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A fully automated portable gas chromatography system for sensitive and rapid quantification of volatile organic compounds in water†

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This paper presents the design, assembly and characterization of a fully automated portable gas chromatography system coupled with a purge-and-trap system for the sensitive and rapid field analysis of volatile organic compounds (VOCs) in water samples. The VOCs were firstly purged by helium gas in the micro-fabricated preconcentrator/injector and then injected into the downstream capillary column and photoionization detector for separation and detection. The purge-and-trap conditions were optimized to efficiently extract VOCs from water samples. The calibration of 6 VOCs with concentrations ranging from 1 $\mu\text{g L}^{-1}$ to 500 $\mu\text{g L}^{-1}$ showed excellent linearity ($R^2 > 0.99$). Detection limits (3σ) of sub- $\mu\text{g L}^{-1}$ (or sub-parts-per-billion level) were achieved, which are orders of magnitude lower than the maximum contaminant level (MCL) established by the US Environmental Protection Agency (EPA). The separation of 26 analytes (in a vapor pressure range from 0.087 Torr to 180 Torr) in a water sample in less than 15 minutes was also demonstrated. Finally, the optimized system was applied to field analysis of a groundwater sample in an environmental remediation site. The quantified results agreed well with those obtained by an analytical lab using standard analytical methods and instruments. Our system offers a lab-on-a-chip solution for sensitive and rapid water analysis compliant with the EPA sample collection method. It will have a wide range of applications in environmental monitoring, industries and healthcare.

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Introduction

Contamination of natural water by volatile organic compounds (VOCs) is a major environmental issue due to their toxicity and various adverse effects on human health.^{1,2} Possible sources of those compounds include industrial effluents, waste disposal, solvents, gasoline or oil spills on the ground surface, pesticides and herbicides used in agriculture, and disinfection processes.³ To protect the public from contaminated water, the Environmental Protection Agency (EPA) established the maximum contaminant level (MCL), which is the highest level of a contaminant allowed in drinking water. Since the MCLs for many VOC contaminants are very low ($\mu\text{g L}^{-1}$ or parts-per-billion in terms of mass), sensitive and quantitative analytical

methods are greatly needed for long-term monitoring and remediation applications.

In recent years, sensor arrays or electronic noses have made significant progress in VOC mixture analysis, including surface acoustic waves (SAWs),⁴ quartz crystal microbalances (QCMs),⁵ metal-oxide-semiconductor field-effect transistors (MOSFETs)⁶ and colorimetric sensors.⁷ These sensor arrays are cost effective and compact in size, some of which have also achieved low detection limits; however, with an increased number of compounds, the complexity of multivariate analysis or pattern recognition for reading the response patterns of the sensor arrays increases. On the other hand, gas chromatography (GC) coupled with spectrometers (such as mass spectroscopy (MS)⁸⁻¹² and ion mobility spectroscopy (IMS)^{13,14}) or other vapor detectors (such as flame ionization detectors (FIDs),¹⁵ photoionization detectors (PIDs),¹⁶ thermal conductivity detectors (TCDs)¹⁷ and electron capture detectors (ECDs)¹⁸) are more suitable for complex analysis, where VOC mixtures are separated and subsequently detected and quantified individually. Nowadays, the well-established analytical method for quantification of VOCs is the EPA Method 5030C/8260B,^{19,20} by which samples are first collected to canisters and then taken to a well-equipped analytical chemistry laboratory for GC-MS analysis. This process is time consuming (from a few days to over a week) and

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costly. Additionally, volatilization losses and contamination of the samples may occur during shipment and storage.

Field-portable GCs^{15,21–28} and MEMS-based micro scale gas chromatography (μ GC) systems^{17,29–33} have been developed for analyzing VOCs on-site. Most portable GC/ μ GC systems consist of a micro-preconcentrator/injector (μ PCI),³⁴ an injection port, a separation column, a detector and a pump or a carrier gas cartridge, all of which are fluidically interconnected. Various detectors have been integrated in these systems, such as chemiresistors,^{21,23} ion trap mass spectrometers,^{23,25,26} SAW microsensors,^{26,35} micro-FIDs¹⁵ and bubble based microfluidic sensors.³⁶ However, most of these portable GC and μ GC systems are focused on air sampling, and only a few systems can be used to analyze VOCs in water samples, such as the portable GC/SAW system with liquid extraction²⁵ or static headspace sampling,²⁶ the portable GC- μ FID systems coupled with headspace solid-phase extraction (HS-SPME),¹⁵ the μ PE (micro purge extraction)- μ GC- μ TCD system³² and static headspace sampling with a micro-helium discharge photoionization detector.²⁹ Those systems have achieved compact sizes and fast analysis (a few seconds to several minutes, including sampling and analyzing time). However, due to the difficulty in stationary phase coating, the microcolumns used in these systems are usually too short to have sufficient separation capability for complex samples (usually fewer than 10 VOCs are analyzed in these systems). In addition, without an efficient sample extraction method, only a small fraction of the VOCs in the water samples can be injected into these systems, so the sensitivity of these systems are also limited (usually hundreds of $\mu\text{g L}^{-1}$).

Here, we report a fully automated portable gas chromatography system integrated with a purge-and-trap water sampling system, a μ PCI, a 10 meter separation column and a flow-through PID (portable P&T-GC-PID) for sensitive and rapid VOC quantification in water. This system has achieved a detection limit of sub $\mu\text{g L}^{-1}$ (or sub-ppb in terms of mass) for VOCs in water, a short analysis time (~ 10 minutes, depending on the target VOCs, and can be shortened further) with a light weight (less than 4 kg) and compact size (40 cm \times 30 cm \times 10 cm). Field studies using a groundwater sample from a recovery well showed that the VOC results obtained with our portable GC system quantitatively matched those generated with standard procedures and instruments by an analytical lab.

Experimental

Materials and sample preparation

All the analytes used in the experiment were purchased from Sigma (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA) and had a purity greater than 97%. CarbopackTM X, adsorbent material for μ PCI, was purchased from Supelco (Bellefonte, PA). Universal quick seal connectors, universal “Y” connectors, 20 mL vials, and Rtx-VMS capillary columns (10 m \times 0.25 mm i.d., 1.4 μm film thickness) were purchased from Restek (Bellefonte, PA). Two-port and three-port solenoid valves were purchased from Lee Company (Westbrook, CT). A mini-diaphragm pump was purchased from Gast Manufacturing (Benton Harbor, MI). Nickel wire (0.32 mm diameter, 1.24 ohm m^{-1}), used as

a heating wire for the capillary column, was purchased from Lightning Vapes (Bradenton, FL). Disposable helium cartridges (95 cm^3 , 2500 psig) were purchased from Leland (South Plainfield, NJ). A commercial PID with a built-in lamp drive circuit and amplifier was purchased from Baseline-Mocon (Lyons, CO). A type K thermocouple was purchased from Omega Engineering (Stamford, CT). A data acquisition card, USB-6003 (16 bits) and a USB-TC01 (for thermocouple measurement) were purchased from National Instruments (Austin, TX).

Water samples at various concentration levels (from 1–500 $\mu\text{g L}^{-1}$ for each analyte) were prepared by serial dilution with ultrapure water obtained from a Milli-Q water purification system (Thermo Fisher Scientific, Wayne, MI). All solutions were stored in 20 mL vials, each of which contained 10 mL of water samples and 10 mL of air-filled headspace. Groundwater samples were collected by Quantum Environmental Inc. (Ann Arbor, MI) from a recovery well (an environmental remediation system). All water samples were stored in a 4 $^{\circ}\text{C}$ refrigerator before use.

Methods

Fig. 1 presents a photograph of the portable GC system. The system is housed in an approximately 40 cm (L) \times 30 cm (W) \times 10 cm (H) plastic case and weighs less than 4 kg. It operates on 110 V AC power with an average power consumption of 25 W for the entire operation. Battery operation is also possible for field applications. The disposable helium cartridge provides purging gas during the sampling mode and carrier gas during the analyzing mode. Each cartridge can provide enough helium for more than 25 analyses. A LabViewTM control program developed in-house is used for automated operation of the system, including flow routing, μ PCI injection, column temperature

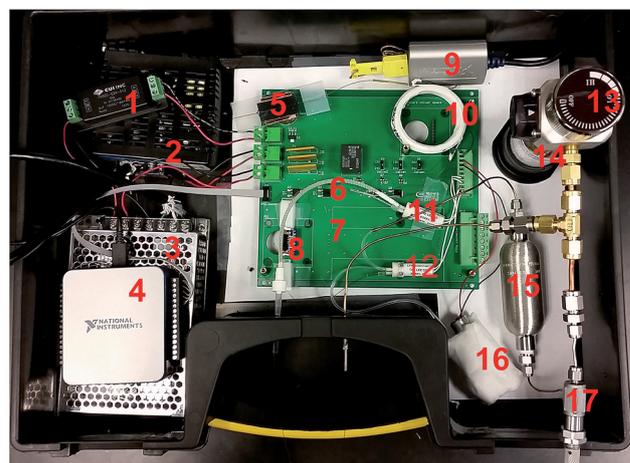


Fig. 1 Photo of a portable GC system. Components on the diagram: (1) 12 V DC–DC converter; (2) 24 V power supply; (3) 36 V power supply; (4) data acquisition card; (5) home-made photoionization detector; (6) scrubber; (7) printed circuit board; (8) μ -preconcentrator/injector; (9) thermocouple data acquisition card; (10) GC column with thermocouple; (11) 3-port solenoid valve; (12) 2-port solenoid valve; (13) regulating valve; (14) helium cartridge; (15) flow buffer; (16) diaphragm pump; and (17) needle valve.

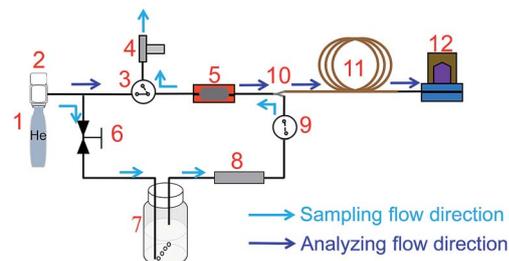


Fig. 2 Schematic of the portable GC system. Flow directions for sampling and analyzing are marked on the figure. Components on the diagram: (1) helium cartridge; (2) regulating valve; (3) 3-port solenoid valve; (4) diaphragm pump; (5) μ PCI; (6) needle valve; (7) purging vial; (8) moisture filter; (9) 2-port solenoid valve; (10) universal "Y" connector; (11) GC column with thermocouple; and (12) PID module.

ramping and data logging. Once started, the program panel shows the status of the system (such as valve on/off and pump on/off), column temperature and PID detector signal.

The μ PCI was used to trap and accumulate low-concentration VOCs and then inject them into the downstream separation column as a sharp peak by thermal desorption. Briefly, a channel with tapered inlet and outlet ports was etched on a Si wafer by deep-reactive-ion-etching (DRIE), and then anodically bonded to a Pyrex plate. A platinum microheater and a resistance temperature detector (RTD) were evaporated onto the backside. Carboxypack™ X granules were loaded into the cavity between the etched channel and Pyrex plate through a third port, which was sealed after loading. For fluidic connection, a guard column was inserted into each port and secured with silicone adhesive. For electrical connection, the microheater and RTD were wire-bonded to a printed circuit board (customarily designed and manufactured by M.A.K.S., Inc.). The μ PCI was preconditioned initially at 300 °C for 12 hours under helium flow.

The Rtx-VMS capillary column and nickel wire (both 10 meters long) were placed in parallel and wrapped by Teflon tape,³⁷ and then coiled into a helix of 10 cm in diameter and 1 cm in height. A type K thermocouple was inserted into the coil to read the column temperature *via* USB-TC01. To achieve a programmed temperature ramping profile, a pulse-width-modulated signal (4.0 Hz square wave) output *via* USB-6003 and was applied to the heater power relay on the printed circuit board. The duty cycle of the square wave was calculated by a proportional-integral-derivative controller in the Lab-View™ program and updated every 0.4 s based on the set-point temperature and measured temperature at that moment.³⁸

A PID module used in this work was assembled using the commercial PID with a built-in lamp drive circuit and amplifier and a home-made flow-through ionization chamber, which has a small dead volume and hence provides sharp chromatographic peaks in comparison with a regular ionization chamber.¹⁶ As shown in Fig. S1,[†] a 2 cm long straight microfluidic channel was created by a 380 μ m gap between two conductive silicon wafers with a resistivity of 0.001–0.005 Ω cm and a thickness of 380 μ m. The bottom and top of the microfluidic channel was covered by a Krypton UV lamp and a glass

Table 1 Physical properties and calibration data summary of the six VOCs

Compound name	Solubility in water (g L^{-1}) at 25 °C	K_{H}^{a} ($\text{mol L}^{-1} \text{atm}^{-1}$) ⁴⁴	ε (K) ⁴⁴	R^2	Detection limit at 3σ ($\mu\text{g L}^{-1}$ or ppb)	MCL ^a ($\mu\text{g L}^{-1}$ or ppb)	Potential health effects
<i>cis</i> -1,2-Dichloroethylene (<i>cis</i> -1,2-DCE)	3.5	0.27	4200	0.9997	0.11	70	Liver problems
Benzene	1.8	0.18	3200	0.9999	0.28	5	Anemia; decrease in blood platelets; increased risk of cancer
Trichloroethene (TCE)	1.1	0.11	4800	0.9997	0.31	5	Liver problems; increased risk of cancer
Toluene	0.52	0.15	3400	0.9962	0.13	1000	Nervous system, kidney, or liver problems
Tetrachloroethylene (PCE)	0.15	0.057	5100	0.9994	0.13	5	Liver problems; increased risk of cancer
<i>p</i> -Xylene	0.20	0.17	4500	0.9991	0.15	10 000 (total xylenes)	Nervous system damage

^a Maximum contamination level. The highest level of a contaminant that is allowed in drinking water defined by the United States Environmental Protection Agency.

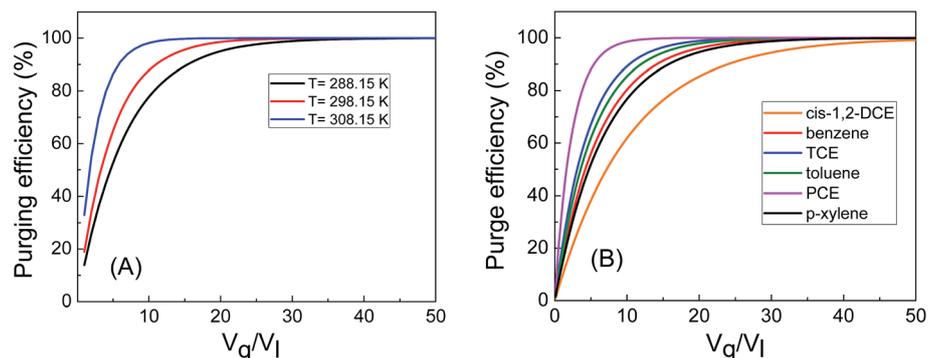


Fig. 3 (A) Purge efficiency for *p*-xylene under different purge temperatures. For all VOCs with $\varepsilon > 0$, the purge efficiency increases with temperature. (B) Purge efficiency at 288.15 K for 6 VOCs with K_{H}^0 ranging from 0.05 to 0.27 mol L⁻¹ atm⁻¹ (see Table 1). A theoretical purge efficiency over 99% can be achieved when $V_{\text{g}}/V_{\text{l}}$ is 50 at 288.15 K.

slide, respectively, which were then glued to the conductive silicon wafers with optical epoxy. Two guard columns (250 μm i.d. and 380 μm o.d.) were inserted into the inlet and outlet of the PID and sealed with optical epoxy. The output signal of PID was sampled at a rate of 40 kHz and averaged every 0.25 s for one data point on the chromatogram. The details of the PID assembly and characterization can be found elsewhere.³⁹

The instrument operates in two modes, as illustrated in Fig. 2. The flow routing components, including the diaphragm pump and the solenoid valves, are controlled by solid state relays driven by the digital outputs from USB-6003. In the sampling mode, the two solenoid valves were actuated. Helium gas was bubbled from a 250 μm i.d. fused silica tubing through the water sample in a purging vial at ambient temperature and drawn by a diaphragm pump through a moisture filter and then a μPCI at a flow rate of 100 mL min⁻¹. The vapors were adsorbed on the Carboxpack X inside the μPCI during the sampling mode. The entire sampling took 5 minutes, which can be further shortened if needed.

In the analyzing mode, the diaphragm pump and solenoid valves were closed. Helium gas was directed through the μPCI , and then the column and the PID module at a flow rate of 1 mL min⁻¹. After 60 seconds of pressure stabilization and PID baseline recovery period, the μPCI was heated to 270 °C in 0.6 s and then kept at 250 °C for 5 s to allow thermal desorption. The column was first heated to and kept at 40 °C for 1 min, and then ramped to 120 °C at a rate of 5 °C min⁻¹.

Theoretical analysis of purge efficiency

Unlike in air samples, a large fraction of VOCs in water samples are contained in the liquid phase rather than headspace. Therefore, several VOC extraction technologies have been developed, such as membrane extraction,^{30,40} static headspace techniques,^{25,29} purge and trap (P&T)^{11,32,41,42} and solid-phase microextraction (SPME).^{9,15,43} Compared to the static headspace and SPME techniques, P&T is capable of transferring all VOCs to the cryo- or sorbent-trap and thus has a better detection limit. In addition, P&T is in compliance with the EPA Method 8260B, which is commonly used by analytical labs in water

sample analysis. Therefore, we adopted P&T in our portable GC system.

Purging organics out of water can be approximated as partitioning between the water and the purge gas. The purge efficiency (η) can be defined as:

$$\eta(\%) = \frac{c_0 - c_r}{c_0} \times 100, \quad (1)$$

where c_0 (mol L⁻¹) and c_r (mol L⁻¹) are the analyte concentrations of the water sample before and after the purge, respectively. Assuming that the analyte is under partition equilibrium during the purging process, the concentration ratio between the gas phase and the liquid phase is constant and can be related by Henry's constant:⁴⁴

$$K_{\text{H}} = \frac{c_r}{p_{\text{g}}}, \quad (2)$$

where K_{H} (mol L⁻¹ atm⁻¹) is the Henry's law solubility constant for the analyte and p_{g} (atm) is the vapor pressure of the analyte in the headspace. The temperature dependence of K_{H} can be expressed as:

$$K_{\text{H}} = K_{\text{H}}^0 \exp \left[\varepsilon \left(\frac{1}{T} - \frac{1}{T^0} \right) \right], \quad (3)$$

where K_{H}^0 is Henry's constant under standard conditions ($T^0 = 298.15$ K) and ε (K) is the temperature dependent constant acquired by the experiment.

Since c_r continuously decreases during the purging process, a differential model can be established. Assuming that the analyte concentration in the water sample decreases by Δc_r after purge gas (e.g., helium) volume ΔV_{g} passes through, and according to the ideal gas law and mass conservation, we have:

$$p_{\text{g}} \Delta V_{\text{g}} = RT \Delta n_{\text{g}}, \quad (4)$$

$$\Delta n_{\text{g}} = -V_{\text{l}} \Delta c_r, \quad (5)$$

where R (L atm mol⁻¹ K⁻¹) is the ideal gas constant, T (K) is the purging temperature, V_{l} (L) is the water sample volume, and Δn_{g} (mol) is the number of moles of the analyte that shifts from the liquid phase to the gas phase. Solving eqn (4) and (5), and

considering the initial condition that $c_r = c_0$ when $V_g = 0$, we have:

$$c_r = c_0 \exp\left(-\frac{V_g}{RTK_H V_1}\right). \quad (6)$$

Thus the purge efficiency is:

$$\eta(\%) = \left[1 - \exp\left(-\frac{V_g}{RTK_H V_1}\right)\right] \times 100. \quad (7)$$

With eqn (3) and (7) and the constants K_H^0 and ϵ listed in Table 1, the purge efficiencies for the six analytes used in our experiment, *i.e.*, benzene, *cis*-1,2-dichloroethylene (*cis*-1,2-DCE), *p*-xylene, trichloroethene (TCE), tetrachloroethylene (PCE), and toluene under different purging conditions are presented in Fig. 3. For the water sample volume of $V_1 = 10$ mL used in our experiment, a purge gas volume of 500 mL results in $V_g/V_1 = 50$, which, according to Fig. 3(B), corresponds to a purge efficiency in excess of 99%, even at a temperature of 15 °C.

Results and discussion

First, we characterized the purge efficiency of our system. Here we used *p*-xylene as a model compound. During the experiment, 10 mL of *p*-xylene solution with concentrations of 5 $\mu\text{g L}^{-1}$, 5 $\mu\text{g L}^{-1}$, 50 $\mu\text{g L}^{-1}$ and 500 $\mu\text{g L}^{-1}$ were placed in four 20 mL purging vials. The helium purging rate and pumping rate were adjusted to 40 mL min^{-1} for the first vial (Column (A) in Fig. 4) and 100 mL min^{-1} for the other three vials (Columns B–D in Fig. 4). The time for each purge was set to 5 minutes, thus making $V_g/V_1 = 20$ for the first vial and $V_g/V_1 = 50$ for the other three vials. All the purge efficiency experiments were performed under a lab

environment and the purging temperature was 21 °C. Other experimental conditions are described in the Methods section.

Each vial was purged and analyzed four times consecutively without changing the solutions within. Due to the fact that the concentration of the solution decreased after each purge, the system actually measured the analyte from a high concentration to low concentration during the four purges. To avoid the possible memory effect between the two adjacent purges, the system was cleaned by triggering the μPCI injection (heated to 270 °C in 0.6 s, and then kept at 250 °C for 5 s at 1 mL min^{-1} helium flow) three times.

The experimental fraction of extraction for each purge presented in Fig. 4 is defined as:

$$\eta_e^i = \frac{A_i}{\sum_{n=1}^4 A_n} \times 100, \quad (8)$$

where n is the number of consecutive purges and A_i is the peak area for the i^{th} purge. Column (A) in Fig. 4 shows that with $V_g/V_1 = 20$, a purge efficiency of only 59.6% was obtained from the

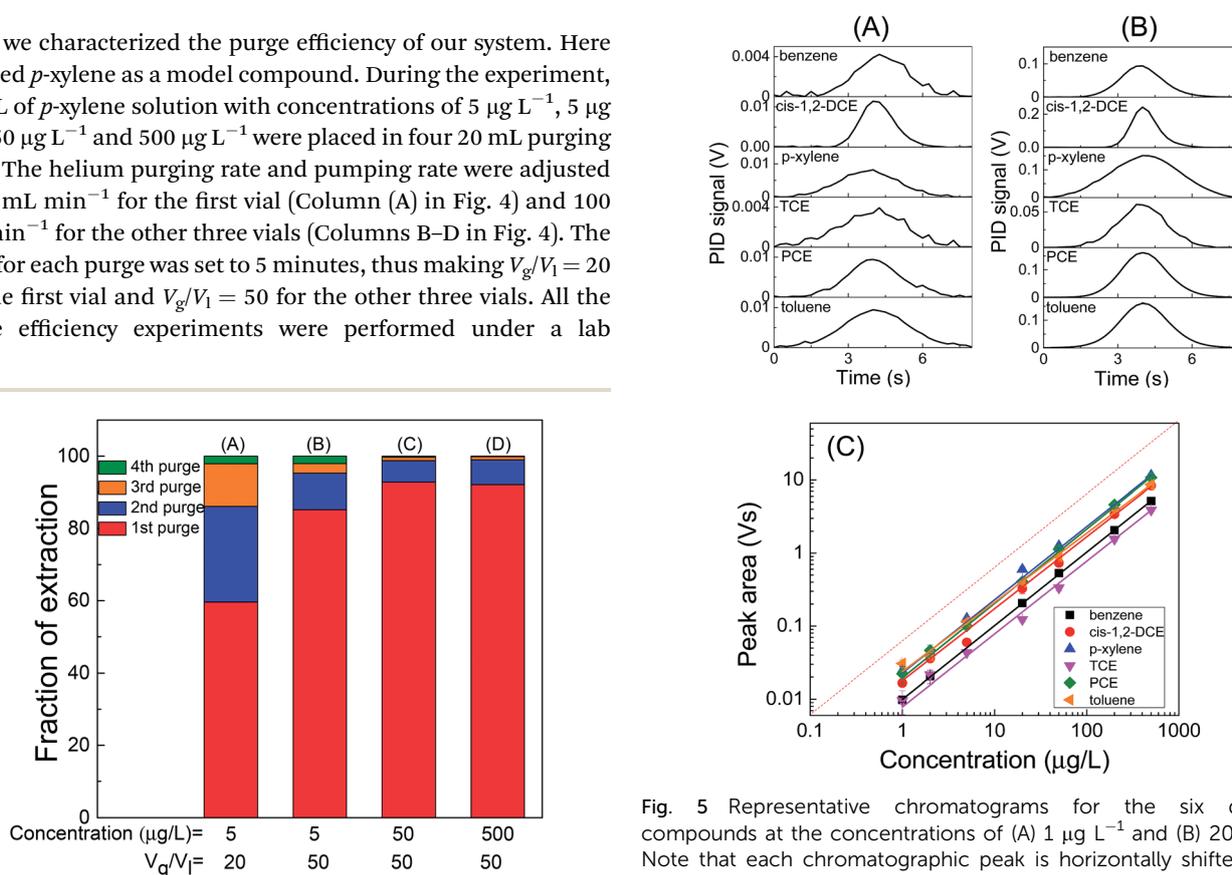


Fig. 4 Comparison of extraction profiles for various concentrations of *p*-xylene in water with different helium purging volumes. Under each set of purging conditions, the water sample was purged four times consecutively. The time for each purge was 5 minutes. The helium flow rate was 40 mL min^{-1} for Column (A) and 100 mL min^{-1} for Columns (B)–(D). V_g/V_1 for each purge was 20 for Column A and 50 for Columns (B)–(D). Details of *p*-xylene detection can also be found in Fig. S2 in the ESI.†

Fig. 5 Representative chromatograms for the six different compounds at the concentrations of (A) 1 $\mu\text{g L}^{-1}$ and (B) 20 $\mu\text{g L}^{-1}$. Note that each chromatographic peak is horizontally shifted to be aligned and centered around 4 seconds. (C) Linearity test for the six compounds in (A) and (B). Peak areas as a function of concentrations are plotted on a log–log scale. Error bars are obtained with three measurements. The solid lines are the linear fit on the log–log scale. The slopes are 1.008, 0.986, 1.003, 0.998, 1.019, and 0.948 for benzene, *cis*-1,2-DCE, *p*-xylene, TCE, PCE and toluene, respectively. The dashed line shows the curve with a unity slope to guide the eye. The details of the linearity, detection limit, and detection precision for those compounds are given in Table 1 and Fig. S3.†

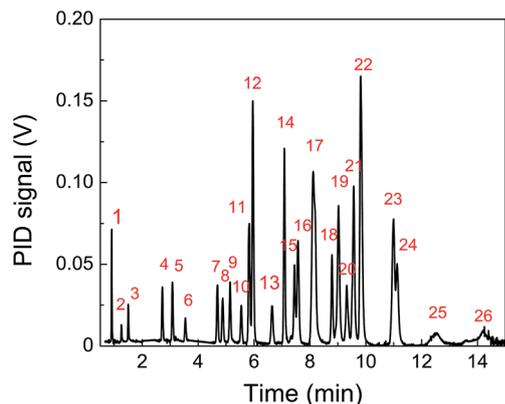


Fig. 6 Chromatogram of a mixture of 26 VOCs in water at a concentration of $5 \mu\text{g L}^{-1}$ for each analyte. (1) *cis*-1,2-Dichloroethylene; (2) benzene; (3) trichloroethene; (4) toluene; (5) tetrachloroethylene; (6) 1,2-dibromoethane; (7) chlorobenzene; (8) ethylbenzene; (9) *p*-xylene; (10) styrene; (11) bromobenzene; (12) propylbenzene; (13) 2-chlorotoluene; (14) mesitylene; (15) 4-chlorotoluene; (16) *tert*-butylbenzene; (17) 1,2,4-trimethylbenzene; (18) *sec*-butylbenzene; (19) 1,3-dichlorobenzene; (20) 1,4-dichlorobenzene; (21) butylbenzene; (22) 1,2-dichlorobenzene; (23) nitrobenzene; (24) hexachlorobutadiene; (25) 1,2,3-trichlorobenzene; and (26) naphthalene.

first purge. With the increased purge flow rate so that $V_g/V_l = 50$, a significant improvement in the purge efficiency (85.2%) can be achieved. Although the experimental purge efficiency at $V_g/V_l = 50$ (85.2%, 92.8%, and 92.1% for the first purge in Columns (B), (C), and (D), respectively) is slightly lower than the corresponding theoretical efficiency (all 99.9%), it is adequate for the system to extract and analyze VOCs in water. Therefore, in the following experiments, we used $V_g/V_l = 50$ with a purge flow rate of 100 mL min^{-1} and a purge time of 5 minutes. The possible reason for the discrepancy between the experimental and theoretical purge efficiency could be that the equilibrium partitioning between the water sample and the helium bubbles was not fully reached.^{45,46}

Linear range, detection limit, and precision

The linearity, detection limit, and detection precision of the portable GC system mentioned above were characterized under the sampling and analyzing conditions previously described in the Methods section at an ambient temperature ($21 \text{ }^\circ\text{C}$) using the six VOCs listed in Table 1 as model systems. The corresponding chromatographic peaks (raw response data) of those six VOCs in water with concentrations of $1 \mu\text{g L}^{-1}$ and $20 \mu\text{g L}^{-1}$ are presented in Fig. 5(A) and (B), respectively. The full-width-at-half-maximum (fwhm) of these VOCs at $1 \mu\text{g L}^{-1}$ varies from 2.25 s to 3 s.

The detection limit LOD for those compounds presented in Table 1 are calculated based on eqn (9):

$$\text{LOD} = \frac{3\sigma}{P_h}, \quad (9)$$

where σ is the standard deviation of the baseline noise and P_h is the peak height at $1 \mu\text{g L}^{-1}$ in Fig. 5(A). Since the LODs (sub- μg

L^{-1} level) of these VOCs are at least one order of magnitude lower than the MCLs listed in Table 1, the sensitivity of our portable GC system is sufficient for field analysis of water samples. Fig. 5(C) presents a set of calibration curves for the six VOCs with water sample concentrations ranging from $1 \mu\text{g L}^{-1}$ to $500 \mu\text{g L}^{-1}$. The peak area in Fig. S3† shows an excellent linear response with R^2 above 0.99 in the linear regression analysis (forced zero Y-intercept on a linear-linear scale). The precisions were calculated using three measurements.

Analysis of a complex VOC mixture

In most applications, the water samples are complex mixtures of target VOCs and many unrelated VOCs. In this scenario, a strong separation capability is required for the system. To test the separation capabilities of the portable GC system, a water sample containing 26 organic compounds, all selected from the EPA Method 8260B¹⁹ analyte list (with vapor pressure ranging from 0.087 Torr to 180 Torr), was analyzed. The concentration for each compound was $5 \mu\text{g L}^{-1}$ in water. The representative chromatogram is presented in Fig. 6, which provides a retention time reference library for us to identify VOCs. It is shown that the six VOCs discussed earlier were eluted in less than 6 minutes and the whole mixture was eluted in 15 minutes. Better separations can be achieved by optimizing the column temperature ramping profile and the analyzing flow rate; and a shorter analysis time can be achieved by increasing the temperature ramping rate at the cost of loss of resolution.

Quantification of VOC concentration in groundwater samples

To test the practical utility of our portable GC system, a groundwater sample obtained from a recovery well located in Pinckney, MI, was field analyzed by our portable GC system with assistance from a local environmental service company. The

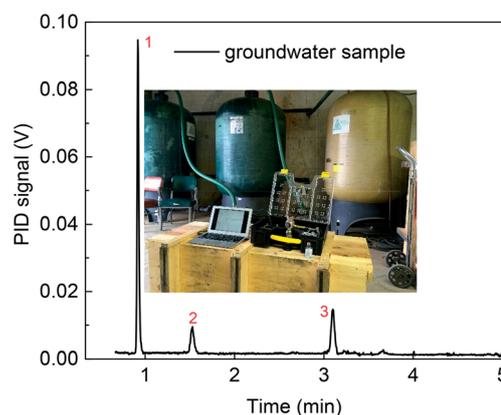


Fig. 7 Chromatogram of a groundwater sample collected from a recovery well. A comparison between the concentration results obtained with our portable GC system and by an analytical lab is given in Table 2. The inset shows that our portable GC system was used to test water samples on site. The three vessels presented in the photo are liquid phase carbon. The three organic compounds shown in the chromatogram are: (1) *cis*-1,2-dichloroethylene; (2) trichloroethene; and (3) tetrachloroethylene, which can be identified by their respective retention times in Fig. 6.

Table 2 Performance comparison of the portable GC system and a benchtop GC system from a local analytical chemistry lab

Compound name	Qualification result ($\mu\text{g L}^{-1}$)		Precision at $50 \mu\text{g L}^{-1}$ (%)		LOD ($\mu\text{g L}^{-1}$)	
	P ^a	A ^b	P ^c	A	P	A
<i>cis</i> -1,2-Dichloroethylene	7.2	7	8.4	2.9	0.11	1
Trichloroethene	2.6	3	9.2	4.0	0.31	1
Tetrachloroethylene	1.7	2	5.8	2.1	0.13	1

^a Portable GC results. ^b Analytical chemistry lab results. ^c Based on Fig. 5(C) and S3.

recovery well is a groundwater remediation system, by which groundwater is pumped through one or more vessels containing activated carbon to adsorb the organic contaminants in the groundwater. The field technicians from Quantum Environmental collect water samples on a monthly basis from the outlets of the vessel and send them to an analytical chemistry lab (Brighton Analytical, Brighton, MI) for determination of VOCs in the water under the EPA Method 5030C/8260B in order to decide whether the vessels can still effectively adsorb pollutants from the groundwater or need to be replaced. The whole procedure (sample collection, transportation, and analysis) normally takes about two weeks.

In our test, as shown in Fig. 7, a 10 mL groundwater sample collected from the outlet of the vessels (inset of Fig. 7) was placed in the purging vials and analyzed by our portable GC system. *cis*-1,2-DCE, TCE, and PCE were identified based on their respective retention times provided in Fig. 6 and their concentrations were calculated using the calibration curves in Fig. 5(C). The whole procedure took 11 minutes (5 minutes of sampling, 1 minute of holding and 5 minutes of analysis). Table 2 presents the quantitative results, precisions and LODs of these three VOCs by our portable GC system and by the benchtop GC system in an analytical chemistry lab. The performance comparison shows that our portable GC system provides faster and more sensitive capabilities for the quantification of VOCs in water samples.

Conclusions

We have developed and characterized the performance of a portable GC system for the highly sensitive, rapid and *in situ* VOC quantification in water. Our results show that our portable GC system is able to complete analytical testing in less than 20 minutes with a sub- $\mu\text{g L}^{-1}$ level detection limit. Quantitative comparison with results obtained with standard procedures and instruments further validated the deployability of the portable GC system in the field. Further development includes the integration of a PID detector with higher sensitivity¹⁶ to achieve a lower VOC detection limit down to ng L^{-1} in water samples. A multiple stage μPCI loaded with different adsorbents can also be implemented to trap VOCs with a wider range of volatilities.^{47,48} A shorter purge time (<1 minute) will be explored to further shorten the overall analysis time. Finally, a multi-dimensional portable GC system will be pursued in order to handle more complicated mixtures. Our ultimate goal

is to be able to analyze and quantify all the VOCs (>100) listed in the EPA Method 8260B¹⁹ *in situ* in less than 20 minutes. It should be noted that, like many other field-deployed devices, our portable GC system will be best used for rapid *in situ* screening when the target VOCs are known. For further confirmation of the VOCs that the portable GC system identifies, or when more complex samples need to be analyzed, another technique (such as mass spectrometry or Fourier transform infrared spectroscopy) should be employed along with portable GC.

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