

Peak tailoring concept in gas chromatographic analysis of volatile organic pollutants in the atmosphere

Chieh-Heng Wang^a, Chih-Chung Chang^b, Jia-Lin Wang^{a,*}

^a Department of Chemistry, National Central University, Chungli 320, Taiwan

^b Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan

Available online 29 March 2005

Abstract

An automated gas chromatographic system aiming at performing unattended analysis of volatile organic compounds (VOCs) was developed in laboratory. To encompass VOCs of a wide range of volatility, two different designs of enrichment and separation methods were adopted and compared with performance in analyzing ozone precursors of C₃–C₁₂. In the dual-trap dual-column design, lower boiling species (C₃–C₆) are enriched and separated by one set of trap and column (porous layer open tubular (PLOT)), whereas the enrichment and separation for the higher boiling species (C₆–C₁₂) are performed by the other set (wall-coated open tubular (WCOT)). Undesired peaks also inevitably appear on both chromatograms often causing annoyances. To reduce complexity of both the apparatus and the resulting chromatograms, the heart-cut technique was adopted as a base for developing a system, which only uses one trap and one flame ionization detector for constructing two-dimensional GC with PLOT and DB-1. Methods were developed to allow the auxiliary flow pressure in the heart-cut device to be programmed to create dual effects, which not only can perform regular heart-cut actions but can also temporally hold up species in the precolumn for prescribed time intervals. Because it is characteristic for PLOT chromatograms to have reproducible blank retention time windows, segments of a DB-1 trace are produced by the auxiliary flow program aligning perfectly in time with the gaps of the PLOT trace. Subsequently, the two column flows are merged and channeled into single flame ionization detector to produce a very condensed “tailored” chromatogram which is equivalent to overlaying a PLOT and a DB-1 chromatogram on top of each other, except that no peaks are overlapped. This innovative “peak tailoring” concept based on the heart-cut technique is simple in design, easy to build, and extremely rugged for long-term continuous operation as fewer moving parts are involved, which is beneficial for deploying in remote monitoring stations.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Volatile organic compounds; Ozone precursors; Monitoring stations

1. Introduction

Ambient volatile organic compounds (VOCs) are known to induce various health or environmental concerns, as most of which are either toxic or precursors of some other secondary air pollutants, e.g., ozone, peroxyacetylnitrate (PAN), aldehydes, etc., photochemically produced in the presence of NO_x. Accurate monitoring of ozone precursors in air with adequate time resolution constitutes the first step towards unraveling emission characteristics by means of source type identification, source strength estimation and apportionment, so that effective ozone abatement strategies can be crafted.

In accordance with the 1990 Clean Air Act Amendments [Section 182 (C) (1)], US Environmental Protection Agency (EPA) developed rules for the initiation of Photochemical Assessment Monitoring Stations (PAMS) located in ozone non-attainment areas targeting 56 VOCs [1] which are either significant in abundance or ozone formation potential or both. In Europe, the new Ozone Directive 2002/3/EC, which has been in effect as of September 2003, obliges member states in the future not only to monitor ozone itself but also its precursors including nitrogen oxides and 31 VOCs. Similar program also has been implemented in other areas of the world such as Taiwan to form VOC monitoring network addressing ozone problem in a more systematic approach [2]. Given the high complexity and low abundance nature associated with ambient VOCs, the chromatographic meth-

* Corresponding author. Fax: +886 3 4227664.

E-mail address: cwang@cc.ncu.edu.tw (J.-L. Wang).

ods are preferred for their efficient separation and sensitivity over other analytical means [3–6]. In order to simultaneously measure VOCs from C₂ to C₁₂ covering large volatility difference, usually two-dimensional gas chromatography (2D GC) is adopted in which two columns of different properties, e.g., porous layer open tubular (PLOT) and wall-coated open tubular (WCOT), are employed. The PLOT column provides sufficient retention for highly volatile compounds which cannot be adequately separated on WCOT columns. Conversely, the less volatile ones are too retentive on the PLOT column and can only be eluted at extremely high temperatures and long retention times. Instead, the higher boiling VOCs can be adequately separated by the WCOT column. Since most ozone precursors are non-polar or less polar compounds, WCOT columns coated with entirely or mostly polydimethylsiloxane can perform satisfactory separation for the less volatile species. To achieve full coverage of the target C₂–C₁₂ ozone precursors, simultaneous use of a PLOT column and a WCOT column is a common approach to obtain all species in one sample aliquot. Using chemical sorbent to pre-concentrate VOCs prior to GC separation is becoming more popular than pure condensation methods with cryogenics such as liquid N₂, Ar, or higher pressure CO₂, since cage effect plus van der Waal's forces exert by the molecular sieve sorbents allow quantitative trapping VOCs at close to ambient temperatures which could eliminate the use of cryogenics [7–9]. Such an advantage helps to extend GC applications outside laboratories, and even unattended continuous field measurement is possible. Using two traps separately for two columns denoted as “dual-trap dual-column” is a straightforward configuration to achieve the objective [10]. Another design uses single trap with heart-cut technique, commonly referred to as Dean's switch device [11–13], also employs dual columns for wide range of VOCs. In either case, usually two flame ionization detectors are needed for the two columns. Both types of systems are commonly employed in monitoring stations for routine measurement of ozone precursors or toxic VOCs. In this work, the heart-cut technique is further improved to ultimately use only one sorbent trap and one flame ionization detector to cover a wide range of VOCs from C₃ to C₁₂. Compared to our earlier design of dual-trap system, the most obvious benefit for the new configuration is that the system not only dramatically reduces the cost of construction but also the cost of maintenance and operation as the tear and ware as well as the gas consumption are greatly reduced, which is centrally beneficial for unattended operation of monitoring stations.

2. Experimental

2.1. Sample preconcentration

An enrichment unit was built in laboratory which is coupled to a GC (Agilent 6890) to perform automated analysis of VOCs. Control hardware and software (Advantech, Taiwan) for the unit was run independently from the commercial

GC integration software (Chem Station provide by Agilent, Wilmington, DE, USA). The enrichment system uses a multi-sorbent trap made by packing some of the following carbon molecular sieves, e.g., Carbosieve SIII, Carboxen 1000, Carboxen 1003, and Carbotrap (Supelco, Bellefonte, PA, USA) into a piece of stainless tubing (3 mm I.D. × 10 cm) with each component occupies roughly 1 cm in length in the trapping tube with glass wool plugs in between. Combination of selected sorbents allows preferential adsorption over certain range of VOCs. The packing sequence and flow direction for sorption and desorption with respect to the sequence is critical to ensure complete desorption, optimal peak shape and thus resolution [14]. The sorption of air sample is performed at 30 °C to enrich VOCs excluding C₂ compounds. Quantitative trapping of three C₂ species, namely ethane, ethene, and ethylene, requires cooling the trap to subambient temperatures, say –30 °C, which can be achieved by common cooling tools, such as a vortex tube, a refrigeration compressor, or a thermoelectric cooler based on Peltier effect,

Table 1
List of compounds in the standard mixture and their concentrations

PLOT column	ppbC ^a	DB-1 column	ppbC ^a
1. Ethane	28	24. Methycyclopentane	31
2. Ethylene	26	25. 2,4-Dimethylpentane	47
3. Propane	47	26. Benzene	36
4. Propylene	25	27. Cyclohexane	48
5. Isobutane	30	28. 2-Methylhexane	30
6. Acetylene	37	29. 2,3-Dimethylpentane	62
7. <i>n</i> -Butane	48	30. 3-Methylhexane	31
8. <i>trans</i> -2-Butene	29	31. 2,2,4-Trimethylpentane	37
9. Isobutene/1-Butene	36	32. <i>n</i> -Heptane	30
10. <i>cis</i> -2-Butene	42	33. Methylcyclohexane	37
11. Cyclopentane	24	34. 2,3,4-Trimethylpentane	31
12. Isopentane	49	35. Toluene	47
13. <i>n</i> -Pentane	31	36. 2-Methylheptane	31
14. <i>trans</i> -2-Pentene	29	37. 3-Methylheptane	32
15. 1-Pentene	30	38. <i>n</i> -Octane	38
16. <i>cis</i> -2-Pentene	41	39. Ethylbenzene	30
17. 2,2-Dimethylbutane	49	40. <i>m/p</i> -Xylene	47
18. 2,3-Dimethylbutane	60	41. Styrene	43
19. 2-Methylpentane	25	42. <i>o</i> -Xylene	30
20. 3-Methylpentane	48	43. <i>n</i> -Nonane	31
21. Isoprene	46	44. Isopropylbenzene	41
22. 2-Methyl-1-pentene ^b	67	45. <i>n</i> -Propylbenzene	36
23. <i>n</i> -Hexane	36	46. <i>m</i> -Ethyltoluene	32
		47. <i>p</i> -Ethyltoluene	46
		48. 1,3,5-Trimethylbenzene	30
		49. <i>o</i> -Ethyltoluene	38
		50. 1,2,4-Trimethylbenzene	48
		51. <i>n</i> -Decane	37
		52. 1,2,3-Trimethylbenzene	31
		53. <i>m</i> -Diethylbenzene	47
		54. <i>p</i> -Diethylbenzene	30
		55. <i>n</i> -Undecane	37
		56. <i>n</i> -Dodecane ^b	40

Concentrations for compounds 1–23 are determined from the PLOT column; and compounds 24–56 are determined from DB-1.

^a ppbC denotes concentration in parts per billion by volume (ppbv) multiplied by the carbon number.

^b These compounds are added for the purpose of retention time verification.

provided that the use of cryogen is not an option. We have designed a cooling device using a thermoelectric device to trap the three C₂ compounds with satisfactory performance [10], but in this work the device was omitted to simply the construction. Nevertheless, the entire heart-cut and peak tailoring concept discussed later in the text will not be affected by the absence of the cooling device.

Thermodesorption for injecting VOCs is made by resistive heating of the s.s. trap tubing. A process controller (Powers 535, Moore Industry, North Hills, CA, USA) regulates a 4 V ac current supplied to the trap tube for reproducible heating which is able to flash-heat the trap from 30 to 250 °C within 7 s and also to confine the fluctuation within ± 1 °C at the high and low setpoints.

2.2. Standard gas mixture containing 56 target species

The system is designed to analyze ambient volatile organic pollutants that are ozone precursors. Monitoring stations that are designated to provide continuous measurement of numerous key ozone precursors in ozone plagued areas have been attempted in some countries to deconvolute the mechanism of ozone formation. For instance, in the US PAMS program, 56 non-methane hydrocarbons (NMHCs) consisting of alkanes, alkenes and single-ring aromatics with molecular size from C₂ to C₁₂ are chosen to be the target species of routine monitoring due to their favorable abundance and reactivity in forming ozone [15,16]. Taiwan EPA also has implemented a similar program trying to elucidate ozone formation mechanism of its own by using automated GCs to provide hourly measurement [10]. High-pressure standard mixture cylinders containing the 56 target species (Spectra, USA) are used in the monitoring stations for daily calibration. Table 1 lists the species and their concentrations for the 56 VOCs in the

cylinders which were used in this work to demonstrate the heart-cut and peak tailoring technique. Other than the 3 early eluting C₂ compounds, i.e., ethane, ethene, and ethyne, the rest of the 53 compounds were tested by the system.

3. Results and discussion

3.1. Dual-trap configuration versus single-trap heart-cut configuration

Prior to the heart-cut configuration our previous design to measure C₂–C₁₂ VOCs was conducted by two parallel components with each containing a multisorbent trap and either a PLOT or a DB-1 column and a flame ionization detector (see Fig. 1 for the schematics). The multisorbent traps were formulated differently for the two traps in which the PLOT trap is packed with stronger sorbents, e.g., Carboxieve SIII or Carboxen 1000, and the DB-1 trap is packed with Carboxen 1000, Carboxen 1003 and Carbotrap. Such a sorbent combination allows the PLOT trap to capture more volatile species and less high boiling ones so that accumulation of higher boiling residuals in the PLOT is minimal. Although the dual-trap configuration performed extremely well and suited for long-term monitoring purpose, the other alternatives were also explored to further simplify the design. One possible drawback with the dual-trap design, if ever is, is that with the PLOT chromatogram higher boiling species from C₆ on also appear even though they are not the intended targets for the PLOT and part of the very high boiling residues could slowly build-up to deteriorate column efficiency. Likewise, the early eluting ones on the DB-1 do not have adequate resolution at close to ambient GC temperatures but appear anyhow causing cosmetic annoyance. As a result, the heart-cut technique

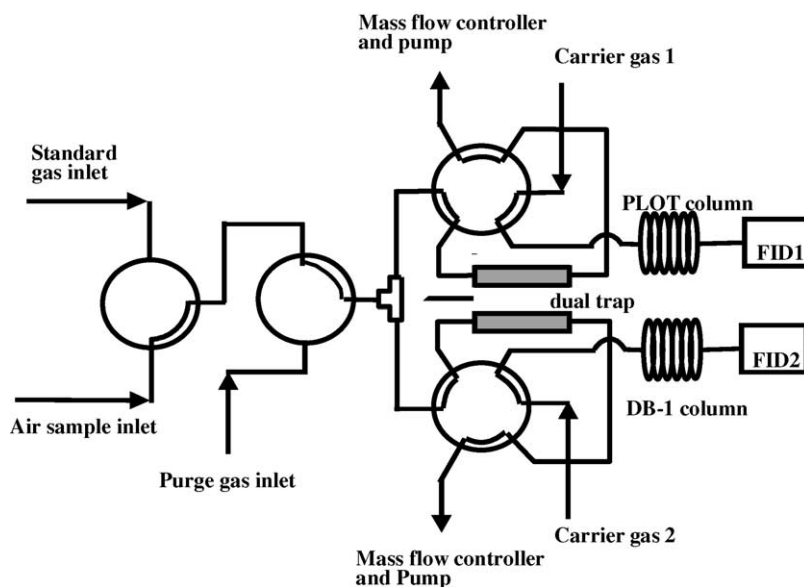


Fig. 1. Schematics for the dual-trap dual-column GC system.

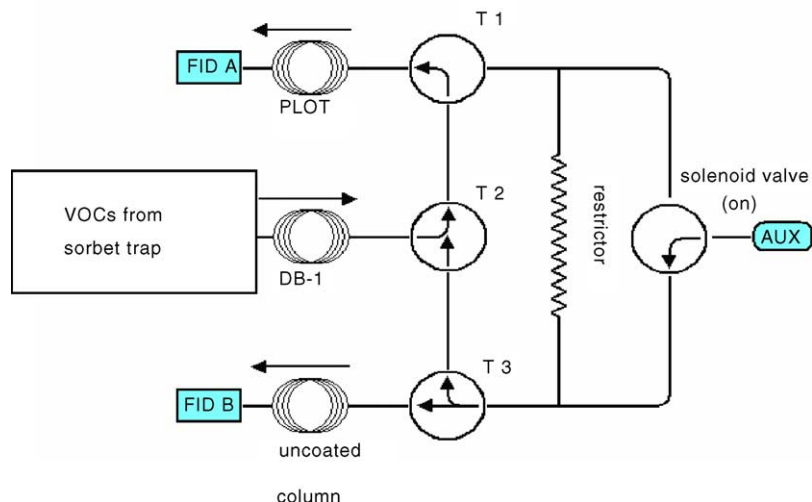


Fig. 2. Schematic diagram of a standard heart-cut GC system for monitoring VOCs which consists of a sorbent thermodesorption unit, a PLOT column, a DB-1 column, an uncoated column and a heart-cut device (in dashed box). In this configuration, all the target VOCs are switched to the PLOT column and the result is shown in Fig. 3a.

was adopted to simplify the construction and to clean up the chromatograms. In Fig. 2, the heart-cut device consists of a solenoid valve (12V DC Parker, USA) placed on the outside of the GC oven and three low dead volume tee connectors installed inside the GC oven. An $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT column ($50\text{ m} \times 0.32\text{ mm}$, $8\ \mu\text{m}$; Hewlett-Packard, San Fernando, CA, USA) and a DB-1 column ($60\text{ m} \times 0.32\text{ mm}$, $1\ \mu\text{m}$; J&W Scientific, Folsom, CA, USA) are used for separation. The DB-1 is used as the precolumn for the PLOT for delivering bulk highly volatile VOCs, but is also the analytical column for the less volatile ones when the flow is switched away from the PLOT. To balance the additional resistance of the PLOT in this heart-cut configuration, a predetermined length of a narrow bore uncoated fused silica column ($0.1\text{ mm I.D.} \times 5\text{ m}$) is installed symmetrically to the PLOT column. As shown in the schematic representation of Fig. 2, the VOCs eluting from the precolumn (DB-1) and T2 can go either to T1 and then PLOT or T3 and then uncoated column depending on the auxiliary flow direction controlled by the solenoid valve. For instance, when the solenoid valve is activated as shown by the configuration in Fig. 2, the auxiliary flow forces the carrier gas to channel through T1 and then PLOT while a split flow of auxiliary enters the uncoated column. Conversely, when the solenoid valve is switched off, the carrier gas flushes VOCs to the DB-1 while keeping a split auxiliary flow entering the PLOT without interrupting its elution. A restrictor in the heart-cut device always keeps a minimal flow in the tee connections to prevent peak broadening.

When no heart-cut action is made and the auxiliary flow direction is fixed to force the carrier gas to the PLOT the whole time, then the result is the same as the set of a sorbent trap plus PLOT as in the dual-trap system. Likewise, if the auxiliary flow is fixed to the other direction the whole time, then all the VOC species will be eluted by the DB-1 and no

advantage of 2D chromatography is achieved (see Fig. 3 for both illustrations). Same as the problems with the dual-trap system mentioned earlier, heavier VOCs (from C_8 on) exhibit poor separation due to excessive retention with the PLOT column (Fig. 3a). Conversely, the species more volatile than C_6 are severely coeluted due to insufficient retention with the WCOT column (Fig. 3b).

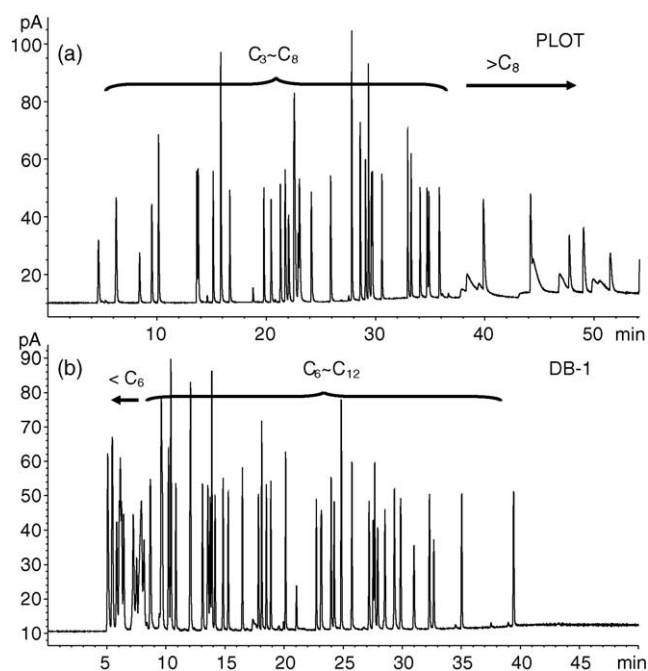


Fig. 3. (a) By switching all VOCs to PLOT, compounds from C_3 to C_{12} are eluted on PLOT column with heavier compounds than C_8 not having adequate peak shape and resolution. No peaks are eluted from DB-1. (b) By switching all target VOCs to DB-1, compounds from C_3 to C_{12} are now eluted on DB-1 column. Early eluting compounds from C_3 to C_5 are poorly separated on DB-1. No peaks are eluted from PLOT.

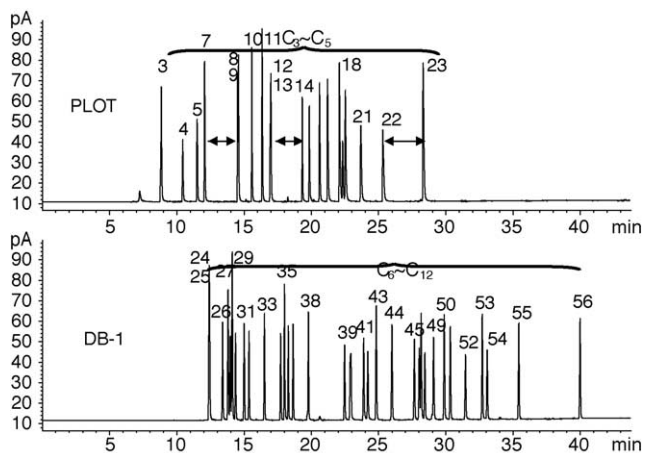


Fig. 4. A standard heart-cut result in which the PLOT separates C_3 – C_5 (upper trace) and DB-1 separate C_6 – C_{12} (lower trace). Selected compounds are numbered in accordance with Table 1. Double arrows indicate the retention time gaps where no peaks are eluted both for the standard mixture and the real ambient air.

To complement the strength of both columns and take advantages of 2D GC, the optimal switching time is determined so that compounds more volatile than C_6 are cut to the PLOT and detector A, and compounds less volatile than C_6 are cut to the uncoated column and detector B (see Fig. 4). Thus, the heart-cut technique successfully avoids problems inherent in the dual-trap system mentioned earlier.

While the heart-cut technique is very well suited for the ozone precursor measurement and such a design has been adopted with great popularity in PAMS program using commercial GC systems [1], there is still room for improvements on the conventional heart-cut device and more innovations to gain additional merits have been attempted.

To design a system that is less complex and requires less attendance, maintenance and running cost is not only beneficial for laboratory use, but also favorable and sometimes even necessary for field operation where logistic support is

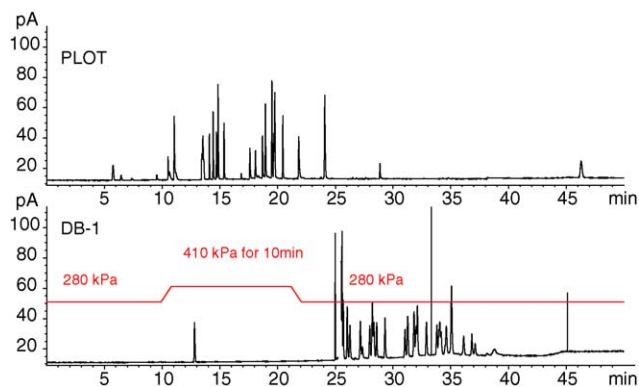


Fig. 5. Delaying C_6 – C_{12} elution on DB-1 (lower trace) until C_3 – C_5 species have eluted from the PLOT (upper trace). Superimposed on the lower panel is the auxiliary pressure program for creating delay effect.

often times difficult and limited. The objective of the following effort is aiming at reducing the complexity and cost of the standard heart-cut system by using only single flame ionization detector instead of two. Using two detectors is currently the standard feature for measuring ozone precursors either with the dual-trap or the heart-cut design. The ultimate goal of simultaneously analyzing all target ozone precursors within one injection with single flame ionization detector requires more sophisticated and innovative manipulation of the heart-cut device which will be discussed further.

3.2. Peak tailoring

The most straightforward way to achieve the goal of one detector for two columns will be to merge the flows at the end of the columns before going to the detector in order to produce one combined chromatogram. Nevertheless, peak overlapping is inevitable and undesirable if using a standard detector is required and a mass spectrometer is not an option. Therefore, an alternative will be to delay the elution of C_6 – C_{12} species from the DB-1 until C_3 – C_5 have eluted from

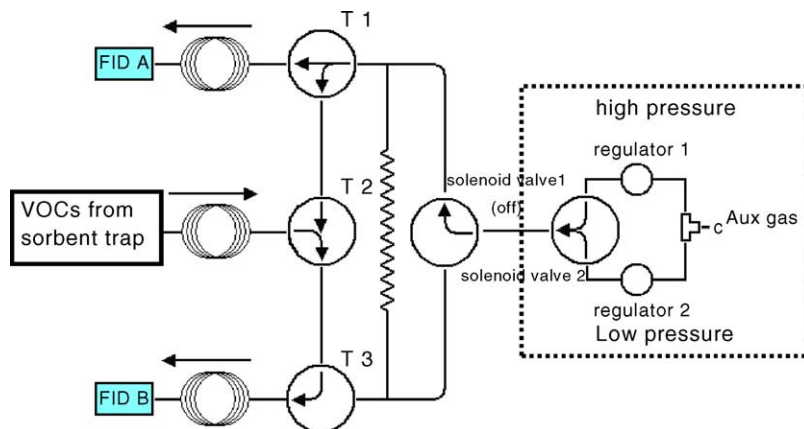


Fig. 6. A pressure switch box is installed prior to the solenoid valve #1 in the heart-cut device. Either high or low pressure can be selected by the solenoid valve #2 to permit responsive and instantaneous pressure changes.

the PLOT so that once the flows are merged a single sequential chromatogram is to be obtained. Although the concept is straightforward, the technique to delay C₆–C₁₂ species in the DB-1 precolumn until full elution of C₃–C₅ from the PLOT is not. It requires a sudden stop of the carrier flow in the DB-1 after C₃–C₅ have cut to the PLOT in order to “freeze” the remaining high boiling species while keeping the carrier in the PLOT undergoing at the same time. It turns out that this goal can be realized by delicate control of the timing and pressure of the auxiliary pressure. The pressure of the auxiliary flow determines whether the carrier gas from the DB-1 can be completely switched either to the PLOT or the uncoated column. If the auxiliary flow pressure is lower than needed, complete switch is not possible and leakage to the undesired column will occur. On the other hand, if the pressure is too high partial or complete blockage of the carrier from the precolumn will take place. It is this phenomenon that is adopted to carry out the delay effect. By rapidly increasing the auxiliary pressure from the standard cutting pressure, the carrier gas flow in the DB-1 can be stopped resulting in temporarily holding up the elution of C₆–C₁₂, which is then released

only at the exact moment when the C₅ species emerges from the PLOT by rapidly decreasing the auxiliary pressure (see Fig. 5 for the sequential elution). The entire cycle of the auxiliary pressure from the solenoid valve proceeds from low (for cutting) and then to high (for holding up) and finally return to low again (for releasing). In this application, two pressure settings for the auxiliary flow are required. However, under the premise of using only one GC oven the sequential elution forces, the separation of C₆–C₁₂ to proceed at higher than optimal temperatures. As a result, even though the sequential elution is feasible, the resolution in the segment of C₆–C₁₂ is compromised and not acceptable for quality analysis.

It is noticed that in the PLOT trace there are several retention time gaps where no peaks appear with the ambient air samples, which is characteristic of the PLOT column (see Fig. 4). It is then imperative to explore the possibility of inserting high boiling segment in these no-elution windows. To do so, multiple hold-ups and releases to cut DB-1 trace into several peak segments that are in alignment with the PLOT gaps needs to be made beforehand, so that the merger can eventu-

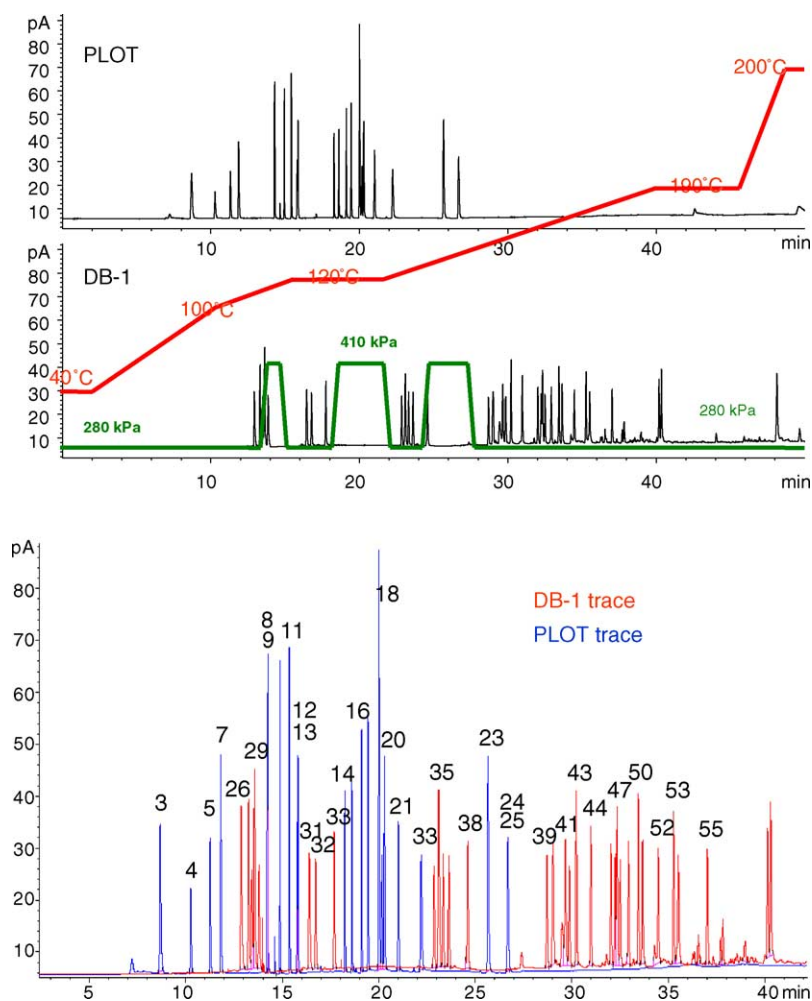


Fig. 7. Pressure and temperature programs to produce four DB-1 segments which are lined up with the empty gaps on the PLOT trace (upper panel). A conceptual chromatogram by overlaying both traces on top of each other (lower panel). Peak assignment is referred to Table 1.

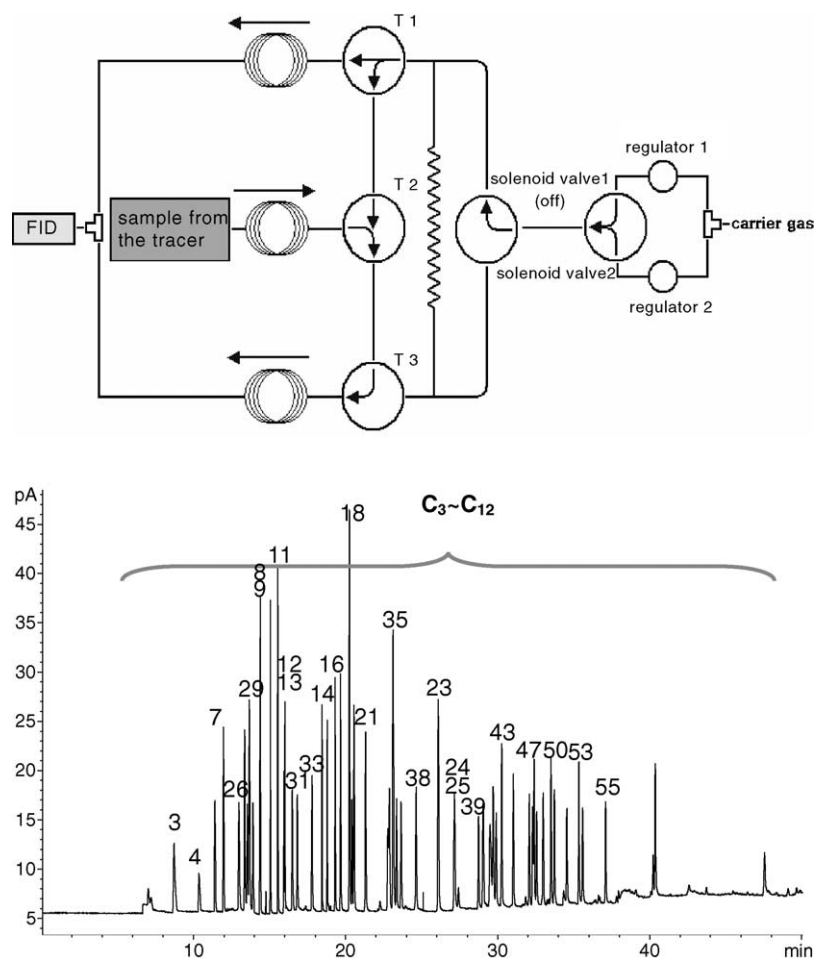


Fig. 8. Two column flows are merged into one before entering the flame ionization detector. Schematic diagram for the plumbing is shown in the dashed circle (upper panel). A synthesized chromatogram is obtained which looks similar to Fig. 7 but is a true elution with single detector (lower panel). Peak assignment is referred to Table 1.

ally produce a synthesized chromatogram covering C_3 – C_{12} with single flame ionization detector.

Because the GC software (Chem Station, Agilent) only allows a three pressure ramps for the electronic pneumatic control (EPC) and it takes two settings (from low changes to high and back to low) to make a cycle for cutting one segment from the DB-1 trace. Furthermore, flow changing from low to high or vice versa with EPC is sluggish and takes some seconds to stabilize. It was because of these two reasons that using standard EPC for “peak tailoring” was abandoned. Alternatively, a pressure switch unit independent from the existing EPC and software was built to replace EPC, in which two auxiliary flows of high (~ 410 kPa) and low (~ 280 kPa) pressures can be selected by another solenoid valve placed upstream of the heart-cut solenoid valve (Fig. 6). With this simple device, high or low pressure can be swung easily by the solenoid valve. In addition, the pressure change and flow stabilization is instant and responsive. As shown in Fig. 7, three pressure cycles made by six pressure changes are made to produce four DB-1 segments in perfect alignment with the three gaps in the PLOT trace. In Fig. 8, merger of the two

flows by a tee connector prior to the detector resulting into a synthesized chromatogram from the unaltered PLOT trace and four DB-1 segments inserted in the gaps of the PLOT trace. By releasing C_6 – C_{12} peak segments timely to catch up with oven temperatures instead of delaying all of them after C_5 as in the sequential case, the resolution becomes comparable to the standard heart-cut results (Fig. 4) and is far more superior to the sequential elution method (Fig. 5). Repeated injection of the standard mixture aliquots produced extremely reproducible chromatograms. While the reproducibility for retention times is within 0.1%, the reproducibility for peak area is better than 2% for most of the target compounds with only a few falling between 2 and 4%, which is comparable to our previous basic heart-cut design or the dual-trap design.

4. Conclusion

Compared to the dual-trap dual-detector design, the new concept only uses single trap and single detector to accom-

plish full range of VOC analysis without compromising any desired performance. The benefits arising from reducing to one trap and one detector are multiple. Consumption of detector gases, i.e., H₂ and zero air is now cut by one half; the construction cost is greatly reduced; the simplified configuration reduces the wear-and-tear as well as the maintenance complexity due to fewer check points. More importantly, the peak tailoring concept opens room for other elaborate detection methods, such as mass spectrometry, which previously would not be practical and sensible to have two MS connected to two columns to form a complete VOC monitoring system.

Acknowledgement

This research is supported by the National Science Council of Taiwan under the contract number of NSC92-2113-M-008-019.

References

- [1] US EPA, Technology Transfer Network, Ambient Monitoring Technology Information Center, Pamsgram, vol. 18, January 2000 (<http://www.epa.gov/oar/oaqps/pams/docs.html>).
- [2] K.L. Yang, C.C. Ting, O.W. Wingenter, C.C. Chan, J.L. Wang, *Atmos. Environ.*, in press.
- [3] T. Maeda, S. Onodera, H. Ogino, *J. Chromatogr. A* 710 (1995) 51.
- [4] K.D. Oliver, J.R. Adams, E.H. Daughtrey Jr., W.A. McLenny, M.J. Yoong, M.A. Pardee, *Atmos. Environ.* 30 (1996) 2751.
- [5] J. Dewulf, V. Langenhove, *J. Chromatogr. A* 843 (1999) 163.
- [6] D. Helmig, *J. Chromatogr. A* 843 (1999) 129.
- [7] E. Matisova, S. Skrabakova, *J. Chromatogr. A* 707 (1995) 145.
- [8] J.L. Wang, S.W. Chen, C. Chew, *J. Chromatogr. A* 863 (1999) 183.
- [9] J.L. Wang, W.L. Chen, Y.H. Lin, C.H. Tsai, *J. Chromatogr. A* 896 (2000) 31.
- [10] J.L. Wang, G.Z. Din, C.C. Chan, *J. Chromatogr. A* 1027 (2004) 11.
- [11] D.R. Deans, *J. Chromatogr.* 203 (1981) 19.
- [12] W.J. Bertsch, *J. High Resolut. Chromatogr.* 1 (1978) 19.
- [13] R.J. Philips, K.A. Knauss, R.R. Freeman, *J. High Resolut. Chromatogr.* 5 (1982) 546.
- [14] J.M. Sanchez, R.D. Sacks, *Anal. Chem.* 75 (2003) 978.
- [15] W.P.L. Carter, *J. Air Waste Manage. Assoc.* 44 (1994) 881.
- [16] R. Atkinson, *Atmos. Environ.* 34 (2000) 2063.