Cryogen free automated gas chromatography for the measurement of ambient volatile organic compounds

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Abstract

An automated gas chromatographic system was constructed for measuring ambient volatile organic compounds (VOCs). Preconcentration of the VOCs was performed by using two separated sorbent traps of different combinations with each designated for either low or high boiling VOCs. Both traps and their associated valve systems were integrated as a complete system sharing a common sample inlet. Precise temperature controls for desorption relied on the use of a process controller with proportional-integral-derivative algorithm to throttle the current supply. No additional cryo-focusing stage prior to the column was needed owing to the flash heating capability for desorption. Other than the cryogen free preconcentration and focusing, the separation of VOCs of large volatility difference was also performed without cryogen. The system employed an Al_2O_3/KCl porous-layer open tubular column for separating C_3–C_7 compounds; and a DB-1 column for C_6–C_{12}. This automated GC system has been deployed in a Taiwan Environmental Protection Agency urban air quality monitoring station of Taiwan for continuous measuring C_3–C_7 ozone precursors. Excellent correlation between the car exhaust type of compounds measured by our GC system and carbon monoxide measured by a non-dispersive infrared spectrometer was observed, suggesting the automated GC system was robust and reliable.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Contamination of the environment with volatile organic compounds (VOCs) has become an important issue during the past decades, since many VOCs are toxic and may cause health risks of different scales. A large number of man-made VOCs are routinely emitted into the ambient environment from industrial, traffic, and energy production sources. Given the high complexity and low abundance nature associated with ambient VOCs, the chromatographic methods are preferred for their efficient separation and detection capability over other analytical means.

Atmospheric concentrations of VOCs are often in their sub-ppb levels and subject to large temporal and spatial variations, and generally insufficient for direct chromatographic analysis. As a result, a preconcentration step is required to remove the matrix of the air, i.e., N_2, O_2, Ar, etc., while retaining VOCs prior to sample injection. Conventional measures of preconcentration involve using cryogens such as liquid nitrogen, argon, or CO_2 to condense VOCs onto some inert solid surface as air sample flowing through [1–6]. Subsequently, the trap that holds the solid particles undergoes rapid heating to have carrier gas flush the enriched VOCs onto a column for separation and detection. This type of method is simple in principle, and is often preferred for its clean and complete thermal desorption. Never-

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theless, inclusion of water and CO_2 in the enrichment process is often inevitable. Common problems include distortion of peak and baseline, shift in retention times, or even plugging the trap or column. Furthermore, the logistical problems arising from cryogen supply when there comes a need to deploy a system in the field renders this preconcentration method very undesirable.

The objective of this work was to develop an analytical system for continuous measurement of atmospheric VOCs by dual trap and dual column approach without the use of cryogen for preconcentration and oven cooling. The use of two different phase systems such as in dual capillary techniques substantially enhances the number of compounds that can be separated [7,8]. The dual capillary technique can be used to cope with the wide volatility range of the components by employing one column for the gaseous compounds and the other for the higher boiling ones. Such a dual column system is already commercially available, it uses a heart-cut technique to route early eluting compounds from a short pre-column to a porous-layer open tubular (PLOT) column for separating C_2–C_6 components and subsequently divert the remaining heavier eluents to a wall-coated open tubular (WCOT) column for separating C_6–C_{12} components [9]. In this work, a different approach from heat-cut techniques was investigated by employing two separate sorbent traps optimized for two columns of different phases to analyze wide range of VOCs without the use of cryogen. The system was built to achieve the following goals: (1) fully automated; (2) can be remotely operated with no attendance (except when changing gas cylinders); (3) can perform highly precise continuous measurements; (4). highly reliable and robust.

2. Instrumentation

2.1. Chromatographic conditions

A HP-6890 equipped with dual sorbent traps, columns, and flame ionization detection (FID) systems were used for simultaneous separating VOCs of wide volatility, i.e., C_3–C_{12}. A PLOT Al_2O_3/KCl column (30 m×0.32 mm; d_f=8 μm, Hewlett-Pac-

kard, San Fernando, CA, USA) was designated to one of the two sorbent traps for separating light VOCs from C_3 to C_7. A DB-1 column (60 m×0.32 mm; d_f=1.0 m, J&W Scientific, Folsom, CA, USA) was connected to the other trap for separating C_6–C_{12} compounds. The temperature program started at 40°C, isothermal for 4 min, followed by a ramp of 8°C/min to 180°C/min, held at 180°C/min for 8 min. To balance the two carrier gas flows to the PLOT and DB-1 columns to about 2.0 ml/min for both, a piece of 5 m×0.25 mm I.D. uncoated column was installed after the PLOT column as a restrictor.

In a separated system, a HP-6850 equipped with a single FID system, which is half the size of HP-6890, was placed in a Taiwan Environmental Protection Agency (Taiwan) EPA air quality monitoring station due to space limitation. Only the PLOT column was used in this system for measuring C_3–C_7. The temperature program for the PLOT column started at 35°C, isothermal for 4 min, followed by a ramp of 4.5°C/min to 55°C, isothermal for 5 min, then a ramp at 7°C/min to 130°C; 8°C/min to 180°C, and isothermal for another 14.4 min. The He carrier gas flow was controlled at a constant rate of 2.0 ml/min by an electronic pressure controller during the whole temperature program.

2.2. Valve system

Fig. 1 illustrates the valve diagram for the dual trap dual column automated GC system. Four electric actuated 2-way multi-port switching valves, i.e., two 3-port, and two 6-port switching valve (Valco, Model 3UWT and 6UWT, Houston, TX, USA) were used to configure this automated system. All the plumbing connecting the valves used 2.0 mm I.D. treated tubing (Silcosteel, Restek, Bellefonte, PA, USA) to minimize possible transfer loss due to surface adsorption [10]. Plumbing to both ends of the trap, however, used 0.5 mm I.D. stainless steel tubing. 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-785, Advantech, Taiwan). Six relays on the relay board were employed to control the 4 valves, initiate the temperature profile controller (Powers 535, Powers Process Controls, Skokie, IL, USA), and start/stop a GC system. Temperature profile was
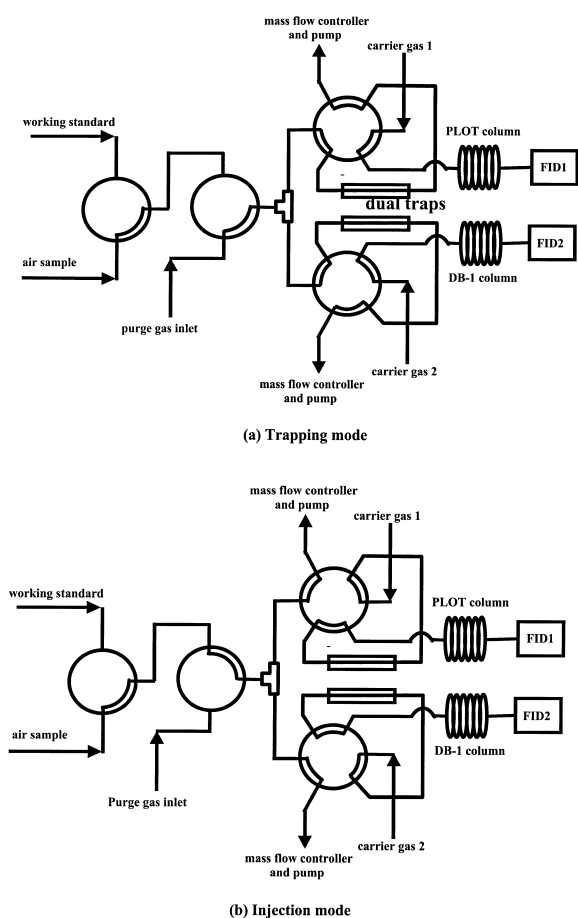
(a) Trapping mode

(b) Injection mode

Fig. 1. Valving and plumbing configuration for the dual trap and column GC system in (a) sample trapping and (b) sample injection modes.

controller (MFC), see Fig. 1a, followed by 1 min dry-purge with He or N_2 to remove excess water and CO_2. The parallel dual trap design allowed the flow-rate to be independently controlled.

The trap was then immediately ramped to 250°C within a few seconds for injection (heating rate >50°C/min), see Fig. 1b. Meanwhile, the GC was started by a relay's contact closure. The injection time lasted for 5 min before the trap temperature rose to 300°C under an inert gas flow for cleaning high boiling residue. At the end of a temperature profile the current was shut off and a fan cooled down the trap to 30°C within 2 min to be ready for the next cycle.

3. Sorbent, plumbing, and resolution

The two sorbent traps in Fig. 1 were made by a piece of 2.0 mm I.D. stainless steel tubing packed with chemical sorbents. Heating of the trap was made by supplying a large current to the stainless steel trap tubing for rapid resistive heating. Using the built-in proportional-integral-derivative (PID) algorithm the controller throttled the incoming current (110 V a.c.) to a large transformer through a solid state relay to generate a pulsed current (40 A, 4 V a.c.) to the trap for resistive heating. In this manner, extremely precise and repeatable temperature control of setpoints was achieved with temperature fluctuation less then 1°C.

Two traps packed with different sorbent combinations were integrated in parallel for efficiently enriching VOCs of different volatility range. For trapping low boiling VOCs, Carboxen 1000 (60–80 mesh, Supelco, Bellefonte, PA, USA) was packed inside a piece of 10 cm×2.0 mm stainless steel tubing, of which the inner diameter provided a good compromise between trapping capacity and sample throughput. Although using smaller bore tubing for the trap improves resolution, the sample throughput and the breakthrough volume would be too small to allow sample trapping in a reasonable time period. Furthermore, 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

prescribed on the controller, which can be activated by relay's contact closure. Detailed description of the profile and time events is referred to in our earlier publications [11,12]. A Windows-based software platform (Genie, Advantech, Taiwan) provided a Visual Basic programming environment for developing our control code. Execution of the control code was displayed in a graphic manner with flashing icons to indicate valve actions and relevant analytical status as an analysis was proceeding, so that an operator can have an instant grasp of system's status. During trapping an air sample the trap temperature was kept at 30°C. Air was drawn from either a canister or open atmosphere at a flow rate of 50 ml/min to each trap controlled by a mass flow

flash heating was effectively reduced and the dead volume was minimized.

The direction of the gas flow was always reversed during thermal desorption so that higher boiling compounds were back-flushed easily from the sampling end of the tube. We have investigated several types of sorbents to obtain optimal combinations for the two columns, and our study suggested that the Carboxen 1000 has better sorption and desorption characteristics than the Carbosieve SIII on the PLOT column, which manifested in sharp and symmetric peaks for low boiling compounds. Although the Carbosieve SIII claims to have better trapping efficiency for C_2–C_3 compounds than Carboxen 1000, it resulted in wider and tailing peaks, probably due to stronger binding force to slow down the desorption process. Furthermore, because the Carboxen 1000 does not efficiently retain high boiling compounds, it provides an excellent match to the PLOT column, which is coincidentally not very tolerable to high boiling compounds. Also, using a short PLOT column (about 30 m) facilitated a faster elution of the remaining trace amount of high boiling residues while maintaining adequate resolution.

Continuous analysis of ambient air showed no sign of accumulation of high boiling residues normally revealed by rising baseline toward the end of elution. In addition, the interference from water and CO_2 was effectively eliminated compared to trapping under cryogen [12], see Fig. 2. Thus, the use of Carboxen 1000 trap to couple with a PLOT column provided a useful tool to analyze low boiling VOCs.

For the second sorbent trap analyzing high boiling VOCs, it was packed with three sorbents, i.e., 1 cm of Carboxen 1000, 1 cm of Carboxen 1003, and 1 cm of Carbotrap B (60–80 mesh, Supelco), in that order, to form a multi-sorbent bed to trap wider range of VOCs. Adding Carboxen 1003 and Carbotrap B significantly increased the trapping efficiency of higher boiling compounds compared to the Carboxen 1000 trap. Our previous study showed that the sorbent trap showed remarkably similar trapping characteristics at ambient temperatures to glass bead trap with liquid N_2 cooling [12]. Thus, with proper formulation the sorbent trap can replace glass bead trap to eliminate the use of liquid N_2.

Since our goal was to completely eliminate the use of cryogen not only in the preconcentration stage,

but also in the GC oven. A thick film column was not an option due to its inferior resolution compared to thinner film counterparts. In this work, we chose a 60 m DB-1 with d_f=1.0 μm to obtain a compromise between resolution and capacity, which when coupled with the multi-sorbent trap provided a satisfactory separation of C_6–C_{12} VOCs.

Minimizing longitudinal diffusion along the transfer line from the trap to column turned out to be a crucial factor for resolution. In Fig. 3 the longitudinal diffusion in 0.5 mm I.D.×1.6 mm O.D. tubing resulted in poor separation of no practical use, see Fig. 3a. Cooling the GC oven with liquid N_2, however, effectively minimized the diffusion and, hence, dramatically improved the resolution, see Fig. 3b. To achieve the objective of minimizing diffusion without using cryogen, dead volume within the transfer tubing must be minimized. We therefore replaced the 0.5 mm tubing with a piece of 0.25 mm I.D.×0.8 mm O.D. stainless steel treated tubing (Silcosteel, Restek) and started the oven temperature from 40°C. Comparable resolution to Fig. 3b (1.6 mm tubing with oven cryogen) for VOCs from carbon number greater than C_6 was achieved, see Fig. 3c. Further gain in resolution was not too obvious for the 0.5 mm tubing with oven cooling. Although this configuration failed to separate compounds lighter than C_6, this task was left to the PLOT column with its matching sorbent trap, as discussed earlier in the text. The plumbing factor was not as critical for the PLOT column as for the DB-1, probably due to the stronger retention of volatile gases on the PLOT column than on the liquid film columns. Our sorbent-column pairs may provide an alternative to the heart-cut technique and can be easily constructed with one trap plus one column for a selected range of VOCs or dual traps plus dual columns for simultaneously analyzing a wide range of VOCs.

4. Reproducibility and linearity

Reproducibility of the system was evaluated by repeatedly analyzing standard mixtures, in which the VOC concentrations were prepared at about 1 ppb (v/v) (ppbv) level. Due to the highly precise execution of valve switching and sorption/desorption
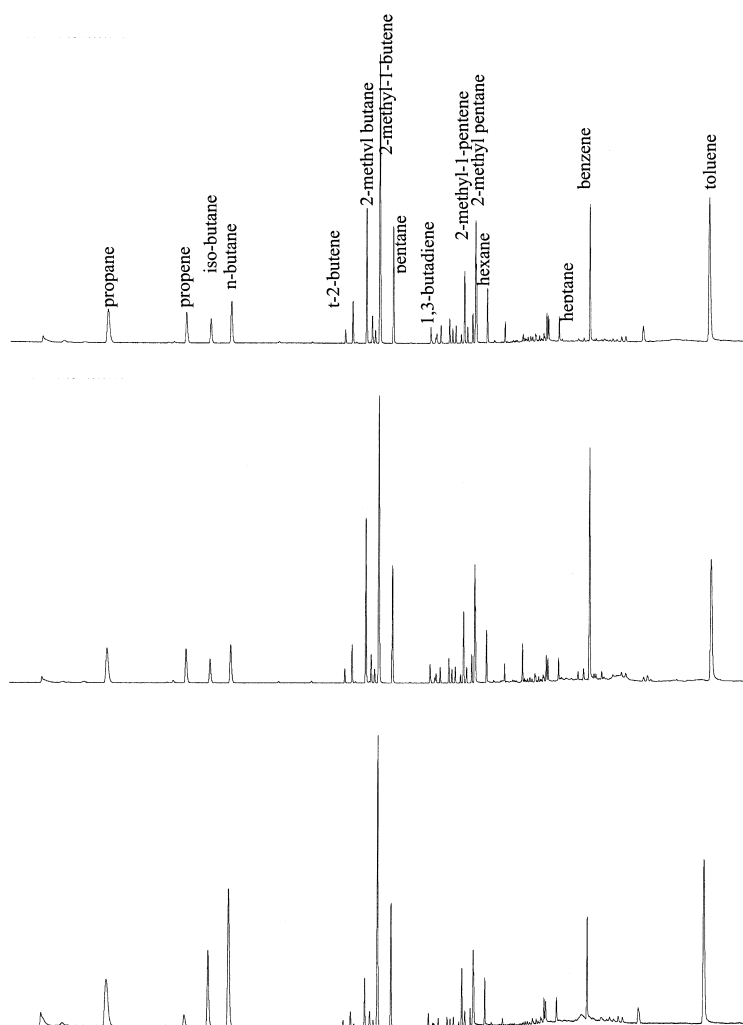
Fig. 2. Continuous analysis of ambient air for C_3–C_7 NMHCs in a Taiwan EPA monitoring station by a Carboxen 1000 sorbent trap and a PLOT column. The upper, middle and lower trace correspond to the first, the 250th and 673th (the last) analysis respectively.

actions, precision for most measured VOCs was within 2%, see Table 1.

Linearity study was investigated by varying the trapping time interval as 1, 3, 5, 10, 15, 20 min under a constant flow rate of 50 ml/min set on the MFC. The air used was a pressurized urban air sample stored in a treated gas cylinder to serve as the working standard, in which the VOC concentrations were calibrated. These six aliquots provided a wide concentration range to cover the working range for our routine analysis. Of the six different trapping

intervals, the 5-min trapping interval was also the standard trapping time for our routine analysis. As a result, the trapping time can be proportionally converted into concentrations, and hence the volume aliquots can be regarded as concentration aliquots. For most of the measured VOCs the calibration curves constructed in this manner were extremely linear with R^2 better than 0.9990 and negligible intercepts. Fig. 4 displays two examples of these curves resulted from the PLOT and DB-1 column, respectively. The linear response with respect to
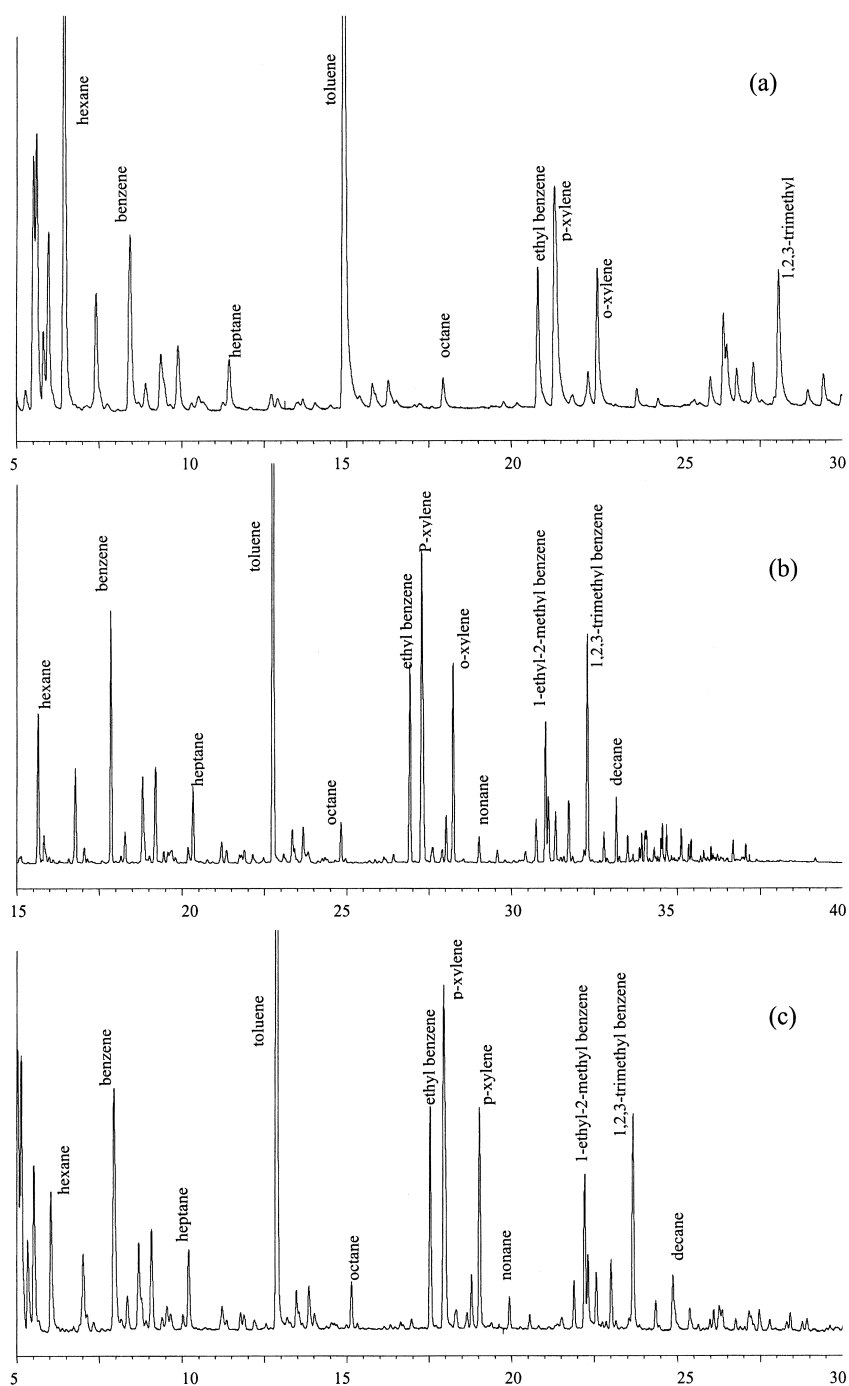
Fig. 3. An urban air sample was analyzed by a multi-sorbent trap coupled to the DB-1 column with (a) 0.5 mm I.D. tubing without oven cooling (starting from 40°C) (b) 0.5 mm I.D. tubing with oven cooling (starting from −50°C) (c) 0.25 mm I.D. tubing without oven cooling. Each chromatogram was optimized to its best resolution by adjusting only temperature programming.

Table 1
Replicate precision for selected VOCs for PLOT and DB-1. RSD% represents the 1 s relative standard deviation at 95% confidence level[a]

PLOT		DB-1	
Compound	RSD% ($n=8$)	Compound	RSD% ($n=8$)
Propane	0.666	Hexane	1.572
Propene	1.703	Benzene	2.120
Isobutane	1.156	3-Methylhexane	0.962
Butane	1.050	Heptane	1.235
2-Methylbutane	2.545	Toluene	0.539
Pentane	0.470	3-Methylheptane	1.587
1,3-Butadiene	1.459	Octane	1.835
2-Methyl-1-pentene	1.879	Ethylbenzene	1.842
2-Methyl-pentane	0.892	*p*-Xylene	1.459
Hexane	1.489	*o*-Xylene	1.533
Heptane	1.510	Nonane	2.111
Benzene	0.988	Decane	2.089

[a] VOCs were analyzed at 1.0 ppb (v/v).

concentration suggests that, within the working range, the sorbent trap exhibited very linear trapping property and no sign of breakthrough was observed.

5. Field measurement

This automated GC system was placed in a Taiwan EPA air quality monitoring station in a downtown area to target ozone precursors. Our system was run in parallel with the existing instruments in the station measuring SO_x, NO_x, CO, THC, and PM_{10} by sharing the same air inlet extruding the rooftop. All instruments, including the automated GC system, took hourly measurements. Due to space limitation in the station, a full size GC system with dual FID systems was not an option, hence a HP 6850 equipped with a single FID system and a PLOT column was used to continuously measure $C_3–C_7$ non-methane hydrocarbons.

The system was remotely controlled from our central laboratory through modems and phone line. The self-developed control software can also be displayed on a lab computer to provide lab personnel with in-situ understanding of system's status quo. During the period of continuous operation starting from 16 September, 1999, the system performed successfully until a severe earthquake struck Taiwan causing a power outage for several days. After that, the continuous measurement resumed for another three weeks. Because the automated GC shared the same inlet with other instruments, the stability and
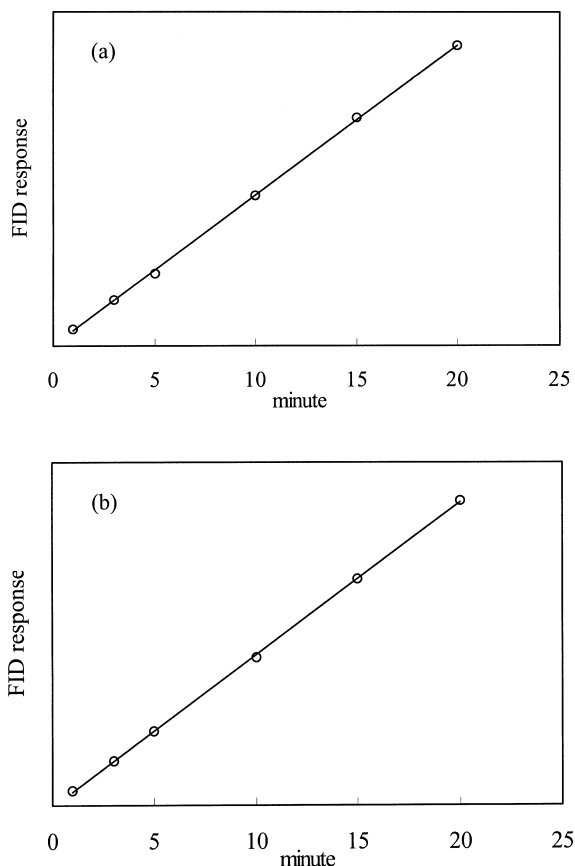

Fig. 4. Linearity of (a) propane from PLOT column; and (b) benzene from the DB-1 column obtained by injecting various amounts of an air standard to provide a wide concentration range covering our routine analysis. The injection volume was controlled by varying the trapping time at a constant flow rate of 50 ml/min set on the MFC.

overall performance can be viewed by comparing with the results obtained from other parallel running instruments. Fig. 5 shows the comparison between the CO measured by the non-dispersive infrared (NDIR) instrument and the vehicular exhaust type of compounds, such as benzene, measured by the automated GC for the first five consecutive days, when the climate was stable and the trace gases revealed clear diurnal variation. Excellent correlation was observed despite the fact that the two instruments had completely different working principles, indicating the performance of the automated GC was robust. The slight disagreement between the NDIR and GC system measurements resulted from the difference in sampling, since our GC system sampled the air for 5 min for every hour, and this sampling was different from that of NDIR which had a much

shorter sampling time. In addition, the time offset in sampling also caused the two instruments probing slightly different air masses. The precise and stable measurement facilitated our source identification, which otherwise would have been impossible or even misleading if systematic problems had occurred. Fig. 6 displays two examples to illustrate the correlation between compounds from the same and different emission sources, respectively. In this example, benzene and hexane are mainly released from car exhaust in an urban environment and, therefore, both are highly correlated. By contrast, the presence of propane in the air largely arises from the leakage of liquefied petroleum gas (LPG), which is a common household fuel in Taiwan, showed poor correlation with benzene [13].
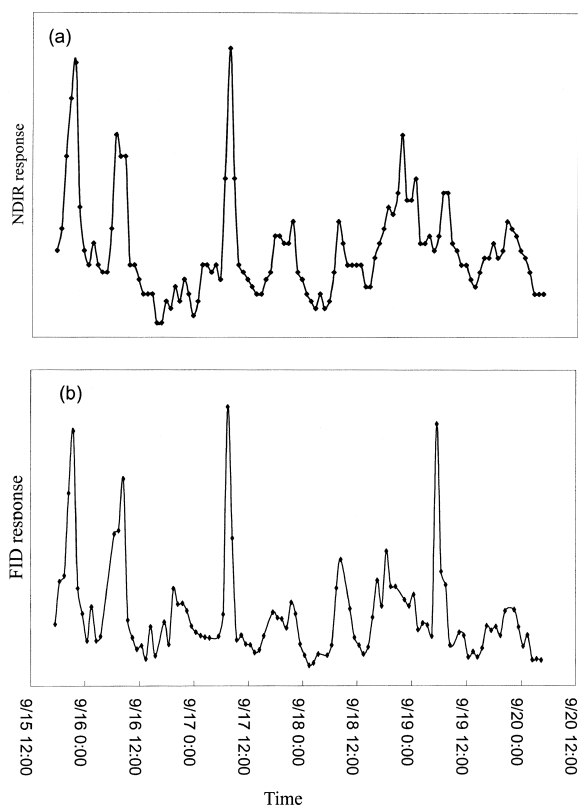

Fig. 5. Hourly measurements of (a) CO by NDIR and (b) benzene by our automated GC–FID in a Taiwan EPA monitoring station. Only five days of data are shown to present clear diurnal features.
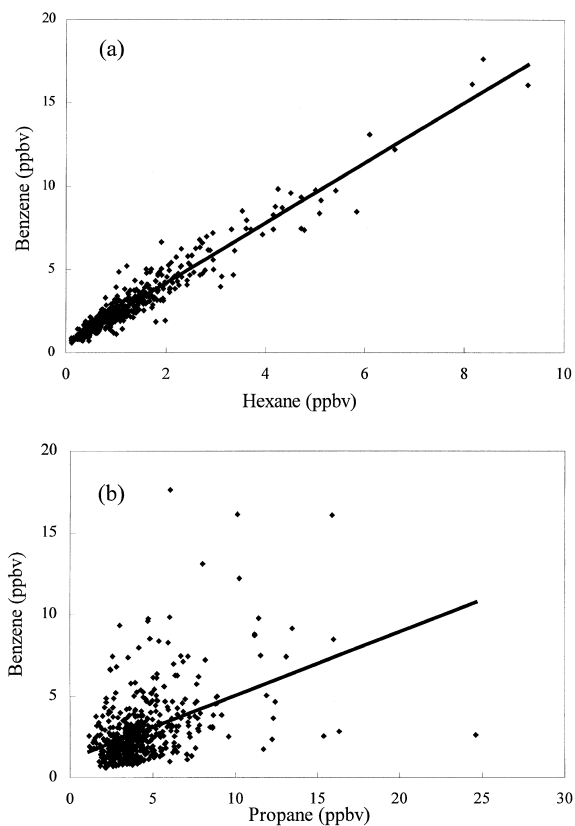

Fig. 6. Scatter plots of (a) benzene vs. hexene with $R^2 > 0.92$ and (b) benzene vs. propane with $R^2 < 0.25$. A total of 673 sample runs were performed during this field measurement.

6. Conclusion

The objective of this work was to build an automated GC system for measuring VOCs either in the laboratory or the field without using cryogen in preconcentration and column separation. This automated system used two sorbent traps with different packing formulas for enriching different range of VOCs. These two traps were coupled to their designated columns to form suitable pairs to provide adequate resolution without cryogen use. Flash heating capability to narrow the bandwidth of the desorbed VOCs and proper plumbing to reduce dead volume were the two decisive factors that controlled the resolution. With this approach, a wide range of VOCs from C_3 to C_{12} was simultaneously analyzed with no need of cryogen.

Field deployment of this automated system in a Taiwan EPA air quality station confirmed the robustness and the long-term stability by making synchronized measurement with existing instruments, such as an NDIR system for CO measurement.

Acknowledgements

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