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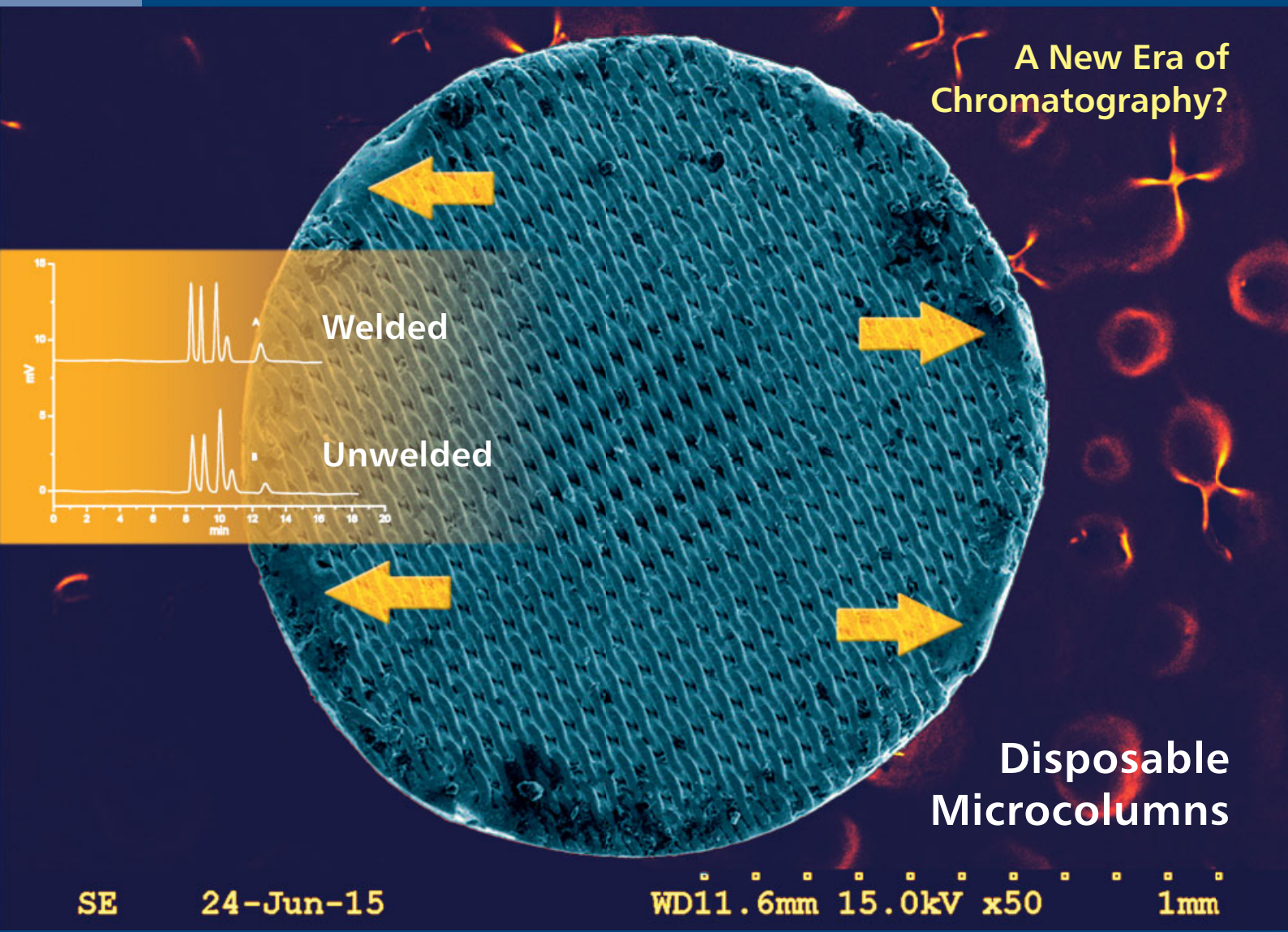

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Research Article

Determination of volatile chlorinated hydrocarbons in water samples by static headspace gas chromatography with electron capture detection

A simple, efficient, solvent-free, and commercial readily available approach for determination of five volatile chlorinated hydrocarbons in water samples using the static headspace sampling and gas chromatography with electron capture detection has been described. The proposed static headspace sampling method was initially optimized and the optimum experimental conditions found were 10 mL water sample containing 20% w/v sodium chloride placed in a 20 mL vial and stirred at 50°C for 20 min. The linearity of the method was in the range of 1.2–240 μg/L for dichloromethane, 0.2–40 μg/L for trichloromethane, 0.005–1 μg/L for perchloromethane, 0.025–5 μg/L for trichloroethylene, and 0.01–2 μg/L for perchloroethylene, with coefficients of determination ranging between 0.9979 and 0.9990. The limits of detection were in the low μg/L level, ranging between 0.001 and 0.3 μg/L. The relative recoveries of spiked five volatile chlorinated hydrocarbons with external calibration method at different concentration levels in pure, tap, sea water of Jiaojiang Estuary, and sea water of waters of Xiaomendao were in the range of 91–116, 96–105, 86–112, and 80–111%, respectively, and with relative standard deviations of 1.9–3.6, 2.3–3.5, 1.5–2.7, and 2.3–3.7% ($n = 5$), respectively. The performance of the proposed method was compared with traditional liquid–liquid extraction on the real water samples (i.e., pure, tap, and sea water, etc.) and comparable efficiencies were obtained. It is concluded that this method can be successfully applied for the determination of volatile chlorinated hydrocarbons in different water samples.

Keywords: Electron capture detection / Gas chromatography / Static headspace sampling / Volatile chlorinated hydrocarbons / Water samples
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1 Introduction

Volatile chlorinated hydrocarbons (VCHCs) such as dichl oromethane (DCM), trichloromethane (TCM), perchlo romethane (PCM), trichloroethylene (TCE), and perchlor oethylene (PCE), which have been extensively used in a variety of industrial and commercial processes as multipurpose solvents, paint removers, chemical intermediates, metal degreasing and dry-cleaning agents for several decades [1–5], are emitted into the environment by vaporization during their production, distribution, storage, handing and final use, and reach the ground and surface water along with other environmental compartments due to their high volatility. Contamination of groundwater with VCHCs is a widespread environmental problem owing to the toxicity, suspected carcinogenity and persistence of these compounds [6,7]. VCHCs have become a public health concern due to their suspected carcinogenic nature (a large population is exposed to them, in particular persons served by public water systems) and their acceptable concentration limits in drinking water are fixed by law [8]. The United States Environmental Protection Agency (EPA) has regulated 0.005 mg/L as the maximum permissible contamination level for DCM, PCM, TCE, and PCE in drinking water. As a result of this low limit, it is necessary to develop highly sensitive and efficient analytical method for determination of VCHCs in the aquatic environment.

Trace analysis of VCHCs in water is usually performed by GC with electron capture detection (ECD) or MS. However, in most cases, sample pretreatment steps are required before the measurement because of the very low levels of analytes and the complicated matrix in real-world samples. Conventional methods, such as LLE [9–12], require the use of large amount of expensive high-purity organic solvents, which are

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Abbreviations: DAI, direct aqueous injection; **DCM**, dichloromethane; **ECD**, electron capture detection; **FID**, flame ionization detection; **HS**, headspace; **P&T**, purge and trap; **PCE**, perchloroethylene; **PCM**, perchloromethane; **SPDE**, solid-phase dynamic extraction; **TCE**, trichloroethylene; **TCM**, trichloromethane; **VCHC**, volatile chlorinated hydrocarbon

often hazardous, and is laborious, time-consuming, and apt to form emulsions. To avoid these drawbacks, several environmentally friendly sample pretreatment techniques, including purge and trap (P&T) [11–18], direct aqueous injection (DAI) [11, 12, 19–22], SPME [18, 23, 24], LPME [25], static headspace (static HS) [10, 12, 26, 27], headspace solid-phase dynamic extraction (HS-SPDE) [28], headspace solid-phase microextraction (HS-SPME) [29, 30], static headspace knotted hollow fiber microextraction (HS-K-HPME) [31], headspace single drop microextraction (HS-SDME) [32, 33], and headspace liquid-phase microextraction (HS-LPME) [34], have been arisen. P&T is the pre-concentration method for VCHCs from water most frequently used in routine analysis in the USA. Several EPA protocols in the 500, 600, and 8000 series, e.g., EPA method 524.2 for the measurement of purgeable organic compounds in water, rely on P&T [13]. But P&T is a time-consuming technique and requires special instrumentation. Buszewski et al. [11] and Golfinopoulous et al. [12] reported a comparison of LLE, P&T, and DAI, indicating that they are similar in precision and accuracy, but DAI has problems with column stability and critical temperatures for column and injector. Lara-Gonzalo et al. [18] reported a comparison between SPME and P&T, indicating that they are similar in precision and accuracy, but SPME is somehow faster and simpler. There are two major types of SPME: direct-immersion and headspace. HS-SPME analysis is the most common technique for the determination of VCHCs as it significantly reduces the interference from dirty matrices, which is generally associated with direct-immersion SPME. However, the extraction fiber of SPME is expensive and fragile, and sample carryover is also a problem. LPME, which emerged as an attractive alternative to conventional LLE, the immersion mode yields high enrichment factors, high sensitivity and ruggedness, while HS-LPME using a hollow fiber presents more challenges than other types of LPME because the extraction solvents compatible with GC usually evaporate quickly in the headspace. But keep in mind that LPME is fast stirring which may cause break up the organic solvent drop and air bubble formation, and time-consuming and in most cases equilibrium is not attained even after a long time.

Despite the rise of other headspace techniques (dynamic, SPME, LPME), static HS remains an ideal technique that has been proven to be an efficient and convenient sampling method in many fields [35–39]. The static HS procedure is free of solvents, demands little sample loading, and can be automated, but its sensitivity is considered low compared to LLE, P&T, and SPME. Nevertheless, the static HS sensitivity can be increased by salt addition, combining with a sensitive detector or optimizing sampling volume, equilibrium temperature etc. Although the International Organization for Standardization (ISO) [10] and Golfinopoulos et al. [12] reported static HS for determination of volatile halogenated hydrocarbons in water, respectively, and had detection limits in the range of hundreds of ng/L. But these detection limits are still too high. With the GC and automated static HS technique developed, new optimized GC and static HS conditions will reach higher sensitivity.

The overall aim of this study was to develop an accurate and sensitive technique, static HS coupled with GC–ECD, to determine five VCHCs in water samples. GC–ECD was the predominant analytical technique for selective and sensitive determination of organohalogens during the past half-century. VCHCs are a class of organohalogens with some chlorine substituents. The static HS, rather than a preconcentration process, was used for the transfer of VCHCs from water to the gas phase, which made the measurement fast and simple. Also, it would avoid errors caused by sample loss or contamination during the pre-concentration. Parameters relevant to the extraction performance of static HS, such as salt addition, gas-to-liquid ratio, equilibration time, and incubating temperature, were studied and optimized. The performance of the developed protocol was validated and detection limits were compared with other reported analytical methods. At last, the applicability of the proposed method was checked through analysis of three natural water samples, and the efficiency of the suggested method was compared with traditional LLE on the real water samples.

2 Materials and methods

2.1 Chemicals and reagents

All the chemicals and reagents were of analytical grade and used without further purification. Ultrapure water (Mili-Q Plus 185, Millipore Corporation) was used throughout this experiment. Methanol (99.9%), pentane and sodium chloride (NaCl) was obtained from Merck (Darmstadt, Germany). dichloromethane (DCM), trichloromethane (TCM), perchloromethane (PCM), trichloroethylene (TCE), and perchloroethylene (PCE) were purchased from Aldrich (Steinheim, Germany).

The stock standard solutions of VCHCs (100 mg/L) were prepared in methanol and were stored in the dark at 4°C. These stock standard solutions were diluted with methanol to prepare a mixed standard solution with a concentration of 12 mg/L for DCM, and 2 mg/L for TCM, and 0.05 mg/L for PCM, and 0.25 mg/L for TCE, and 0.1 mg/L for PCE. Then, working standard solutions were freshly prepared by diluting the mixed standard solution with ultrapure water to the required concentrations. NaCl was used to adjust the ionic strength of the aqueous samples. Before use, ultrapure water was heated at 100°C for 1 h, and then cooled to room temperature.

2.2 Instrumentation

The analysis of VCHCs was performed on a Varian CP3800 gas chromatograph equipped with an electron capture detector. The GC was fitted with PTE-5 capillary column (30 m × 0.25 mm, id, 0.25 μm phase thickness, 5% phenyl – 95% methyl polysiloxane) from Varian (USA). The

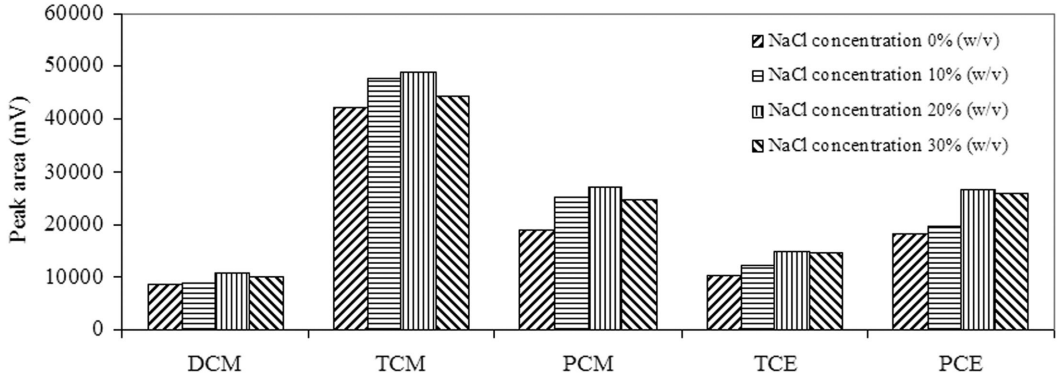

Figure 1. Effect of salt addition on the volatilization efficiency of the 5 VCHCs. Working solution: 24 μg/L DCM, 4 μg/L TCM, 0.1 μg/L PCM, 0.5 μg/L TCE,and 0.2 μg/L PCE; incubating temperature: 50°C; equilibration time: 35 min; gas-to-liquid ratio: 1:1.

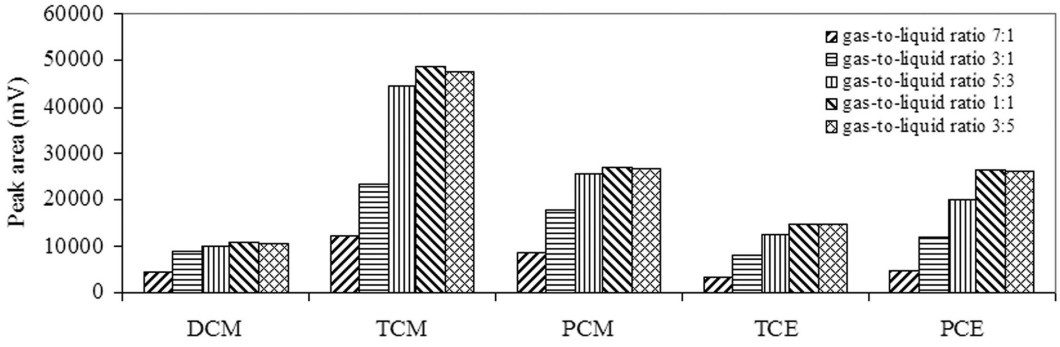

Figure 2. Effect of gas-to-liquid ratio on peak area of the 5 VCHCs. Working solution: 24 μg/L DCM, 4 μg/L TCM, 0.1 μg/L PCM, 0.5 μg/L TCE and 0.2 μg/L PCE; salt concentration: 20% w/v; incubating temperature: 50°C; equilibration time: 35 min.

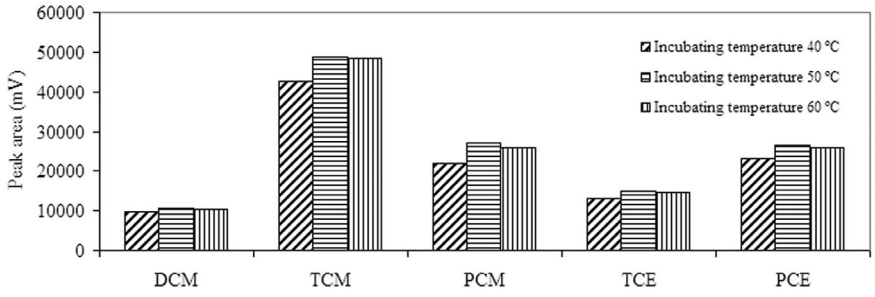

Figure 3. Effect of incubating temperature on peak area of the five VCHCs. Working solution: 24 μg/L DCM, 4 μg/L TCM, 0.1 μg/L PCM, 0.5 μg/L TCE, and 0.2 μg/L PCE; salt concentration: 20% w/v; equilibration time: 35 min; gas-to-liquid ratio: 1:1.

injection port was held at 220°C and used in the split mode with a split ratio of 10:1 in 0.75 min, and after 0.75 min, the split ratio was 50:1. A constant flow (1 mL/min) of nitrogen was used as a carrier gas. The analysis was performed with an initial column temperature of 40°C held for 5 min followed by heating to 100°C at 8°C/min, and finally, followed by heating to 200°C at 20°C/min and holding at 200°C for 1 min to clean the column. The total GC analysis time was 18.5 min. The ECD temperature was maintained at 300°C.

The CTC Combi PAL GC multifunction auto sampler (CTC Analytics GmbH) with headspace mode was used for auto sampling. Under the headspace mode, the incubating temperature was 50°C, and the equilibration time was 20 min.

Data acquisition and processing were carried out by a Varian Star450C chromatogram workstation (Varian).

2.3 Sampling and preservation

For the current experiment, pure water was obtained from a shop, tap water was collected from a laboratory, and sea water was collected from Jiaojiang Estuary (Taizhou, Zhejiang, China) and waters of Xiaomendao (Wenzhou, Zhejiang, China). In detail, there were three sea water sampling positions in the Jiaojiang Estuary, and nine sea water sampling positions were set up in the waters of Xiaomendao. These tap and sea water samples were collected in 250 mL amber glass bottles with polytetrafluoroethylene (PTFE)

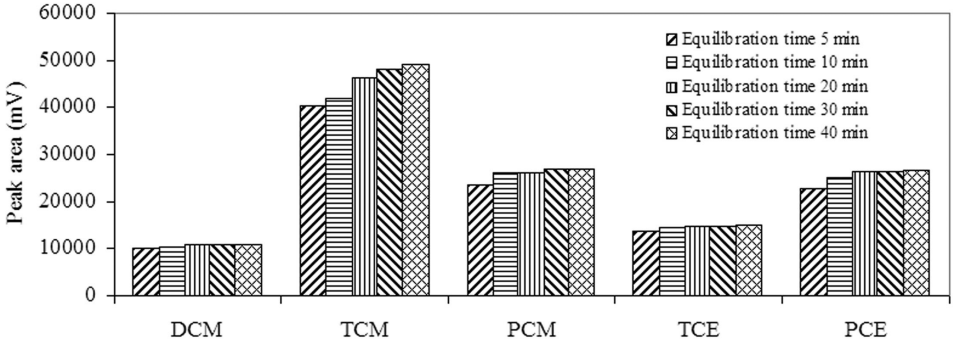

Figure 4. Effect of equilibration time on the five VCHCs signal. Working solution: 24 μg/L DCM, 4 μg/L TCM, 0.1 μg/L PCM, 0.5 μg/L TCE and 0.2 μg/L PCE; salt concentration: 20% w/v; incubating temperature: 50°C; gas-to-liquid ratio: 1:1.

screw caps and without headspace to avoid the evaporation of volatile compounds. The water samples were stored at 4°C and should be analyzed within 1 day of collection. When the time between sample collection and analysis exceeded 1 day, samples were stored at –20°C for up to 7 days.

2.4 Static headspace GC–ECD procedure

10 mL of pure water, or tap water, or sea water samples, or VCHCs standards prepared in ultrapure water was added to a 20 mL headspace clear vial with 2 g of NaCl. The vial was immediately tapped with a silver aluminum cap and PTFE-silicon septum and vortexed for 30 s for homogenization. Finally, the vial was placed in the 32-space autosampler and the robotic arm took each one and introduced it in the headspace oven to release VCHCs from the liquid to the gas phase in the aforementioned conditions. In the next step, the injection valve was switched and the nitrogen stream carried the sample loop content (injection volume 400 μL) towards the GC–ECD instrument. VCHCs separation through the chromatographic column was performed using the temperature programme mentioned above. Finally, the retention time was used for identification and external standard method for quantification.

2.5 Traditional LLE

Traditional LLE procedure was adopted from ISO 10301 [10]. Briefly, 200 mL of water was extracted with 10 mL of pentane by a mechanical shaker for 5 min. 2 μL of the pentane layer was injected into GC–ECD in splitless mode, and after 0.75 min, the split ratio was 50:1. The CTC Combi PAL GC multifunction auto sampler with liquid mode was used for auto sampling. The other GC–ECD conditions were carried out as described in Section 2.2.

3 Results and discussion

This study explored the applicability of static headspace to the analysis of VCHCs in aqueous matrices. The effect of a number of variables, including salt addition, gas-to-liquid ratio, equilibration time, and incubating temperature were investigated and optimized to achieve high sensitivity of the proposed method.

3.1 Effect of salt addition

The so-called salting-out effect is commonly used to improve the release of organic volatile compounds from an aqueous sample matrix to its headspace. The salting-out increases the ionic strength of the aqueous solution and, in this way, could decrease the solubility of target analytes; therefore, the vapor–liquid equilibrium system would be changed [40]. For investigating the influence of ionic strength on the performance of static headspace, experiments were performed by adding different amounts of NaCl (0∼30%). As shown in Fig. 1, salt addition influenced the headspace concentration of the analytes, and a higher salt concentration lead to a higher peak area. It was found that the peak area reached maximum around 20% for all analytes. Hence, the NaCl concentration was fixed at 20%.

3.2 Effect of gas-to-liquid ratio

The ratio of the volume of the gas and liquid in the vial can affect the concentration of the VCHCs in the headspace. To investigate the effect of gas-to-liquid ratio on peak area of VCHCs, 2.5, 5, 7.5, 10, and 12.5 mL working solution were added into a 20 mL headspace vial, respectively, which obtained gas-to-liquid ratio at 7:1, 3:1, 5:3, 1:1, and 3:5. As shown in Fig. 2, the signal abundance increased on decreasing the gas-to-liquid ratio up to 1:1, probably as the result of the increasing VCHCs concentrations in the headspace. Meanwhile, the results obtained for 3:5 were a little less than those provided for 1:1. Hence, the gas-to-liquid ratio was selected at 1:1.

3.3 Effect of incubating temperature

The incubating temperature had a profound effect on the sensitivity of the method because incubating temperature had a direct impact on the equilibrium concentration of the

Table 1. Dynamic linear ranges, regression equations, coefficients of determination, and limit of detections of VCHCs using the proposed static HS GC-ECD method; limits of detection obtained by other methods reported in the literatures

Analyte	DLR (μg/L)	Regression equation (y ~ x)[a)]	r^2	LODs (S/N = 3, μg/L)											
				Static GC HS ECD[b)]	LLE GC ECD[9]	P&T GC MS[15]	DAI GC ECD[22]	SPME GC ECD[23]	LPME GC ECD[25]	Static HS GC MS[12]	HS SDME GC MS[28]	HS SPME GC ECD[29]	HS SDME GC μECD[30]	HS LPME GC μECD[34]	HS-K-SPME GC MS[31]	HS SPME GC MS MS[30]
DCM	1.2 ~ 240	y = 351.32x + 2065	0.9980	0.3	__	0.062	0.6	__	__	__	0.119	__	__	__	5	__
TCM	0.2 ~ 40	y = 19780x − 24261	0.9979	0.04	0.055	0.002	0.05	0.03	0.45	0.1	0.176	0.0014	0.035	0.116	__	0.6
PCM	0.005 ~ 1	y = 280588x -1377.7	0.9988	0.001	0.002	0.002	0.07	0.001	__	0.5	0.019	__	0.004	0.006	__	__
TCE	0.025 ~ 5	y = 29592x +2321.1	0.9986	0.005	0.002	0.010	0.036	0.005	__	0.1	0.013	0.0013	0.025	0.146	__	0.2
PCE	0.01 ~ 2	y = 149980x+527.31	0.9990	0.002	0.002	0.014	0.024	0.001	__	0.05	0.028	0.00008	0.002	0.003	__	0.6

a)y and x stand for the peak area and the concentration of the analytes in 10 mL ultrapure water in 20 mL vial, respectively.
b)Data taken from the present work, and LODs stand for the concentration of the analytes in 10 mL of ultrapure water in 20 mL vial, GC-ECD analysis.

Table 2. Comparison of the optimized static HS procedure with other traditional LLE for concentrations (μg/L) of VCHCs in pure water, Tap water, 3 sea water samples from Jiaojiang Estuary, and 9 sea water samples from waters of Xiaomendao

Analyte	Pure water		Tap water		Sea water from Jiaojiang Estuary						Sea water from waters of Xiaomendao								
	Static HS	LLE	Static HS	LLE	Static HS Position 1	LLE	Static HS Position 2	LLE	Static HS Position 3	LLE	Static HS								
											Position 1	Position 2	Position 3	Position 4	Position 5	Position 6	Position 7	Position 8	Position 9
DCM	ND	ND	ND	ND	94.4	94.7	55.7	55.4	62.5	62.7	ND	ND	ND	7.7	10.2	10.9	28.2	13.9	16.6
TCM	3.21	3.25	4.58	4.55	23.82	23.84	22.53	22.56	15.37	15.36	1.26	1.28	1.56	1.42	1.28	1.35	23.53	8.35	5.77
PCM	0.025	0.027	0.033	0.034	0.293	0.295	0.298	0.295	0.095	0.096	0.029	0.136	0.138	0.147	0.145	0.167	0.490	0.198	0.191
TCE	ND	ND	ND	ND	0.063	0.061	0.048	0.049	0.144	0.147	ND	ND	ND	0.077	0.071	0.185	0.267	0.233	0.493
PCE	ND	ND	ND	ND	0.075	0.076	0.068	0.066	0.022	0.025	ND	ND	ND	0.032	0.033	0.043	0.182	0.054	0.052

"ND" stands for analyte is not detected.

Table 3. Results of relative recoveries and relative standard deviations ($n = 5$) obtained by applying the proposed static HS GC-ECD approach to the analysis of spiked water samples with external calibration

Analyte	Pure water				Tap water				Sea water from position 1 of Jiaojiang Estuary				Sea water from position 1 of waters of Xiaomendao			
	Add (μg/L)	Found (μg/L)	Recovery (%)	RSD (%)	Add (μg/L)	Found (μg/L)	Recovery (%)	RSD (%)	Add (μg/L)	Found (μg/L)	Recovery (%)	RSD (%)	Add (μg/L)	Found (μg/L)	Recovery (%)	RSD (%)
DCM	12.0	10.9	91	3.2	2.4	2.3	96	3.5	240.0	332.4	95	2.6	12.0	9.6	80	3.7
TCM	2.00	5.40	110	3.6	0.40	5.00	105	3.1	40.00	58.22	86	2.7	2.00	3.48	111	2.9
PCM	0.050	0.083	116	2.1	0.010	0.043	100	2.8	1.000	1.273	98	1.6	0.050	0.080	102	2.1
TCE	0.250	0.247	99	1.9	0.050	0.045	90	2.3	5.000	5.663	112	1.9	0.250	0.214	86	2.6
PCE	0.100	0.111	111	2.4	0.020	0.020	100	2.5	2.000	2.035	98	1.5	0.100	0.089	89	2.1

VCHCs in the headspace of the vial. Generally, the higher the temperature, the higher the concentration of VCHCs in the headspace of the vial will be. But if the incubating temperature was too high, the air tightness of the vial would have been poor and a large amount of water vapor could have entered into the headspace of the vial, which would have decreased the concentration of VCHCs. Incubating temperature at the stage of equilibrium was set up by investigating the response at different temperatures (40∼60°C). As shown in Fig. 3, when the temperature was less than 50°C, there were notable changes in response. But when the temperature was more than 50°C, the peak areas of VCHCs decreased slightly. Considering the response of all the analytes, it was demonstrated that 50°C was the optimal incubating temperature.

3.4 Effect of equilibration time

Another crucial factor of static HS refers to the equilibrium between the vapor and analyzed phases. The equilibrium time of its attainment depends on the desorption rate, which is determined by the slow migration of the retained chemicals from microscopic pores of the adsorbent, i.e., water samples, into the gas phase, this step limits the entire process. If the slowness of desorption is determined by the diffusion process, the only way to accelerate it is provided by temperature elevation. The elevation of the incubating temperature reduces the distribution ratio and enhances the sensitivity of the static HS process while equilibrium is attained. Figure 4 shows the influence of equilibration time on the signal of VCHCs at the incubating temperature of 50°C. As can be seen, from 5 to 20 min, the peak areas increased rapidly with equilibration time increasing within 20 min. When the equilibration time was more than 20 min, the peak areas tended to change a little, meaning that their static headspace equilibriums were nearly achieved. Since 18.5 min was needed for GC–ECD analysis, to realize the continuous sample analysis, the equilibration time was fixed at 20 min.

3.5 Evaluation of the method of performance

Calibration curves were drawn using seven points in the concentration range of 1.2–240 μg/L with respect to DCM, 0.2–40 μg/L with TCM, 0.005–1 μg/L with PCM, 0.025–5 μg/L with TCE, and 0.01–2 μg/L with PCE. Three replicate analytical processes were performed at optimal conditions (salt concentration: 20% w/v; gas-to-liquid ratio: 1:1; incubating temperature: 50°C; equilibration time: 20 min). The dynamic linear range (DLR), coefficient of determination (r^2) and the LODs were calculated and summarized in Table 1. The RSDs ($n = 3$) were in the range of 2.1–3.7% for the five VCHCs. A good linear correlation ($r^2 > 0.99$) between the concentration and peak area of analytes was obtained for all target analytes from the linearity test solutions.

Table 1 also present the reported LODs values found in the literature for analysis of VCHCs in water samples when

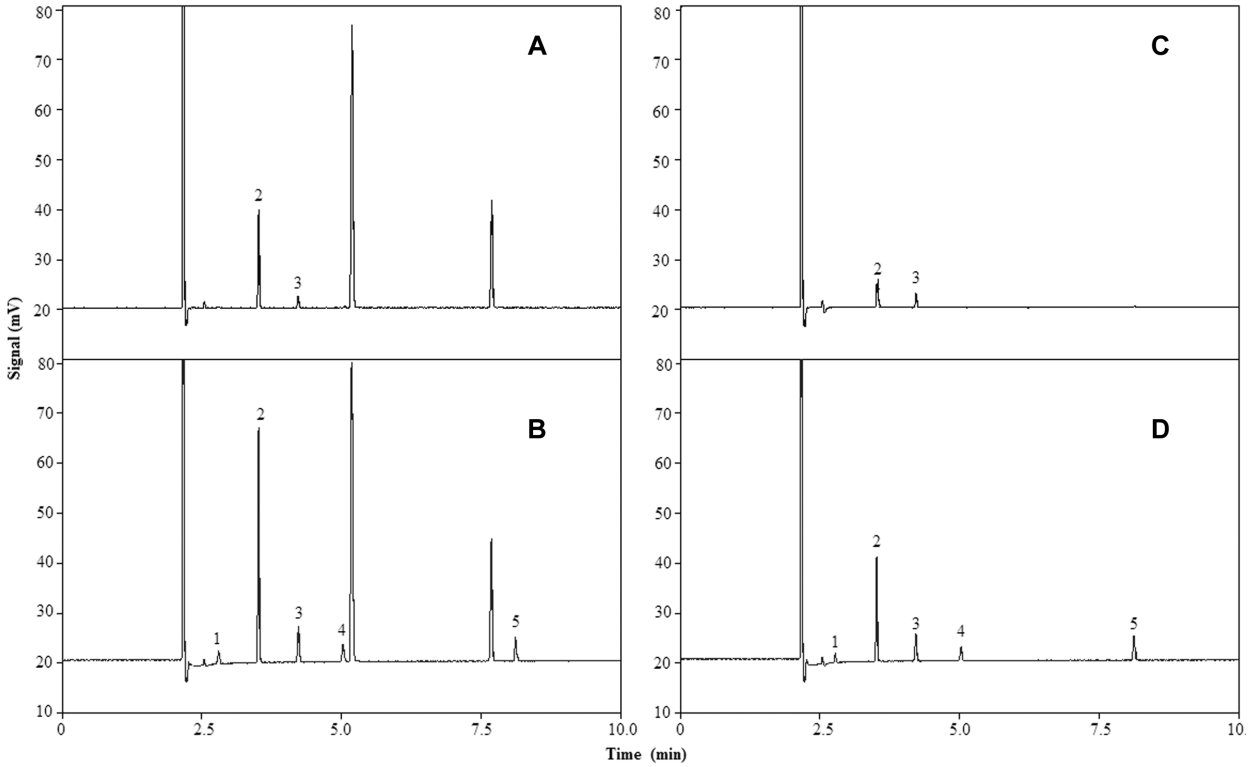

Figure 5. Chromatogram of (A) pure water, (B) spiked pure water, with 12 μg/L DCM, 2 μg/L TCM, 0.05 μg/L PCM, 0.25 μg/L TCE and 0.1 μg/L PCE, (C) sea water from position 1 of waters of Xiaomendao, and (D) spiked sea water from position 1 of waters of Xiaomendao, with 12 μg/L DCM, 2 μg/L TCM, 0.05 μg/L PCM, 0.25 μg/L TCE and 0.1 μg/L PCE. Gas-to-liquid ratio: 1:1; salt concentration: about 20% w/v; incubating temperature: 50°C; equilibration time: 20 min. Peaks: 1. DCM; 2. TCM; 3. PCM; 4. TCE; 5. PCE.

using LLE GC–ECD [9], P&T GC–MS [15], DAI–GC–ECD [22], SPME–GC–ECD [23], LPME–GC–ECD [25], static HS–GC–MS [12], HS-SDME–GC–MS [28], HS-SPME–GC–ECD [29], HS-SDME–GC–μECD [32], HS-LPME–GC–μECD [34], HS-K-SPME–GC–MS [31], and HS-SPME–GC–MS/MS [30]. It is seen in Table 1 that the LODs of VCHCs obtained with the proposed static HS–GC–ECD are superior to those obtained with DAI–GC–ECD [22] as well as with LPME–GC–ECD [25], static HS–GC–MS [12], HS-LPME–GC–μECD [34], HS-K-SPME–GC–MS [31], and HS-SPME–GC–MS/MS [30]. In comparison with P&T–GC–MS [15], HS-SDME–GC–MS [28], and HS-SDME–GC–μECD [32], the LODs obtained from the static HS–GC–ECD are lower (except for DCM or TCM). The proposed static HS–GC–ECD shows comparable LODs with LLE–GC–ECD [9] and SPME–GC–ECD [23]. Furthermore, HS-SPME–GC–ECD [29] gave lower LODs than those obtained with our proposed static HS–GC–ECD. As was discussed in Section 1, LLE requires a large volume of organic solvent and it is time-consuming procedure. The main disadvantage of SPME and HS-SPME is that the extraction fiber is expensive and fragile, so it has a limited lifetime. Nonetheless, in contrast to other methods, the static HS–GC–ECD does not require an organic solvent for extraction. Furthermore, the static HS–GC–ECD requires no additional instrumentation minimizing the cost of analysis per sample. Therefore, the present method is a simple, sensitive technique and can be used for the determination of VCHCs in the water samples.

The validation of the developed static HS was carried out using spiked real water samples with three different concentration levels. In addition, the efficiency of the proposed method was also compared with traditional LLE on the same spiked water samples. The details are given in Section 3.6.

3.6 Real water analysis

To investigate the matrix effect on the efficiency of the proposed method, pure water, tap water, and sea water were examined under a set of optimal conditions. The results are shown in Table 2. As can be seen, the results were similar to pure water and tap water. They were free of DCM, TCE, and PCE, but contained traces of TCM and PCM. This may due to that chlorine in one form or another is by far the most commonly used chemical for the disinfection of water supplies. Furthermore, when chlorine has an interaction with impurities in water, the degradation products such as TCM and PCM are emerged. The five VCHCs were all detected in sea water samples which from three sea water sampling positions in the Jiaojiang Estuary and six sea water sampling positions in the waters of Xiaomendao. Sea water samples from the other three sea water sampling positions

in the waters of Xiaomendao only contained TCM and PCM. The total content of the five VCHCs in the Jiaojiang Estuary was higher than that in waters of Xiaomendao. The detected five VCHCs in sea water samples could be because of to the influence of the harbor chemical industry. Additionally, TCM and PCM were present in all samples because they were produced during disinfection but they were also widely used in industry. Comparable results were also obtained when traditional LLE was applied to the same pure water, tap water, and three sea water samples from Jiaojiang Estuary (Table 2).

VCHCs with three different concentration levels were spiked into 10 mL water samples to assess matrix effects and test recovery (Table 3). Table 3 shows that the relative recoveries of the VCHCs with external calibration from pure water, tap water, sea water of Jiaojiang Estuary, and sea water of waters of Xiaomendao were in the range of 91–116, 96–105, 86–112, and 80–111%, respectively, with RSDs of 1.9–3.6, 2.3–3.5, 1.5–2.7, and 2.3–3.7% ($n = 5$), respectively. The results indicated that the matrices of the pure water, tap water and sea water had a negligible effect on the performance of the method. The results obtained were satisfactory, and these data supported the suitability of the proposed static HS–GC–ECD method for its application to real samples.

Moreover, the efficiency of the proposed static HS was also compared with traditional LEE on the same spiked pure water, tap water, sea water of Jiaojiang Estuary. The relative recoveries of the VCHCs using traditional LLE methods from pure water, tap water, and sea water of Jiaojiang Estuary were in the range of 90–105, 91–102, and 83–94%, respectively, with RSDs of 2.8–4.9, 3.3–5.4, and 3.1–5.9% ($n = 5$), respectively. The results showed that the proposed method gave comparable results with traditional LLE method. However, it should be emphasized that the optimized static HS is not laborious procedure and it is not necessary to re-concentration before the GC analysis. Furthermore, it is free of solvents, demands little sample handing, and is automated in this study.

Figure 5 shows the chromatogram obtained for pure water, spiked pure water, sea water from position 1 of the waters of Xiaomendao and spiked sea water from position 1 of the waters of Xiaomendao at certain concentration level of VCHCs. It showed that the selected chromatographic conditions resulted in good chromatographic resolution, with good peak separation.

4 Conclusions

This study has outlined the successful development and application of a static HS technique for the determination of five VCHCs in aqueous matrices by using GC–ECD. The optimized extraction conditions for 10 mL of sample were as follows: a sodium chloride addition of 20%, a gas-to-liquid ratio of 1:1, an equilibration time of 20 min, and an incubating temperature of 50°C. Analysis of real water samples showed that sample matrices had no adverse effect on the efficiency of proposed static HS method. As a consequence, the proposed method is simple, convenient, precise, and solvent-free as well as sensitive. In addition, the developed static HS–GC–ECD method has been demonstrated to be viable, rapid and easy to use for the qualitative and quantitative analysis of VCHCs in pure water, tap water, and sea water.

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