Automated gas chromatography with cryogenic/sorbent trap for the measurement of volatile organic compounds in the atmosphere

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Abstract

An automated gas chromatographic system was constructed to easily adapt either the cryogenic trap or chemical sorbent trap for preconcentrating ambient levels of volatile organic compounds. Remarkable similarity in chromatograms from C_3 to C_{10} was found between these two enrichment methods, except that the sorbent trap did not quantitatively trap the C_2-hydrocarbons. In contrast to cryogenic trapping, the chromatographic conditions for more volatile compounds were substantially improved using the sorbent trap. Water interference on the porous-layer open tubular column was also better managed using the sorbent trap for the continuous analysis of humid room air. The similarity in peak profiles between the GC–flame ionization detection (FID) and a commercial GC–MS system, regardless of concentration levels, facilitated compound identification on the FID chromatograms based on a field mission involving analysis of 106 air samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Air analysis; Environmental analysis; Volatile organic compounds

1. Introduction

Natural and anthropogenic forces have continually modified the Earth's atmospheric composition, particularly during the industrial era. In clean environments, the presence of volatile organic compounds (VOCs) contributes to the formation and transportation of oxidants and, therefore, partially determines the oxidative capacity of the atmosphere [1–3]. In non-background environments, however, elevated VOC concentrations of e.g., vehicular or biogenic origin, in the presence of NO_x, produce surface ozone and deteriorate the air quality [4–6]. The US Clean Air Act Amendments of 1990 lists 189

chemicals as hazardous air pollutants, and nearly 100 of them have been classified as VOCs [7].

The VOC concentrations in ambient air normally range from hundreds of ppb (v/v) to tens of ppt (v/v), and are generally insufficient for direct chromatographic separation and detection. As a result, a preconcentration step is required to remove the major constituents of air, e.g., O_2 and N_2, CH_4, 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. Subsequently, the enriched VOCs are vaporized and flushed to the analytical columns as the surface is heated up [8–12]. This type of method is simple in principle, and is often preferred for its clean and complete thermal desorp-

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tion. Nevertheless, inclusion of water and CO_2 in the enrichment process is often inevitable, which later creates problems in column separation, particularly for porous-layer open tubular (PLOT) columns used for separating very volatile compounds. Common problems include peak distortion, shift in retention times, baseline rise, plugging the trap, etc. By contrast, using hydrophobic chemical sorbents trapping VOCs at near ambient temperatures can alleviate the above mentioned problems [13–18], but the adsorption and desorption onto sorbent bed could involve forming and breaking chemical interaction and, thus, may not be as straightforward as the cryo-trapping counterpart. Systematic errors could arise if compounds are not being quantitatively absorbed or desorbed. Recent studies in searching of new sorptive preconcentration techniques and materials showed promising prospects in terms of water management and sorption and desorption properties [19,20].

Since either preconcentration method has its pros and cons, and a chromatographic system that can easily adapt either device adds tremendous flexibility and convenience to VOC analysis and also facilitates comparison between these two methods, we therefore designed our system to easily interchange either trapping device. In addition, the system also meets the following criteria: It (1) is fully automated; (2) can be operated in either in-situ or flask analysis mode; (3) consumes little (for cryogenic-trap) or no cryogen (for sorbent trap); (4) can be connected to GC system of any manufacturer with various detection methods such as electron-capture detection (ECD), flame ionization detection (FID), and mass spectrometry (MS).

2. Experimental

2.1. Chromatographic conditions

Fig. 1 illustrates the systematic diagram of the automated system. Two different GC systems and analytical columns were used in this study: A Varian 3400 GC accommodating the DB-1 column (60 m× 0.32 mm; d_f=1.0 μm, J&W Scientific, Folsom, CA, USA) was employed for separating VOCs with 4 or more carbon atoms. The flow eluting from this DB-1
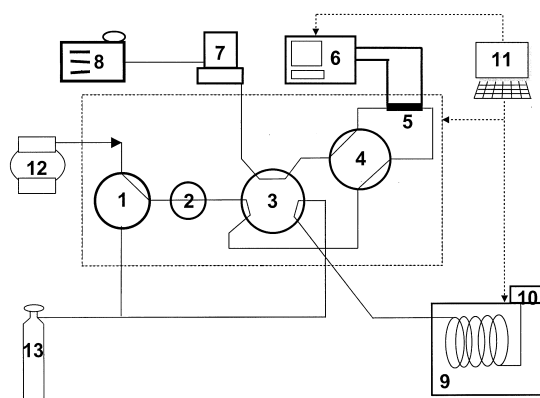

Fig. 1. Plumbing diagram of the automated GC–FID system. Components are numbered as: (1) 3-port switching valve; (2) pneumatic bellows valve; (3) 6-port switching valve; (4) 4-port switching valve; (5) 1/8 in. O.D. absorbent trap; (6) temperature controller; (7) mass flow controller; (8) oil-free pump; (9) GC column; (10) FID; (11) personal computer; (12) 2-L sample canister; (13) He gas. Dotted lines with arrows denote control directions. Heated zone is encircled by the dashed rectangle. As shown, the system is in trapping condition. For desorption, only valve 3 needs to be switched.

column was split into two streams, with the smaller stream (approximately 1/3) going to an ECD system and the larger stream going to an FID system. The temperature program started at −50°C, isothermal for 2 min, followed by a ramp of 8°C/min to 180°C, and maintained at 180°C for 8 min. In the second GC system (Hewlett-Packard HP-6890 GC), a PLOT Al_2O_3/KCl column (50 m×0.32 mm; d_f=8 μm, Hewlett-Packard, San Fernando, CA, USA) and a FID system were used to separate and detect VOCs from C_2 to C_7. The temperature program for the PLOT column started at 35°C, isothermal for 4 min, followed by a ramp of 6°C/min to 180°C, and maintained at 180°C for another 20 min.

2.2. Preconcentration trap

Depending upon mission objectives, either single column or dual column arrangement was employed. In the applications where dual columns were needed for analyzing VOCs of wider volatility range, an adjustable splitter was used with the larger flow

entering the DB-1 column and the smaller flow entering the PLOT column.

The preconcentration trap labeled as component 5 in Fig. 1 can be either a cryogenic trap or a sorbent trap, but only the schematic diagram with the sorbent trap is shown. The interchange only required minor work involving changing an inlet and outlet Swagelok connections, two electric wire connections to the trapping tube, and a thermocouple connection to the temperature controller, plus providing the cryogen supply. The complete cryo-trap device used in this system was built in-house. The cryo-trap unit was placed right on top of a flange-sealed 10-L liquid nitrogen dewar with a head pressure of about 20 p.s.i. (1 p.s.i.=6894.76 Pa). A piece of 10 cm× 0.32 mm (1/8 in.) O.D. stainless steel tubing was filled with 4 cm long, 80–120 mesh glass beads. Cooling of the trap was made possible by purging liquid N_2 into the trap housing. A thermocouple was attached to the trap tubing to provide temperature feedback. The design purpose of this cryogenic trap was to conserve liquid N_2 by reducing vaporization due to long-distance transfer. Thus, more than 30 analyses can be made with one liquid N_2 filling (about 8 L). Detailed description of this cryo-trap is referred to our previous publication [12].

The sorbent trap was also made by a piece of 10 cm×0.32 mm O.D. stainless steel tubing, but packed with 1 cm of Carboxen 1000 (60–80 mesh, Supelco, Bellefonte, PA, USA), 1 cm of Carboxen 1003 (60–80 mesh, Supelco), and 1 cm of Carbotrap B (60–80 mesh, Supelco), in that order. These sorbents were held in place by deactivated glass wool plugs and then some glass beads on either side. Immediately adjacent to the glass bead plugs, the empty sections on either side were slightly pressed with pliers to tightly secure the packing material. Otherwise, the flush and back-flush flows would push the sorbent plug back and forth inside the tubing owing to its light mass, and possibly out of the trap. 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. Prior to analysis, the trap was conditioned by heating to 280°C and purging with ultra-pure He. Afterwards, blank runs were made to ensure clean baseline. Heating of the trap was made by supplying a low-voltage large-current (4 V a.c.; 40 A) to the

stainless trap tubing, which enabled a maximum heating rate of 50°C/s.

2.3. Valve system

The valve system used three air actuated 2-way multi-port switching valves, i.e., a 3-port, a 4-port and a 6-port switching valve (Valco, Model 3UWT, 4UWT, and 6UWT, Houston, TX, USA), and a pneumatic bellows valve (Parker; 4A-P4K-11ACSS, Jacksonville, AL USA). All the plumbing used 0.32 cm O.D. treated tubing (Silcosteel, Restek, Belle-fonte, PA, USA) to minimize possible transfer loss due to surface adsorption [21]. Actuating these 4 valves was made possible by four 110 V a.c. solenoid air valves controlled by relays. The control hardware used in this system consisted of an input/output board (PCL-724, Advantech, Taiwan), a 16-channel power relay output board (PCLD-885, Advantech, Taiwan), and a wiring terminal board (PCLD-8115, Advantech). Seven relays were employed to control the four valves, initial the temperature profile controller (Powers 535, Powers Process Controls, Skokie, IL, USA), and start/stop both GC systems. A Windows-based software platform (Genie, Advantech) provided a Visual Basic programming environment for writing control code. Since the operation conditions for the two trapping devices were different, two different sets of control code were written and saved as method files. Fig. 2 illustrates the time events and temperature programs for the sorbent trap during repetitive operation of this system for continuous measurements.

2.4. Test with a field mission

A field mission was made on 7 August, 1998 to collect 106 samples in 2 L stainless steel canisters over the Taipei metropolitan area. These samples were first analyzed by this automated GC–FID system with the cryogenic trap and the DB-1 column. Subsequently, the samples were randomly analyzed again by an independent commercial GC–MS (Varian Saturn 2000) system, also equipped with a glass-bead cryo-trap (made by Varian called SPT) and a RTX-1 column (60 m×0.32 mm; d_f=1.0 μm, Restek), using the same temperature program as the
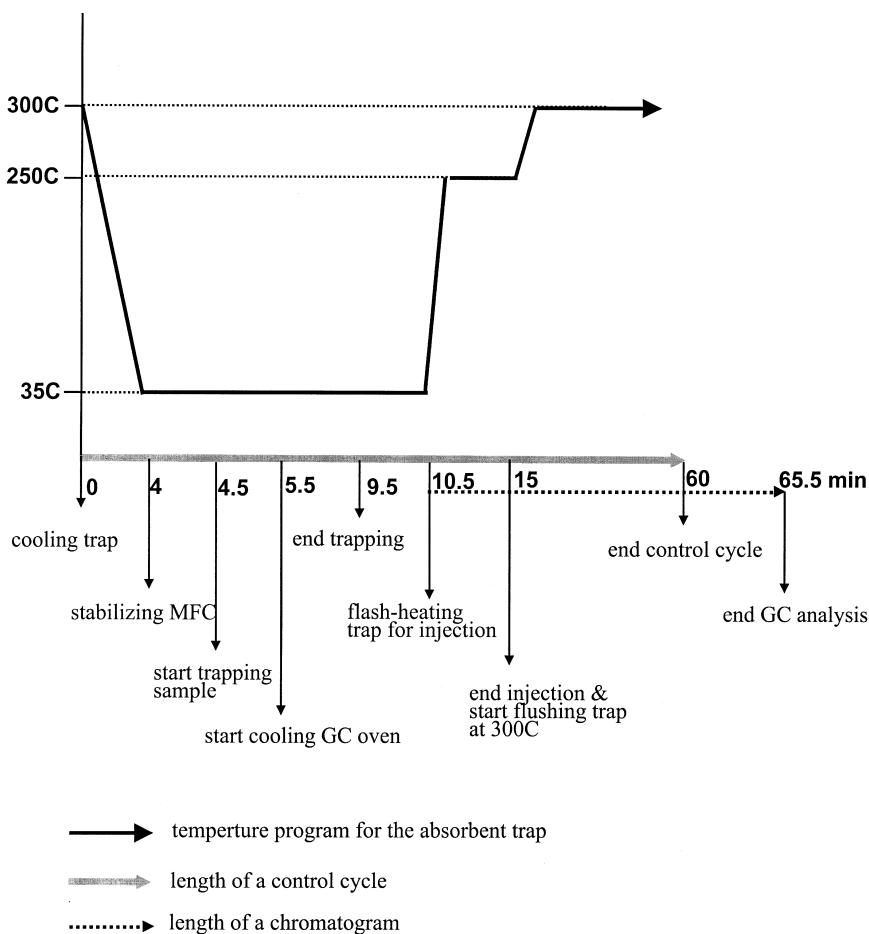
Fig. 2. Temperature and control event programs during the course of an analysis.

DB-1 in our system. Detailed discussion will be given later in the text.

3. Results and discussion

3.1. Comparison of traps for less volatile compounds

Fig. 3 exhibits DB-1 column chromatograms using either trap analyzing the less volatile compounds starting from C_4 in the same air sample. Remarkable resemblance was observed between the two, implying the absorbing and desorbing behaviors associated with the chemical sorbent trap can mimic those with the cryogenic trap which is less prone to artifacts or

systematic errors based on atmospheric CCl_4 measurements of 106 air samples collected in the Taipei metropolitan area. Due to the implementation of the Montreal Protocol, the atmospheric concentrations of CCl_4 have become homogeneous in many parts of the world [22,23], hence the CCl_4 ECD response was closely monitored during the course of continuous analysis of the 106 samples for halocarbons. These samples were collected on 7 August 1998 in the Taipei metropolitan area with one half of the samples collected between 5:00 and 5:30 a.m. and the other half collected between 6:00 and 6:30 p.m. The sampling strategy was designed to obtain a distribution profile of anthopogenic halocarbons in this metropolis. As a result, samples were spread out as evenly as possible and collected over an area of 30
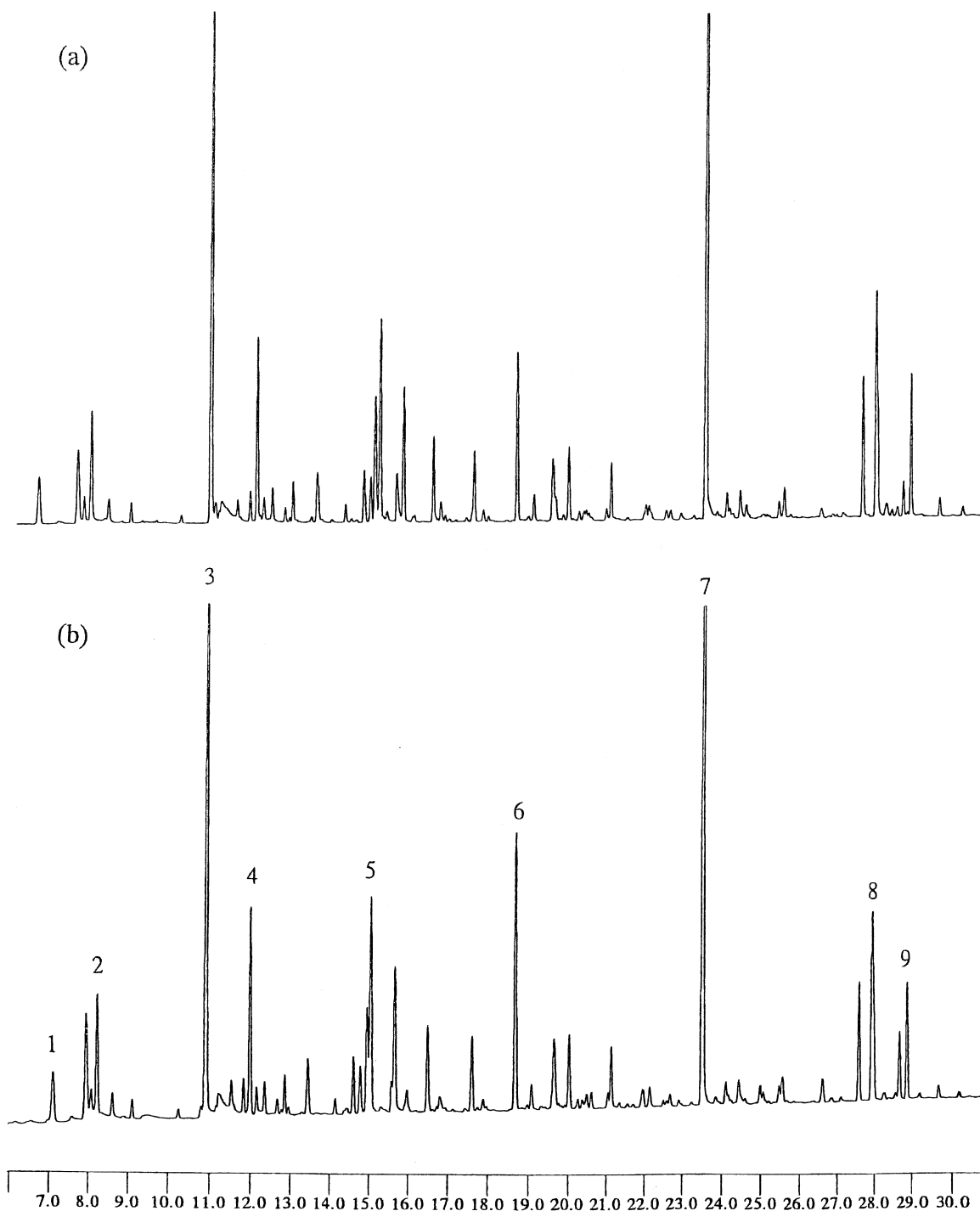
Fig. 3. A typical air sample analyzed by automated GC with the DB-1 column using (a) cryogenic trapping and (b) sorbent trapping. Each injection aliquot is 250 ml. Selection peaks are assigned as: (1) isobutane; (2) butane; (3) 2-methylbutane; (4) pentane; (5) 2-methlypentane; (6) benzene; (7) toulene; (8) 1,3-dimethylbenzene; (9) 1,2-dimethylbenzene.

km^2 in open field such as parks or schoolyards to avoid direct influence by point sources. The average concentration of CCl_4 of the 106 samples was about 101 ppt (v/v), with 1σ standard deviation as small as 1.41 ppt (v/v), suggesting that this automated system was stable and precise [12,22]. Consequently, the cryogenic trap was employed to serve as a reference to compare against the sorbent trap.

3.2. Comparison of traps for more volatile compounds

Likewise, both traps were tested on the PLOT column with the same air sample, and the results are displayed in Fig. 4. The overall profile with the sorbent trap is similar to the cryogenic trap, except that the C_2 hydrocarbons, i.e., ethane, ethene and ethyne, were missing in Fig. 4b, suggesting operating at ambient temperature, the sorbent trap was not able to trap the extremely volatile components. Losing C_2 hydrocarbons could sometimes be a disadvantage, particularly in ozone precursor measurement [24], since they contribute an important fraction of the total photochemical reactivity [25]. However, in many environmental applications, measurement excluding C_2 hydrocarbons may still be quite applicable. For instance, the system with sorbent trap was successfully used in accordance with the US Environmental Protection Agency (EPA) TO-15 compendium method [26]. Even the most volatile target compounds, such as CCl_2F_2, CH_3Cl, vinyl chloride, etc., can be measured by this setup.

3.3. CO_2 and water management in sorbent trapping

A major advantage of sorbent trap over the cryogenic trap was reflected on the early eluting peaks, see Fig. 4b. Propane's peak shape improved dramatically with sorbent trapping at ambient temperatures. By contrast, the propane peak in Fig. 4a suffered from CO_2 interference because the atmospheric abundance of CO_2 is overwhelmingly larger than that of VOCs, and its retention time on PLOT column coincides with propane. The propane plug inside the column is diluted and thereby broadened by the presence of large amount of CO_2. Increasing GC oven temperature to force a faster elution does not really circumvent the interference problem, but merely makes the CO_2 plug longitudinally less diffused. The asymmetric propane peak with cryogenic trapping reveals a serious overloading problem caused by CO_2. The nonlinear FID response for propane could occur if the CO_2 content in air samples are highly variable, particularly when samples are collected near combustion sources. By contrast, enriching air sample using sorbents solves the problem by not retaining the CO_2 in the trap. Subsequently, a very rapid thermal desorption to 250°C immediately followed by flushing with He carrier gas for injection was necessary to obtain sharp peaks for early eluting VOCs. Owing to using a large transformer (110 to 4 V a.c.), a current as high as 40 amperes can be instantaneously drawn to the trap tubing, producing a heating rate as fast as 50°C/s. A process controller (Powers 535, Skokie, IL, USA) with proportional-integral-derivative (PID) algorithm helps controlling the temperature profile and preventing the temperature over-shoot. We have found that flash-heating is crucial for sorbent trap to obtain sharp peaks for early eluting compounds, as shown by the propane, propene, isobutane and butane peaks in Fig. 4b. On average, a reduction in peak width and an increase of peak height by a factor of 2 was achieved for these four volatile compounds by using the sorbent trap.

After flushing the trap for 4 min, the carrier gas flow by-passed the trap, while another faster flow of He was purging the sorbent trap maintained at 280°C, 30°C higher than injection temperature, so as to remove the firmly retained high boiling residue and refresh the trap for subsequent injections. The valve configuration for this arrangement can be referred to Fig. 1, except the 3-port valve (component 1) is switched to the He gas supply.

Water management has been a troublesome issue facing the PLOT column with Al_2O_3/KCl layer due to its large concentration and strong retention [27]. Excess water on the PLOT column can change the adsorption properties of the solid phase and cause unpredictable changes in the retention times [28] and, in some instances, irreparable damage to the column [29]. Common practice to remove excess water involves the use of desiccant [28,30,31], cooling to dew point [32], Nafion tubing [33], etc., before the cryogenic trap. However, these treatments
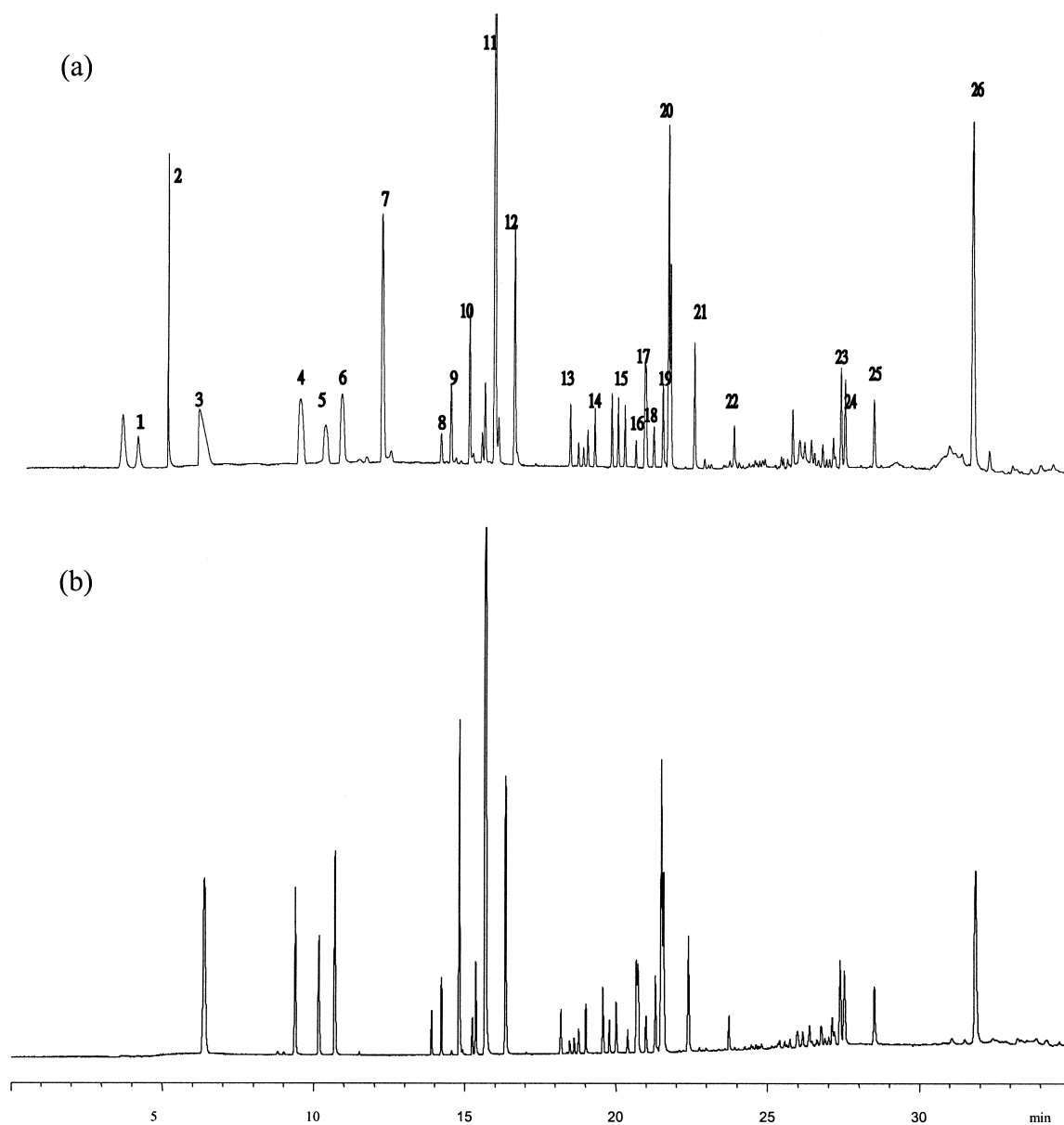
Fig. 4. A typical air sample analyzed by automated GC with the PLOT column using (a) cryogenic trapping and (b) sorbent trapping. Each injection aliquot is 250 ml. Peak assignment: (1) ethane; (2) ethene; (3) propane; (4) propene; (5) isobutane; (6) *n*-butane; (7) ethyne; (8) *tert.*-2-butene; (9) 1-butene; (10) 2-methyl-1-butene; (11) 2-methylbutane; (12) pentane; (13) 1,3-butadiene; (14) cyclopentene; (15) 1,1-dimethylcyclopropane; (16) pentene; (17) 2-methyl-1-pentene; (18) cyclohexane; (19) 2,3-dimethylbutane; (20) 2-methylpentane; (21) hexane; (22) 2-methyl-1,3-butadiene; (23) 3-methylhexane; (24) 2-methylhexane; (25) heptane; (26) benzene.

may possibly open room for artifacts. Analogous to CO_2 management, using hydrophobic sorbents provides a fundamental solution by simply not retaining water in the trap. We have tested the system with

sorbent trap for water problems by continuously injecting room air (over 40% humidity) for 3 days and accumulated 60 chromatograms. Other than observing variation in peak height with some com-

pounds on these chromatograms, the baseline remained extremely flat during the whole time, see Fig. 5. Lowering sorbent-trap temperature by cryogen or thermoelectric cooling (using Peltier device) to subambient temperatures, e.g., $-30°C$, help quantitatively trapping the extremely volatile components, which has also been reported [34]. However, water vapor was inevitably trapped, which was undesirable for repetitive measurement using Al_2O_3/KCl PLOT column.

3.4. Linearity and breakthrough in sorbent trapping

The sorbent was further tested for linearity and breakthrough by injecting various amounts of a standard air mixture to create a range of concentration loadings, which was large enough to encompass our routine measurement extremes. This was accomplished by varying the trapping time interval prescribed in the control code. The valve
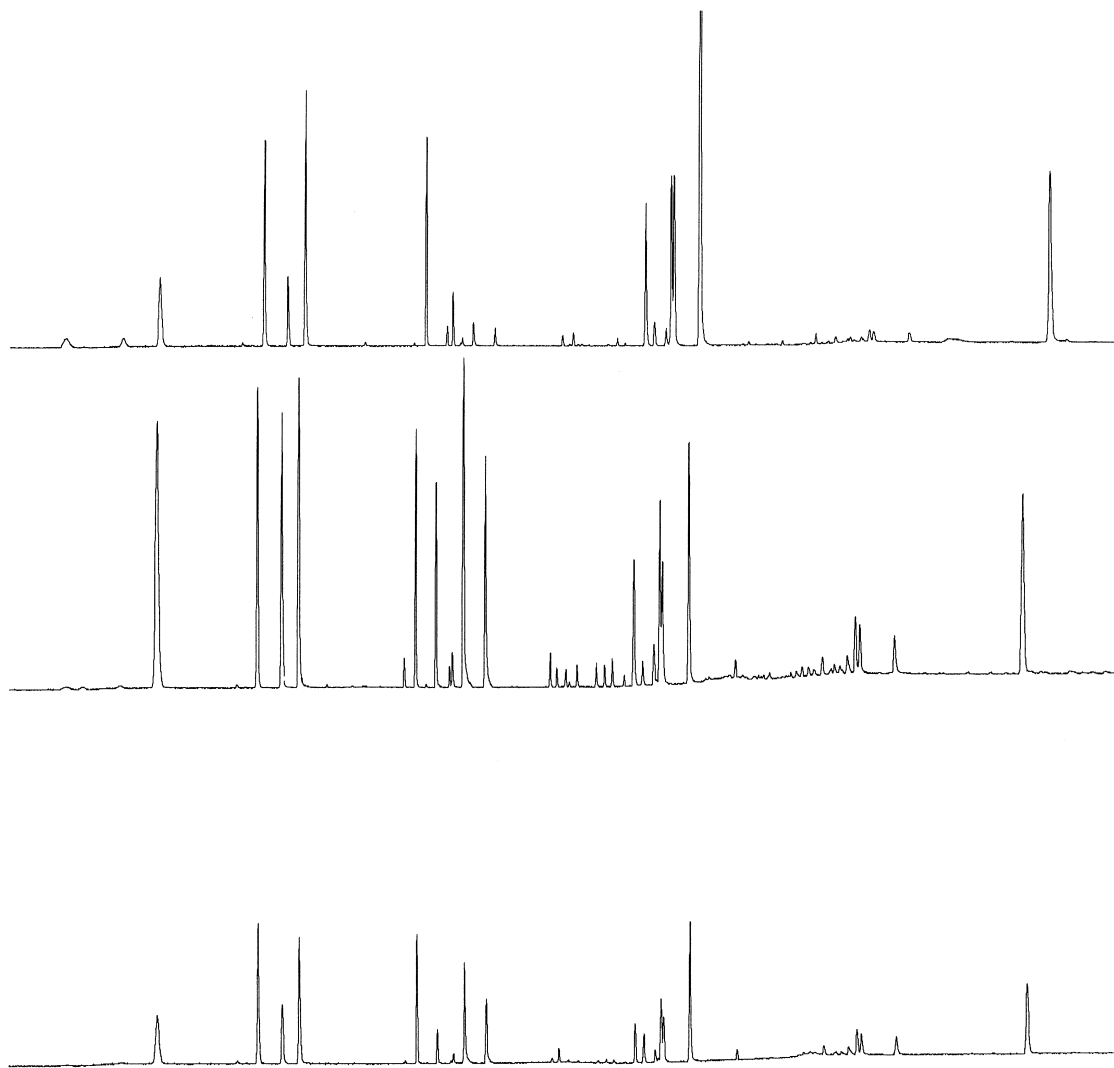

Fig. 5. Repetitive analysis of humid room air for 3 days for testing water interference. The upper, middle and lower traces correspond to the first, the 30th and the 60th (the last) analysis, respectively. The sorbent trap was used, and the PLOT column for analysis.

assembly was controlled in such a way that allowed an initial 30 s of air sample to by-pass the trap in order to stabilize the mass flow controller (MFC) placed downstream of the system. After that the valve was immediately switched to the trapping position for a prescribed time period, while the MFC remained at the fixed flow rate of 50 ml/min. All the compounds exhibit excellent linearity with negligible intercepts. Fig. 6 illustrates the linearity results for two well-separated hydrocarbons on the PLOT column. The linear response with respect to concentration suggests that, within the working range, the measured VOCs did not breakthrough the sorbent trap in our routine operation conditions.

3.5. Compound identification by GC–MS
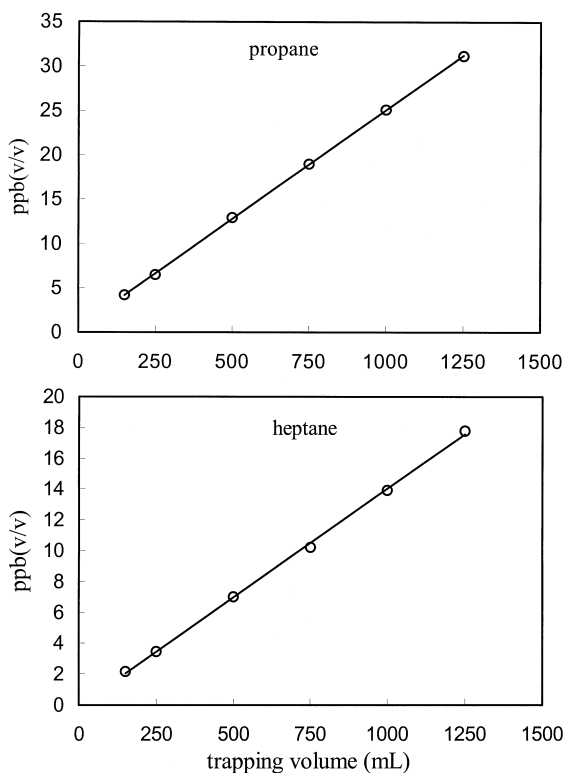
We used this system with the cryogenic trap to

Fig. 6. Linearity check on the system by injecting various amounts of a standard air mixture containing propane and heptane. Our routine injection volume is 250 ml (5 min×50 ml/min on the MFC).

analyze 106 samples collected in the Taipei metropolitan area. These canisters were later analyzed again by another independent commercial GC–MS system with a built-in cryogenic trap and a 16-canister auto-sampler. We then compared the chromatograms obtained from our automated GC–FID system with those obtained from GC–MS and found that all the 106 samples consistently exhibited remarkable resemblance in peak profiles between the two independent systems, regardless of concentration levels, see Fig. 7 for a typical air sample. Starting the mass scanning from m/z 46 to avoid detecting CO_2 slightly lowers the sensitivity of early eluting compounds on the GC–MS chromatogram, since their major ions are excluded.

The resemblance to GC–MS in separation and detection tremendously facilitated species confirmation on the FID chromatograms. Provided that the speciation is accurately known, using GC–FID is more desirable than GC–MS in that the FID system is substantially less costly in purchasing and maintenance, more rugged and reliable, linear in response over a wide dynamic range, proportional in response to carbon number, etc. We therefore routinely use automated GC–FID to perform analyses of large sample quantity, and only randomly selected a small number of samples for subsequent GC–MS analyses at identical chromatographic conditions solely for species identification purpose.

4. Conclusion

An automated gas chromatographic system was designed and constructed in order to accommodate either a cryogenic trap or a sorbent trap. The chromatographic profiles obtained from the sorbent trap remarkably resembled those from the cryogenic trap, except that the C_2 hydrocarbons were lost in sorbent trapping owing to their high volatility. Nevertheless, CO_2 and water interference, as well as the peak shape of early eluting compounds on the PLOT column, was dramatically improved using the sorbent trap. Water interference was further tested based on repetitive injecting humid air over a period of 3 days.

Consistency and similarity between the GC–MS and GC–FID chromatograms, regardless of concen-
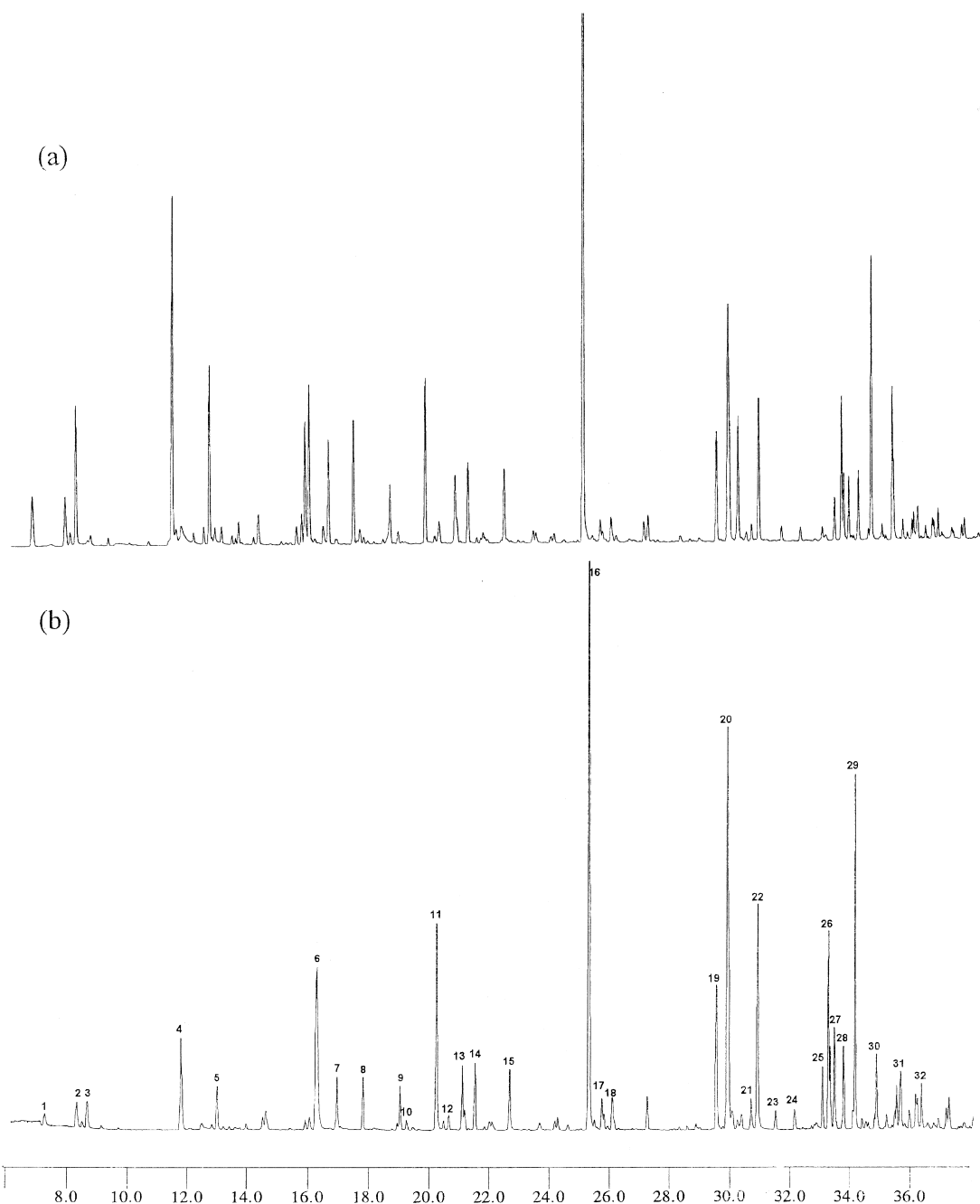
Fig. 7. A typical air sample analyzed by (a) automated GC–FID and later analyzed by (b) an independent GC–MS system. Both systems employed the cryogenic trapping method of different designs. Peak assignments: (1) isobutane; (2) 2-methyl-1-propene; (3) butane; (4) 2-methylbutane; (5) pentane; (6) 2-methylpentane; (7) 3-methylpentane; (8) hexane; (9) methylcyclopentane; (10) 2,4-dimethylpentane; (11) benzene; (12) cyclohexane; (13) 2-methylhexane; (14) 3-methylhexane; (15) heptane; (16) toluene; (17) 2-methylheptane; (18) 3-methylheptane; (19) ethylbenzene; (20) *p*-xylene; (21) styrene; (22) 1,3-dimethylbenzene; (23) nonane; (24) 1-methylethylbenzene; (25) propylbenzene; (26) 1-ethyl-3-methylbenzene; (27) 1,2,3-trimethylbenzene; (28) 1-ethyl-2-methylbenzene; (29) 1,3,5-trimethylbenzene; (30) 1,2,4-trimethylbenzene; (31) 1-methyl-3-propylbenzene; (32) 1-methyl-2-(1-methylethyl)-benzene.

tration levels, facilitated compound identification on the FID chromatograms by analyzing samples at identical chromatographic conditions.

Acknowledgements

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