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Simultaneous determination of halogenated neutral and acidic disinfection by-products in drinking water by closed-loop stripping extraction and capillary gas chromatography

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Abstract

The analytical capabilities of Grob closed-loop stripping analysis technique were evaluated for the determination, in drinking water, of trihalomethanes, haloacetonitriles, haloacetic acids, chloropicrin, halogenated ketones and chloral hydrate, reported as chlorination disinfection by-products. Thus by one-step enrichment and isolation procedure and subsequent analysis by capillary gas chromatography with electron-capture detection, organic polar and non-polar disinfection by-products could be analyzed at levels as low as 0.5 ng/l for trihalomethanes, 1 ng/l for haloacetonitriles and 45–72 ng/l for haloacetic acids.

Keywords: Water analysis; Closed-loop stripping analysis; Extraction methods; Halogenated compounds; Trihalomethanes; Haloacetonitriles; Haloacetic acids; Halogenated ketones; Organochlorine compounds

1. Introduction

Water chlorination for disinfection purposes leads to the formation of a wide range of halogenated compounds from natural organic matter [1,2]. The most common disinfection by-products (DBPs) are trihalomethanes (THMs), haloacetonitriles (HANs), haloacetic acids (HAAs), chloropicrin (CP), halogenated ketones (HAKs) and chloral hydrate (CH) [3–6]. In addition, high bromide levels in water reservoirs used as sources of drinking water, can significantly contribute to the formation of brominated and mixed bromo/chloro-DBPs during chlorination [7–9]. This can be explained by the oxidation of bromide to hypobromous acid (HOBr), which reacts in an analogous manner to hypochlorous acid (HOCl), to form the brominated species [7].

Screening methods for various DBPs in drinking water generally consist of an appropriate extraction and isolation step by which compound enrichment is achieved. This is then followed by derivatization (e.g. for HAAs) and chromatographic determination. Due to the differences in the chemical structures, polarity, and volatility of DBPs the determination of trace concentration (e.g. ng/l) in drinking water is not a trivial matter. Purgeable halocarbons, such as THMs, are usually analyzed in drinking water by the ''purge and trap'' technique followed by gas chromatography [10–13]. Although this method is very well suited for the most volatile fraction of DBPs, giving

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low method detection limits (MDLs) for THMs (0.05–0.2 μg/l), it is not appropriate for the more polar DBPs such as HANs and HAAs. The determination of THMs is only a specific parameter used to characterize the presence of chlorination DBPs in drinking water. THMs represent only the very volatile fraction of DBPs, which does not represent the bulk of total halogenated organic compounds [2]. Previous studies have shown that most of the mutagenic activity in chlorinated drinking water has been associated with non-volatile fraction [14]. Among the major components of this fraction are the HANs and especially HAAs. Liquid–liquid extraction (LLE) by using various solvents has been used for the determination of THMs, HANs, HAKs, CP, CH [4,9] and HAAs [15,16]. LLE for the neutral halogenated DBPs was achieved by methyl *tert*-butyl ether (MTBE) [4] or *n*-pentane [9]. In both cases gas chromatography with electron-capture detection (GC–ECD) and/or gas chromatography with mass spectrometry (GC–MS) were used for qualitative and quantitative determination. MDLs ranging from 0.002 (chloroform) to 0.092 (trichloroacetonitrile) μg/l were reported [4]. The determination of HAAs, on the other hand, requires a second extraction procedure with subsequent esterification [15–17]. Simultaneous extraction–derivatization [18] and ion chromatography [19], have also been proposed for the determination of HAAs. MDLs values for the HAAs determination varied in the ranges 0.05–0.10 μg/l [15–17], 0.06–0.2 μg/l [18] and 8–80 μg/l [19].

The determination of semi-volatile organic compounds in drinking water at the ng/l level has been reported by Grob and co-workers [20–23] using a closed-loop stripping analysis (CLSA). Later Giger et al. [24] applied this method to trace the source of chlorinated volatile hydrocarbons in ground and lake water. Coleman et al. [25] used a modified CLSA methodology to concentrate organic contaminants and disinfection by-products, which were then analyzed by GC–ECD or GC–MS. A method based on Grob's CLSA technique is also proposed by Standard Methods [26] for the analysis of drinking water contaminants, such as US Environmental Protection Agency (EPA) priority pollutants and the earthy-musty-smelling compounds (e.g. methylisoborneol and geosmin).

The main objective of the present study was to evaluate the analytical capabilities of Grob CLSA technique for the determination (at the low ng/l level) of the most common non-polar, and polar halogenated DBPs [27,28] by one-step enrichment and isolation procedure and subsequent capillary gas chromatography GC–ECD analysis.

2. Experimental

2.1. Reagents

The Trihalomethane Calibration Standard Mix [containing trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM)], tetrachloromethane (TCC) and the Halogenated Volatiles Mix 551B [containing trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), 1,1-dichloro-2-propanone (1,1-DCP), 1,1,1-trichloro-2-propanone (1,1,1-TCP), chloropicrin (CPN)] were purchased as high-purity stock solutions from Supelco (Deisenhofen, Germany). Supelco also supplied dibromoacetic acid (DBAA), dichloroacetic acid (DCAA) (purity>95%) and the internal standards 2-bromo-1-chloropropane and 1,2,3-trichloropropane (purity 99%).

Anhydrous sodium sulfate, for organic trace analysis was purchased from Merck (Darmstadt, Germany), and was baked at 550°C for at least 4 h before use. Carbon disulfide was of Uvasol grade, while acetone, methanol and dichloromethane were of SupraSol grade. All solvents were obtained from Merck. Organic-free water was made by Modulab system from US-Filter (Lowell, MA, USA).

Stock solutions of all the above compounds were fresh weekly prepared in methanol and stored in dark in a refrigerator (at − 5°C).

2.2. Sampling and storing

Nineteen chlorinated drinking (tap) water samples were collected from the Athens urban area (center of Greece, $4 \cdot 10^6$ inhabitants) from July 1996–April 1998, and twenty-eight chlorinated drinking (tap) water samples from the urban area of Heraklion

(northeastern coast of the Island of Crete, 150 000 inhabitants) from July 1995–October 1997.

Each water sample was collected and analyzed in the same glass bottle (1.2 l stripping gas bottle) to minimize contamination and errors introduced by sample transfer [25,26]. The stripping bottle was rinsed before sampling with the water sample. A 1 ml volume of a concentrated aqueous solution of sodium thiosulfate was then added as dechlorinating agent. In Standard Methods (Method 6040B [26]) was reported that dechlorinating agents may affect the disinfection by-products. For this reason the use of sodium thiosulfate was checked for both recovery studies and real samples. No relevant impact on quantitation (>5%) and qualitative composition was observed. The bottle was filled to the top with the sample leaving no headspace, and sealed with the appropriated glass stopper. Samples were stored at 4°C and analyzed, the latest, within three days [29].

2.3. CLSA apparatus

CLSA was performed in a commercially available apparatus (Brechbühler, Zurich, Switzerland) designed according to Grob and co-workers [20–23]. Briefly, the organic compounds were air stripped from a water sample and trapped on 1.5 mg activated carbon filter (Brechbühler). Air was continually recirculated through the hermetically closed-loop system by means of a pump. The water sample was immersed in a thermostatically controlled water bath. The gas stream leaving the sample was heated about 12–13°C above the water bath temperature in order to prevent water condensation, and optimize the absorption of organics onto the activated carbon filter [23].

2.4. CLSA procedure

The activated carbon filter (ACF) was cleaned before each application by successive rinsing with the following solvents: carbon disulfide, organic-free water, acetone and finally methylene chloride. The filter was then placed in the oven at 150°C for 2 h. Before stripping ACF was rinsed five times with CS_2 and dried in the hood.

The PTFE connections were cleaned with methylene chloride and acetone, and then stored in acetone until next use. Stripping bottles were cleaned by rinsing with Nanopure water, acetone (three times) and methylene chloride, and then placed in the oven at 180°C for at least 4 h. Likewise, vials were flushed seven times with acetone and methylene chloride, and baked at 180°C. Before use, vials were rinsed several times with CS_2 and dried with a drier in the hood.

Prior to the CLSA, samples were prepared according to Hwang [30]. In the water sample (ca. 900 ml), 70 g of pre-cleaned and oven-dried sodium sulfate [30] were added. The sample was stirred with a magnetic stirrer for 30 s. The stirrer was then removed and the sample was spiked with 10 μl of the internal standard solution (in methanol). The internal standards were used for identification purpose [through adjusted retention time (ARt); see below]. The sample was then immersed in the 35°C water bath. The ACF was inserted in its holder of the closed-loop, and the sample was stripped of organics for 2 h with the use of the pump. After this the ACF was removed from the holder and linked to a clean vial via a dry PTFE connection. The extraction of DBPs from ACF was performed as described by Grob and Zürcher [23], and Coleman [25] using 30 μl of carbon disulfide. The extraction efficiency of the ACF by CS_2 was evaluated. The ACF (after the CLSA) was extracted three consecutive times in order to examine if more than one extraction is needed in order to obtain the highest stripped amount of each analyte from the filter. With a single extraction more than 90% of each stripped compound was recovered, except for DCAN, BCAN and DBAN which by one single extraction were recovered with yields ranging from 73 to 79% of the stripped amount.

A 1 μl volume of CS_2 DBPs of the final solution was injected to the capillary GC–ECD for the analysis.

2.5. GC–ECD and GC–MS analysis

Aliquots of the activated carbon trap extracts were analyzed in a Hewlett-Packard gas chromatograph 5890IIB equipped with a ^{63}Ni electron-capture detector. Separation was performed in two different Hewlett-Packard HP-5 (column A: 1.05 μm film thickness, 50 m×0.32 mm I.D. and column B: 1.00

μm film thickness, 60 m×0.32 mm I.D.) fused-silica capillary columns. Hydrogen (purity 99.999%) was used as carrier gas with a back-pressure of 80.5 (50 m) and 97.2 (60 m) kPa. Nitrogen (ECD quality) was used as make-up gas (60 ml/min). Injection, at 200°C, was accomplished in the split-less mode (30 s). The chromatographic conditions were the following: (a) for the 50 m HP-5 column, 35°C (10 min), 35–100°C (5°C/min), 100°C (3 min), 100–180°C (8°C/min) and 180°C (3 min). The ECD temperature was set at 300°C; (b) for the 60 m HP-5 column, 35°C (15 min), 35–100°C (5°C/min), 100°C (3 min), 100–180°C (8°C/min) and 180°C (5 min). The ECD temperature was set at 300°C. The capillary fused-silica column (Hewlett-Packard HP-5MS with 0.25 μm film thickness, 30 m×0.25 mm I.D.) was directly connected to a Hewlett-Packard 5971A mass-selective detector, which operated by electron ionization, in the full scan mode. The electron impact ionization mode conditions were the following: electron energy 70 eV; ion source temperature 195°C; mass range 35–450 m/z; electron multiplier voltage 1700–1800 V. The same chromatographic and injection conditions as for the 50 m column were used for the GC–MS analysis. Helium was used as carrier gas with a back-pressure of 80.5 kPa.

2.6. Ion and organic carbon analysis

Ground water samples were filtered, prior to analysis, with two filters: a 0.45 μm (Gelman IC polyethersulfone), and a 0.2 μm Whatman Anotop IC. The ion chromatograph pump (Alltech 325) was equipped with an Ionpac (50×4 mm) pre-column and an Ionpac AS12A (200×4 mm) analytical column (Dionex, Sunnyvale, CA, USA). A 100 μl loop was used for the sample injection. The eluent consisted of 2.7 m*M* Na_2CO_3 and 0.3 m*M* $NaHCO_3$, with a flow-rate of 1.5 ml/min. The conductivity was measured using an Alltech 320 conductivity detector. Chemical suppression was obtained with a Dionex Anion Micro-Membrane Suppressor AMMS-I. We followed the ion analysis procedure according to EPA Method 300 [31].

For total organic carbon (TOC) analysis an O.I. Analytical Model 700 TOC Analyzer was used. This instrument uses the persulfate oxidation procedure at 100°C, with subsequent purging and trapping of CO_2 followed by a non-dispersive infrared (NDIR) detection. We followed the TOC analysis procedure according to Standard Methods (Method 5310 [32]). TOC concentration was taken as the average of six replicate injections.

2.7. Definitions and calculations

(I) The adjusted retention time (ART) for each analyte was calculated as follows:

$$\mathrm{ART} = \frac{t_x - t_s}{t_s} \tag{1}$$

where t_x and t_s are the retention times of compound and internal standard, respectively. The 2-bromo-1-chloropropane (BCP) was used as chromatographic identification standard for trihalomethanes and the 1,2,3-trichloropropane (TCP) for all the other compounds.

(II) The percent recovery of each standard was calculated, according to the following equation:

$$\%\mathrm{Recovery} = \frac{C_x(\mathrm{ng}) - C_b(\mathrm{ng})}{C_o(\mathrm{ng})} \times 100 \tag{2}$$

where C_x, C_b and C_o are the amounts of each analyte determined in the sample, in the blank and in the spiked replicate, respectively.

(III) The bromine incorporation factor, n(Br) [33] is given by the equation:

$$n(\mathrm{Br}) = \frac{\mathrm{TTHMs} - \mathrm{Br}}{\mathrm{TTHMs}} \tag{3}$$

where TTHMs (μmole/l) is the sum of the four trihalomethanes and TTHMs−Br (μmol/l) is given by the following equation:

$$\mathrm{TTHMs} - \mathrm{Br} = \sum_{i=0}^{3} i \times \mathrm{CHCl}_{3-i}\mathrm{Br}_i \ (\mu\mathrm{mole/l}) \tag{4}$$

The value of n(Br) can vary between 0 and 3 depending on the degree of bromine substitution on trihalomethanes.

(IV) The World Health Organization (WHO)

index for additive toxicity I_{WHO} [27] was calculated as follows:

$$I_{WHO} = C_{TBM}/GV_{TBM} + C_{DBCM}/GV_{DBCM} + C_{BDCM}/GV_{BDCM} + C_{TCM}/GV_{TCM} \quad (5)$$

where C is the concentration of each trihalomethane and GV: WHO guideline value [27].

2.8. Recovery studies

Aliquots of stock solutions containing the analytes were diluted in carbon disulfide. Carbon disulfide solutions were directly injected into the GC–ECD system in order to determine ARTs (according to Eq. (1)) and to establish calibration curves for the quantitation each compound (external standard method). For the quantitation of the analytes twelve different carbon disulfide solutions with concentrations ranging from 0.4 to 32 ng/μl for THM and 0.02 to 12 ng/μl for HAN, HAA, TCC and CPN were prepared. An aliquot of 1 μl was injected three times into the GC–ECD system. A high linearity ($R^2 \geq 0.97$) was obtained for the above concentration ranges. Quantitation curves were controlled prior to sample analysis with solutions of known concentration. If the determined concentration deviated from the known concentration more than 10% the above procedure was repeated to establish new calibration curves.

The flow-rate through the activated carbon filter was adjusted to be greater than 0.9 ml/min [25,26].

Different temperature-purging and water bath conditions were examined in order to optimize the CLSA procedure. The salting out effect of sodium sulphate (Na_2SO_4) was also evaluated. The water sample (900 ml) was spiked with 10 μl of methanol solution containing the analytes in order to obtain concentrations of 50, 200, and 500 ng/l for each compound. A 70 g amount of Na_2SO_4 was then added to the water sample prepared as above. CLSA procedure recoveries were obtained according to Eq. (2). Procedural CLSA blanks were determined with organic-free (Nanopure grade) water samples. The above-described recovery study and determination of procedural CLSA blanks were also established by using ground water used for drinking water (after disinfection).

3. Results and discussion

3.1. Evaluation of CLSA in comparison to liquid–liquid extraction and purge-and-trap techniques

Fig. 1A shows the gas chromatogram (column B) of the ACF CS_2 extract after the CLSA of Nanopure water. Fig. 1B (column B) and 1C (column A) show the corresponding gas chromatograms of Nanopure water spiked with 100 ng/l of each DBP after the CLSA. Only THMs could be determined as blanks in nanonpure water in concentrations lower than 7 ng/l. The same observation concerning procedural blanks was done when ground water was used. The highest THM blank concentration was found for TCM. The other DBPs, such as HAANs, HAAs, HAKs, CP and CH, were not present in the blank.

Mean percent recoveries of each DBP for the three different CLSA conditions are presented in Table 1. Sodium sulfate was added before stripping in order to raise the ionic strength of the water and thus enhance the air stripping of DBPs [30]. The use of sodium sulfate (Na_2SO_4) is favored over that of sodium chloride since the later contains traces of bromide ions, which by reacting with HOCl, could alter the composition of DBPs to the more brominated species, creating thus an analytical artifact. CLSA recoveries for four trihalomethanes (TCM, DCBM, DBCM, TBM), tetrachloromethane (TCC), four halogenated acetonitriles (TCAN, DCAN, BCAN, DBAN), two haloketones (1,1-DCP, 1,1,1-TCP), dichloroacetic and dibromoacetic acids (DCAA, DBAA), and chloropicrin (CPN) were obtained. As shown in Table 1 when the water bath temperature was maintained at 35°C during CLSA, without addition of Na_2SO_4 (A in Table 1), the lowest recoveries for all compounds were observed, except for TCM. The addition of Na_2SO_4 had a clear positive effect on the efficiency of the DBPs recovery. The recoveries for HANs, THMs, TCC, 1,1-DCP and HAAs increased considerably with the addition of Na_2SO_4 (B in Table 1). The reproducibility (in % of standard deviation) ranged between 6–15%. A further temperature increase to 40°C of the water bath affected negatively the efficiency of CLSA for THMs, CPN and TCAN (C in Table 1), whereas the recoveries for the other

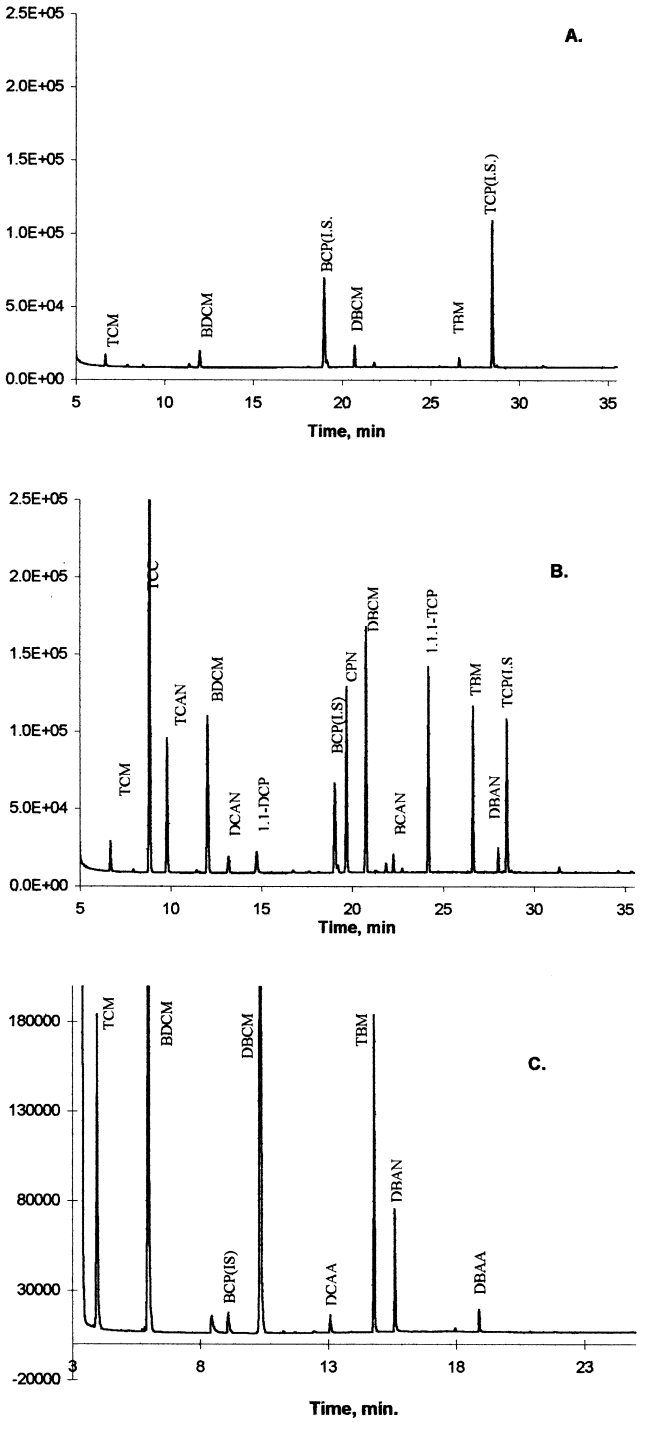

Fig. 1. (A) Gas chromatogram of Nanopure water after CLSA (60 m capillary column, see Experimental). (B) Gas chromatogram of Nanopure water with a concentration of ca. 200 ng/l for each DBP, after CLSA (60 m capillary column, see Experimental). (C) Gas chromatogram of Nanopure water with a concentration of ca. 200 ng/l for each DBP, after CLSA (50 m capillary column, see Experimental). For compound abbreviations see Table 1.

Table 1
Mean recovery efficiency (in %) of spiked water samples with disinfection by-products under different closed-loop stripping analysis (CLSA) conditions

Compounds	A[a]	B[a]	C[a]
Trichloromethane (TCM)	22.80±3.30	12.18±1.43	7.25±1.93
Bromodichloromethane (BDCM)	5.60±0.05	24.72±2.87	11.60±2.18
Dibromochloromethane (DBCM)	10.43±1.05	42.85±5.44	19.81±3.26
Tribromomethane (TBM)	21.04±1.72	59.37±5.20	31.44±4.02
Tetrachloromethane (TCC)	n.d.	38.63±9.08	27.65±4.55
Trichloroacetonitrile (TCAN)	n.d.	19.46±2.57	8.99±2.44
Dichloroacetonitrile (DCAN)	n.d.	4.95±0.63	6.03±1.00
Bromochloroacetonitrile (BCAN)	n.d.	6.29±0.77	8.88±1.82
Dibromoacetonitrile (DBAN)	2.00±0.20	8.86±1.06	10.69±2.59
1,1-Dichloro-2-propanone (1,1-DCP)	n.d.	6.88±0.10	9.17±2.00
1,1,1-Trichloro-2-propanone (1,1,1-TCP)	n.d.	28.78±0.66	35.72±3.30
Dichloroacetic acid (DCAA)	4.52±0.83	15.08±2.77	n.d.
Dibromoacetic acid (DBAA)	10.40±1.25	29.84±7.71	n.d.
Chloropicrin (CPN)	n.d.	33.66±2.89	19.06±4.76
Bromo-1-chloropropane (BCP, I.S.))	35.30±0.08	73.71±10.06	28.12±2.57
1,2,3-Trichloropropane (TCP, I.S.)	n.d.	94.21±5.79	89.98±6.84

[a] A: Without Na_2SO_4; water bath temperature 35°C; 6 trials. B: With Na_2SO_4; water bath temperature 35°C; 9 trials. C: With Na_2SO_4; water bath temperature 40°C; 6 trials. n.d.: Not determined; I.S. = internal standard.

halogenated acetonitriles and the halogenated ketones were slightly higher, but less reproducible. These results led to the conclusion that the addition of Na_2SO_4 to the water sample and a water bath temperature of 35°C are the optimum CLSA conditions for the determination of neutral and acidic chlorination DBPs. In addition, with a water bath temperature of 40°C we observed salt deposition (scavenged by water steam) on the active carbon filter. This is an undesired effect for the efficiency and lifetime of ACF.

Table 5 shows the absolute recovery and the recovery efficiency and their standard deviation (for fifteen trials or five trials for each concentration) for each disinfection by-product determined in this study by using the optimum purging conditions (see above and Table 1). Our data indicate that all compounds do not have the same recoverability, because of the differences in water solubility and vapor pressure. We can also notice that the quantity of the spiked amount for each compound does not affect the recovery efficiency (Table 2). The recovery efficiency obtained in this study for THM (12 to 59%, Table 2) was higher than this obtained in other studies [25,34] which, ranged from 4 to 12%. The reproducibility of the recovery efficiency for THMs, taking into consideration the three different concentrations of the water (Table 2), was satisfactory. From these results and in agreement with the results of Coleman and co-workers [25] is clear that the CLSA recoveries obtained are higher for the brominated THMs than for the chlorinated ones. Tetrachloromethane (TCC) recovery efficiency (Table 2) is also very reproducible for the three different concentrations. If, we consider the haloacetonitriles the highest recovery efficiency was obtained for TCAN (ca. 19%). For the other components of haloacetonitriles, the recovery efficiency, although very reproducible (Table 2), was the lowest for DCAN and BCAN. Low but very reproducible recovery efficiency was obtained for the haloketon 1.1-DCP (Table 2). The other haloketon 1.1.1-TCP, the two haloacetic acids (DCAA and DBAA) and chloropicrin (CP) gave reproducible recovery efficiencies ranging from 13 to 33% (Table 2). To our best knowledge there are not other reports concerning the recovery of haloacetonitriles, haloacetic acids, chloropicrin, and halogenated ketones. The same recovery studies were conducted by using ground water samples spiked with a concentration of ca. 50 ng/l for each compound. We observed recoveries of the same order of magnitude as those obtained for nanopure water. The low organic carbon content of ground water used (see Section 3.2) could explain the absence of a noticeable matrix effect. Nevertheless, our results are in agreement with those

Table 2
Repetitive purge study with quantitation

Compound	Spiked amount[a] (ng)	Mean recovered amount[a] (ng)	Recovery efficiency[a] (%)	Spiked amount[a] (ng)	Mean recovered amount[a] (ng)	Recovery efficiency[a] (%)	Spiked amount[a] (ng)	Mean recovered amount[a] (ng)	Recovery efficiency[a] (%)
TCM	50.03	6.09±0.93	12.20±1.90	200.10	24.37±4.78	12.20±2.39	500.25	61.03±3.43	12.20±0.70
BDCM	49.99	12.35±1.68	24.70±3.36	199.95	49.39±6.32	24.70±3.16	499.88	123.57±12.45	24.72±2.49
DBCM	50.01	21.43±3.87	42.90±7.74	200.05	83.72±11.69	41.90±5.85	500.13	219.31±33.10	43.90±6.62
TBM	50.01	29.70±3.38	59.39±6.76	200.05	118.77±14.10	59.37±7.05	500.13	296.93±30.26	59.40±6.05
TCC	47.67	18.40±4.03	38.60±8.10	158.90	61.05±7.19	38.42±3.60	476.70	185.32±26.93	39.00±5.40
TCAN	49.91	9.58±1.53	19.20±3.08	199.64	39.17±2.80	19.62±1.40	499.10	97.62±17.94	19.60±3.60
DCAN	46.71	2.31±0.37	5.00±0.74	186.85	9.25±1.44	5.00±0.72	467.13	23.12±3.62	5.00±0.72
BCAN	47.28	2.99±0.41	6.32±0.82	189.12	11.88±0.21	6.30±0.11	472.80	29.74±4.06	6.30±0.81
DBAN	49.19	4.42±0.61	9.00±1.22	196.77	17.23±2.27	8.80±1.14	491.93	43.52±5.68	8.90±1.14
1.1-DCP	50.50	3.43±0.05	6.80±0.12	201.99	13.88±0.22	6.90±0.11	504.98	35.30±0.55	7.00±0.11
1.1.1-TCP	50.33	14.49±0.33	28.80±0.68	201.33	57.94±1.34	29.03±0.67	503.33	143.27±3.35	28.50±0.67
DCAA	93.78	12.58±0.20	13.00±0.22	187.56	28.27±5.19	16.00±2.60	468.90	78.04±25.70	16.24±5.14
DBAA	96.60	28.94±5.46	30.00±5.63	193.20	56.99±13.19	29.50±6.60	483.00	145.00±23.95	30.00±4.79
CPN	49.83	16.44±1.34	33.00±2.70	199.33	68.75±2.07	35.10±1.04	498.33	163.87±17.56	33.00±3.51

[a] Average value±standard deviation based on five experiments for each quantity of spiked amount For abbreviations see Table 1.

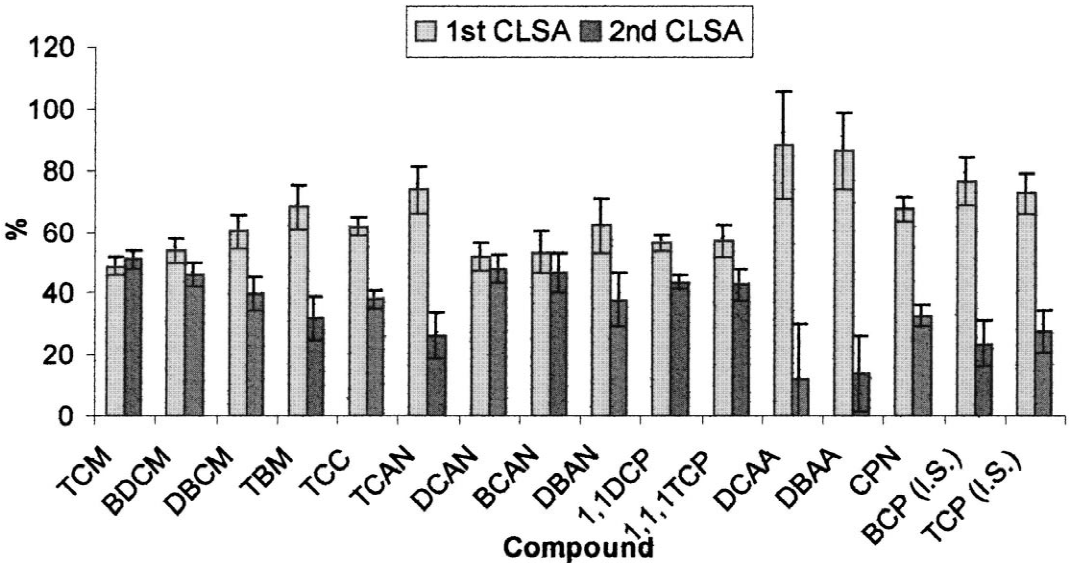

Fig. 2. Closed-loop stripping efficiency (in % of the total stripped quantity). For compound abbreviations see Table 1.

obtained by Nicholson et al. [35]. According to the above work, the Henrys Law constant for each trihalomethane was not affected by the presence of other trihalomethanes or by the water composition (e.g. ions, total organic carbon and humic acid content).

By using the above optimum purging conditions, the efficiency of stripping was also examined. Fig. 2 presents the results of the two consecutive CLSA for a single sample. Fig. 2 shows the mean percent efficiency (3–5 trials) of each stripping in relation to the total stripped amount (sum of the absolute analyte amount of each stripping) for each analyte. The second stripping was performed for each sample under the same CLSA conditions. With the exception of chloroform, equal or lower CLSA recoveries were obtained from the second stripping. As it was established (see Tables 1 and 2) the reproducibility of the CLSA recovery from the first stripping (expressed through the relative standard deviation of five replicates for each concentration) was satisfactory.

In order to check the MDLs, we added Na_2SO_4 in the water sample, we set the water bath temperature at 35°C, we performed only one CLSA and we extracted the ACF only once (see Experimental). From each amount obtained the corresponding procedural blank was subtracted. We integrated the chromatographic peaks only when a signal-to-noise ratio (S/N) higher than five was obtained. The results for each analyzed DBP are shown in Table 3. The CLSA method gave substantially lower MDLs, than the other methods mostly in use, namely LLE and the purge-and-trap (PT) technique. The four THMs could be determined at the lowest ng/l level. Actually TCM, BDCM, DBCM and TBM could be de-

Table 3
Closed-loop stripping analysis method detection limits for each compound

Compound	Method detection limit (μg/l)		
	CLSA	LLE[a] [4]	PT[a] [10]
TCM	0.0005	0.002	0.05
BDCM	0.0005	0.006	0.10
DBCM	0.0005	0.012	0.09
TBM	0.0005	0.012	0.20
TCC	0.00045	0.004	0.12
TCAN	0.00114	0.092	n.m.
DCAN	0.00107	0.019	n.m.
BCAN	0.00108	0.011	n.m.
DBAN	0.00112	0.034	n.m.
1.1-DCP	0.00115	0.005	n.m.
1.1.1-TCP	0.00115	0.012	n.m.
DCAA	0.04510	0.054 [15]	n.m.
DBAA	0.07245	0.065 [15]	n.m.
CPN	0.00115	0.012	n.m.

[a] LLE: Liquid–liquid extraction; PT: purge and trap. For compound abbreviations see Table 1. n.m.: Not measurable.

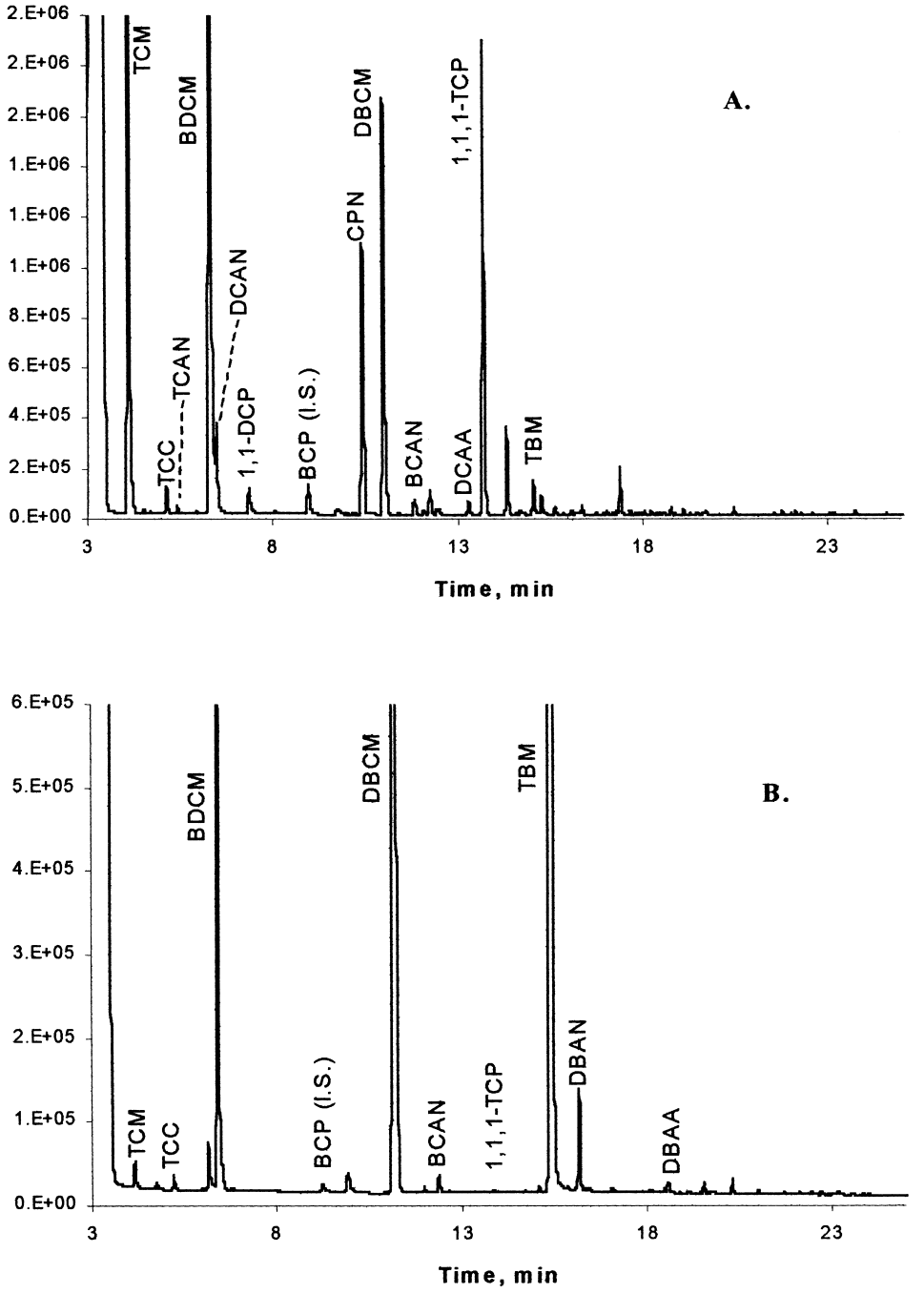

Fig. 3. (A) Gas chromatogram of Heraklion drinking water after closed-loop stripping analysis. (B) Gas chromatogram of Athens drinking water after closed-loop stripping analysis. For compound abbreviations see Table 1.

termined reliably at 0.0005 μg/l, ca. an order of magnitude lower than LLE (0.002 to 0.012 μg/l, Table 3) and almost two orders of magnitude lower than PT (0.05 to 0.2 μg/l, Table 3). The same observation can be done for TCC and the more polar DBPs such as, the four HANs (TCAN, DCAN, BCAN and DBAN), 1,1-DCP and 1,1,1-TCP (Table 3). The examined HAAs could be determined with MDLs of the same order of magnitude as those with LLE.

Although the recovery efficiency of the CLSA for the chlorinated disinfection by-products is relatively low, the enrichment factor of the method (1:33.333), the reproducibility of the recovery independently of the concentration and the absence of artifacts, are strong points in its favor. In addition, when one compares CLSA with PT the advantage of CLSA is obvious. The larger range of compounds, which can be determined with CLSA (THMs, HANs, HAAs and HAK) is another factor to take into consideration. The PT method is suitable only for the THMs. The advantage of CLSA over LLE consists of the lower obtained MDLs and of the fact that the HAAs can be reliably determined with CLSA in a one-step procedure. When LLE is used, two different water sample extractions (and subsequent derivatization of extract) are needed [16–18]. Another advantage of CLSA is the absence of artifacts. Formation of artifacts was reported when extraction with solvent was used, presumably from the reaction with traces of olefins present in the solvent [2]. Grob's CLSA can be reliably used for the monitoring of chlorinated disinfection by-products at the low ng/l level, provided that recovery data are available for all compounds of interest. Our study allows the use of Grob's CLSA for the reliable determination of the most common chlorinated DBPs by providing these recovery data.

3.2. Application of CLSA to the analysis of DBPs in drinking water

Fig. 3A and B (both with column A) show characteristic gas chromatograms of chlorinated drinking (tap) water from Athens and Heraklion. In Table 4 the concentration range of each DBP and some diagnostic parameters such as total trihalomethanes (TTHM), bromine incorporation factor [n(Br); Eq. (3)] and the WHO additive toxicity index (I_{WHO}) are presented. In addition and for comparison reasons the concentration ranges of chlorination DBPs and n(Br) obtained for Barcelona (Spain)

Table 4
Concentration ranges and diagnostic parameters of disinfection halogenated by-products determined in chlorinated drinking waters

Compound	Concentration (μg/l)			
	Athens	Heraklion	Barcelona [32,33]	D.W.O.[a] [9,16]
TCM	2.74–22.41	0.02–2.41	8.40–40.20	n.r.[a]
BDCM	0.71–7.15	0.01–7.24	19.20–69.80	n.r.
DBCM	0.57–5.81	0.02–19.47	24.00–112.10	0.4–1.1
TBM	0.03–1.15	0.41–51.26	23.20–156.10	19.0–27.0
TTHM	3.63–29.15	0.83–55.62	n.r.	n.r.
TCAN	0.0007–0.0190	0.0000–0.0006	n.r.	n.r.
DCAN	0.606–1.389	0.000–0.016	n.r.	n.r.
BCAN	0.213–0.650	0.005–0.324	0.0–9.8	n.r.
DBAN	0.02–2.81	0.00–5.32	0.0–7.0	0.9–1.1
DCAA	0.00–0.91	n.d.[a]	n.r.	0.0–0.3
DBAA	0.09–2.50	0.00–0.91	n.r.	0.15–1.20
1.1 DCP	0.145–0.461	0.000–0.021	n.r.	n.r.
1.1.1 TCP	0.585–1.220	0.000–0.013	n.r.	n.r.
TCC	0.007–0.018	0.005–0.050	n.r.	n.r.
CPN	0.051–0.260	0.000–0.003	n.r.	n.r.
n(Br)[a]	0.20–0.92	1.64–2.93	1.58–1.75	3.00
I^{a}_{WHO}	0.03–0.22	0.01–0.59	n.r.	n.r.

[a] D.W.O.: Drinking water prepared off-shore; n.d.: not determined. n.r.: not reported; n(Br): bromine incorporation factor; I_{WHO}: WHO index for additive toxicity. For compound abbreviations see Table 1.

chlorinated tap water [36,37] and chlorinated drinking water produced offshore [9,16] are presented.

As can be seen in Fig. 3A, B and Table 4, chloro-, bromo- and bromo/chloro non-polar and polar DBPs were observed in all chlorinated drinking water samples collected in the two Greek cities. Using GC–MS analysis, comparison with the authentic standards and ARTs (Eq. (1) in Experimental), we identified all compounds reported here. Internal standards were used for the determination of ARTs. Quantification was achieved by GC–ECD (external standard technique, see Experimental).

There are important differences in the THM distribution between the Athens and Heraklion drinking waters (see Fig. 3A and B and Table 4). In drinking water from Athens chloro- and chloro/bromo-THMs were observed in higher concentrations than TBM. Conversely, in Heraklion the brominated THMs were in higher concentrations. TBM was the most abundant DBP in almost all samples examined. These results correspond to the higher value of the bromine incorporation factor *n*(Br), 2.93, which approached that of chlorinated desalted seawater (see Table 4).

The brominated species DBCM, TBM and DBAN were the most abundant products found in chlorinated drinking water in Heraklion and also in desalted seawater, used as a source on many offshore installations to produce potable water [10,16]. With regard to HAAs, in Athens drinking water DCAA was determined in concentration up to 0.91 μg/l (Table 4) and DBAA range from 0.09 to 2.50 μg/l. In Heraklion drinking water only DBAA was determined in concentration up to 0.91 μg/l. These observations concerning the presence of HAAs comply with those of Benanou et al. [18], according to which chlorinated surface waters (e.g. Athens) contain higher amounts of HAAs than chlorinated ground waters (e.g. Heraklion).

The concentrations of individual DBPs are significantly lower than those determined in Barcelona (Table 4) [36,37]. Nevertheless, the THM bromine incorporation factor of Heraklion drinking waters was higher than the corresponding *n*(Br) of Barcelona (Table 4) and was approaching that of chlorinated drinking water prepared off-shore (Table 4). TBM DBCM and DBAN were the most abundant DBPs found in chlorinated drinking water prepared off-shore [9,16]. Desalted seawater contained variable amounts of dissolved organic carbon (DOC, 2.50–2.90 mg/l) and very high amounts of bromide (63–67 mg/l) [9,16]. Brominated THMs in Barcelona reached values as high as 75.30% of TTHMs [36,37]. Bromide concentrations of 0.95 to 3.66 mg/l, due to discharges of salt mines, were measured in the Llobregat River from which water is chlorinated for Barcelona's drinking water supply [36,37].

Free available chlorine (FAC) initial and final concentration, and bromide to chlorine (Br^-/Cl^+) molar ratio relate to potential for bromine substitution into the trihalomethanes. Because the key variable, the Br^-/Cl^+ molar ratio, cannot be calculated at every moment during chlorination, we used the average FAC concentration (([initial Cl+]+[final Cl+])/2) and initial bromide concentration. It has been demonstrated that initial[Br^-]/average[Cl^+] molar ratio (Table 5) controls bromine substitution on THMs and HAAs [32,38]. In Table 5 characteristic parameters for Heraklion ground water are shown such as bromide ion concentration range, total organic carbon (TOC) concentration range, and as well as chlorination parameters such as free available chlorine (FAC) dose and residual. The degree of bromine substitution *n*(Br) increases when the bromide concentration increases or the average free available chlorine (FAC) decreases [38]. Indeed *n*(Br) can change from 0.7 to 1.75 when the initial[Br^-]/average[Cl^+] molar ratio changes from 0.003 to 0.302 [38]. The low FAC doses and the

Table 5
Characteristics parameters of Heraklion ground water and chlorination conditions

[Br^-] (mg/l)	0.1–1.0
[Cl^-] (mg/l)	24.0–293.9
[Cl^-]/[Br^-]	256.1–304.9
[TOC] (mg/l)	0.12–1.31
FAC-Dose (mg/l)	1.00–1.20
FAC-Residual (mg/l)	0.40–0.60
Mean (initial Br^-/average Cl^-)	0.52
	Mean TTHMs (%)
TCM	4.22
BDCM	4.25
DBCM	18.02
TBM	73.50
n(Br)	2.48

TOC: total organic carbon. FAC: free available chlorine. TTHMs: total trihalomethanes. *n*(Br): bromine incorporation factor.

relatively high bromide concentrations encountered in Heraklion drinking water (Table 5) make that the mean initial[Br^-]/average[Cl^+] molar ratio takes a mean value of 0.52 (Table 5). This mean value is very high and can elucidate the higher levels of TBM compared to TCM (Table 5) in Heraklion drinking waters and also the very high n(Br) ranges (Table 4).

In Table 4, values are given for total trihalomethane (TTHM), by using the WHO standard approach [12]. The concentrations for TTHM determined in Athens and Heraklion, shown in Table 4, comply with the EPA [28] and European Commission rules [39]. If we consider the WHO total trihalomethane fractionation approach [27], to account the additive toxicity I_{WHO}, we can conclude that the trihalomethane concentrations observed for Athens and Heraklion comply also on the WHO guidelines.

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