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Evaluation of the liquid–liquid extraction technique and application to the determination of volatile halo-organic compounds in chlorinated water

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ABSTRACT

The experimental conditions of a simple liquid–liquid extraction method for the determination of sixteen volatile halo-organic compounds, including the main trihalomethanes (THMs), in water were evaluated. The volatile halo-organic compounds were extracted with *n*-pentane and analysed by gas chromatography using a semi-capillary column and an electron-capture detector. The extraction recoveries for the four THMs were almost complete and the detection limits were lower than 1 μg/l. The method was applied to the analysis of raw and chlorinated water from the river Tormes for distribution in the city of Salamanca (Spain). Chloroform and bromodichloromethane were detected in all the chlorinated water samples; the mean concentrations determined in the finished water were 9.59 and 2.58 μg/l, respectively, from February to July, 1991.

INTRODUCTION

Disinfection of water destined for human consumption by chlorination has the drawback that substances potentially harmful to health may be formed [1,2]. Of the organic halogen derivatives that may be formed in chlorinated water, the compounds known as trihalomethanes (THMs) occur frequently; these mainly include chloroform, bromodichloromethane, chlorodibromomethane and bromoform.

As the toxicity and carcinogenic potential of chloroform depends on the breed, species, sex and age of experimental animals, controversy exists with respect to its toxic and mutagenic effects [3–6]. Despite this, the concentrations of chloroform detected in treated water may cause hepatotoxicity and nephrotoxicity [7]. The other three THMs show mutagenicity according to the Ames assay and genetotoxicity in *in vitro* experiments [8,9].

As a result of the possible risks to health, the World Health Organization has recommended a limit of 30 μg/l of chloroform [10] and US legislation has established a limit of 100 μg/l for total THMs [11]. Like the EEC report [12], Spanish technical-sanitary legislation [13] for the supply and quality of public drinking water does not establish maximum admissible concentrations of organochlorinated compounds and the limit for THMs is not clear.

Among the numerous methods used for the determination of volatile halo-organic compounds in water, the technique used for the separation and quantification of each of the different compounds is gas chromatography (GC). The compounds can be determined by direct injection [14] or, more commonly, following isolation or preconcentration, or

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both, of the organic compounds from the aqueous sample, adsorption onto solid materials [15], gas extraction (head space [16,17] purge and trap [18,19] and closed-loop stripping [20]), permeability through membranes [21] and liquid–liquid extraction [22–24]. The two methods used by the US. Environmental Protection Agency are the purge and trap method and the liquid–liquid extraction method. Comparison of these two methods shows that extraction-based procedures offer two primary advantages: analysis times can be significantly reduced, and the recovery and precision for all four THMs are better by liquid–liquid extraction. These advantages are especially important in the routine analysis of large numbers of samples.

In this work the application of a simple extraction step with *n*-pentane was applied to the analysis of sixteen halo-organic compounds, including the THMs, by GC with a capillary column. The proposed procedure was applied to the identification and quantification of these organic compounds in raw and supply water of the city of Salamanca (Spain), studying the effect of the different treatments (chlorination, flocculation and filtration) applied in the two town drinking water treatment plants on the formation of halo-organic compounds.

EXPERIMENTAL

Apparatus

The analyses were performed on a Varian Model 3700 gas chromatograph equipped with a ^{63}Ni electron-capture detector and a VOCOL fused-silica semi-capillary 30 m × 0.53 mm I.D. column with a 3.0-μm film.

The carrier and make-up gases were N-52 nitrogen at flow-rates of 5 and 20 ml/min, respectively.

After each 1-μl injection the column temperature was kept at 30°C for 8 min, then increased to 90°C at a rate of 2°C/min.

The temperatures of the electron-capture detector and the injector were 300 and 150°C, respectively.

The gas chromatograph was coupled to a Varian Model 9176 recorder and a Varian CDS Model 111 integrator.

Reagents

The extraction solvent was *n*-pentane, residues grade (Merck). Na_2SO_3 [analytical grade (Panreac)] was used as a sample preservative.

The individual standards of the halo-organic compounds were of analytical standards stockroom quality supplied by Kromxpek Analítica. The concentrations were 0.1 mg/ml in methanol.

The working solutions used for the qualitative and quantitative analyses and for control of the results (reagent purity, extraction recovery and detection limit) were prepared immediately before use by dilution of the standards with *n*-pentane.

Sample collection

Samples were collected in 120 ml amber-coloured glass vials previously washed with special detergents and dried at 110°C. As a preservative, 10 mg of Na_2SO_3 were added, without headspace in the vials, which were sealed hermetically by a septum and an aluminium cap.

Extraction technique

Aliquots of 5.0 ml of *n*-pentane were injected through the septum. These displaced an equal volume of water which was collected in another syringe. Both phases were shaken for 120 s and when equilibrium was reached 1 μl of the organic phase was injected into the chromatograph.

Quantification

The concentrations of the halo-organic compounds were determined by the addition to the samples of *cis*-1,3-dichloropropene as an internal standard before extraction at a concentration at which the height of the peak was similar to that of the halo-organic compounds present in the samples.

For control of the results, periodic calibration graphs were obtained of the compounds identified in the samples in the working concentration zone.

RESULTS AND DISCUSSION

Optimization of the method

Using standard working solutions, the optimum chromatographic conditions for the detection and quantification of the sixteen halo-organic compounds were determined (Table I).

n-Pentane was chosen as the extraction solvent

TABLE I

VOLATILE HALO-ORGANIC COMPOUNDS DETERMINED IN THIS STUDY

Compound	Retention time (min)	Detection limit (μg/l)
Methylene chloride (**a**)	4.3	4.3
1,1-Dichloroethane (**b**)	6.0	5.2
Chloroform (**c**)	8.0	0.9
Carbon tetrachloride (**d**)	9.9	0.4
1,2-Dichloroethane (**e**)	11.2	2.6
Trichloroethylene (**f**)	13.7	1.7
1,2-Dichloropropane (**g**)	14.7	3.5
Bromodichloromethane (**h**)	16.0	0.4
2-Chloroethylvinylether (**i**)	18.3	4.3
cis-1,3-Dichloropropene (**j**)	18.9	1.7
trans-1,3-Dichloropropene (**k**)	22.0	2.6
1,1,2-Trichloroethane (**l**)	22.6	2.6
Tetrachloroethylene (**m**)	23.5	1.7
Chlorodibromomethane (**n**)	25.3	0.4
Bromoform (**o**)	34.7	0.9
1,1,2,2-Tetrachloroethane (**p**)	36.7	0.9

because it induces fewer interferences in the response of the electron-capture detector (Fig. 1).

Extraction rate. The extraction rate with *n*-pentane was determined by shaking 120 ml of ultrapure water containing the four main THMs at three concentration levels: 2.0, 5.0 and 9.0 μg/l. The two phases were in equilibrium after 120 s (Fig. 2). The

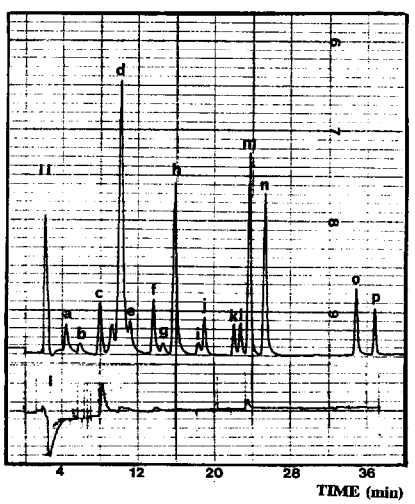

Fig. 1. (I) Chromatogram of *n*-pentane; (II) chromatogram of the multicomponent solution.

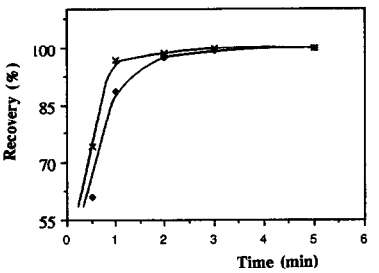

Fig. 2. Extraction rate for: (◆) chloroform and (×) bromoform at concentrations of 5.0 μg/l.

graphs obtained at the other concentrations and for the four THMs are similar to those shown here.

Extraction efficiency. Extraction efficiency was determined by shaking 120 ml of ultrapure water containing the sixteen halo-organic compounds at three concentrations ranging between 2.0 and 9.0 μg/l. The shaking time was 120 s and the concentrations of the compounds in the extracts were compared with standards prepared directly in *n*-pentane. Table II gives the recoveries obtained for the THM compounds; it is seen that they do not depend on concentration (small standard deviation) and are almost complete.

Detection limit. To determine the detection limits, ten different blank assays were performed, the interferences being negligible except for chloroform, an impurity of *n*-pentane, which was taken into account to obtain the detection limit of this compound.

The detection limit (Table I) ranged from 0.4 to 5.2 μ/l; for chloroform and bromoform it was 0.9 μg/l and for bromodichloromethane and chlorodibromomethane it was 0.4 μg/l.

Precision. By applying the optimum experimental conditions to eight vials containing 5.0 μg/l of the four main THMs and *cis*-1,3-dichloropropene as an internal standard a standard deviation ranging between 0.32 and 0.78 was obtained, together with a relative standard deviation in the range 8.7–18%.

Application of method

The method was applied to the determination of halo-organic compounds in raw water and in treated water in the city of Salamanca. The treated water is a mixture of water treated in two different plants (the "old" and "new" plants) and the water in each

TABLE II

EXTRACTION EFFICIENCY AT 2.0, 5.0 AND 9.0 μg/l

Compound	Extraction efficiency (%)			
	2.0 μg/l	5.0 μg/l	9.0 μg/l	Mean ± S.D.
Chloroform	90	98	97	95 ± 4
Bromodichloromethane	106	95	94	98 ± 6
Chlorodibromomethane	110	99	113	107 ± 7
Bromoform	108	105	106	106 ± 1

is treated in a slightly different way. To study the effect of the different treatments and processes on the formation of the halo-organic compounds samples were taken at different points, the locations of which in the different plants are shown in Fig. 3.

Eighty-eight duplicate analyses were made. These were raw (eleven) and treated (eleven) water samples, as well as samples from six selected steps (sixty-six) during the plant treatments from February

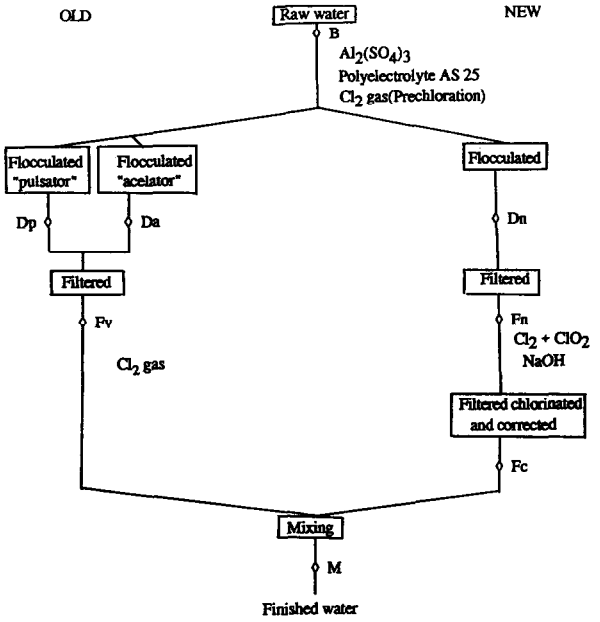

Fig. 3. Location of sampling points in the water treatment plants of the city of Salamanca. B = Raw water; Dp, Da = water treated with gaseous Cl_2 and flocculated with the "pulsator" or "acelator" in the "old" plant; Fv = water filtered in "old" plant after prechlorination step; Dn = water treated with gaseous Cl_2 and flocculated in the "new" plant; Fn = water filtered in "new" plant after prechlorination step; Fc = water treated with Cl_2 and ClO_2, filtered and pH corrected with NaOH in "new" plant; M = mixing point for Fc and Fv treated again with Cl_2.

to July 1991. The sampling frequency was fortnightly.

None of the sixteen halo-organic compounds was detected in any of the raw water samples. Chloroform and bromodichloromethane were formed in all the samples of treated water, whereas dichlorobromomethane and 1,1,2-trichloroethane were detected in 98.7 and 23.4%, respectively. Chloroform was always formed at the highest concentrations and chlorodibromomethane and 1,1,2-trichloroethane were present at values lower than the detection limit in most instances.

The concentrations of chloroform and bromodichloromethane were higher at the sampling points (Dn, Fn and Fc) in the "new" plant than in those corresponding to the "old" plant (Da, Dp and Fv) (Table III) because although the chlorination levels are similar in both plants (5–6 g Cl_2 per m^3), the greater efficiency of the flocculation and filtration processes in the "old" plant produces smaller amounts of organic matter (absorbance measurement at 254 nm). Additionally, it is seen that in sample Fc the maximum concentrations of both compounds are detected (a new treatment with Cl_2 and ClO_2 is performed) and that filtration does not significantly affect the level of formation of chloroform and bromodichloromethane in this plant (Student's *t*-test applied to Dp and Fv, and to Dn and Fv).

In the treated water, point M, an increase is seen in the concentration of chloroform during the sampling period, probably due to the increase in the temperature of the raw water between February and July, whereas the concentration of bromodichloromethane remained almost constant (Table IV). However, the mean respective concentrations, 9.59 and 2.58 μg/l, during the period from February

TABLE III

MEAN, MAXIMUM AND MINIMUM CONCENTRATIONS OF HALO-ORGANIC COMPOUNDS AT SAMPLING POINTS OF THE WATER TREATMENT PLANTS IN SALAMANCA (SPAIN)

Values given are mean ± standard deviation of eleven determinations with maximum and minimum concentrations during sampling in parentheses.

Sampling point	Concentration (μg/l)	
	Chloroform	Bromodichloromethane
Da	4.38 ± 2.05 (1.4–7.8)	0.99 ± 0.32 (0.5–1.4)
Dp	6.00 ± 2,31 (2.0–9.5)	1.31 ± 0.36 (0.8–1.8)
Fv	6.51 ± 3.08 (2.0–12.7)	1.54 ± 0.59 (1.0–2.6)
Dn	9.18 ± 4.35 (4.3–17.6)	1.96 ± 0.40 (1.4–2.7)
Fn	9.14 ± 4.49 (3.6–15.8)	1.99 ± 0.70 (1.0–3.2)
Fc	11.81 ± 5.89 (4.0–25.2)	2.61 ± 0.89 (1.5–4.1)

TABLE IV

VARIATION IN CONCENTRATIONS OF CHLOROFORM AND BROMODICHLOROMETHANE IN THE TREATED WATER IN SALAMANCA (SPAIN)

Sampling point	Concentration (μg/l)	
	Chloroform	Bromodichloromethane
1	5.3	2.8
2	3.1	1.9
3	7.3	3.0
4	7.2	1.7
5	17.2	2.8
6	7.1	1.8
7	10.6	2.4
8	15.4	2.3
9	15.8	2.8
10	6.5	2.5
11	10.0	4.3
Mean	9.59	2.58
Standard deviation	4.69	0.81
Relative standard deviation (%)	49	32

to July, 1991, are lower than the limits established by the World Health Organization.

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