



ELSEVIER

Journal of Chromatography A, 976 (2002) 39–45

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Sub-second thermal desorption of a micro-sorbent trap for the analysis of ambient volatile organic compounds

Tai-Yi Chen^a, Ming-Jay Li^b, Jia-Lin Wang^{b,*}

^a*Institute of Earth Sciences, Academia Sinica, Taipei 11529, Taiwan*

^b*Department of Chemistry, National Central University, Chungli 320, Taiwan*

Abstract

This study investigates a novel approach of fast thermal desorption on a micro-sorbent trap for analyzing ambient volatile organic compounds (VOCs) by gas chromatography with flame ionization detection. Unlike conventional approaches, the temperature feedback mechanism for temperature control was abandoned, which often poses a limit to the heating speed due to slow response of the sensor and the control algorithm. Instead, a series of programmed a.c. pulses was given to the Ni–Cr wire coiled around the micro-trap to perform instant heating from room temperature to 250 °C within a fraction of a second, maintained at 250 °C during injection, and subsequently to 300 °C for trap cleaning. Temperature fluctuation around a high temperature set point could be maintained within ± 10 °C. Significant improvement in resolution and peak height was obtained compared to a trap with temperature feedback and control algorithm. While keeping resolution at a satisfactory level, the sub-second desorption approach allows faster chromatography and at the same time increases the sensitivity of VOC analysis.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermal desorption; Air analysis; Sample handling; Volatile organic compounds

1. Introduction

Ambient concentrations of volatile organic compounds (VOCs) are usually too low to allow direct injection without preconcentration. Common methods for preconcentration involve using a sorbent trap to enrich VOCs at ambient or subambient temperatures, which upon thermal desorption are then delivered to a column for separation [1–6]. The chromatographic resolution is often limited by the longitudinal diffusion within the column during elution or within the trap during thermal desorption. While optimizing the flow-rate and the temperature program helps minimizing the diffusion within a

given column, fast delivery of a very focused sample out of the sorbent trap can be even more effective in controlling peak broadening. Hence, to reduce dead volume and to increase the speed of thermal desorption of a sorbent trap are always high priorities for achieving good resolution and sensitivity in VOC analysis, and could become more decisive for more volatile compounds than for less volatile ones.

Thermal desorption of a sorbent trap in a feedback and controllable manner uses a temperature sensor such as a thermocouple or a Pt wire to measure the temperature in-situ. The response time of a typical temperature sensor is often in the range of a few milliseconds to a second, which together with the temperature control algorithm, often limits the temperature ramping rate to several tens of degrees Celsius per second if a precise and accurate tempera-

*Corresponding author. Fax: +886-3-427-7972.

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

ture control is desired. As a result, the time period of several seconds needed for thermal desorption, say, from room temperature to 300 °C could inevitably broaden the compound bands within the sorbent trap prior to migration onto the column. Hence, adding a re-focusing stage or cooling the entire GC oven is often exercised for VOC analysis [7–11]. In this work, a super fast, sub-second thermal desorption method is illustrated, which, when combined with a narrow bore trap and low dead volume plumbing, not only eliminates the need for re-focusing, but also dramatically improves the resolution, and consequently could allow faster chromatography.

2. Experimental

2.1. Chromatographic conditions

A DB-1 column (60 m×0.32 mm; $d_f=3\ \mu\text{m}$, J&W Scientific, Folsom, CA, USA) installed in a Hewlett-Packard HP6850 system was used for VOC separation with the temperature program started at 40 °C, isothermal for 5 min, followed by a ramp of 10 °C/min to 180 °C, held at 180 °C for 38 min. An electronic pneumatic controller (EPC) was used to provide a programmable control over the He carrier and N₂ for the make-up gas, which were set at constant flow-rates of 3 ml/min and 60 ml/min, respectively. A flame ionization detection system (FID) was used for halocarbon detection with temperature set at 250 °C.

2.2. Sample injection system

A description with regard to the design and configuration of the self-built preconcentrator can be found in our earlier publications [5,6]. In brief, the system used three air-actuated two-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). A Windows-based software platform (Genie, Advantech, Taiwan) provided a Visual Basic programming environment for writing control codes.

The sorbent trap was made by a piece of 20 cm×1.0 mm I.D. stainless steel (s.s.) narrow bore tubing, called the micro-trap, or 10 cm×3 mm I.D.

s.s. wide bore tubing, of which only the middle section was packed with 1 cm of Carboxen 1000 (60–80 mesh, Supelco, Bellefonte, PA, USA), 1 cm of Carboxen 1003 (60–80 mesh), and 1 cm of Carbotrap B (20–40 mesh), in that order. Sample trapping was performed by drawing an air sample through the trap with the flow-rate set at 20 ml/min by a mass flow controller placed downstream while the trap temperature was maintained at 30 °C. A 5-min sampling time period was prescribed in the control codes, which allowed an aliquot of 100 ml/min to be trapped for each analysis. Injection was performed by flash heating the trap to 250 °C for 5 min to flush VOCs onto the column. Subsequently, the trap temperature was raised to 300 °C for trap cleaning. The direction of the gas flow was reversed during thermal desorption to back-flush higher boiling residuals from the sampling end of the tube. Two types of heating methods were employed in this study for comparison, i.e. direct resistive heating and Ni–Cr wire heating. For the resistive heating a thermocouple tip was welded on the central part of the trap to provide signal feedback to the temperature controller. Heating was made possible by supplying a large 4 V alternating current to the trap. 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 (proportional integral derivative) algorithm, which regulates the power so that the actual temperature on the trap sensed by the thermocouple closely matches the prescribed temperature ramp. Under the PID control, the maximum heating speed was about 50 °C/s [5,6]. In this study the feedback design was used as a reference to be compared with the pulsed design.

2.3. Pulse generation for flash heating

In our pulsed heating design the thermocouple only provided temperature reading with no feedback circuit. A piece of thin glass tubing (10 cm×3 mm O.D.×2 mm I.D.) with I.D. slightly larger than the O.D. of the trap was used to serve as the insulator on the outside of the sorbent packing section, around which the Ni–Cr wire was closely coiled. Through a solid state relay the 110 V a.c. power was supplied to

the wire for heating but in a pulsed manner. Pulse generation was made by the contact closure of a solid state relay with the pulse intervals prescribed by the control codes based on the personal computer clocking. To simulate a useful feature found in a typical feedback method with a heating process consisting of multi-steps of ramping and soaking (maintaining at a fixed temperature), several series of pulses with various width and frequencies were combined as a complete cycle. Once the injection started to call for thermal desorption, a pulse of 0.4 s was produced to provide sufficient power to raise the trap temperature instantly from 30 to 250 °C. As soon as the trap temperature reached 250 °C, a series of shorter pulses was used (0.1 s for the pulse width and 5 s between pulses) to maintain the trap temperature at 250 °C during the injection period. Subsequently, for baking out high boiling residuals, the trap temperature was further raised to 300 °C by another series of more frequent pulses (0.1 s for the width and 3 s between pulses), see Fig. 1.

The rapid on and off of the power switching inevitably created temperature fluctuation, however the insulating glass shield helped damp the ripples to some degree so that the temperature fluctuation can be kept within ± 10 °C either at 250 or 300 °C. We were also aware that the reading from the thermocouple always lags behind the actual temperatures because of its slow response in sensing temperature. Consequently, the actual rate of temperature ramping was not easy to determine and as a result, after the first 0.4-s pulse was fired, it took more than a second for the thermocouple to reach 250 °C, but the actual rate was expected to be shorter than 1 s.

Note that the trap temperature either at low or high temperature was left to equilibrate with the room temperature. As a result, large room temperature variation could affect the consistency of the high–low temperature set points and, hence, the repeatability. From this standpoint, it seems inferior to the temperature feedback method in which the low and high temperature set points are reached in a controlled manner. However, such a deficiency can be easily overcome by enclosing the trap with a miniaturized constant temperature housing. Since our experiments were conducted in an air-conditioned lab, the inclusion of a housing in the system was not necessary.

3. Results and discussion

It is widely perceived that, while keeping other chromatographic conditions the same, both dead volume and desorption speed are considered to be the two most important factors affecting the peak width and hence the resolution. These two factors are particularly true for VOC analysis as these compounds exhibit a highly gaseous nature and thus great diffusion power along the flow path of a chromatographic system, which could include the transfer tubing, trap, connection fittings, and column. To put these two factors into perspective, two traps of different dimensions with two different heating methods were explored under similar chromatographic conditions, see Fig. 2. To serve as the comparison basis, the wider bore trap (10 cm \times 3 mm I.D.) with temperature feedback and PID control capable of greater than 50 °C/s heating rate was employed to represent the most common feature found in most VOC analysis applications. Both carrier gas flow-rate and GC temperature program were adjusted to yield sufficient separation for two pairs of compounds labeled as A and B. The elution took ~ 35 min to separate a gas standard containing VOCs from C₃ to C₈ using a 60 m \times 0.32 mm \times 1.0 μ m DB-1 column, see Fig. 2a.

In order to seek better resolution, the narrower bore trap (10 cm \times 1.0 mm) packed with the same sorbents was employed to substitute the wide bore trap. In contrast to the larger trap, which used two reducing unions on both ends to connect a piece of 1/16 in. (1 in.=2.54 cm) tubing to the switching valve, we connected the remaining unfilled portion of the trap tubing directly to the switching valve ports without connection fittings to reduce dead volume. The same method of resistive heating was applied with the same temperature feedback as in the previous case, and also took 6 s to raise the temperature from 30 to 250 °C as for the larger trap. Because no connectors were used for the trap, the “all-in-one” assembly by making the trap also part of the transfer line completely eliminated the dead volume, and together with the reduction in longitudinal diffusion within the smaller bore tubing, noticeably improved the resolution as well as narrowed the peak height for the same amount of air injected (Fig. 2b), as compared to Fig. 2a.

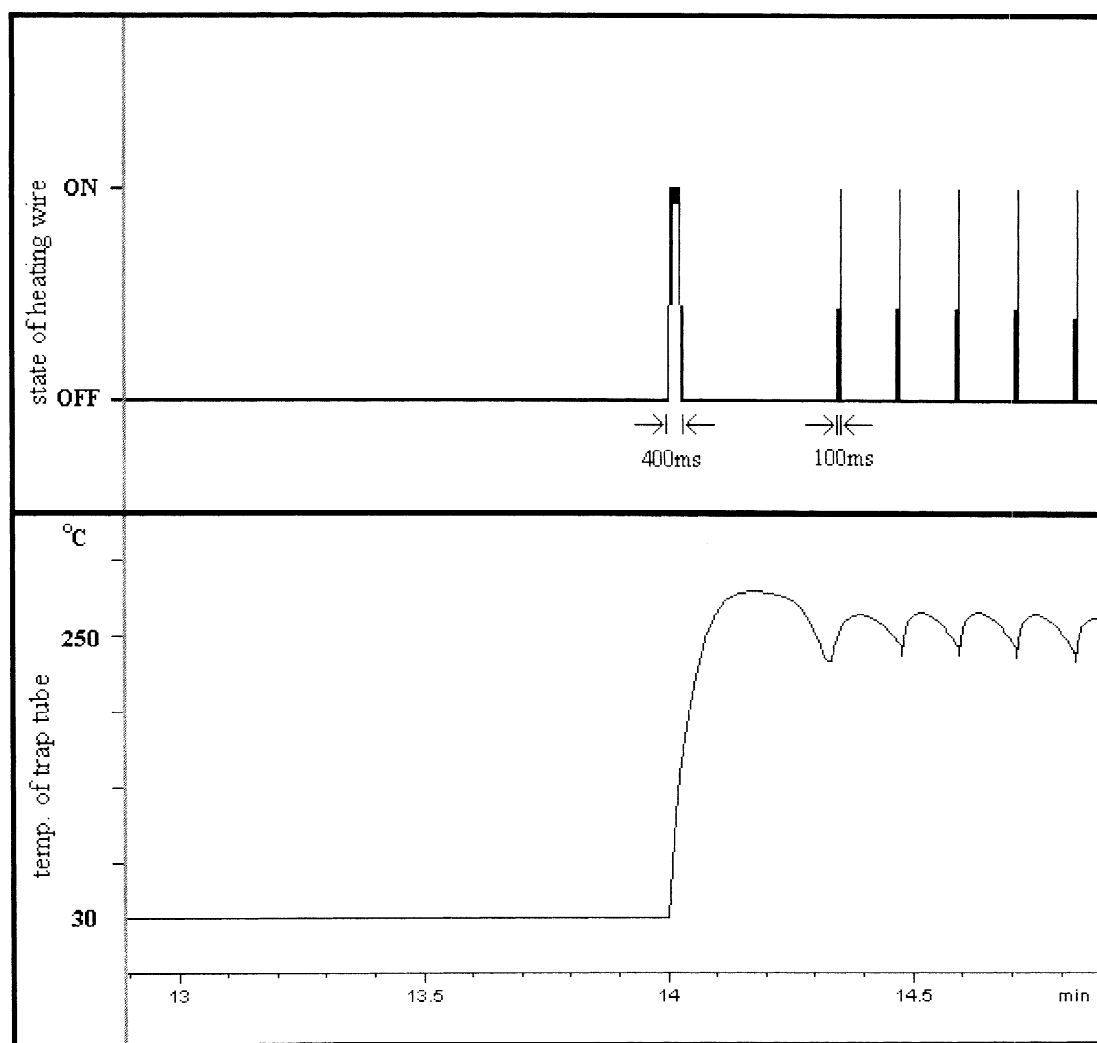


Fig. 1. Progression of pulses. (a) Pulses are continuously generated during thermal desorption. Shown in the figure is a long pulse for rapid temperature ramping followed by a series of shorter pulses for keeping temperature at about 250 °C. (b) The corresponding conceptual temperature profile.

Once the dead volume has been minimized, we further studied the effect of desorption speed on resolution. It is also noted that the speed for the thermal desorption is more crucial to the resolution of early elution compounds, which are more volatile and subject to greater longitudinal diffusion within the trap tubing, hence manifesting in broader peak width and hence poorer resolution. As discussed earlier, that although using temperature feedback and PID function can precisely control the temperature

ramp to the set points for desorption, its ramping speed however is limited by the response time of the sensor and the calculation speed of the microprocessor. Pulse heating was used instead to emphasize the extremely fast ramping speed, as none of the above two limiting factors existed. By giving a pre-determined set of pulses to ramp temperature from 30 to 250 °C with an emphasis on the first pulse for the extremely fast ramping effect, the improvement in resolution became every evident, see Fig. 2c.

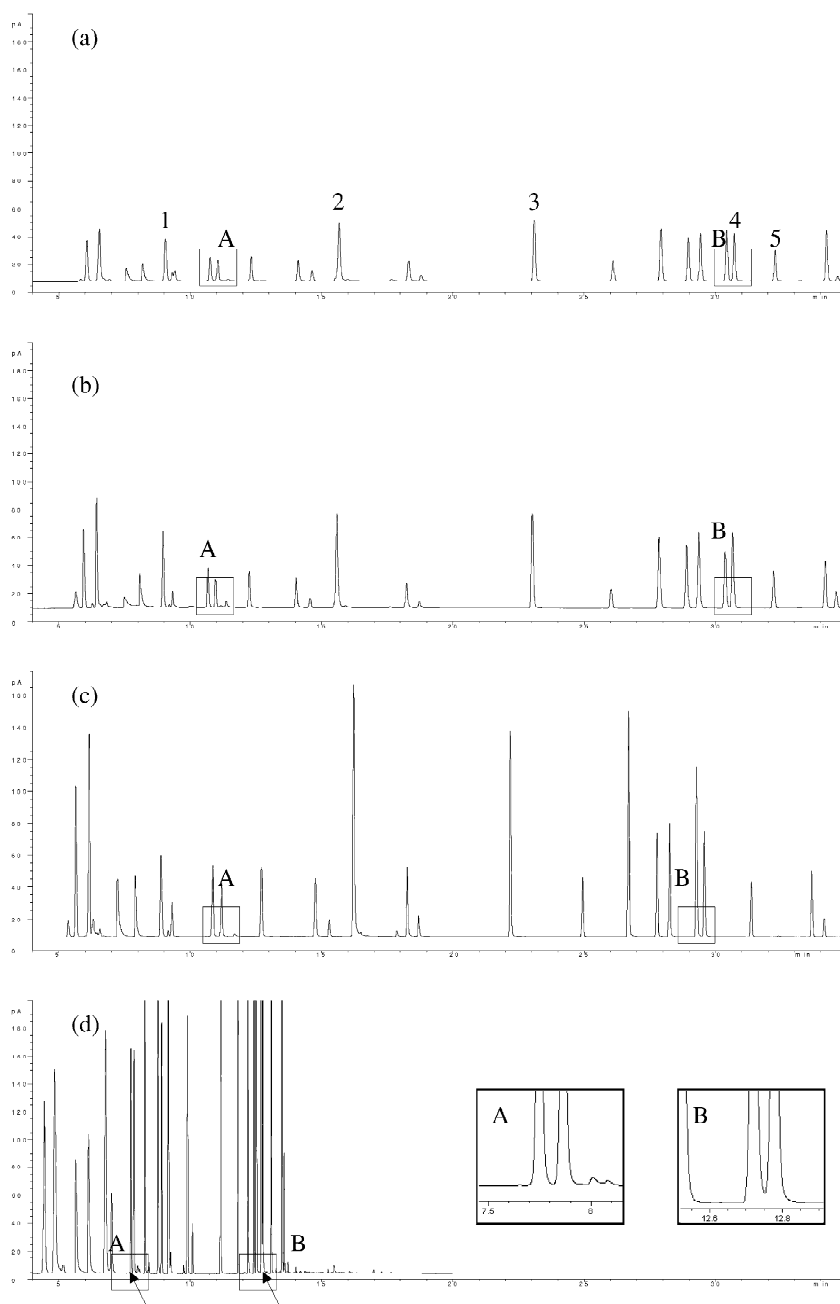


Fig. 2. Comparison of resolution and sensitivity between two traps of different dimensions and two different heating methods. (a) The wide bore trap with resistive heating and temperature feedback control. (b) The small bore trap with resistive heating and feedback to show the effect of low dead volume. (c) The small bore trap with pulse heating and no feedback to show further improvement in peak shape. (d) Same as (c) but with a faster oven ramping. For showing carbon range, selected peaks are labeled as (1) 1,3-pentadiene; (2) benzene; (3) toluene; (4) *o*-xylene; (5) 1-methylethylbenzene. Two pairs of compounds A and B are enclosed and enlarged in (d) for a clearer view of separation.

For the large trap as in Fig. 2a, representing the average dimension used in most applications, both flow-rate and temperature program were optimized to yield sufficient resolution to separate A and B pairs of compounds. The elution took ~35 min to separate from C₃ to C₉, which is the range where most VOCs belong in terms of abundance and speciation [3]. The improved separation shown in Fig. 3c opens room for faster chromatography. While keeping all compounds with satisfactory separation, e.g. keeping A and B pairs of compounds properly separated, the improved separation seen in Fig. 2c allowed the elution to be completed within 14 min by a faster ramping program, which consequently resulted in higher signal levels and thus lower detection limits, see Fig. 2d.

Linearity of the pulse heating method was examined by trapping various amounts of the standard air to mimic aliquots of various concentrations, see

Fig. 3. The breakthrough volume apparently goes beyond the level of 40 parts per billion by volume (ppbv) equivalent, which is way above most ambient concentrations encountered in normal conditions ranging between several tens of ppbv for the very polluted air to several ppbv for a moderately clean environment. The extremely linear behavior of this method and the excellent precision both in retention time and response as listed in Table 1 suggests that this sub-second desorption method is highly applicable and particularly advantageous for in-situ analysis of ambient VOC, which often demands a large variety of species to be measured with short turn-over time.

4. Conclusion

A novel approach of sub-second thermal desorp-

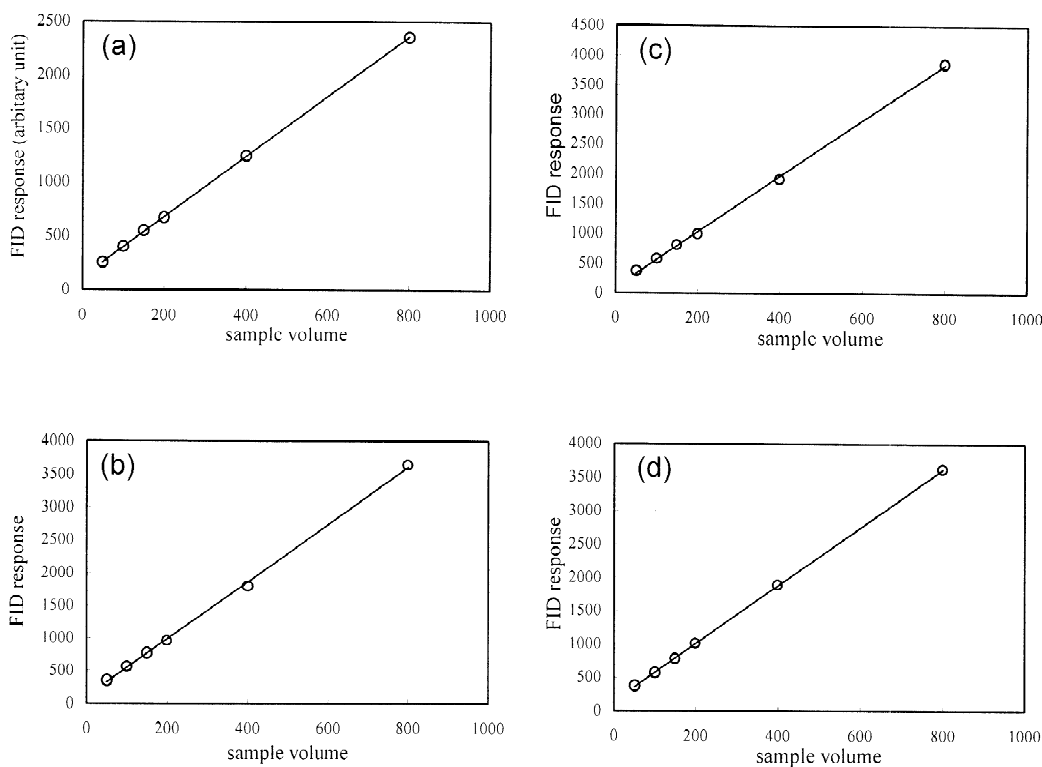


Fig. 3. Linearity of the pulse heating method by trapping various amounts of the standard air of 20 ppbv to mimic aliquots of various concentrations. For instance, trapping 800 ml of air is equivalent to trapping 400 ml of air with twice the concentration, which in this case is 40 ppbv. R^2 is greater than 0.9990 for the following compounds: (a) 1,3-pentadiene; (b) benzene; (c) toluene; (d) 1-methylethylbenzene.

Table 1
Precision in response and retention time from repeated injections of a standard air at about 20 ppbv ($n=10$)

Compound	Detector response		Retention time	
	Mean (pA s)	RSD (%)	Mean (min)	RSD (%)
1,3-Pentadiene	669.72	0.83	8.08	0.047
Methylenechloride	195.62	0.60	8.25	0.036
1,2-Dichloroethene	324.16	0.36	8.87	0.031
1,1-Dichloroethane	322.22	0.56	9.00	0.033
1,1-Dichloroethene	318.13	0.43	9.55	0.025
1,2-Dichloroethane	347.16	0.29	10.25	0.017
1,1,1-Trichloroethane	314.01	1.53	10.41	0.018
Benzene	961.08	0.44	10.66	0.014
2-Propenoic acid	11.89	5.55	11.05	0.009
Trichloroethylene	354.58	0.31	11.16	0.009
2-Methylester	68.55	3.12	11.24	0.010
Toluene	1009.36	0.53	11.91	0.006
Tetrachloroethylene	403.06	0.37	12.32	0.006
Chlorobenzene	881.43	0.59	12.56	0.007
Ethylbenzene	860.36	1.24	12.69	0.008
<i>p</i> + <i>m</i> -Xylene	979.01	0.81	12.74	0.008
Styrene	806.40	4.90	12.87	0.009
<i>o</i> -Xylene	1013.43	2.49	12.91	0.009
1-Methylethylbenzene	543.31	1.49	13.11	0.010

tion of a micro-sorbent trap in a pulsed heating manner was constructed and studied for the measurement of ambient VOCs. Significant improvement in peak shape was obtained compared to conventional methods with temperature feedback, which inevitably slows down the heating speed. The improved peak shape opened room for faster elution of the VOCs and consequently better sensitivity at a satisfactory resolution level.

Acknowledgements

The authors would like to thank the National Science Council for the financial support of this research under contract no. NSC90-2113-M-008-005.

References

- [1] S. Mitra, A. Lai, J. Chromatogr. Sci. 33 (1995) 285.
- [2] C. Feng, S. Mitra, J. Chromatogr. A 805 (1998) 169.
- [3] D. Helmig, J. Chromatogr. A 843 (1999) 129.
- [4] J. Dewulf, H.W. Langenhove, J. Chromatogr. A 843 (1999) 163.
- [5] J.L. Wang, S.W. Chen, C. Chew, J. Chromatogr. A 863 (1999) 183.
- [6] J.L. Wang, W.L. Chen, Y.H. Lin, C.H. Tsai, J. Chromatogr. A 896 (2000) 31.
- [7] J.P. Greeberg, D. Helming, P.R. Zimmerman, J. Geophys. Res. 101 (1996) 14581.
- [8] J.W. Bottenheim, M.F. Shepherd, Atmos. Environ. 29 (1995) 647.
- [9] T.S. Clarkson, R.H. Martin, J. Rudolph, Atmos. Environ. 31 (1997) 3763.
- [10] N. Moschonas, S. Glavas, Atmos. Environ. 30 (1996) 2769.
- [11] J.W. Bottenheim, P.C. Brickell, T.F. Dann, D.K. Wang, F. Hopper, A.J. Gallant, K.G. Anlauf, H.A. Wiebe, Atmos. Environ. 31 (1997) 2079.