Construction and validation of an automated spray-and-trap gas chromatograph for the determination of volatile organic compounds in aqueous samples

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Abstract

An automated spray-and-trap (ST) chromatographic system was constructed for fast and efficient extraction of volatile organic compounds (VOCs) in aqueous samples with the capability to be deployed in the field for unattended continuous monitoring of surface or ground water. This system was built upon a commercial gas chromatograph with full automation capability using self-developed hardware and software. For sample analysis, fine droplets of the aqueous solution were generated in the extraction chamber by pressure expansion of a clean air stream through a spray nozzle. A portion of the VOCs distributed into the gas phase was retained by a multi-sorbent micro-trap kept at ambient temperature. Flash heating of the sorbent trap desorbed the enriched VOCs onto the gas chromatography (GC) with flame ionization detection (FID) for hydrocarbons or electron-capture detection (ECD) for halocarbons. In order to validate the performance of the ST method, it was compared with a more conventional method, i.e., a purge-and-trap (PT), by analyzing a serious of standard solutions containing benzene, toluene, ethylene, and *o*-, *m*-xylenes. Using a purge-and-trap method as a reference for complete extraction, the ST method showed less sensitivity. Extraction recoveries are in consistent with Henry's law constants. To test response time the ST–GC–ECD was periodically switched between tap and underground waters. Negligible carry-over of halogenated species and reproducibility better than 2% relative standard deviation (R.S.D.) can be achieved regardless of large concentration difference between the two sources, thus demonstrating applicability of the ST system for on-site monitoring.
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1. Introduction

Various gas extraction techniques have been developed to extract dissolved volatile organic compounds (VOCs) in aqueous samples for qualitative and quantitative determination. These techniques consist of static headspace (HS) [1,2], dynamic headspace [3–11], spray-and-trap (ST) [12–14], solid-phase microextraction (SPME) [15,16], membrane inlet [17–20], etc. which are then combined with gas chromatography (GC) or mass spectrometry (MS) for analyzing dissolved VOCs. Among these techniques the static or dynamic headspace methods have become the most widely used methods in environmental laboratories, even though other emerging techniques such as the SPME

method have gained increasing attention from various research disciplines [21]. Conventional dynamic headspace (so called purge-and-trap (PT) method), which was first described by Swinnerton et al. [3], extracts dissolved VOCs by passing a stream of inert gas through a glass frit or a small-bore needle to generate many small gas bubbles in an aqueous sample held within a sealed glass tube. This way, large interfacial surface area between gas and liquid is created thus speeding up the distribution of VOCs between phases. The dissolved VOCs are eventually removed almost completely from the water sample as the inert gas constantly strips VOCs from the liquid phase. This exhaustive extraction method is in theory more sensitive than equilibrium techniques like the static HS method which does not result in a full extraction of VOCs. Using these techniques (both static and dynamic) cryogenic traps and/or sorbent traps are very useful to enrich extractable analytes. Generally, these traps must be flash-heated to desorb retained VOCs

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onto a GC as narrow injection bands for separation and detection.

Purge-and-trap has two main drawbacks: foaming and slowness of the purging step. Foaming is often caused by high content of surfactants (nearly 30% of all industrial water waste contains some degree of surface-active compounds); it often creates the risk of contaminating the chromatographic system. Moreover, to achieve low detection limits and to increase precision, large sample volumes and long purging times are usually employed. Typical extraction times are in the 10–30 min range, which can significantly limit sample throughput especially using high-speed GC or direct MS, which are inherently fast analytical techniques and potentially useful in achieving short turn-over time for real-time monitoring of aquifer bodies [19,22,23].

These shortcomings of PT can be overcome by employing the spray-and-trap extraction device, which was first developed by baykut and Voigt [12], and then applied in field analyses by Matz and Kesners [13]. In the ST approach a spray nozzle based on Bernoulli effect generates very small droplets of sample within an extraction chamber. This accelerates the partition of VOCs because a small volume of water sample contacts a large volume of extracting gas, an opposite process of PT. In this manner, extraction of a sample aliquot can be faster than PT, and could be useful to monitor waste waters in cases where fugitive release of toxic organic solvents may occur, for which fast response to a sudden rise in concentration is sometimes an important advantage.

This work reports the construction of an automated ST–GC system for on-line determination of dissolved VOCs in water. This system required minimum cost both in the construction and routine operation. For validation purpose the new PT was compared with our previously designed PT system by analyzing target toxic substances using flame ionization detection (FID) for non-halogenated compounds and electron-capture detection (ECD) for halogenated compounds.
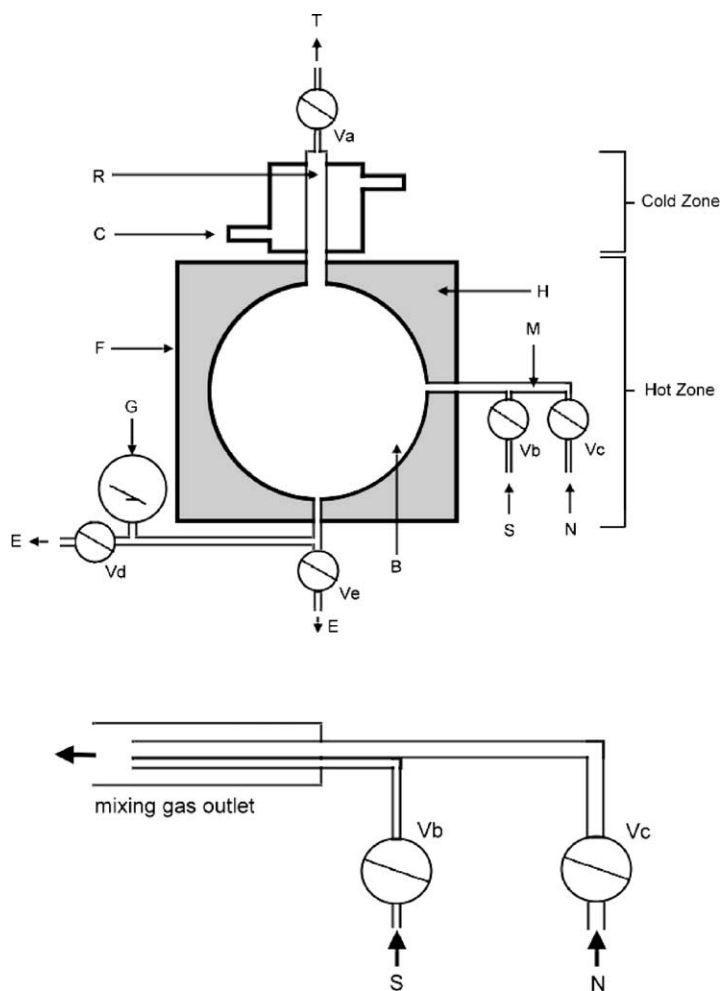

Fig. 1. Schematic diagram of the ST chamber with the spray nozzle enlarged for viewing details. Important components are labeled as following: T, extracting gas outlet going to the enrichment device; R, water condenser with circulating ice water; C, ice water inlet; H, heated zone; F, aluminum enclosure; M, nozzle assembly; B, spray chamber; G, pressure gauge; S, water sample inlet; N, extracting gas (N_2); E, drain port; and V(a, b, c, ...), solenoid valves.

2. Construction of the ST system

2.1. Controlled hardware and software

Operation of the ST–GC was automated by synchronizing the ST chamber actions with the GC. The control hardware used in this system consisted of an I/O board (PCL-724, Advantech, Taiwan), a power relay board (PCLD-785D) for controlling solenoid valves and initiating a process controller (Powers 535, Skokie, IL, USA) for temperature ramping of the trap, and to start/stop the GC. A Windows-based software platform (VisiDAQ3.1, Advantech, Taiwan) provided a Visual Basic programming environment for writing the control code with graphical display of key actions including parameters like time elapsed, valve position, GC on/off status, and current trap status (such as trapping, dry purging, or injecting), so that the operator can be aware of the analytical status.

Preconcentration and focusing of analyses required a micro-sorbent trap made by a stainless-steel tube of $8\,cm \times 1\,mm$ i.d. $\times 1/16$ in. o.d. (1 in. = 2.54 cm) packed with 2 cm each of Carboxen 1000 and Carbonxen 1003 (60–80 mesh, Supelco, Bellefonte, PA, USA). No additional focusing stage was needed as the micro-trap provided suffi-
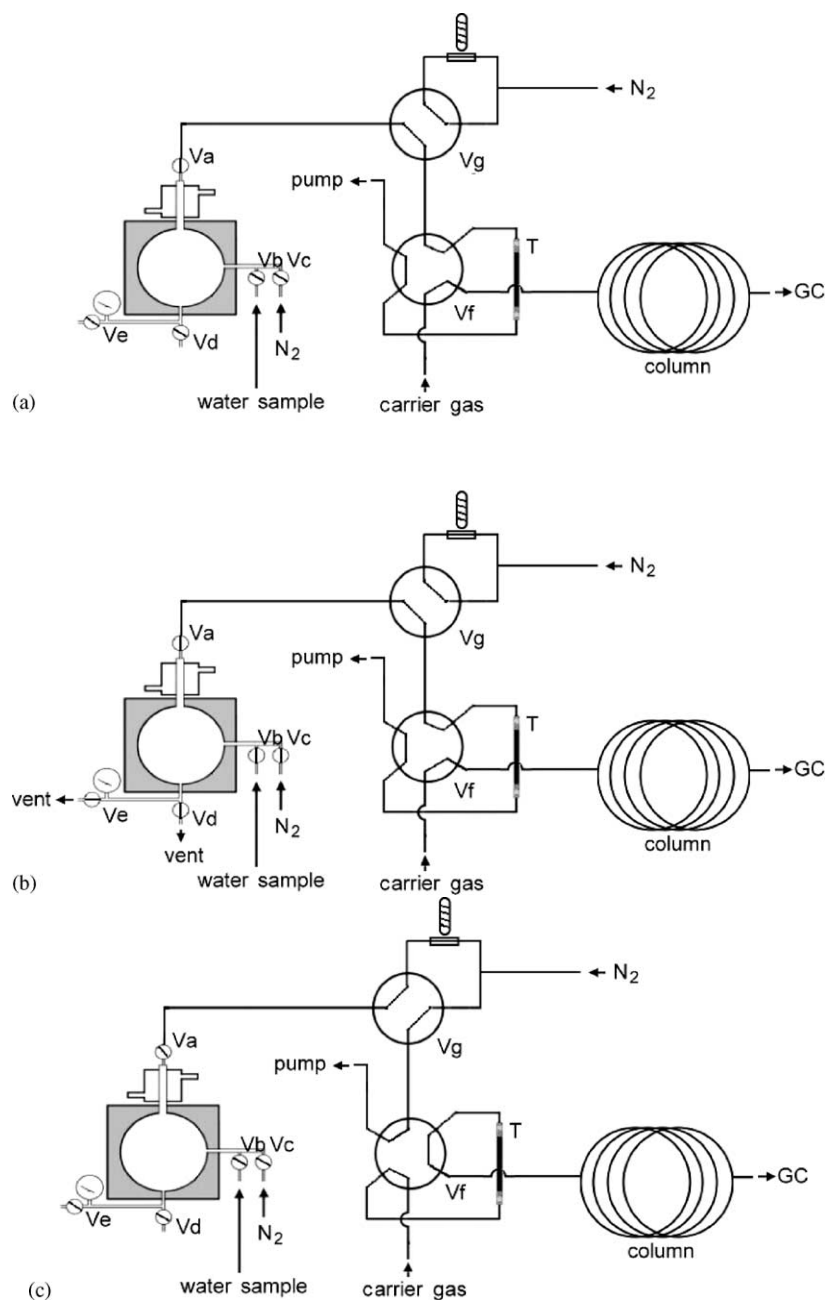

Fig. 2. Schematic diagram of the entire auto ST–GC system consisting of a spray chamber; an enrichment stage, and a GC. (a) Short-pulsed ST operation; (b) long-pulsed ST action; and (c) sample injection.

cient trapping capacity and, at the same time, fast desorption speed to minimize broadening effect.

A process controller was used to control the trap temperature, so that a temperature fluctuation of $\pm 1\,^{\circ}C$ was achieved at any setpoint. VOC molecules with sizes between C_3 and C_{12} could be quantitatively trapped at room temperature including very volatile compounds such as CCl_2F_2 (CFC-12). Detailed description for the enrichment and thermal desorption design can be referred to our previous publication [11,24].

2.2. Spray-and-trap device

A spray chamber was made with a 1200 ml Pyrex round bottle with three side arms connecting to a nozzle, a drainage port, and a vent port each arm having a solenoid valve (see system configurations reported in Fig. 1). The entire glass chamber was wrapped around with a heating tape to keep its temperature at $90\,^{\circ}C$ to facilitate rapid gas–liquid distribution. During spray the temperature dropped slightly due to cooling by spray gas and water droplets. Because the process was repetitive, the temperature change was reproducible. The spray nozzle was made by welding a piece of 1.0 mm i.d. $\times$ 1/16 in. o.d. tubing onto the outside of another piece of 2.1 mm i.d. $\times$ 1/8 in. o.d. tubing. Suction and spray of the liquid sample at the opening of the smaller bore tubing occur when a high speed N_2 flows through the closely attached larger bore tubing (see Fig. 1). The dual tubing nozzle was housed in a 4.3 mm i.d. $\times$ 1/4 in. o.d. tube inserted to the side opening of the chamber and sealed by a

PTFE stopcock. All the materials used for construction of the chamber were cheap and of common use.

The chamber was then coupled to an enrichment unit consisting of two valves (Vf and Vg parts), and a sorbent trap (Fig. 2). Glass chamber valves and enrichment unit were automated permitting repetitive ST cycles for continuous analysis of an aqueous sample. Repeatability of the operations with the ST device was assured by the control software.

2.3. Analysis procedure

A series of valve combinations were attempted to optimize the spray condition. Described below are some of the relevant steps in an analytical cycle designed for fast extraction with adequate precision and sensitivity.

2.3.1. Spray-and-trap

As shown in Fig. 2a, at the onset of the spray action all the valves on the chamber were opened except valve Va so that the high pressure N_2 extraction gas was expanded into the chamber, at the same time drawing and spraying water sample into the chamber for a predetermined time period. Two spray-and-trap modes were attempted for studying the spray efficiency and sensitivity. In one mode, immediately after the spray action, the two venting valves, Ve and Vd, were closed along with the valve Vb. Vc was shut off 1 s later to pressurize the chamber to exceed 1.5 bar so that more N_2 molecules were to be in contact with the water droplets to facilitate rapid extraction. The amount of water that can be sprayed was limited by the chamber pressure, which was never al-
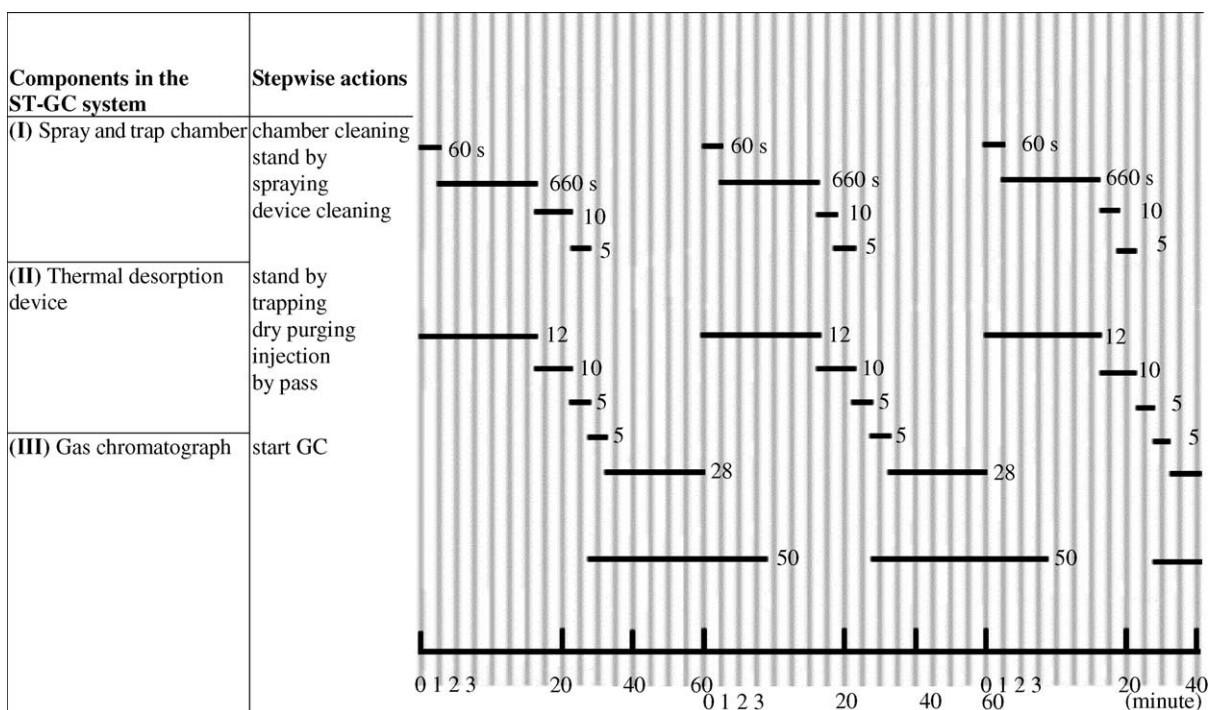

Fig. 3. Time sequence of a complete ST–GC analytical cycle.

lowed to exceed 1.5 bar for safety concerns. Approximately 2 ml of water sample was able to be introduced in one short pulse of spray. Subsequently, Va was opened while Vb and Vc were closed to allow the extraction gas to be sampled by the preconcentrator. The sensitivity of this method is determined by at least three factors, namely spraying conditions, amount of sample that can be sprayed, and amount of extraction gas that is sampled. While the spraying conditions, such as the size of droplets, the extracting gas flow rate, the design of the nozzle, etc. were fixed, such a short-pulsed mode of ST constrained the sensitivity by only introducing a limited amount of sample and extraction gas, of which a portion was also lost from the drainage port. By contrast, the extraction with the PT method is more complete, as no extraction gas and water sample is allowed to escape.

Such a restriction with the short-pulsed mode of ST can be lifted if both the spray and the enrichment time are extended. However, when taking into account the pressure limit, the vent port at the bottom had to be opened to prevent the pressure from exceeding 1.5 bar (see Fig. 2b). Maintaining a slight positive pressure within the chamber is advantageous to facilitate longer residence time for VOC molecules within the chamber later to be enriched by the trap. In this mode of spraying a portion of the N_2 into the chamber was constantly drawn through the trap at a flow rate of 100 ml/min with excess water vapor condensed by a condenser chilled by ice water. Since the spraying was continuous, excess N_2 pressure and the water inside the chamber continued to drain through the bottom port. Inevitably, a large portion of the extracted VOCs in the chamber never traveled to the trap and was lost in the ventilation. In this long-pulsed action, each spraying consumed about 25 ml of water sample. Nevertheless, the sensitivity was not increased proportionally to the sample amount, because of the lower recovery arising from pressure venting compared to the short-pulsed spray-

ing. However, because the device was intended for on-line monitoring of a water body such as a surface runoff or a ground water source, presumably the system should have an unlimited supply of water sample. So long as the trapping volume is kept below the breakthrough volume of the trap, the spray action can continue to compensate the poorer recovery.

2.3.2. Sample injection

Upon injection the temperature of the trap tubing was rapidly ramped from 30 to 250 °C by ohmic heating within a few seconds. Immediately valves were switched to route He carrier gas to the trap flushing VOCs onto the column (see Fig. 2c).

2.3.3. System cleaning

Prior to the start of an analytical cycle a N_2 flow was allowed to flush the chamber (Fig. 2a) to force any remaining water sample from previous cycle out of the chamber. At the same time a stream of N_2 flowed through the trap kept at 300 °C to flush out any remaining high boiling residual. Detailed time sequence and analytical conditions for a complete ST–GC analysis are shown in Fig. 3 and Table 1.

3. Analysis and performance validation

To assess the performance and applicability, ST method was compared with the PT method which has become the backbone of various standard methods for determining VOCs in water samples announced by the US Environmental Protection Agency (EPA) [25–27]. Both methods were optimized for their best performance during the comparison and their performance was based on analyses of standard solutions containing benzene, toluene, ethylbenzene, and *o*-

Table 1
Analytical conditions for ST and PT methods

| Condition	ST	PT
Sampling		
Temperature	90 °C (spray extraction chamber) Room temperature (condenser)	Room temperature (purge tube)
Pressure	20 psi (spray by N_2) 0.5 bar (spray extraction chamber)	
Flow rate		30 ml/min (N_2)
Sample amount	2.0 ml	5.0 ml
Thermal desorption (same for ST and PT)		
Adsorbent bed	Carboxen 1000, Carboxen 1003	
Sorption temperature	30 °C	
Desorption temperature	250 °C	
GC (same for ST and PT)		
Detector	FID, ECD	
Column	Supelco SPE-1 (60 m × 0.25 mm i.d.; film thickness 1.5 μm)	
Temperature programming	Initial $T = 90$ °C (hold 15 min) → 10 °C/min → 200 °C (hold 24 min)	
Carrier (He) pressure	Initial $P = 30$ psi (hold 15 min) → 5 psi/min → 50 psi (hold 31 min)	

1 psi = 6894.76 Pa.
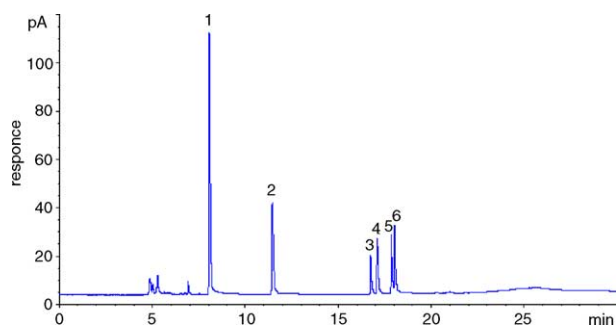
Fig. 4. A typical ST–GC–FID chromatogram for a standard mixture containing (1) benzene; (2) toluene; (3) ethylbenzene; (4) *m*-xylene; (5) styrene; and (6) *o*-xylene.

and *m*-xylenes (BTEX). These standard solutions were prepared by dissolving reagent grade solvents into methanol, from which further dilution with water was made to prepare approximately 10, 20, 30, 40, and 50 μg/l of water solutions. Since the ST–GC–FID method was automated, the only manual labor involved was the change of sample bottles. These bottles had a large volume of 1.2 l to allow several injections of a water sample without a significant change in the headspace volume, so that for repeated injections the depletion of BTEX due to the slightly increased headspace was negligible. Fig. 4 shows the chromatogram from extracting a standard mixture of 50 μg/l of BTEX by the ST method using the short-pulsed operation mode. Styrene was present as the impurity in the reagents. Similar result was also obtained by the PT method.

Both modes of ST operation were tested for sensitivity. Even though the long-pulsed mode consumed about 10 times

the sample amount used for the short pulsed mode, the signal strength only increased by a factor 1.5–2.4 for BTEX, suggesting rather poor recoveries than the short-pulsed mode. The ratios of short-pulsed ST response to PT response on per ml basis for BTEX can be regarded as the recoveries of ST method since the extraction of PT method was exhaustive (see Table 2). Not only the recoveries of ST were lower in general than those of PT, as the extraction of ST is not as complete as that of the PT, also they varied between BTEX and exhibited compound dependence which may be controlled by the Henry's law. In theory, the Henry's law constant, K_H, which has the unit of atm (1 atm = 101 325 Pa), l/mol, determines the distribution of a compound between the solution and its headspace. As described by the Henry's law, the vapor-phase partial pressure of the species is proportional to its mole fraction in the solution by assuming the solution being ideal. Compounds with smaller K_H values suggest higher solubility in water and lower vapor pressure in the headspace and, in theory, are more difficult to extract. Consequently these compounds should show lower sensitivities than the ones with larger K_H values (Table 2). A lower concentration (e.g., 10 μg/l) BTEX recoveries by ST show a trend consistent with K_H values. At higher concentrations the relationship with K_H values failed presumably because of the non-ideality of the solution when the interaction between compound and compound or compounds and solvent became more pronounced, and the solution environment were different from the environment in their pure forms.

Linearity and reproducibility of both methods were examined by analyzing five standard mixtures diluted in series from the of 50 μg/l BTEX stock solution and seven repli-

Table 2
Recoveries (%) of ST method for BTEX represented by the ratios of the ST response to the PT response at various concentrations[a] for unit of sample volume

Compound	K_H[b]	10 μg/l	20 μg/l	30 μg/l	40 μg/l	50 μg/l
Benzene	0.23	71.0 ± 3.6	83.1 ± 3.6	75.6 ± 2.7	80.6 ± 3.6	78.9 ± 2.4
Toluene	0.272	96.4 ± 4.0	81.8 ± 3.4	86.6 ± 3.5	85.0 ± 3.9	84.8 ± 4.7
Ethylbenzene	0.336	108.8 ± 8.4	89.5 ± 4.4	72.9 ± 3.8	72.2 ± 5.4	69.5 ± 3.1
m-Xylene	0.32	95.6 ± 6.7	65.8 ± 3.4	64.2 ± 2.2	54.8 ± 2.6	54.8 ± 2.0
o-Xylene	0.212	61.0 ± 3.9	2.2 ± 2.7	52.9 ± 2.2	51.7 ± 1.4	51.1 ± 1.1

[a] $n = 7$.
[b] Henry's law constant at 25 °C.

Table 3
Detection limits (DL), precision (R.S.D.) and linearity (R^2) for BTEX determined by both ST and PT[a]

Compound	Concentration range (μg/l)	ST			PT		
		DL (μg/l)	R.S.D. (%)	Linearity (R^2)	DL (μg/l)	R.S.D. range (%)	Linearity (R^2)
Benzene	10.14–50.70	0.93	0.71–2.78	0.9996	1.18	1.27–3.93	0.9984
Toluene	10.84–54.20	1.12	2.06–3.89	0.9977	0.51	1.07–2.07	0.9962
Ethylbenzene	10.32–51.60	1.37	0.7–5.51	0.9996	1.88	1.77–6.25	0.9965
m-Xylene	10.46–52.30	1.70	2.16–4.88	0.9904	1.32	1.14–4.42	0.9972
o-Xylene	10.19–50.95	1.71	3.44–7.27	0.9989	0.92	0.62–3.08	0.9995

[a] $n = 7$.

cates for each concentration were made by both the ST and the PT methods (see Table 3). Comparable to the PT method, the ST method showed satisfactory results with R^2 better than 0.990 and the relative standard deviation (R.S.D.) in the range of 1–7%, mostly within 4%.

The ST method was further tested for its applicability to be used in unattended continuous monitoring of surface or ground water. For these applications a fast response to an abrupt concentration changes in these water bodies (e.g., fugitive dumping or discharge of waste organic compounds into rivers, lakes, and ground water) is a clear advantage. Tape water was chosen to be the target samples and ECD was used for detecting on-line halogenated species commonly found in tap water due to the chlorination treatment in the water plants. To assess the carry-over and blank prob-

lem and, more importantly, the fast response to the rapid change in concentrations, an underground water source was analyzed in between the tap water analyses to serve as a blank, as no halogenated compounds should exist in the underground. Fig. 5 shows the chromatograms of these two water sources. Several halocarbons were found in tap water in relatively high concentrations including $CHCl_3$, $CHCl=Cl_2$ and $CHBrCl_2$. Only traces of halocarbons residuals could be detected in the underground water possibly due to minor contamination of the underground water since ECD is extremely sensitive in detecting these halogenated species. By switching the water sources between the tap water and the underground water, the PT–GC–ECD was able to sensitively detect the change in concentration (Fig. 6) and maintain its stability during continuous operation.
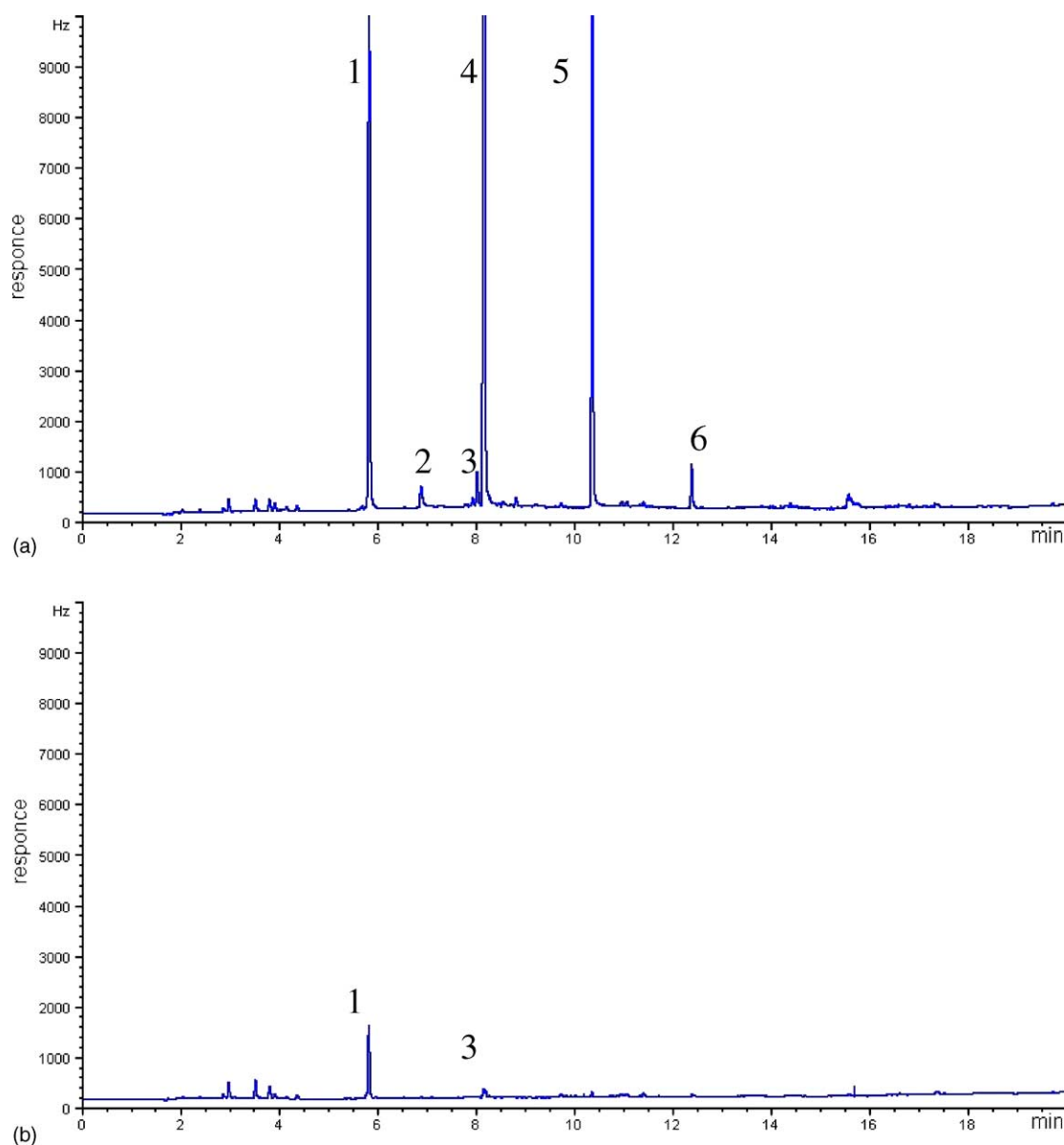

Fig. 5. Chromatograms of ST–GC–ECD for: (a) tap water and (b) underground water. Both chromatograms are on the same scale for easy comparison of species abundance. Peaks are identified as: 1, $CHCl_3$; 2, CCl_4; 3, CH_2Br_2; 4, $CHCl=CCl_2$; 5, $CHBrCl_2$; 6, $CCl_2=CCl_2$.
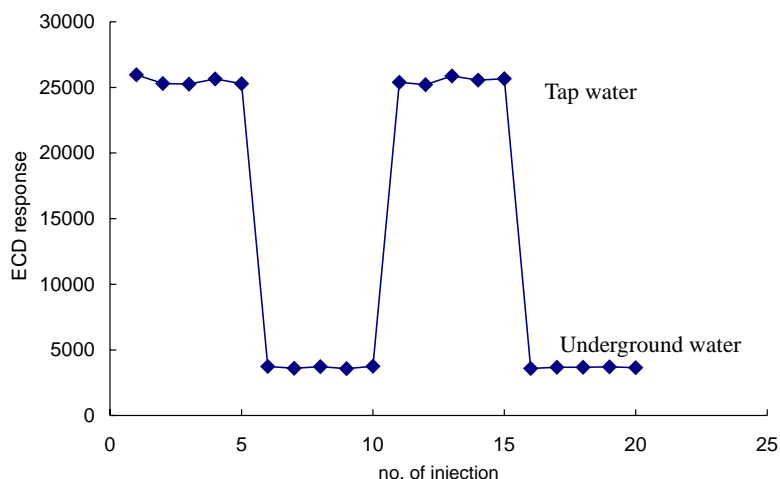
Fig. 6. Test of ST–GC–ECD system's fast response to concentration change by alternating between tap water and underground water for every five consecutive runs.

4. Conclusion

An automated spray-and-trap device was built in the laboratory and coupled to GC–ECD or GC–FID in an attempt to on-line monitor the dissolved VOCs in water bodies, which conventionally was performed by field sampling followed by in-laboratory PT analysis. The studied ST method was validated in comparison with classic PT: recoveries, precision, and linearity are reasonable, though inferior to PT.

When compared to the PT which permitted exhaustive extraction of BTEX, the ST showed poorer recoveries for BTEX, which however when performed at the lowest concentration were in consistent with their Henry's law constants.

The ST method shows a fast response to abrupt changes in sample quality, which makes it suitable for on-site monitoring of a water body.

Acknowledgements

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