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Optimization of the gas stripping and cryogenic trapping method for capillary gas chromatographic analysis of traces of volatile halogenated compounds in drinking water

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Abstract

A simple laboratory-made gas stripping and cryogenic trapping system coupled to a gas chromatograph with flame ionization detector as a universal detector has been developed for the determination of traces of volatile halogenated compounds (VHCs) in drinking water. The effects of inert gas velocity, stripping time, temperature and salting out on the extraction efficiency and the efficacy of different adsorbents for water vapour elimination were studied. The VHCs were trapped in a stainless-steel coil (50 cm × 1.5 mm I.D.) placed in liquid nitrogen. The trapped compounds were released by thermal desorption and injected in the capillary column. To prevent peak tailing arising from the injection of the sample spread in a large volume of the carrier gas, VHCs were retrapped in the beginning of the capillary column with a cryofocusing system. The chromatographic analyses were run with a suitable temperature program.

The present method allows the determination of 0.1–10 ppb of each VHC. The relative standard deviation of 5–10% ($n = 5$) was obtained at 2 ppb for different VHCs. The detection limits (signal-to-noise ratio 3) were 0.01–0.05 ppb for the studied compounds which are comparable with US Environmental Protection Agency method 502.2.

1. Introduction

Volatile organic compounds (VOCs) such as volatile halogenated compounds (VHCs) are found virtually in all homes and workplaces in our modern technological society. Chlorine reacts with organic matter during water disinfection, produces VHCs and increases our exposure to these compounds [1,2], and numerous studies have confirmed the mutagenic effects of these compounds [3–7]. The combination of ubiquitous exposure and possible serious health effects makes VHCs a public health concern [8]. As a result of the possible risk to health, the World Health Organization has recommended a limit of 30 ppb for chloroform [9] and USA legislation has established a limit of 100 ppb for total VHCs [10].

Gas chromatography is often used for the analysis of these compounds [11–15]. However, due to the very low concentration of VHCs in drinking water, a preextraction and preconcentration step is needed. So far several techniques have been used for this purpose: liquid–liquid extraction [12,16–18], adsorption onto solid phase [15,19], permeability through membranes

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[20,21], head-space [21–23], closed-loop stripping [24], cryofocusing [25] and spray extraction [26,27]. These methods are subjected to the solvent, airborne or solid-phase contaminations, which often gives high background and different interferences [11].

The purge-and-trap technique is free from these problems because it uses a purified inert gas to extract VHCs from water; once introduced to the system it is never in contact with the atmosphere and the relatively high concentrating factor obtained by this method allows analysis of very-low-concentration samples [28,29].

This paper describes a new analytical method for the trace analysis of some VHCs using a simple laboratory-made gas stripping and cryogenic trapping system coupled to gas chromatography (GSCT–GC) with flame ionization detection (FID) as a universal detector.

2. Experimental

2.1. Chemicals and reagents

Helium 99.999% was purchased from Air Products (Middle East), Dubai, U.A.E.; chloroform, carbon tetrachloride, dibromochloromethane, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene, 1,1,2-trichloroethane, 1-chloro-2-bromoethane, dibromomethane, KBr, NaCl, LiCl, $CaCl_2$, Na_2SO_4, $MgSO_4$ and all other reagents were from E. Merck (Germany).

Stock solutions of VHCs were prepared by dissolving 1 mg of each in 5 ml methanol (200 ppm); stock solution of internal standard was prepared by dissolving 1 mg of dibromomethane in 5 ml methanol. Model aqueous solutions at 2 ppb level were prepared by adding 2.5 μl of stock solutions of each VHC into 250 ml doubly distilled and stripped water. $MgSO_4$, $CaCl_2$ and alkali metal salts were activated in 400°C for 60 min and used as dryer for the elimination of water vapour from released VHCs.

2.2. Apparatus

The GC apparatus consisted of a Shimadzu (Japan) GC-15 A, equipped with a FID system, a data processor Model C-R4 A Chromatopac, hydrogen generator Model OPGU-1500 S and split/splitless injector. A Shimadzu Hicap CBP10-S25-050 (OV-1701) capillary column was used.

2.3. Stripping and trapping process

A general view of the laboratory-made GSCT–GC system is shown in Fig. 1. In this system, impurities in the helium gas are eliminated in cryogenic trapping interface (1) kept at −196°C with liquid nitrogen; the pure He is then passed via a stainless-steel filter (2) into the stripping column (100 × 2 cm I.D. glass tube) containing 250 ml of the water sample (3) kept at 80°C; the released VHCs accompanying water vapour are passed through the dryer column packed with activated adsorbents (4), in which the water vapour is retained; dried VHCs are trapped in a cold trapping coil (50 cm × 1.5 mm I.D. stainless-steel tube) kept at −196°C with liquid nitrogen (5). When the stripping process is completed (75 min), the liquid nitrogen is removed and the trapping coil is warmed with hot air, hence the analytes are thermally desorbed and introduced into the GC system (6); to prevent peak tailing arising from the injection of the sample in a large volume, the VHCs are cryofocused in the beginning of the capillary column (the first 50 cm of the column is placed in liquid nitrogen) (7); after 2 min the liquid nitrogen is removed and the GC analysis is started with a suitable temperature program.

2.4. Quantitative analysis

For quantitative analysis by GSCT–GC, the internal standard method was used. This approach is less attentive and offers better precision than other calibration methods [30,31]. To 250 ml model aqueous solution containing 0.1–10 ppb of each VHC are added 2.5 μl of stock

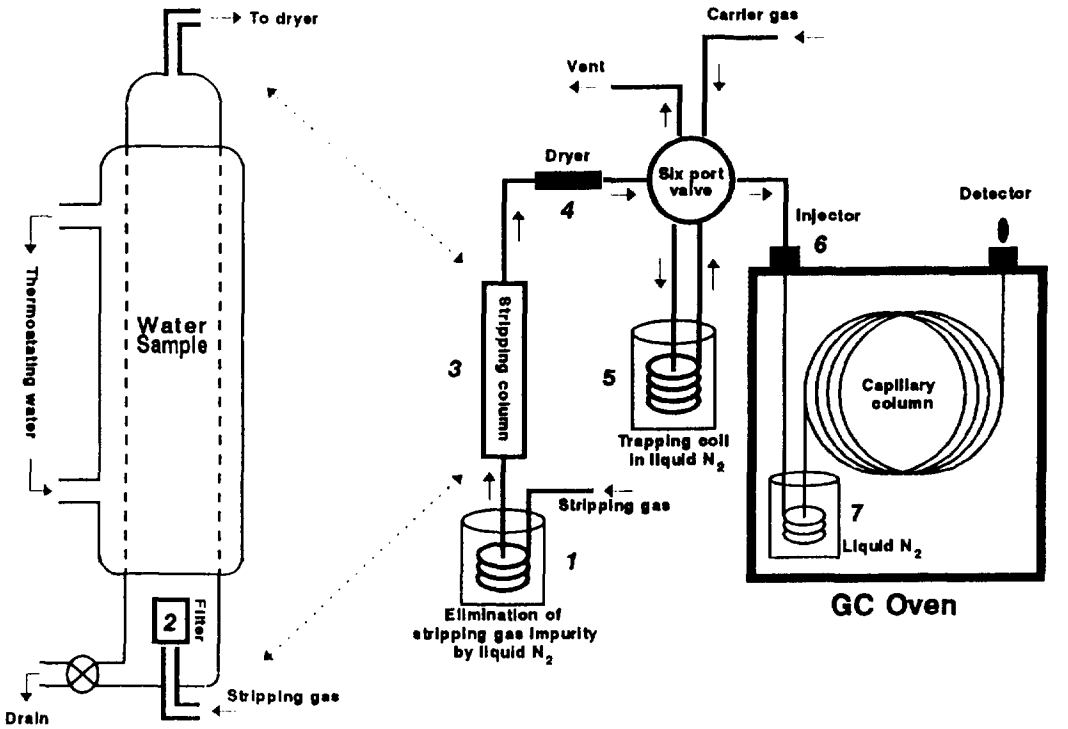

Fig. 1. Schematic diagram of on-line gas stripping and trapping system coupled with GC. See text.

dibromomethane solution rendering an internal standard concentration of 2 ppb.

3. Results and discussion

3.1. Optimization of chromatographic conditions

In order to optimize the chromatographic conditions a 1-μl portion of the VHC mixture was directly injected at a split ratio of 80:1. The best capillary column, suitable oven temperature program, optimum carrier and makeup gas flow-rates and injector temperature were determined on the basis of peak resolutions and reproducibility of the retention times. A typical chromatogram obtained under optimized conditions is shown in Fig. 2. The observed resolution (R_s) for chloroform and carbon tetrachloride was 1 and for other VHCs the R_s value was >1.5. The calculated standard deviation for the retention times of 0.03–0.08 for various VHCs show that under the selected conditions, a good separation and identification of VHCs seem possible.

3.2. Analysis of model aqueous solution

Under the optimized GC conditions, 250 ml of the model aqueous solution were analysed using GSCT–GC. Fig. 3 shows that a good identification of the studied VHCs can be achieved.

3.3. Effect of stripping time on stripping efficiency

The stripping efficiencies of the studied VHCs in model aqueous solutions were determined over the time range 30–105 min, in 15-min intervals. The results obtained are shown in Fig. 4. Since the stripping curve of each compound

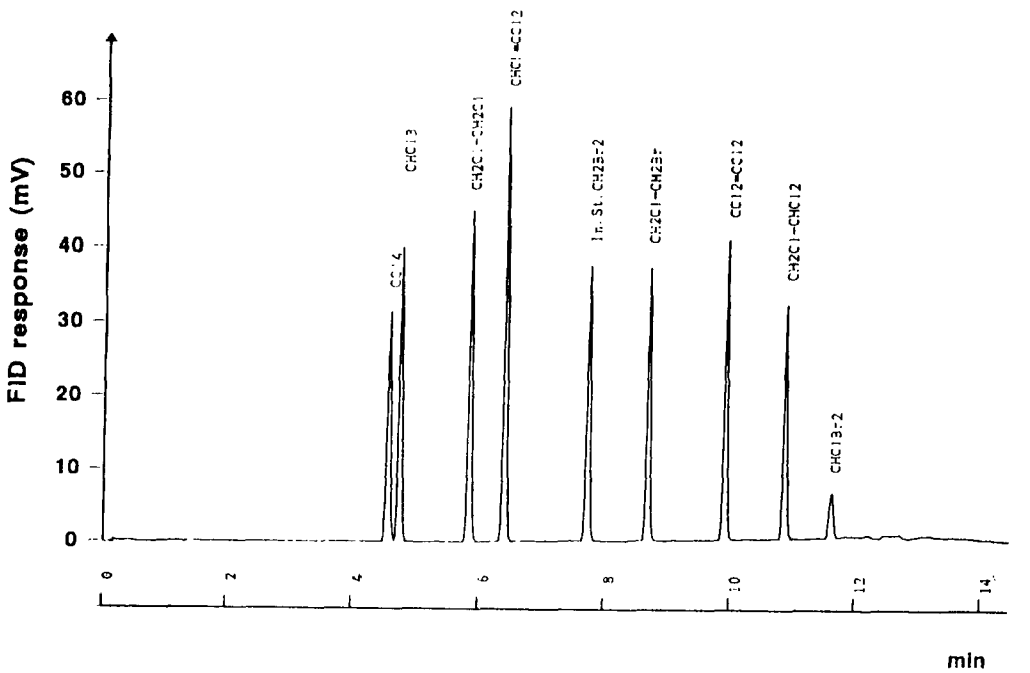

Fig. 2. Typical chromatogram of VHCs. Column CBP-10 (OV-1701), 25 m × 0.33 mm I.D., film thickness 0.5 μm; carrier gas velocity 25 cm/s; split ratio 80:1; injection volume 1 μl; injector temperature 150°C; oven temperature program 30°C with a 5-min hold rising at 7°C/min to 120°C, and hold 5 min; makeup gas 25 ml/min; FID temperature 150°C.

reaches a quasi plateau over 75 min, we can accept 75 min stripping as optimum stripping time.

3.4. Effect of stripping temperature on stripping efficiency

For this study, the stripping was carried out for the same model aqueous solution at 75 min and various temperatures (20–80°C). Representative plots of the peak areas against temperature for each VHC are shown in Fig. 5. It can be seen that the stripping efficiencies of all studied compounds increase with temperature. However, due to the inconvenient interference of water molecules in the cold trap device, increasing the temperature over 80°C is not practically suitable. Therefore we took the stripping temperature of 80°C as the optimum.

3.5. Effect of salting out on stripping efficiency

For this investigation we have studied the effect of various amount of Na_2SO_4 on the stripping efficiency of VHCs. Fig. 6 plots the peak area versus Na_2SO_4 quantities in water. We observe that the addition of 30–40 g Na_2SO_4 in 250 ml model aqueous solution increases the stripping efficiency of VHCs two-fold.

3.6. Study of the drying device efficiency

Since the stripping temperature is relatively high, some quantity of the water vapour is transferred along with VHCs which freezes in the cold trap coil and clogs this device. For this reason the elimination of water before entering the cold trapping device is necessary. Therefore we have investigated the usefulness of various inorganic salts such as NaCl, LiCl, KBr, $CaCl_2$,

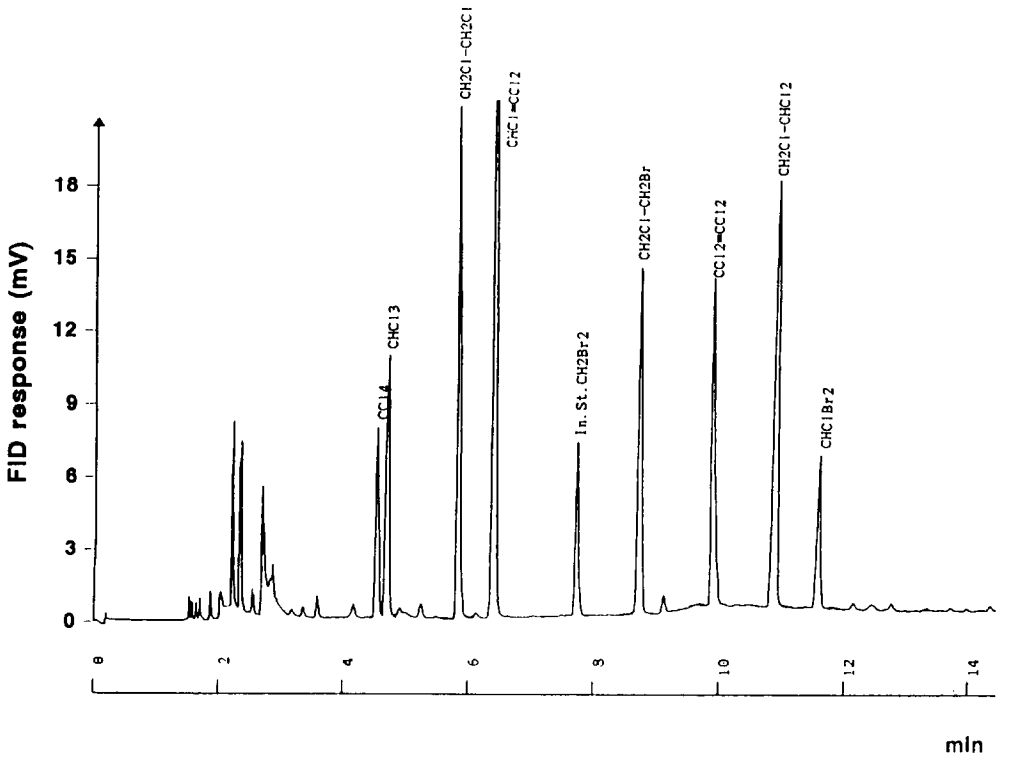

Fig. 3. Typical chromatogram of model aqueous solution. Chromatographic conditions as in Fig. 2; sample volume 250 ml containing 2 ppb of each VHC in which 30 g Na_2SO_4 was dissolved; stripping time 75 min; stripping temperature 80°C.

Na_2SO_4 and $MgSO_4$ as dryers. The investigations show that KBr and Na_2SO_4 have not much affinity towards water molecules. The others are very effective for water elimination, but they can also adsorb VHCs. Table 1 shows the adsorption strength of water and VHCs using various dryers. The results obtained from this study, reveal that activated NaCl and $CaCl_2$ have a

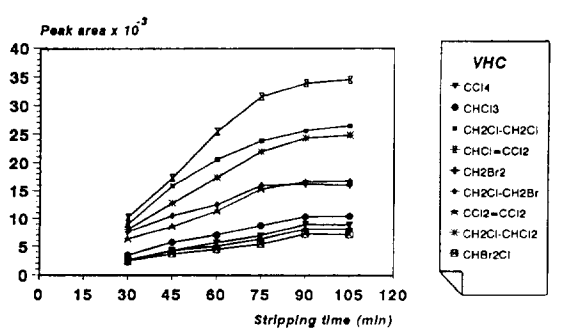

Fig. 4. Effect of time in stripping efficiency. Conditions as in Fig. 3. Dryer $CaCl_2$.

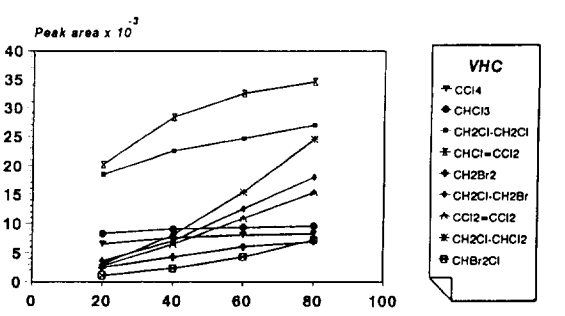

Fig. 5. Effect of temperature in stripping efficiency. Conditions as in Fig. 3. Dryer $CaCl_2$.

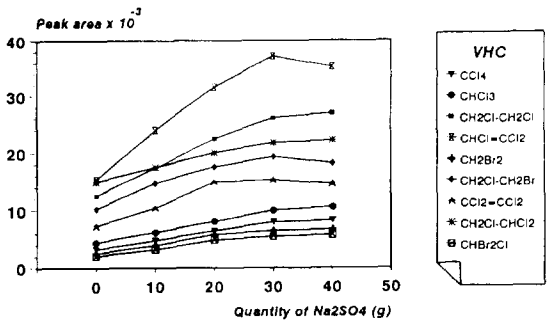

Fig. 6. Effect of salting out in stripping efficiency. Conditions as in Fig. 3. Dryer $CaCl_2$.

Table 1
Adsorption strength of water and VHCs onto various adsorbents

Dryer	Water adsorption strength	VHC adsorption strength
LiCl	VL	VL
KBr	VS	S
NaCl	M	VS
$CaCl_2$	L	S
$MgSO_4$	L	L
Na_2SO_4	M	M

VL = Very large; VS = very small; L = large; M = medium; S = small.

relatively good affinity for water and adsorb very little and negligible quantities of the VHCs; therefore they are suitable dryers in these experiments.

3.7. Recovery study

Five replicates of 2-μl portions of diluted standard solution in *n*-pentane containing 500 ng of each VHC were analysed by direct splitless injection (split valve opened at 1 min) and five replicates of 250-ml portions of model aqueous solution containing the same quantities of VHCs were analysed by GSCT–GC. With comparing the peak areas of each VHC in two sets of experiments, recoveries of 75–86% were obtained (Table 2).

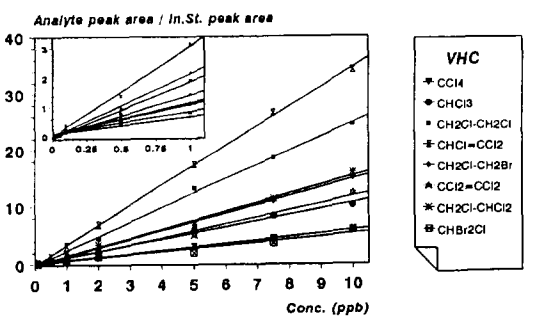

Fig. 7. Calibration graphs of VHCs. Internal standard (CH_2Br_2) 2 ppb. Conditions as in Fig. 3. Dryer $CaCl_2$.

Table 2
Recoveries of tested compounds with GSCT–GC method

Formula	Peak area, mean ± S.D. ($n = 5$)[a]	Peak area, mean ± S.D. ($n = 5$)[b]	Recovery (%), mean ± S.D.
CCl_4	10 400 ± 150	8 600 ± 450	83 ± 4.6
$CHCl_3$	13 100 ± 210	10 200 ± 720	78 ± 5.6
CH_2Cl-CH_2Cl	31 700 ± 410	26 000 ± 1300	82 ± 4.2
$CHCl=CCl_2$	40 700 ± 670	35 000 ± 1700	86 ± 4.4
CH_2Br_2	8 800 ± 170	7 100 ± 460	80 ± 5.4
CH_2Cl-CH_2Br	22 700 ± 430	17 000 ± 1000	75 ± 4.6
$CCl_2=CCl_2$	19 000 ± 250	15 000 ± 1300	79 ± 6.9
$CH_2Cl-CHCl_2$	29 300 ± 480	24 000 ± 1800	82 ± 6.3
$CHClBr_2$	9 200 ± 220	6 900 ± 690	75 ± 7.7

[a] The peak area of VHCs from direct injection of 2 μl standard solution in *n*-pentane with 500 ng of each compound.
[b] The peak area of VHCs after extraction from 250 ml standard water with 2 ppb of each compound.

Table 3
Characteristic parameters of the calibration graphs and analytical features of the determination of VHCs

Formula	Retention time (min)	LOD (ppb)[a]	D.r. (ppb)[b]	Regression equation[c]	r[d]	R.S.D. (%) ($n = 5$)
CCl_4	4.60 ± 0.06	0.04	0.1–10	$y = 0.077 + 0.58x$	0.999	5.3
$CHCl_3$	4.75 ± 0.06	0.04	0.1–10	$y = 0.110 + 1.04x$	0.997	7.1
CH_2Cl–CH_2Cl	5.90 ± 0.08	0.02	0.1–10	$y = -0.141 + 2.48x$	0.999	5.0
$CHCl{=}CCl_2$	6.44 ± 0.07	0.01	0.1–10	$y = -0.143 + 3.47x$	0.999	4.9
CH_2Cl–CH_2Br	8.71 ± 0.05	0.04	0.1–10	$y = -0.120 + 1.47x$	0.999	5.9
$CCl_2{=}CCl_2$	9.94 ± 0.04	0.04	0.1–10	$y = -0.113 + 1.17x$	0.996	8.5
CH_2Cl–$CHCl_2$	10.86 ± 0.03	0.03	0.1–10	$y = 0.010 + 1.51x$	0.995	7.6
$CHBr_2Cl$	11.65 ± 0.04	0.05	0.1–10	$y = 0.085 + 0.52x$	0.973	10

[a] Limit of detection ($S/N = 3$).
[b] Dynamic range; internal standard = CH_2Br_2 (2 ppb).
[c] y = Analyte peak area/internal standard peak area; x = analyte concentration (ppb).
[d] Correlation coefficient.

Table 4
Comparison of LOD in GSCT–GC with LOD in EPA method 502.2

Formula	EPA 502.2 (ppt)	GSCT–GC (ppt)
CCl_4	20	40
$CHCl_3$	10	40
CH_2Cl–CH_2Cl	ND	20
$CHCl{=}CCl_2$	60	10
CH_2Cl–CH_2Br	ND	40
$CCl_2{=}CCl_2$	20	40
CH_2Cl–$CHCl_2$	40	30
$CHBr_2Cl$	ND	50

ND = Not detected.

3.8. Quantitative analysis

The calibration graphs of the studied VHCs representing the ratios of analyte peak area to internal standard peak area versus concentration in ppb are shown in Fig. 7. Some statistical data for these curves and five replicate analyses are illustrated in Table 3. From the results obtained the quantitative analysis of the VHCs can be carried out with a good precision and accuracy. Data in Table 4 illustrate the LOD of this method and US Environmental Protection Agency (EPA) method 502.2 [32]. The results show that the proposed method using FID is comparable to the EPA method. Table 5 shows

Table 5
Measured VHCs in Tabriz drinking water

Formula	Drinking water, mean ± S.D. (ppb, $n = 5$)	Added (ppb)	Found, mean ± S.D. (ppb, $n = 5$)
CCl_4	0.51 ± 0.03	1.0	1.45 ± 0.11
$CHCl_3$	3.90 ± 0.20	1.0	4.72 ± 0.28
CH_2Cl–CH_2Cl	< 0.05	1.0	1.03 ± 0.05
$CHCl{=}CCl_2$	0.29 ± 0.02	1.0	1.21 ± 0.08
CH_2Cl–CH_2Br	0.30 ± 0.02	1.0	1.32 ± 0.09
$CCl_2{=}CCl_2$	0.49 ± 0.04	1.0	1.40 ± 0.13
CH_2Cl–$CHCl_2$	< 0.1	1.0	0.96 ± 0.07
$CHBr_2Cl$	0.70 ± 0.07	1.0	1.85 ± 0.17

the measured quantity of some VHCs in Tabriz drinking water.

4. Conclusions

The results show that the GSCT method is very convenient for sensitive analysis of trace amounts of dissolved VHCs in water. The concentration factor is very high and the method is free from airborne, solvent and solid-phase contaminations. Minute amounts of contaminants of the stripping gas (helium) can also be eliminated completely.

Acknowledgement

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