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Purge-and-trap capillary gas chromatography with atomic emission detection for volatile halogenated organic compounds determination in waters and beverages

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Abstract

A method for the simultaneous determination of 10 volatile halogenated organic compounds (VHOCs), including four trihalomethanes (THMs), in waters and beverages was developed. The analytes were stripped from the aqueous sample by a flow of helium, preconcentrated in a capillary trap and thermally desorbed using a purge-and-trap (PT) system. This was followed by capillary gas chromatography with microwave-induced plasma atomic emission spectrometry (GC–AED). For element-specific detection, three wavelengths were monitored, corresponding to chlorine (479 nm), bromine (478 nm) and iodine (193 nm). Each chromatographic run took 21 min, including the purge time. After careful choice of the experimental conditions, the performance of the system was evaluated. Calibration curves were obtained by plotting peak area versus concentration and the correlation coefficients for linear calibration were at least 0.9987. Detection limits, calculated for 5 ml sample volume, ranged from 0.05 $\mu g\,l^{-1}$ for chloroform to 0.5 $\mu g\,l^{-1}$ for tetrachloromethane. The method was successfully applied to the quantitative analysis of water samples of different origin and also of several beer and juice samples. The tap water samples analyzed contain variable concentrations of the four trihalomethanes, ranging from 1.0 to 66.5 $\mu g\,l^{-1}$, depending of the compound. Whereas chloroform, bromodichloromethane and bromoform were found in some of the juice samples, only chloroform was detected in the beer samples. The method is reliable and can be used for routine monitoring in water and beverages.

Keywords: Water analysis; Atomic emission detection; Beverages; Purge-and-trap methods; Volatile halogenated organic compounds; Trihalomethanes

1. Introduction

Volatile halogenated organic compounds (VHOCs) are an important chemical class of water pollutants. The water used as drinking water or in a wide variety of industrial applications is frequently disinfected with chlorine. However, the reaction of chlorine with the organic matter present in waters, particularly humic and fulvic acids or seaweed metabolic breakdown products [1], produces a number of volatile chlorination by-products, some of which are suspected of being carcinogenic. Furthermore, high bromide levels in reservoirs used as sources of drinking water contribute to the formation of brominated and mixed bromo/chloro-disinfection by-products (DBPs). The first category of DBP identified in water was the trihalomethanes (THMs), with dichlorobromomethane, dibromochloromethane, tribromomethane and trichloromethane being by far the most common.

VHOCs have potentially adverse effects on human health, and are incorporated in the body via the lungs or by food and drinking water via the gastrointestinal tract and, to some extent, via the skin [2]. The US Environmental Protection Agency (EPA) has published a list of contaminants and their maximum contaminant level (MCL) in drinking water [3], which includes eight of the VHOCs analyzed in this paper. The maximum contaminant level permitted in drinking water for tetrachloromethane, 1,2-dichloroethane and dichloromethane has been set at 5 and 80 $\mu g\,l^{-1}$ for total trihalomethanes (TTHMs). These tolerance levels are less restrictive under Spanish Legislation (R.D. 140/2003), which has established an MCL for TTHMs of 150 $\mu g\,l^{-1}$, which is to be reduced to 100 $\mu g\,l^{-1}$ [4] on 31 December 2008.

Analytical methods for the determination of volatile organic compounds in water samples generally imply a

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preconcentration step, which, besides being the most labor-intensive step, is also the source of many errors. The compounds of interest must be separated from the matrix and concentrated in order to reach the levels necessary for the methods and detectors used. A wide number of techniques has been described in the literature for this purpose, including classical solvent extraction [5], and variations of the same, such as single-drop extraction (SDE) and solid-phase microextraction (SPME) [6], in an attempt to reduce the time needed and the volumes of organic solvent required. Headspace analysis (HS) and purge-and-trap (PT) techniques are commonly used for volatile organic compounds (VOCs) analysis in liquid samples. In the former, a part or all [7] of the headspace gas is introduced into the separation column, which can be at low oven temperatures, being the "cryogenic oven-trapping (COT)" [8]. With PT, the analytes are purged out of the sample by a gas-flow and subsequently trapped prior to analysis using either cryogenic [9–13] or sorbent traps [2,14–20]. Comparisons of the different methods for treating samples for volatile organic compound determination can be consulted in the bibliography [21–23]. Due to its high degree of sensitivity, purge-and-trap still remains the most frequently used preconcentration system for VOCs in water samples when gas chromatography is used, although to the best of our knowledge, few reports have been published on VOC determination using AED as a detection method in PT–GC [13–15]. In AED, the solutes eluting from the GC column are atomized in a microwave-induced plasma (MIP), while the resulting excited atoms and ions emit light as they return to the ground state. The polychromatic light is dispersed in a spectrometer and the emission intensity of the characteristic wavelengths is measured by a photodiode array. AED is a sensitive detection system for gas chromatography, providing selective information which cannot be obtained with other commonly used element-selective detectors [24,25].

In this study, procedures for the determination of ten volatile halogenated organic compounds, including trihalomethanes, in water, beer and juice samples, using AED as detection method in PT–GC are discussed. The method is rapid and involves minimal sample treatment.

2. Experimental

2.1. Chemicals

The studied VHOC standards came from various suppliers, Dr. Ehrenstorfer (Augsburg, Germany), Lab-Scan (Dublin, Ireland) and Supelco (Bellefonte, PA, USA) and their purity was, in every case, better than 98.3%. Their boiling points were between 40 and 150 °C, as shown in Table 1. Standard solutions of 3000 μg ml^{-1} of each compound were prepared by dissolving the standards in methanol of analytical-reagent grade (Merck, Barcelona, Spain) and stored in the dark at 4 °C. Working standard solutions were prepared daily by diluting the methanolic standards with high quality water obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) and also stored at 4 °C in the refrigerator. Silicone antifoam 30% (w/v) in water was obtained from Fluka (Buchs, Switzerland).

Table 1
List of compounds

Compound	Molecular formula	Boiling point (°C)	Monitored emission line (nm)	Retention time (min)
Iodomethane	CH_3I	42	I 193	5.97
Dichloromethane	CH_2Cl_2	40	Cl 479	6.24
Chloroform	$CHCl_3$	68	Cl 479	7.72
Tetrachloromethane	CCl_4	76	Cl 479	8.10
1,2-Dichloroethane	$C_2H_4Cl_2$	83	Cl 479	8.23
Bromodichloromethane	$CHBrCl_2$	87	Br 478	9.12
Tetrachloroethene	C_2Cl_4	121	Cl 479	10.19
Dibromochloromethane	$CHBr_2Cl$	117	Br 478	10.35
Bromoform	$CHBr_3$	149	Br 478	11.45
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	146	Cl 479	11.73

Hellium, nitrogen, oxygen and hydrogen (99.9999%) were purchased from Air Liquide (Madrid, Spain).

2.2. Instrumentation

The purge-and-trap sample enrichment system was a Tekmar Dohrmann 3100 model (Agilent, Waldbronn, Germany) which was controlled by Teklink (2.02 Version) software. The purging vessel was a 5 ml glass U-tube with frit sparger 0.5 in. top fit. This was rinsed three times with the sample before each experiment, and further rinsed three times with deionized Milli-Q water after each analysis. The purge vessel was thermostated using a lab-made system. A classic PT operating process was applied, including the three main steps: sample purging, analyte desorption and baking. Analytes were purged out from 5 ml of aqueous solution with a helium flow-rate of 40 ml min^{-1} and carried to a trap column (30.5 cm × 0.312 cm o.d.) packed with Tenax GC, silica gel and activated carbon, as recommended by the US EPA Method [26]. The purge-and-trap system includes a moisture control module (MCM). The volatile organic compounds were desorbed from the trap, after being concentrated, by opening the valves at 260 °C for 4 min. During the desorption step, the carrier gas was drawn through the trap in the opposite direction to the purge flow onto the column, in order to minimize band broadening at the beginning of the chromatographic column. Once the analytes had been desorbed, the trap was cleaned at 270 °C for 8 min, to avoid possible memory effects of the tailing compounds. The purge-and-trap system was directly coupled to the gas chromatograph in a direct split interface (DSI) configuration, set at 200 °C in order to avoid analyte condensation during the analyses. The end of the transfer line was directly inserted into the split injector of the GC.

An Agilent 6890 gas chromatograph was directly coupled by a transfer line to a G2350A microwave-induced plasma

Table 2
Experimental conditions of the PT–GC–AED system

PT conditions	Sample volume	5 ml
	Gas flow	40 ml min^{-1} He
	Purge cycle	9 min at 30 °C
	Desorb cycle	4 min at 260 °C (preheat 245 °C)
	Bake cycle	8 min at 270 °C
	Trapping material	Tenax-silica gel/charcoal
GC conditions	Injection port	250 °C, split ratio (40:1)
	Capillary column	DB-624 (30 m × 0.32 mm i.d. × 1.80 μm)
	Carrier gas	Helium, 1 ml min^{-1}
	Oven program	40 °C (3 min)
		100 °C at 30 °C min^{-1} (2 min)
		200 °C at 25 °C min^{-1} (1.6 min)
GC–AED interface parameters	Transfer line	DB-624
	Transfer line temperature	200 °C
AED conditions	Reagent gases	Cl and Br: O_2 at 25 psi
		I: H_2 and O_2 at 7.1 and 25 psi
	Spectrometer purge flow	Nitrogen, 2.5 l min^{-1}
	Helium make-up flow	40 ml min^{-1} (measured with reagent gases turned on)
	Solvent vent off-time	0–4 min
	Cavity temperature	200 °C

atomic emission detector (Agilent). Updated G2070AA ChemStation application with the G2360AA GC–AED software was used to control and automate many features of the GC and AED systems, and for data acquisition and treatment. The experimental conditions for the chromatographic separation and the detection system are summarized in Table 2. Filter and backamount adjustment in the AED were set according to Agilent default specifications. The elements analyzed and their emission lines, in nanometers, were: chlorine 479, bromine 478 and iodine 193.

Since the retention time for the most retained compound was 11.73 min, as shown in Table 1, the analysis of the 10 VOCs studied can be performed within 45 min after sampling, taking into account that two separate injections have to be performed to monitor the chlorine, bromine and iodine emission lines.

An S.P. Selecta centrifuge (Selecta, Spain) was used for the juice samples. A domestic microwave oven (maximum heating power 1450 W) was used for stability studies of the volatile organic compounds.

2.3. Sampling

Ten tap water samples were obtained from different cities of Spain. Two 100 ml volumes of tap water were collected in glass bottles and care was taken to ensure that all the recipients were completely filled with the samples to avoid the presence of a gaseous phase. Two different mineral waters and a rain water sample were also obtained. All water samples were kept at 4 °C before their analysis (which was performed normally within 48 h of arrival at the laboratory).

Three beer samples of different trademarks and five juice samples were also analyzed.

2.4. Sample treatment and recovery assays

No sample treatment was required for any of the water samples, but in the case of some of the tap waters a 1:10 dilution was required, because of the high THM content. Two drops of silicone antifoam were added to 20 ml of beer and juice to avoid the foam normally produced during the purge step. Besides, the juice samples were centrifugated prior to the addition of the antifoam agent. Beverages were not submitted to dilution for quantification purposes.

Sample volumes of 5 ml (the maximum volume permitted in the purging vessel) were submitted to the optimized procedure.

All samples were spiked by adding from 7.5 to 140 ng of the volatile organic compounds, depending on the compound, to 5 ml of sample.

3. Results and discussion

Two sequential chromatographic runs were required to obtain chromatograms for C (496 nm), Cl (479 nm), Br (478 nm) and I (193 nm), since GC–AED permits elements to be scanned in groups on condition that close emission line wavelengths and the same scavenger gases are used.

3.1. Optimization of the purge-and-trap conditions

The parameters were varied in order to obtain the highest degree of sensitivity and the best repeatability for the compounds investigated. For this, standard solutions of the analytes at 10 μg l^{-1} in deionized water were used. Evaluation of the purge-and-trap step was made for each compound by comparing peak areas obtained by either purge-and-trap

injections under different experimental conditions. All experiments were carried out in triplicate. Care was taken to remain below the breakthrough volume of the trap for all the experiments. When purge flow is too low, quantitative purging is impossible, whereas if purge flows are too high, an ineffective removing of the water happens, and the trap gets blocked. Therefore, the purge gas flow-rate was set at 40 ml min^{-1} in accordance with the manufacturer's recommendations. A certain time is necessary to purge the compounds out of the sample, depending on the polarity and the boiling point of each analyte. The purge time was varied between 7 and 11 min with a desorption cycle of 4 min at 220 °C and a purge temperature of 35 °C. Finally, a value of 9 min was chosen as optimal, since purge times higher than 9 min led to a slight decrease in the peak area of most of the studied compounds or had no significant effect. Indeed, very long purging times decreased the signals because the helium itself causes stripping of the trapped analytes. The results obtained are shown in Fig. 1A for iodomethane, chloroform, bromodichloromethane and bromoform (covering in this way the whole range of boiling points of the studied compounds), where the influence of the purge time on the extraction yield is expressed as peak area. As regards desorption time, it was varied between 2 and 6 min, finally being fixed at 4 min, which provided the highest peak areas for all the compounds (Fig. 1B).

The purge vessel temperature during the purging step was varied from ambient to 45 °C. As can be seen in Fig. 1C, purge efficiencies did not vary significantly between 25 and 35 °C. For temperatures higher than 35 °C the peak areas decreased for all the studied compounds, including the least volatile, probably due to the amount of water reaching the trap which decreased sensitivity, so ambient temperature was maintained in all the experiments. The influence of the trap temperature during the adsorption step was studied between 25 and 40 °C, and the results obtained appear in Fig. 1D. Although this parameter did not have a significant influence on the efficiency of the process, the maximum peak area for all analytes was obtained at 30 °C, for which reason this value was chosen as optimal. Experiments were performed to check the influence of the trap temperature used during the desorption step by increasing it from 180 to 280 °C. The peak areas for all the compounds slightly increased up to 260 °C, while higher temperatures decreased the signals, as can be seen in Fig. 1E. This parameter was therefore fixed at 260 °C. Finally, the transfer line temperature was varied between 100 and 250 °C and, as expected, increasing the temperature up to 200 °C improved the extraction efficiency since high temperatures theoretically prevent condensation of the compounds inside the transfer line. However, temperatures above 200 °C decreased the signal, and so this was selected as the transfer line temperature (Fig. 1F). The chosen conditions for the purge-and-trap system are summarized Table 2.

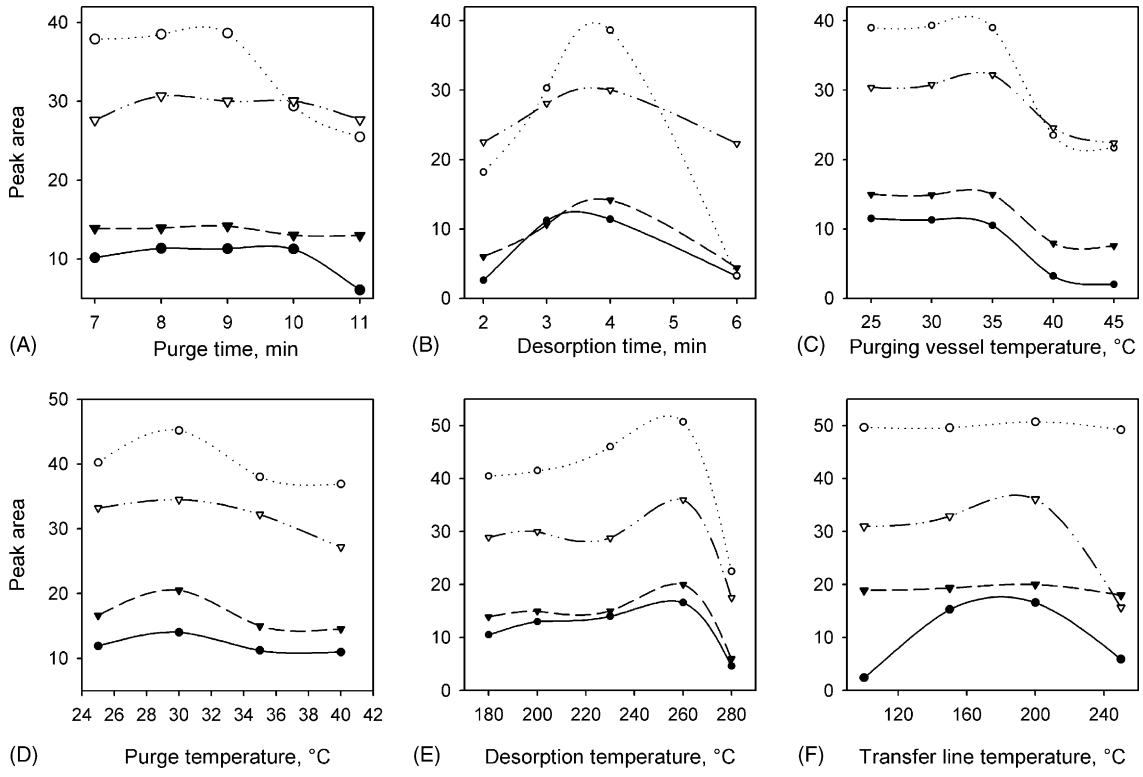

Fig. 1. Effect of: (A) purge time; (B) desorption time; (C) purging vessel temperature; (D) purge temperature; (E) desorption temperature and (F) transfer line temperature on the purging of iodomethane (●), chloroform (○), bromodichloromethane (▼) and bromoform (▽). Concentration of each compound is 10 μg l^{-1}.

3.2. Chromatographic and AED parameters

Preliminary experiments were conducted to choose the temperature program that best allowed separation of the ten volatile organic compounds in the lowest possible time. The selected program temperature allowed elution of the 10 compounds between 5.8 and 12 min, as shown by their respective retention times in Table 1. The chromatogram started at 40 °C before being increased to 100 °C which was maintained for 2 min to elute iodomethane and dichloromethane; as the oven temperature was increased to 200 °C thus permitting chloroform, tetrachloromethane, 1,2-dichloroethane, bromodichloromethane, tetrachloroethene and dibromochloromethane to elute. Once the oven temperature was established at 200 °C bromoform and 1,1,2,2-tetrachloroethane were eluted. Separation was carried out using a constant helium flow rate of 1 ml min^{-1}, since higher flow rates resulted in overlapping peaks and lower flow rates increased peak widths and hence analysis time. The injection temperature is the temperature of the compounds entering the analytical column after passing through the transfer line between the purge-and-trap system and the GC. This temperature, therefore has to be higher or equal to 200 °C. The injection temperature was varied between 200 and 300 °C. A maximum value was obtained at 250 °C for five of the studied compounds, iodomethane, tetrachloroethene, dibromochloromethane, bromoform and 1,1,2,2-tetrachloroethane. No effect was observed on the rest of the compounds by varying the injection temperature and so, 250 °C was the selected injection temperature.

After choosing the most suitable chromatographic parameters, the detector operating conditions were studied to obtain the highest sensitivity for the studied volatile organic compounds. The detector parameters investigated were reagent gases pressure and make-up gas flow rate.

To monitor the chlorine and bromine emission lines, oxygen is the only scavenger gas needed, since it prevents carbonaceous deposition on the wall of the discharge tube. The influence of oxygen pressure was studied between 20 and 35 psi since it is known that pressures under 20 psi do not prevent the accumulation of elemental carbon in the AED discharge tube [27]. A slight increase in sensitivity was observed at 25 psi for all the studied compounds (Fig. 2A), and so this value was adopted. Both hydrogen and oxygen are required for monitoring the iodine emission line, and so, to determine the optimum hydrogen pressure, oxygen pressure was held constant at the previously optimized value, 25 psi, while the hydrogen pressure was varied between 5 and 15 psi. The sensitivity was maximum for iodomethane at 7 psi, which was the value adopted.

To select the optimum value for the helium make-up gas flow that allows maximum sensitivity, the flow-rate was varied from 30 to 45 ml min^{-1}. No signals were obtained for the studied compounds for 30 ml min^{-1} make-up flow rate. Maximum sensitivity was obtained at 35 ml min^{-1} in the case of the four most retained compounds, while the rest of the compounds provided a maximum signal at 40 ml min^{-1}, as can be seen from Fig. 2B. The helium make-up gas flow was therefore adjusted to 40 ml min^{-1}.

The transfer line and the cavity temperatures were optimized between 150 and 300 °C, for a standard mixture solution. The best results were obtained at 200 °C for the transfer line temperature, while no significant effects on sensitivity were obtained when the cavity temperature was varied. Therefore 200 °C was the selected value, following the manufacturer's recommendations of using similar temperatures for the transfer line and the cavity.

Fig. 3 shows the chromatograms obtained for a standard mixture under the optimized conditions. Note that, although tetrachloromethane and 1,2-dichloroethane are eluted very close to each other, this poses no problems for quantification purposes, as can be seen from the results obtained.

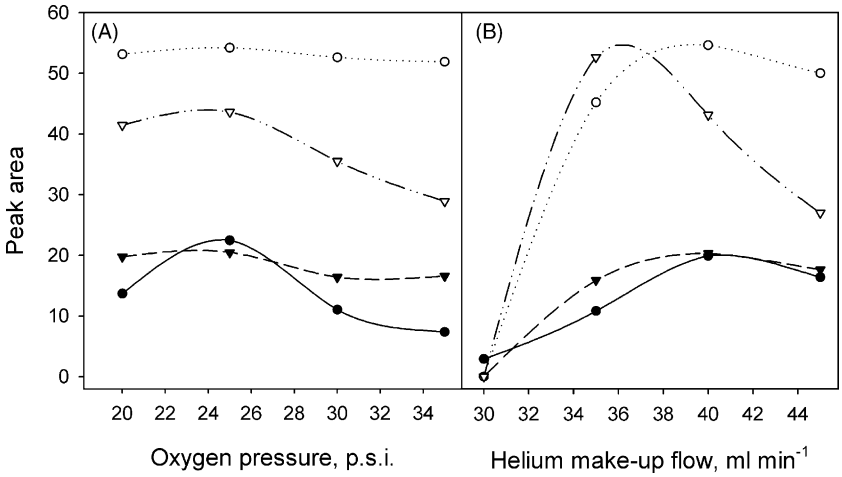

Fig. 2. Influence of: (A) the reagent gases and (B) the helium make-up flow on the responses of iodomethane (●), chloroform (○), bromodichloromethane (▼) and bromoform (▽). Concentration of each compound is 10 μg l^{-1}.

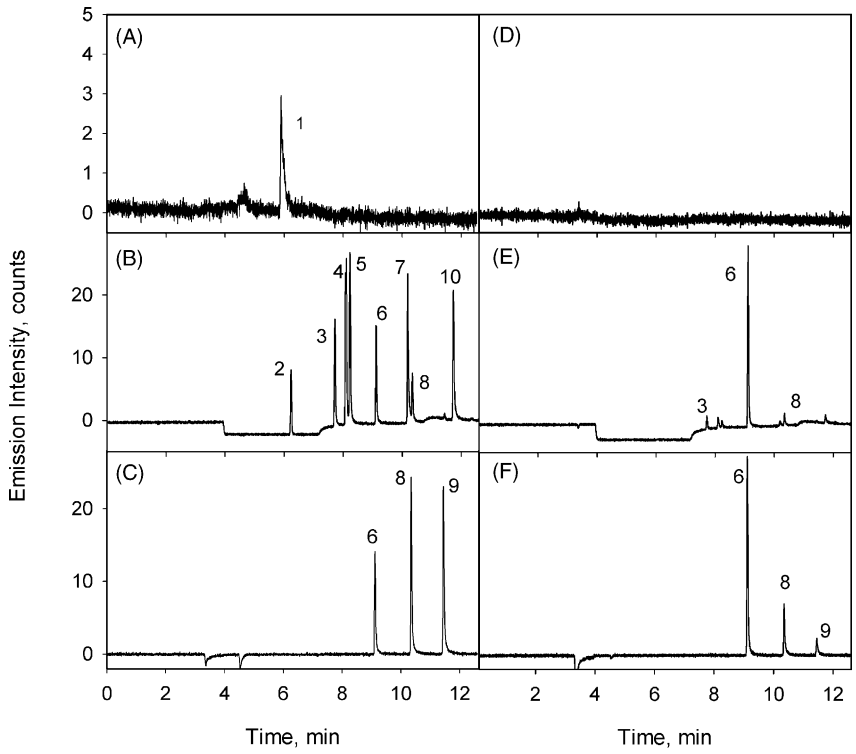

Fig. 3. PT–GC–AED chromatograms obtained from a standard mixture of the volatile organic compounds (A, B, C) and tap water 6 (D, E, F). (A, D) I 193 nm, (B, E) Cl 479 nm, and (C, F) Br 478 nm. Concentrations of the standard mixture: (1) iodomethane, 10 $\mu g\,l^{-1}$; (2) dichloromethane, 20 $\mu g\,l^{-1}$; (3) chloroform, 3 $\mu g\,l^{-1}$; (4) tetrachloromethane, 18 $\mu g\,l^{-1}$; (5) 1,2-dichloroethane, 4 $\mu g\,l^{-1}$; (6) bromodichloromethane, 7 $\mu g\,l^{-1}$; (7) tetrachloroethene, 10 $\mu g\,l^{-1}$; (8) dibromochloromethane, 4 $\mu g\,l^{-1}$; (9) bromoform, 4 $\mu g\,l^{-1}$ and (10) 1,1,2,2-tetrachloroethane, 5 $\mu g\,l^{-1}$.

Tetrachloroethane and dibromochloromethane are also eluted very close, but because they are monitored on different emission lines, there is no possibility of quantification errors arising.

The depression of the baseline observed between 4 and 8 min approximately, for the chromatograms corresponding to chlorine emission line, is produced by the water entering the analytical column. On the other hand, the two negative peaks appearing in the chromatograms corresponding to the bromine emission line, are due to the selected value for the backamount, which eliminates the interference of carbon.

3.3. Calibration, precision and detection limits

For calibration, Milli-Q water standards at five concentration levels were prepared and 5 ml aliquots of each standard were purged and analyzed. Two replicates for each calibration level were made. Linear calibration curves were obtained for all the compounds in different concentration ranges, depending on the compound. Table 3 shows the characteristics of the calibration graphs used to quantify each compound, with the emission wavelength indicated in Table 1 being the most sensitive in every case. Correlation coefficients showed a high degree of correlation

Table 3
Analytical data for the target compounds (as the entire compounds)

Compound	Slope[a] ($l\,\mu g^{-1}$)	Ordinate[a]	Correlation coefficient	Linearity range ($\mu g\,l^{-1}$)
Iodomethane	1.7236 ± 0.0359	−0.1928 ± 0.1460	0.9994	2.0–20.0
Dichloromethane	0.5766 ± 0.0131	0.6357 ± 0.1144	0.9992	2.5–25.0
Chloroform	5.4870 ± 0.0828	−0.7827 ± 0.2445	0.9989	0.4–5.0
Tetrachloromethane	0.5940 ± 0.0144	−0.0614 ± 0.1551	0.9994	2.5–30.0
1,2-Dichloroethane	4.4825 ± 0.0374	−0.7629 ± 0.1212	0.9999	0.5–10.0
Bromodichloromethane	2.0845 ± 0.0352	−0.5118 ± 0.1600	0.9994	1.0–10.0
Tetrachloroethene	0.7580 ± 0.0381	−0.2403 ± 0.1180	0.9989	2.0–10.0
Dibromochloromethane	4.0692 ± 0.0959	−0.2626 ± 0.1876	0.9988	0.5–10.0
Bromoform	4.3626 ± 0.1743	−0.4975 ± 0.1546	0.9987	0.5–10.0
1,1,2,2-Tetrachloroethane	3.6893 ± 0.0683	−0.4491 ± 0.1349	0.9993	0.5–10.0

[a] Mean ± standard deviation ($n = 3$).

Table 4
Accuracy and sensitivity for the studied VOCs (as the entire compounds)

Compound	R.S.D. (%)[a]	Detection limit ($\mu g\,l^{-1}$)	Quantification limit ($\mu g\,l^{-1}$)
Iodomethane	3.9 (5.0)	0.20	0.70
Dichloromethane	8.5 (5.0)	0.40	1.30
Chloroform	8.5 (1.0)	0.05	0.16
Tetrachloromethane	7.3 (4.0)	0.50	1.70
1,2-Dichloroethane	4.7 (2.5)	0.06	2.00
Bromodichloromethane	3.7 (3.0)	0.18	0.60
Tetrachloroethene	10.0 (3.0)	0.30	1.00
Dibromochloromethane	3.1 (3.0)	0.08	0.26
Bromoform	4.0 (2.0)	0.05	0.17
1,1,2,2-Tetrachloroethane	5.5 (2.0)	0.06	2.00

[a] Values in brackets are the compound concentrations in $\mu g\,l^{-1}$.

between concentration and peak area for the studied compounds, ranging from 0.9987 for bromoform to 0.9999 for 1,2-dichloroethane. The repeatability was calculated using the relative standard deviation for 10 successive injections of a standard mixture and was in the range of 3.1–10.0% (R.S.D.) as shown in Table 4. Detection limits were calculated using a signal-to-noise ratio of 3 for all the investigated compounds. The values are also given in Table 4, along with the quantification limits calculated using a signal-to-noise ratio of 10.

3.4. Real samples

The developed method was used to analyze the 10 analytes in different tap water samples and the results obtained appear in Table 5. Only trihalomethanes were found in the tap water samples. For the water sample purified using a domestic filter system, the concentrations of the four THMs decreased notably, as shown in Table 5. The water sample named as Tap water 1 provided a TTHM concentration higher than the maximum contaminant level permitted by the Spanish Legislation [4]. No VHOCs were detected in the two mineral waters or the rain water analyzed. All samples were analyzed in triplicate. Fig. 3 shows the chromatograms obtained for a tap water sample using different emission lines.

The influence of high temperatures on the THMs was studied for a real tap water sample. When the sample was heated in a domestic microwave oven for 2 min at maximum power, the THM concentrations decreased. When the sample was submitted to heating times higher than 2 min these concentrations decreased even more, and signals were obtained for 1,2-dichloroethane, tetrachloroethylene and 1,1,2,2-tetrachloroethane, as can be seen in Fig. 4.

The optimized procedure was also applied to the determination of VHOCs in beer and juice samples after the addition of antifoam to the sample in the purge vessel [2] since the matrix of these samples causes serious foaming during the purge step. The slopes of the calibration graphs with the standards prepared in deionized water and the standard addition calibration graphs obtained for a beer and a juice sample spiked with three levels of concentration were similar, confirming the absence of any matrix effect. The results obtained for the beverages (Table 5) show that chloroform was the only analyte found in the analyzed beer samples, whereas bromodichloromethane and bromoform were also found in some of the analyzed juice samples. The recoveries of the VOCs from a spiked beer varied from 96.5 to 103.4 and from a spiked juice from 96.4 to 104.2, with an average recoveries ± S.D. ($n = 90$) of 99.8 ± 2.0 and 100.0 ± 1.8 for beer and juice, respectively.

Table 5
Concentrations[a] of trihalomethanes in different matrices ($\mu g\,l^{-1}$)

Samples	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform
Tap water 1	28.4 ± 1.9	55.3 ± 5.6	66.5 ± 5.5	24.7 ± 2.1
Tap water 2	30.5 ± 3.2	42.0 ± 5.1	47.9 ± 2.4	16.1 ± 0.4
Tap water 3	15.6 ± 0.1	25.8 ± 1.4	40.0 ± 2.5	24.7 ± 0.3
Tap water 4	17.7 ± 0.2	25.4 ± 2.8	30.0 ± 1.3	15.1 ± 0.1
Tap water 5	40.8 ± 0.1	5.0 ± 0.3	ND	ND
Tap water 6	5.4 ± 0.1	3.1 ± 0.1	2.7 ± 0.1	2.1 ± 0.1
Tap water 7	1.0 ± 0.1	10.0 ± 0.1	2.0 ± 0.8	1.8 ± 0.2
Tap water 8	1.0 ± 0.1	ND	4.4 ± 0.1	7.7 ± 0.1
Tap water 9	27.6 ± 0.5	38.9 ± 2.6	46.2 ± 0.7	16.0 ± 0.1
Filtered tap water 9	9.7 ± 1.4	10.8 ± 0.2	5.5 ± 0.1	ND
Beer sample 1	5.0 ± 0.4	ND	ND	ND
Beer sample 2	1.5 ± 0.1	ND	ND	ND
Beer sample 3	2.8 ± 0.3	ND	ND	ND
Pineapple juice	1.0 ± 0.1	2.1 ± 0.2	ND	4.2 ± 0.4
Lemon juice	2.1 ± 0.2	ND	ND	ND
Apple juice	ND	ND	ND	3.5 ± 0.1
Orange juice	3.0 ± 0.1	ND	ND	ND
Forest fruits juice	1.1 ± 0.1	ND	ND	2.5 ± 0.1

ND means non detected.
[a] Mean ± standard deviation ($n = 3$).

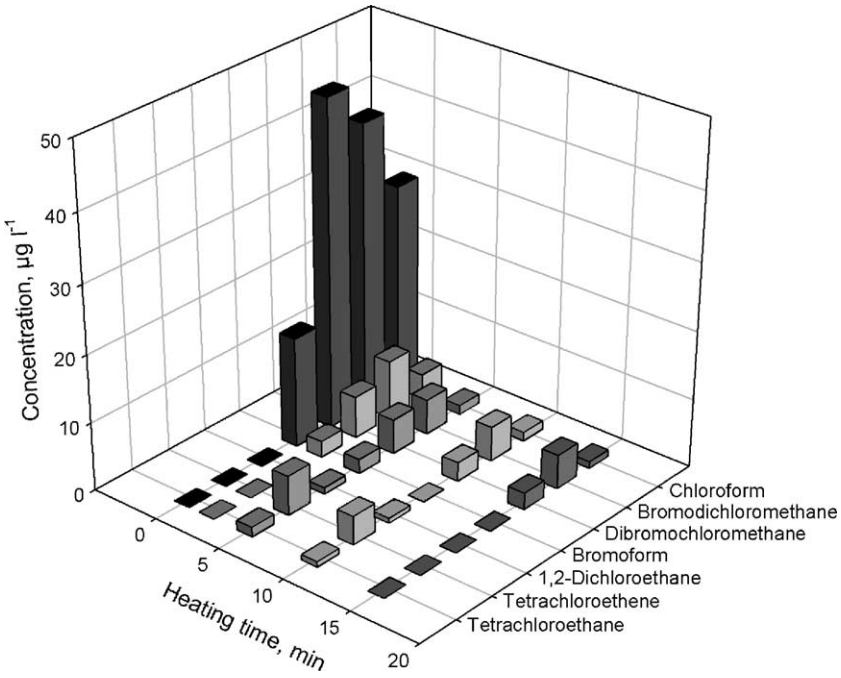

Fig. 4. Variation in the concentrations of the volatile halogenated organic compounds in tap water 7 with heating time.

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