this sample with the same sample spiked with 15 $\mu g\,l^{-1}$ of a standard solution. These samples were also analysed by LLE–GC–MS under selected ion monitoring conditions [23] and DCAA, DBAA and TCAA were determined in the sample after the chlorination step. This confirmed the previous results obtained by CE. Table 3 shows the analytical data.

The evolution of these compounds at different points in the mains was also investigated, because the concentration of chlorinated by-products varies with the distance from the water treatment plant [27]. Three water samples collected at different distances from the treatment plant were analysed using the proposed method. The first water sample corres-

Table 2
Calibration data and precision for the haloacetic acids studied

Compound	Linear range ($\mu g\,l^{-1}$)	Slope	Intercept	r^2	R.S.D. (%)[a]	LOD ($\mu g\,l^{-1}$)
MCAA	15–80	−0.7	2.5	0.9954	9.8	5
MBAA	15–80	−1.1	3.3	0.9960	6.3	5
DCAA	5–80	−5.1	1.6	0.9981	5.5	2
DBAA	7–80	−1.8	1.1	0.9970	7.4	3
TCAA	5–80	−2.5	1.0	0.9973	6.7	2

[a] Obtained for a standard solution of 40 $\mu g\,l^{-1}$ ($n=6$).

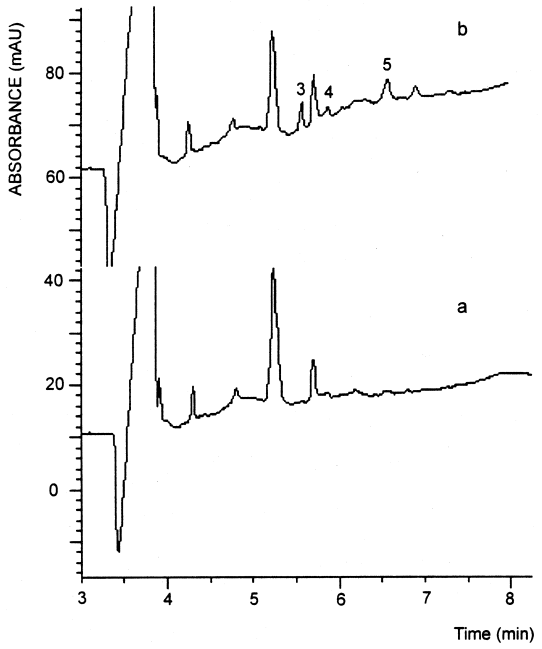

Fig. 3. Electropherogram obtained by passing 500 ml of water, from the water treatment plant of L'Ampolla, (a) before and (b) after the chorination step, through LiChrolut EN cartridge. For peaks, see Fig. 1.

ponded to the outlet of the treatment plant. The second and third water samples were collected 75 and 120 km from the treatment plant which represent residence times of 1.5 and 2 days, respectively. The samples were collected in March 1998 and they were analysed within 48 h. Table 3 shows the results of these analyses. Only three haloacetic acids were found in these samples: DCAA, DBAA and TCAA. They were also found when these samples were analysed by LLE–GC–MS. The measured concentrations were below the maximum contaminant levels (60 $\mu g\,l^{-1}$ for the sum of the five regulated HAAs) established by EPA regulations. The concentration of these compounds increased as they passed through the distribution system.

4. Conclusions

This paper demonstrates that SPE followed by CE with indirect UV detection can be applied to determine haloacetic acids from water samples at $\mu g\,l^{-1}$ levels. It has also been observed that LC-SAX cannot be used in the SPE process because of the incompatibility between the low pH of the solution used in the elution step and the capillary of the CE system. The best of the sorbents studied was LiChrolut EN which gave recovery values over 80% for DCAA and TCAA in the preconcentration of 500 ml of tap water samples. However, MCAA was determined with less precision in these samples because of a peak from the matrix. Furthermore, when the water at different points in the mains was investigated, the concentration of HAAs was seen to increase in water samples that have higher residence times when they have been chlorinated with free chlorine.

In comparison with the GC–MS method, the CE method enables HAAs to be detected in only 8 min whereas the GC method requires 30 min. Other important advantages are that the derivatization step is not necessary to analyse these compounds, and the

Table 3
Analytical results of different water samples

Compound	CE[a]					GC–MS[a]				
	Inlet	Outlet	0 km	75 km	125 km	Inlet	Outlet	0 km	75 km	125 km
MCAA	–	–	–	–	–	–	–	–	–	–
MBAA	–	–	–	–	–	–	–	–	–	–
DCAA	–	7.6	7.8	8.6	9.3	<LOQ[b]	4.9	5.1	6.2	7.3
DBAA	–	<LOQ	<LOQ	<LOQ	<LOQ	–	2.1	2.8	3.6	4.3
TCAA	–	9.8	10.6	13.5	17.4	<LOQ[b]	6.1	6.8	10.1	13.6

[a] All the values are defined in $\mu g\,l^{-1}$.
[b] Linearity of the LLE–GC–MS method is between 1 and 40 $\mu g\,l^{-1}$ for DCAA and TCAA and between 2 and 40 $\mu g\,l^{-1}$ for DBAA, for the rest of haloacetic acids was between 5 and 40 $\mu g\,l^{-1}$ [23].
LOQ=Limit of quantification.

equipment involved is simpler and cheaper than GC–MS equipment.

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