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Construction and validation of automated purge-and-trap–gas chromatography for the determination of volatile organic compounds

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Abstract

An automated purge-and-trap chromatographic system for the determination of dissolved volatile organic compounds in aqueous samples was built in the laboratory with minimum cost both in the construction and routine operation. This system was built upon a commercial gas chromatograph with full automation capability using self-developed hardware and software. The use of a multi-sorbent bed quantitatively trapped a wide range of volatile organic compounds at ambient temperature, including the extremely volatile ones such as dichlorofluoromethane (CFC-12). Flash heating for rapid desorption and adequate plumbing for minimizing dead volume resulted in excellent chromatographic separation at above-ambient temperatures, which eliminated the need for cryogen for cooling at the head of the column, a second refocusing stage, or entire GC oven for refocusing. This cryogen-free system was tested with standard solutions and environmental samples for determining hydrocarbons with flame ionization detection, and halogenated compounds with electron-capture detection. An innovative method was also developed for validating the system's linearity for extremely volatile compounds. By introducing ambient air, which usually contains constant levels of anthropogenic halocarbons, e.g., CFC-12 and CFC-11 (CCl₃F), the need to prepare aqueous standards containing extremely volatile compounds is avoided, hence providing a convenient method for evaluating a purge-and-trap system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) are found in virtually all homes and workplaces in our modern society. Their use as solvents, cleaning agents, fuels, and chemical reagents in a number of industrial and commercial applications has led to their ubiquitous presence in air, water, food, etc. Many of the VOCs

are either toxic or carcinogenic and exposure to these compounds through diet and inhalation may cause adverse effects in human health. The link between ubiquitous exposure and possible health effects make VOCs a major public health concern.

Purge-and-trap–gas chromatography (P&T–GC) as described first by Swinnerton and Linnenbom [1] and developed by Bellar and Lichtenberg [2] has become a valuable and widely accepted method for the analysis of VOCs in aqueous samples and was adopted by the US Environmental Protection Agency

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(EPA) in various methods [3–6]. Using flame ionization detection (FID) or electron-capture detection (ECD) with gas chromatography is advantageous for VOC analysis as it offers a wide linear dynamic range and is extremely sensitive for detecting halocarbons and hydrocarbons, respectively [7,8]. Moreover, the fact that these two types of detection methods are very rugged and less costly makes them the most widely used detection methods in VOC analysis. We therefore designed and built a P&T device with minimum cost employing both detection methods for our routine analysis.

The concentration range of VOCs in aqueous samples are in the $\mu\text{g}/\text{l}$ to ng/l range, generally insufficient for direct GC analysis. As a result, a preconcentration step is required to retain VOCs prior to sample injection. Conventional measures of preconcentration involve using cryogenics such as liquid nitrogen to condense VOCs with boiling points as low as, e.g., -29.8°C (dichlorodifluoromethane; CFC-12), onto some inert solid surface. Subsequently the enriched VOCs are vaporized and flushed to the GC column as the surface is heated up [9–12]. This method is simple in principle, and is often preferred for clean and complete thermal desorption. However, a large amount of water vapor from a sparger carried by the purge gas also condenses onto the cold surface and later creates chromatographic interference. Removing water by physical or chemical means prior to the preconcentration step inevitably opens room for artifacts [13–15]. In addition, cryogenic focusing by liquid nitrogen or CO_2 is often employed for the P&T method to help retain highly volatile compounds and increase chromatographic resolution, which also adds cost and inconveniences to a laboratory.

In light of these common problems, a P&T–GC technique that does not require cryo-cooling either for preconcentration or refocusing, and at the same time provides high resolution for VOC analysis is worth investigation. Thus, the goal of this work was to present the hardware and software design of a cryogen-free automated P&T system which can be easily constructed in a laboratory with comparable or superior performance in comparison with commercial counterparts. The low cost in construction and routine operation, simple and rugged design, plus complete automation capability provide a useful

recipe for budget-concerned laboratories to build a system of their own with satisfactory performance.

2. Experimental

2.1. Chemicals and water

Standards containing benzene and toluene >99.5 were prepared and issued by an independent laboratory as part of a quality assurance program between laboratories. The helium gas was UHP grade ($>99.999\%$). The water used for preparing standard solutions was purified by a Milli-Q system from Millipore equipped with a Milli-Guard filter, an activated carbon cartridge, and two ion-exchange mixed-bed cartridges. Water passed through the Milli-Q unit was boiled and further sparged with N_2 for several hours.

2.2. Instrumentation

Fig. 1 illustrates the schematic diagram for the complete automated P&T–GC system. Three air-actuated two-position multi-port switching valves (Valco, $2\times 4\text{UWT}$, and $1\times 6\text{UWT}$) were used. All the connecting plumbing for transferring sample air used $0.32\text{ cm}\times 0.16\text{ cm}$ O.D. treated tubing (Silcosteel, Restek, Bellefonte, PA, USA) to minimize surface adsorption [16].

The sparger used in this setup consisted of a 20-ml glass vial sealed by Swagelok fittings with PTFE and Vespel ferrules. No thermal device was built for the vial and the sparging was operated at around 26°C in an air conditioned laboratory. The plumbing of the sparger however was heated with heating tapes to 60°C to minimize condensation and surface adsorption. A 0.02 cm I.D. stainless steel needle intruded near the bottom of the vial, through which He gas was purged at $20\text{ ml}/\text{s}$ controlled by a mass flow controller placed downstream.

The control hardware used in this system consisted of an I/O board (PCL-724, Advantech, Taiwan), and a 16-channel power relay output board (PCLD-8115). Actuation of the three valves was made possible by three solenoid air valves controlled by relays with each routing compressed air to actuate its corresponding switching valve. Five relays were

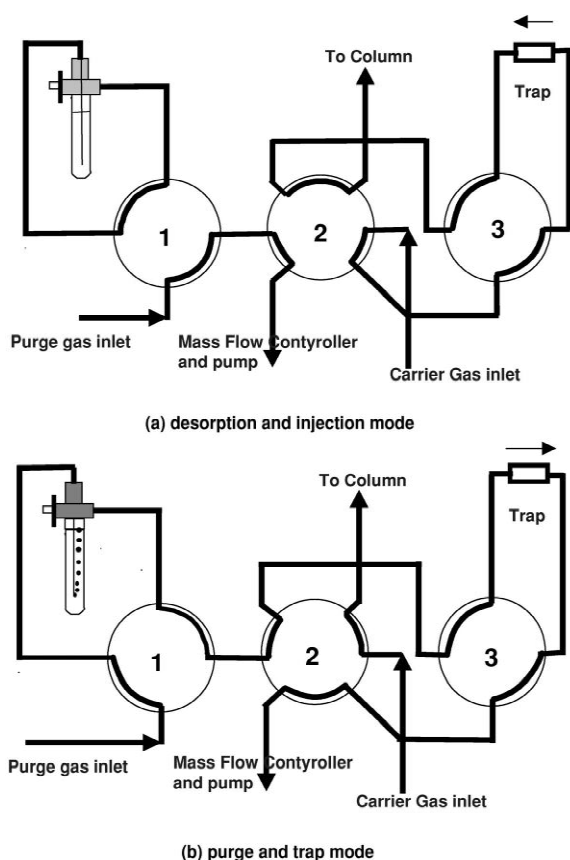


Fig. 1. Instrumental setup for the purge-and-trap GC system. Two configurations are shown to illustrate actions such as (a) desorption and injection; (b) purge and trap.

employed to control the three solenoid valves, initiate the temperature profile controller (Powers 535, Skokie, IL, USA), and start/stop the GC system. A Window-based software platform (Genie, Advantech, Taiwan) provided a Visual Basic programming environment for writing our control codes. We also designed the software to graphically display important information such as the time elapsed, valve actions, GC on/off, and the current analytical status such as trapping, dry purging, injecting, so that the operator can be easily aware of the analytical status.

Preconcentration and focusing relied on a sorbent trap made from a piece of 8 cm × 2 mm I.D. (3.2 mm O.D.) stainless steel tubing, packed with 1 cm each of Carboxen 1000, Carbonxen 1003, and Carbotrap

B (60–80 mesh, Supelco, Bellefonte, PA, USA) in that order, for sample trapping. Using the trap of this dimension provided a good compromise between trapping capacity and sample throughput. In order to achieve the focusing effect, the tubing was only packed with 3 cm of sorbents more towards the trapping end (the left end in Fig. 1), so that the bandwidth of the desorbed VOCs during flash heating was effectively reduced and the dead volume was minimized. No additional focusing stage was needed, which is usually conducted by adding a microtrap or a section of the column cooled with cryogen prior to entering the GC oven. The direction of the gas flow was always reversed during thermal desorption so that higher-boiling compounds were easily back-flushed from the sampling end of the trap.

Heating of the trap was performed by supplying a low-voltage large current (4 V a.c.; 40 A) to both ends of the stainless steel trap tubing, which enabled a maximum heating rate greater than 50°C/s. A process controller was used to control the trap temperature, of which the proportional-integral-derivative (PID) algorithm with relay output to responsively throttle current to the trap, so that a temperature fluctuation of merely ±1°C was achieved at different setpoints. A K-type thermocouple was welded on the trap tubing to provide temperature feedback to the temperature controller. Most of the VOCs could be quantitatively trapped at room temperature including the most volatile compounds, i.e., CFC-12, which will be discussed later in the text.

A DB-1 column (60 m × 0.32 mm, $d_i=1 \mu\text{m}$; J&W Scientific, Folsom, CA, USA) was used on a HP 6890 GC system equipped with an FID system for analyzing hydrocarbons and a micro-ECD system for analyzing halogenated compounds. The oven temperature program started from 40°C to 80°C at 10°C/min, and to 120°C at 5°C/min; and then to 180°C at 20°C/min, holding at 180°C for 10 min.

2.3. Automation sequence

Fig. 2 displays the time events and their corresponding analytical significance for a complete control process of a sample run. Critical steps are described as follows.

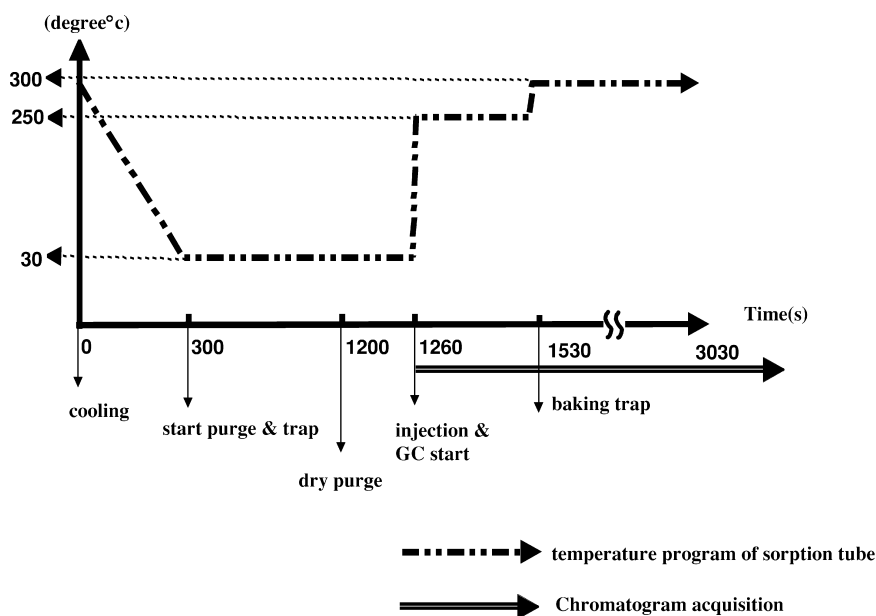


Fig. 2. Time events for a complete analytical cycle for analyzing hydrocarbons. Temperature profile for the sorbent trap is controlled by a process controller to synchronize with valve actions.

2.3.1. Sample purge

Prior to starting an analysis the trap was maintained at 30°C by the temperature controller as one of the setpoints. Switching valve 1 routed the purge gas from its by-pass configuration (Fig. 1a) to the sparger, purging VOCs from a liquid sample to the trap (Fig. 1b). The use of a two-way four-port switching valve (valve 1) gave extremely precise and clean action to start/stop purging with no obvious pressure surge. The purge time in this study was set for 15 min for hydrocarbons and 25 min for halo-carbons to yield a compromise between speed and trapping efficiency. Its by-pass configuration to isolate the sparger avoided the possibility of contamination and pressure build-up.

No cryogen was needed for VOC trapping, as most VOCs except C_2 hydrocarbons can be quantitatively retained in the trap at room temperature [17,18]. Using 2.0 mm I.D tubing packed with 3 cm of sorbent provided a balance between trapping capacity and focusing effect, facilitating both sensitivity and resolution. Linearity was tested by analyzing standards covering the working range of our routine analysis, which will be discussed later in the text.

2.3.2. Dry purge

After purging for a prescribed time period, valve 1 was switched to isolate the sparger, while valves 2 and 3 remained the same configuration as in Fig. 1b to allow dry-purge the trap at 30°C for 1 min with the flow set at 20 ml/min. Because the carbon-based sorbents packed in the trap were fairly hydrophobic, most water vapor carried by the He purge gas was not retained. The slight amount of water, O_2 and CO_2 remaining in the trap can be further removed from the trap by dry purge at 30°C. Dry purge also has been successfully employed in air analysis using a similar concept to manage water and CO_2 [18–24]. By doing so, no desiccants or other means of water-removal techniques were needed, as frequently adopted by other P&T work [13–15,17]. Blank runs of purified water were tested to confirm free of residue from previous sample runs. After finishing dry purging the trap was isolated by switching valve 3 to be ready for injection.

2.3.3. Sample injection

Upon injection the temperature controller was initiated by a relay's contact closure to begin feeding

large current (40 A; 4 V a.c.) to the trap tubing, resulting in extremely rapid ohmic heating to 250°C within a few seconds. Immediately valves 2 and 3 were switched to route He carrier gas to the trap flushing VOCs onto the column for 4.5 min. The He carrier gas stream was precisely controlled and programmed by routing the gas through an electronic pressure controller (EPC) prior to entering the trap, see Fig. 1. Simultaneously, the GC system was started to ramp oven temperature, see Fig. 1a for the valve configuration and Fig. 2 for the control process and the corresponding temperature profiles for both the trap and the GC system.

2.3.4. Trap cleaning

After 4.5 min of injection, the trap temperature ramped from 250 to 300°C and the valves returned to the dry-purging configuration for cleaning high-boiling residuals. This conditioning stage lasted for more than 20 min until the trap temperature returned to 30°C by cooling with a fan to be ready for trapping the next sample and restarting a new cycle, see Fig. 2 for a complete temperature profile.

2.4. Standard and sample analysis

We have employed this automated P&T–GC system equipped either FID or ECD for our routine analysis of environmental samples. The system's versatility and applicability are illustrated with the following two case studies.

2.4.1. P&T–GC–FID

The system was employed in an evaluation program to monitor the effectiveness of a remedial treatment of a contaminated underground aquifer underneath a decommissioned chemical plant. Tons of waste benzene based solvent were directly dumped into subsurface as a means of disposal when the plant was in use 2 to 3 decades ago. Recent passage of the underground water and soil act of Taiwan mandated the site to be cleaned up. Remediation involved pumping underground water to a surface pool and treating it by sparging air through to purge out the VOCs before discharging into a river. Water samples were collected from the pool before and after the purge treatment and were stored at 4°C. Because the level of contamination in the ground

water was high, only 1.0 ml of water sample was introduced to the vials and filled to 7.0 ml with purified water, see Fig. 3 for the effectiveness of the treatment. A clean water sample collected from a background well is also included in Fig. 3 to serve as a reference. The clean baseline observed for the blank runs after analysis of high concentration samples suggests the flash desorption to 250°C did not produce artificial compounds, which is often encountered with polymer-type sorbents such as Tenax during thermal desorption [25]. This comparison illustrates that the purge treatment effectively removed benzene, whose concentrations were in the mg/l range before the treatment and dropped to the µg/l level after the treatment. Most VOCs were effectively removed by this treatment except toluene. Because the pool is not a well-controlled experimental apparatus, but rather a process facility, which previously was used for processing waste water in the plant, contamination of toluene from the slurry was inevitable.

Owing to fast desorption, most of the species were adequately resolved under cryogen-free conditions. In Fig. 4 the resolution of cryogen-free conditions for the treated water sample is compared with that for oven cooling which is often necessary to retain more volatile compounds within a column for reducing longitudinal diffusion and therefore improving the peak shape or resolution for early-eluting species. In this case, the DB-1 phase separates compounds based upon their volatility and lower-boiling compounds are eluted sooner than higher-boiling compounds. In Fig. 4, even the most volatile compounds on the upper trace exhibit comparable resolution to the cryogen condition shown on the lower trace, suggesting that the separation efficiency was not compromised even without oven cooling.

It is also noted that the speed for the ohmic heating is crucial to the resolution of early-eluting compounds, which are more volatile and subject to greater longitudinal diffusion within the trap tubing and, thus, manifests in broader peak width and poorer resolution. The instantaneous provision of a large current from the transformer was capable of melting the 10 cm stainless steel trap tubing within a few seconds. Nevertheless, in our application the current was supplied in a controlled manner by the PID algorithm, which regulates the power so that the

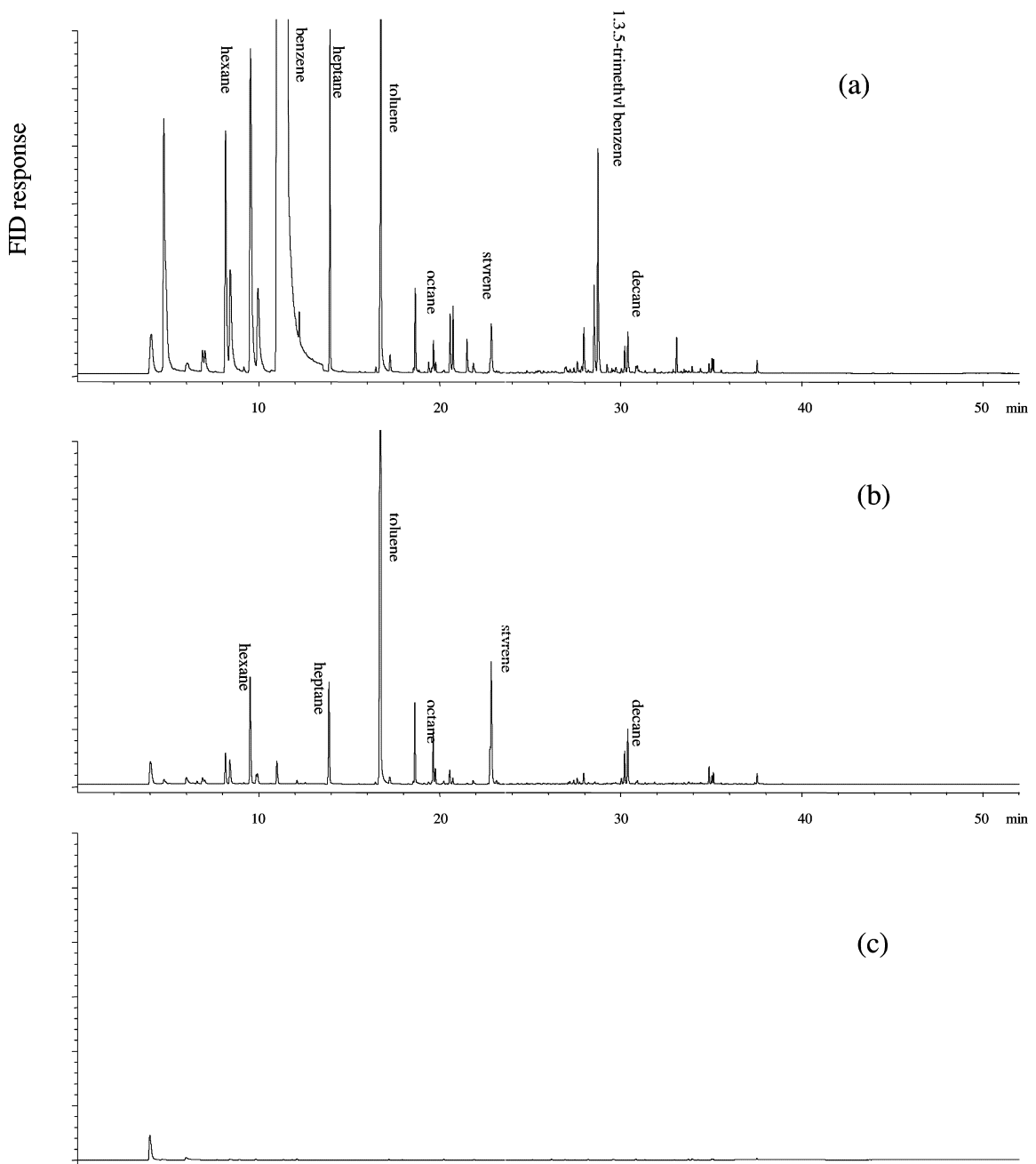


Fig. 3. Evaluation of the remedial treatment by analyzing water samples with P&T-GC-FID. (a) Contaminated groundwater pumped to the surface; (b) after purging treatment to remove VOCs; (c) a clean sample collected from a background well. Responses of the three analyses are on the same scale for ease of comparison.

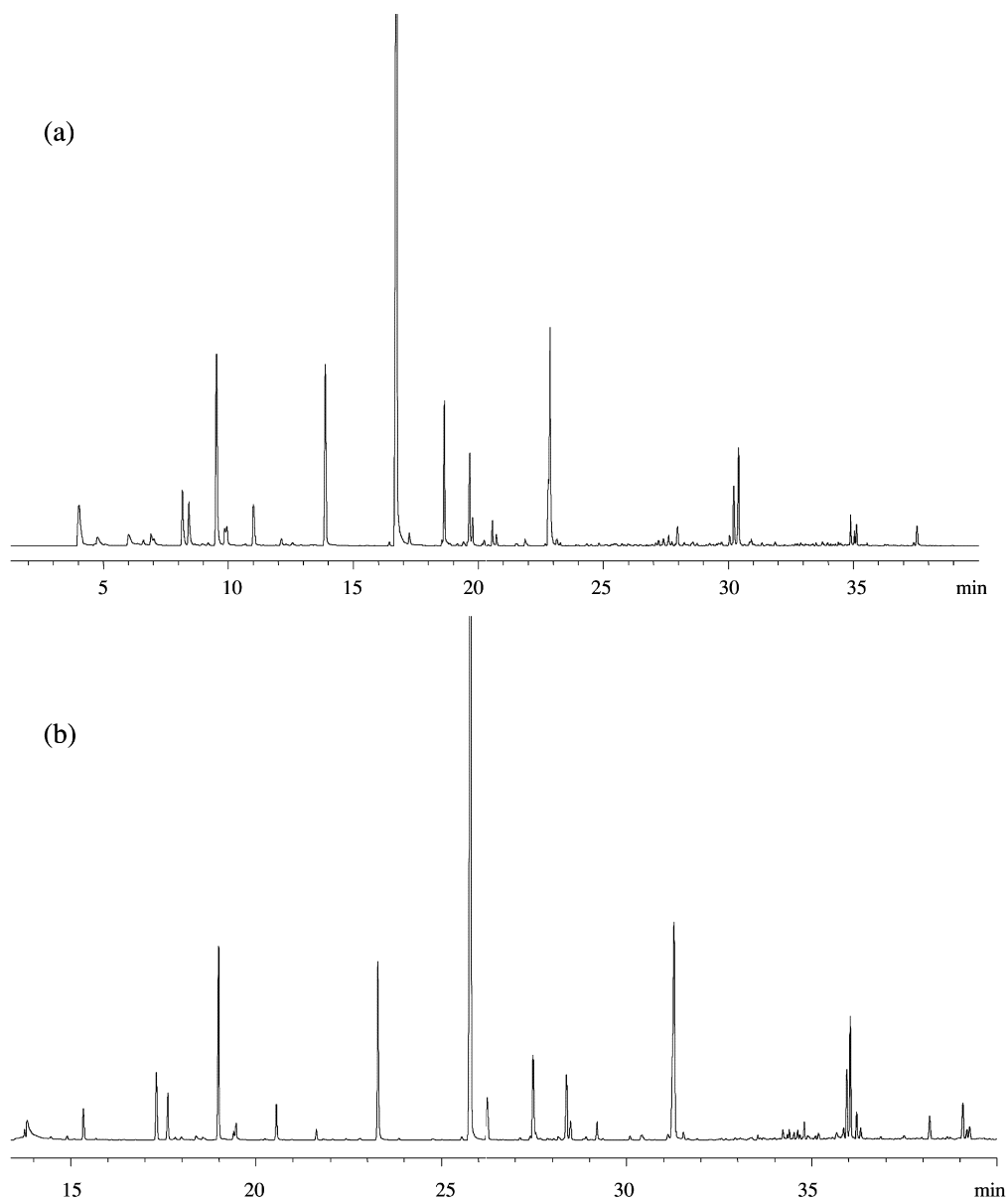


Fig. 4. Comparison between two oven conditions with the same sample as of Fig. 3(b). (a) The sample was analyzed with oven temperature started from 40°C. (b) Same conditions except oven temperature started from -50°C.

actual temperature on the trap sensed by the thermocouple closely matches the prescribed temperature ramp. The plumbing for connecting the trap with the transfer line, the switching valve, followed by a column was carefully fabricated to minimize dead volume, which is also crucial for obtaining narrow and symmetric peaks. Fig. 5 shows the effect of

desorption speed on the peak width. For the same amount of air injected, not only the peaks became sharper with faster heating, the peak height was significantly increased, which could translate into lower detection limits.

Standards of hydrocarbons containing benzene and toluene were prepared at 0.5, 1.0, 5.0, 10.0, 20.0 and

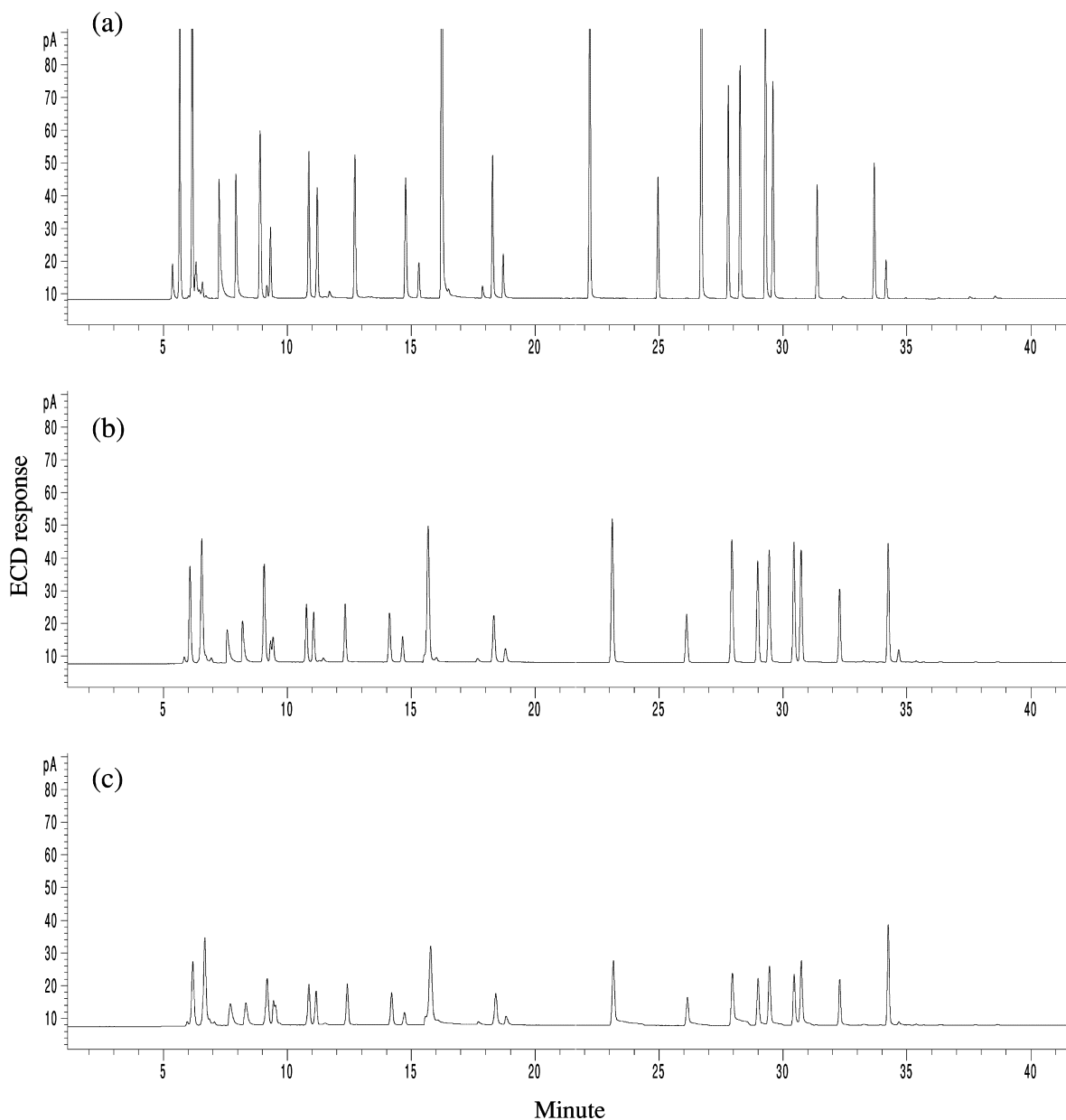


Fig. 5. Desorption speed on the peak shape. (a) Desorption within 1 s; (b) within 6 s; (c) about 12 s. Same amount of air was injected and the ECD response was adjusted to the same scale.

40.0 $\mu\text{g}/\text{l}$, respectively. Analyses were made from low to high concentrations with each aliquot containing 7 ml withdrawn from their chilled stock solutions. Extremely linear response was observed with R^2 greater than 0.99. Precision for the two

compounds was better than 2.0% by analyzing seven replicates of the 0.5 $\mu\text{g}/\text{l}$ standard mixture.

2.4.2. P&T-GC-ECD

Owing to their toxicity and carcinogenicity, or-

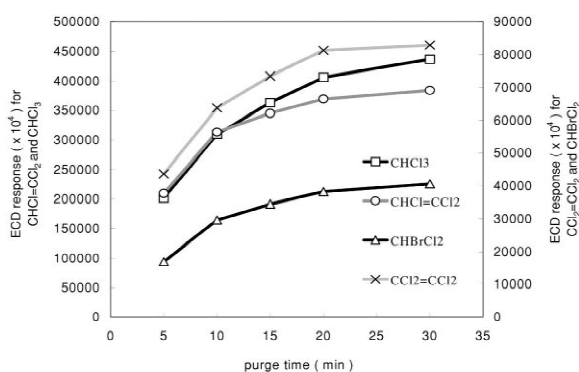


Fig. 6. Purge time optimization for halocarbons.

ganohalogenated compounds are often determined at very low levels in environmental samples. We routinely used P&T-GC-ECD to analyze halogenated compounds in environmental and biological

samples. Quantification of halogenated compounds in those samples requires standard solutions made from pure water largely free of these contaminants. Since the tap water contains substantial amounts of halogenated compounds with some arising from the chlorine treatment in water plants, purification was performed to remove these contaminants in the water used for preparing standards. Fig. 6 shows the purge efficiencies of halogenated compounds in the tap water with respect to the purge time. The increase in efficiency begins to level off after 20 min of purging. As a result, the purge time of 25 min was chosen to be the compromise between the sensitivity and the analysis time. Fig. 7a displays the chromatogram for analyzing 7 ml of a typical tap water sample. Both chlorinated and brominated compounds were observed with the most obvious ones being CHCl_3 , C_2HCl_3 , and CHBrCl_2 , for which chlorine treatment and biological process in water may be responsible

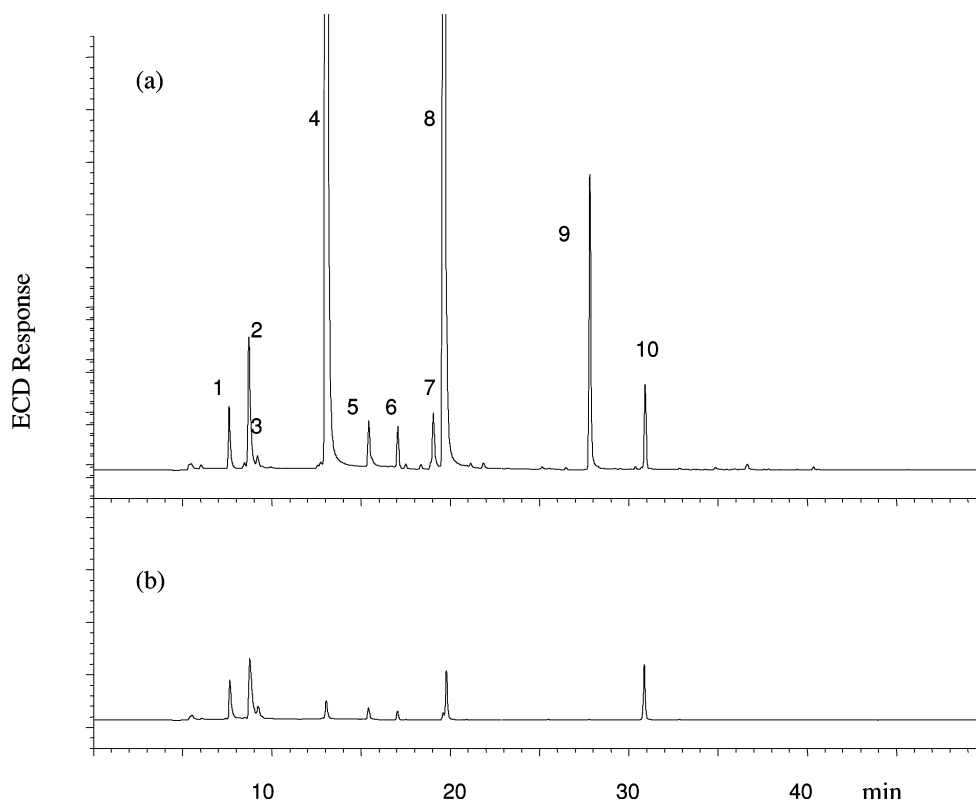


Fig. 7. P&T-GC-ECD analysis of (a) tap water and (b) tap water treated by Milli-Q and sparging while boiling. Peak assignment: 1=CFC-11, 2= CH_2Cl_2 , 3=CFC-113, 4= CHCl_3 , 5= CH_3CCl_3 , 6= CCl_4 , 7= CH_2Br_2 , 8= CHCl=CCl_2 , 9= CHBrCl_2 , 10= $\text{CCl}_2=\text{CCl}_2$.

for their dominance [26]. Determination of these three compounds gave a precision better than 2.5% based on 10 replicate analyses. To serve as blank solution, the tap water was purified by Milli-Q followed by N_2 sparging before using for preparing standard, see Fig. 7b for the effectiveness of the treatment. Most of the halocompounds can be largely removed from tap water after the treatment, although slight amount of residue can still be observed in this blank analysis. This is not surprising since micro-ECD is highly sensitive with detection limits less than a few ng/l [27]. The residue was mainly contributed by the laboratory air in the headspace of about 10 ml, in which halocarbons from anthropogenic emissions into the atmosphere, e.g., CFC-11, $CFCl_2CF_2Cl$ (CFC-113), $CHCl_3$, CH_3Cl_3 , CCl_4 , C_2HCl_3 and C_2Cl_4 , can be easily measured by GC-ECD [28,29]. By contrast, the two bromo-compounds, which do not have an atmospheric source, were not observed in the blank analysis indicating efficient removal in the treatment process. A blank run was needed for a batch of samples in our routine analysis to determine the contribution from the headspace.

The system could quantitatively analyze the most volatile target compound, such as CFC-12 listed in the EPA standard method [30], should it present in the liquid sample. We realized that analyzing liquid standards containing adequate amount of CFC-12 and other extremely volatile compounds with high precision is difficult, because either the preparation or preservation will be too elusive due to their gaseous nature and low solubility. Instead, we exploited the homogeneous nature of chlorofluorocarbons as the “intrinsic” standards. The long lifetimes and negligible emissions of anthropogenic chlorofluorocarbons render their ambient levels rather uniform in the atmosphere worldwide [31,32]. For instance, the abundance of CFC-12 and CFC-11 are quite uniform in clean atmospheric environments with minimum concentrations of about 520 parts per trillion by volume (pptv) and 250 pptv, respectively [33–35]. In this practice, the He purge gas stream was replaced by an pressurized ambient air stream to bubble through the sparger for moisturizing the air and artificially providing volatile chlorofluorocarbons that are sensitive to ECD. Fig. 8 shows the result from this approach. Without using cryogen excellent

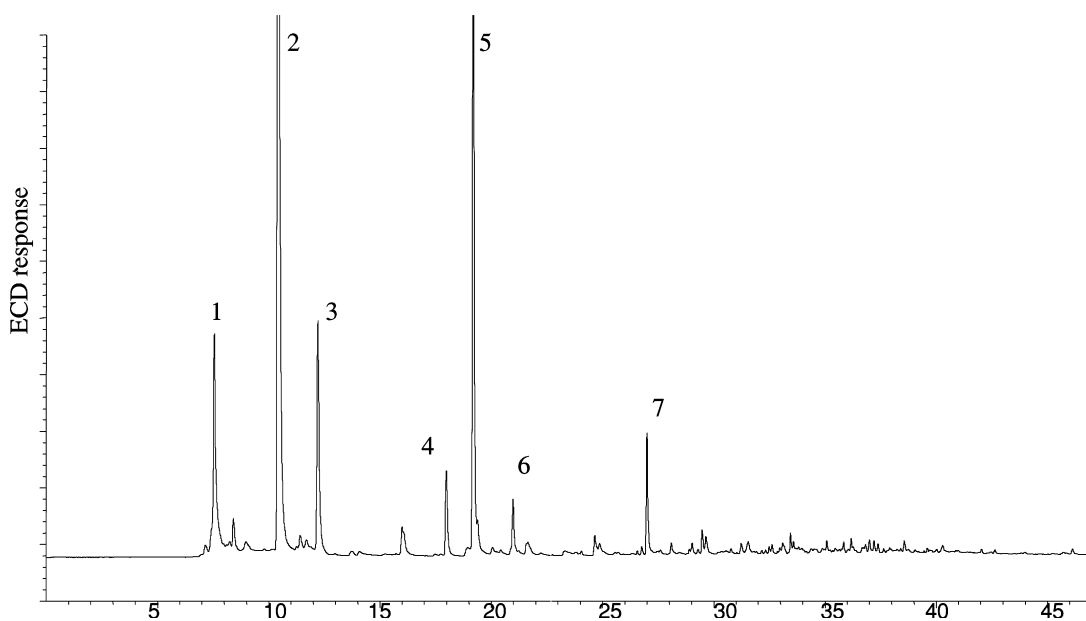


Fig. 8. A pressurized ambient air sample was fed through the sparger to provide chlorochlorocarbons to be trapped and analyzed by the automated P&T-GC-ECD system. Selected halocarbons are labeled as (1) CFC-12, (2) CFC-11, (3) CCl_2FCClF_2 , (4) CH_3CCl_3 , (5) CCl_4 , (6) $CCl_2=CClH$, and (7) $CCl_2=CCl_2$.

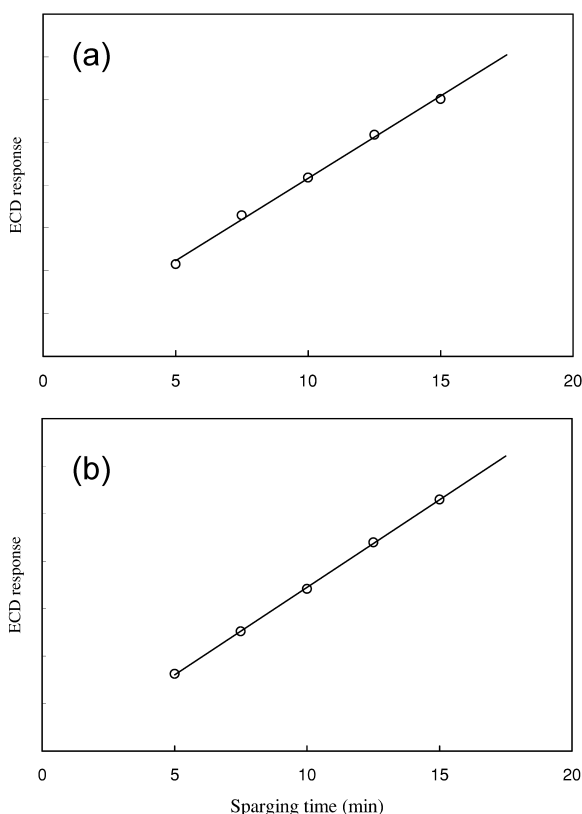


Fig. 9. Linearity study on the extremely volatile compounds, i.e., (a) CFC-12 with $R^2=0.9973$; (b) CFC-11 with $R^2=0.9993$. Compounds were provided by feeding clean air through the sparger, and concentrations were controlled by the feeding time period.

resolution could still be obtained for these extremely volatile halocarbons on the wall coated open tubular column. By sparging with the clean ambient air with various time periods to simulate generating various amounts of halogenated compounds of high volatility and low solubility, the system could be examined for trapping linearity or breakthrough for this type of compounds. For instance, 5 min sparge time at 20 ml/min with clean ambient air is equivalent to purge a water sample containing about 40.12 ng/l of CFC-12 and 21.68 $\mu\text{g/l}$ of CFC-11, respectively. Likewise, feeding 10 min of clean air would be equivalent to analyzing a water sample of twice amount of concentrations. In Fig. 9, the range of linearity for CFC-12 and CFC-11 was far beyond the levels of they can reside in normal aqueous samples and

exhibit no sign of breaking through, suggesting that trapping at near room temperature could quantitatively enrich even the very volatile compounds.

3. Conclusion

An automated P&T–GC system consisting of both hardware and software was constructed with minimum cost and successfully employed in our routine analysis. The use of a small bore multi-bed carbon-based sorbent trap avoided the use of cryogen for preconcentration and, at the same time, largely eliminated water interference, which has been the major problem encountered by most cryo-cooling preconcentration techniques. Extremely fast desorption by direct resistive heating resulted in very narrow peaks, particularly for more volatile compounds, which eliminated the need for a cryofocusing stage behind the trapping stage, which is commonly seen in many applications.

By exploiting the homogeneous nature of chlorofluorocarbons in the atmosphere, the introduction of ambient air through the sparger avoided the standard preparation and made the evaluation of analyzing extremely volatile compounds rather easy.

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