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Full-range analysis of ambient volatile organic compounds by a new trapping method and gas chromatography/mass spectrometry

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ABSTRACT

This study investigated the feasibility of analyzing a full range of ambient volatile organic compounds (VOCs) from C_3 to C_{12} using gas chromatograph mass spectrometry (GC/MS) coupled with thermal desorption. Two columns were used: a PLOT column separated compounds lighter than C_6 and a DB-1 column separated C_6–C_{12} compounds. An innovative heart-cut technique based on the Deans switch was configured to combine the two column outflows at the ends of the columns before entering the MS. To prevent the resolved peaks from re-converging after combining, two techniques were attempted (hold-up vs. back-flush) to achieve the intended "delayed" elution of heavier components. Thus, the resulting chromatogram covering the full range of VOCs is a combination of two separate elutions, with the heavier section following the lighter section. With the hold-up method, band-broadening inevitably occurred for the delayed C_6–C_7 DB-1 compounds while the light compounds eluted from the PLOT column. This broadening problem resulted in peak tailing that was largely alleviated by adding a re-focusing stage while the DB-1 compounds were back-flushed, and this modified technique is referred to as the back-flush method. With this modification, the separation of the C_6–C_7 compounds improved dramatically, as revealed by the decrease in peak asymmetry (As) and increase in resolution. Linearity and precision for these peaks also improved, yielding R^2 and RSD values better than 0.9990 and 2.8%, respectively.

1. Introduction

Determination of the composition of volatile organic compounds (VOCs) in ambient air often serves as the cornerstone for air quality diagnosis and improvement. Not only do VOCs cause adverse health effects under long-term exposure at elevated levels, but they are also precursors of secondary pollutants, such as ozone, aldehydes, organic nitrates and fine particles [1–5]. With this knowledge available, effective air-quality improvement strategies can be planned and ultimately assessed for effectiveness. Thus, choosing a suitable VOC measurement technique is a pre-requisite to the representative characterization of VOC composition. Of all the available monitoring methods, gas chromatography (GC) is often favored for its superb separation power and sensitivity [6–8]. For instance, on-site automated GCs have been widely deployed in many ozone non-attainment areas to continuously assess the composition and levels of ambient VOCs as part of an effort to reduce ozone [8–11]. In GC techniques, mass spectrometry (MS) is the most powerful means of detection due to its remarkable ability to identify compounds and its virtually unmatched sensitivity. When analyzing VOCs at the ambient level, an on-line enrichment device often must be coupled with the GC/MS system to provide sufficiently low detection limits at the level of parts per billion (ppbv) or trillion by volume (pptv) [6,7,12–14]. Either cryogenic or non-cryogenic enrichment methods can be used; each method has its own advantages and disadvantages [15–19].

When using MS as the detection method, usually only a single column is connected to the MS. However, due to the broad volatility range of air-borne VOCs, finding a single column type that can separate VOCs, normally from C_2 to C_{12}, is extremely difficult. As a result, porous layer open tubular (PLOT) columns are often employed for the lower boiling species, whereas wall-coated open tubular (WCOT) columns are used for the higher boiling species [20]. To perform full-range VOC analysis from one GC injection, a strategy using dual PLOT and WCOT columns simultaneously is often adopted. This strategy can be implemented either by simply splitting the flow after the enrichment unit into the PLOT and WCOT columns with two detectors or by using the more elaborate heart-cut technique. With the splitting technique, the carrier gas is divided into multiple streams, each stream flowing into a separate column with the split ratio determined by the resistance of the columns. In principle, each split flow contains an identical VOC composition to that of the original sample aliquot. This situation causes a problem for the PLOT column because excessive retention may occur for the high boiling

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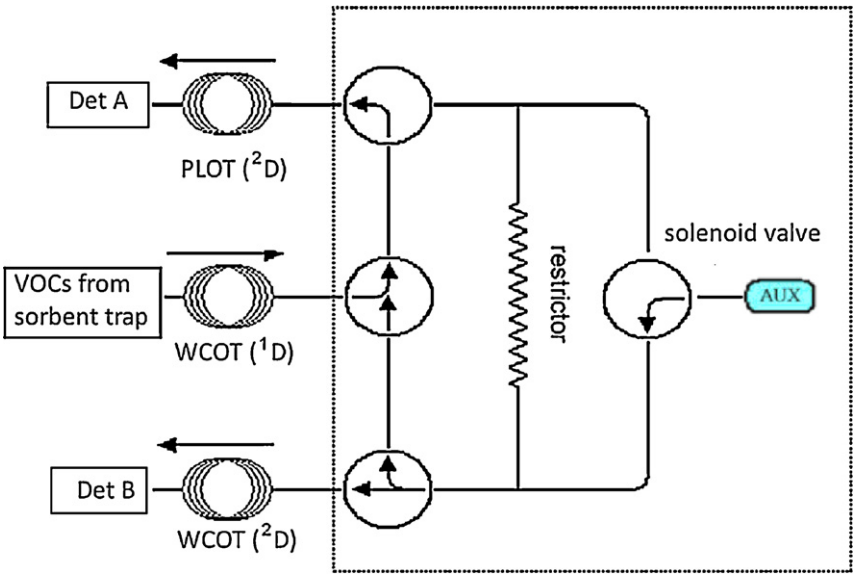

Fig. 1. Schematic diagram of a typical Deans switch that cuts eluents from the primary (^{1}D) column to either of the two secondary (^{2}D) columns.

constituents, thus prolonging the time to complete a full analysis cycle. Although higher oven temperatures could speed up elution, PLOT columns usually have much lower temperature limits than those of the WCOT columns, rendering elution within a reasonable cycle time difficult. The alternative is to use the heart-cut technique, in which either a multi-port switching valve or a Deans switch is connected to the two columns in the GC oven. Although the Deans switch concept has been transferred into other non-conventional applications, e.g., comprehensive GC × GC and dynamic flow splitting [21–28], heart-cutting is still the main application for the Deans switch. A typical Deans switch consists of a micro-fluidic manifold and an electric three-way solenoid valve. The solenoid valve acts as a flow switch for guiding the carrier flow from the primary (denoted as ^{1}D) WCOT column to a secondary (denoted as ^{2}D) column, either a PLOT or a WCOT column, via the introduction of an auxiliary flow (Fig. 1). Unlike the manifold, the solenoid valve is installed outside the GC oven and, thus, is not subject to high GC temperatures. From this standpoint, the Deans switch is more desirable than the switching valve due to the minimal wear-and-tear; thus, the Deans switch is very reliable and heavy-duty for applications that require long-term repeated analyses. When analyzing VOCs, the solenoid valve cuts the early-eluting but unresolved light components from the ^{1}D WCOT column to the ^{2}D PLOT column for better separation while cutting the mostly resolved higher boiling components to the ^{2}D WCOT column, usually of the same type, to the detector (Fig. 1) [21,23,26]. With few exceptions [24,26], two GC detectors are usually used for the typical heart-cut operation. Although MS is the preferred means of detection, the instrumentation is complex and costly if both channels are needed. As a result, one channel is commonly chosen for the MS, leaving the

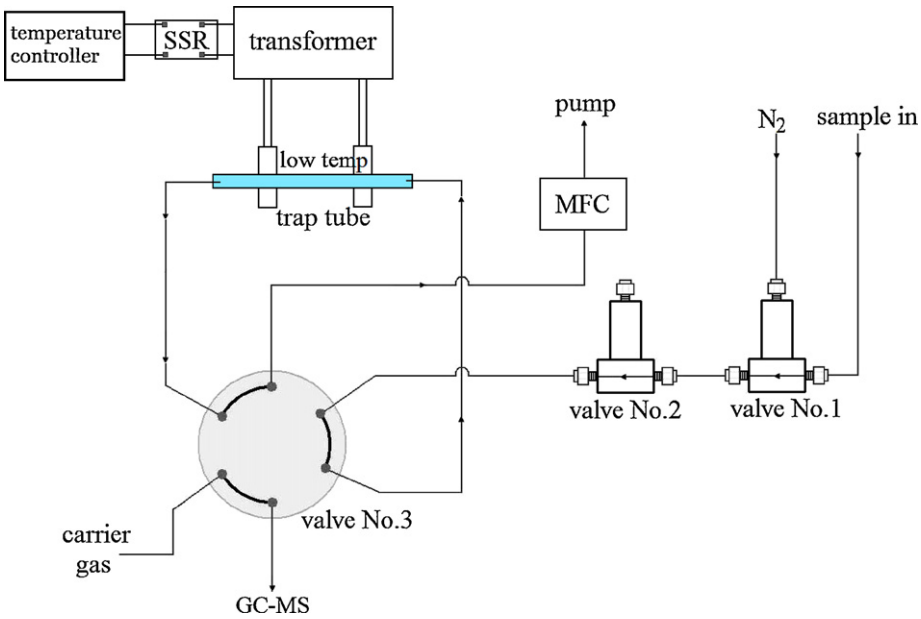

Fig. 2. Schematic diagram of the TD unit. SSR denotes the solid state relay and MFC denotes the mass flow controller. The trapping stage is shown in this figure.

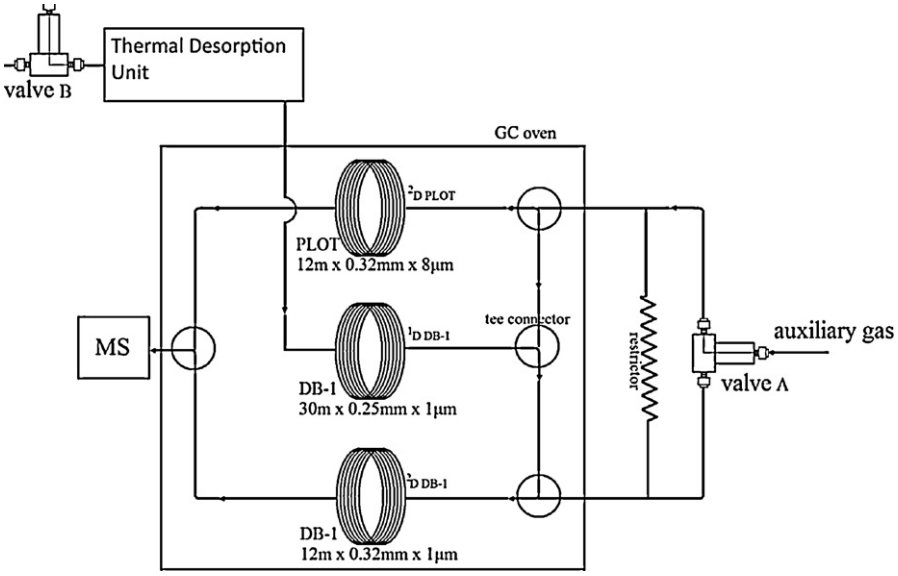

Fig. 3. Schematic diagram of the Deans switch assembly with both ^{2}D columns channeling into the MS.

other channel for a conventional GC detector [28,29]. For instance, Wang et al. [28] used the Deans switch heart-cutting technique and two detection methods of flame ionization detection (FID) and electron capture detection (ECD) to simultaneously analyze atmospheric non-methane hydrocarbons and halocarbons, respectively. Fahrenholtz et al. [29] used the Deans switch and two detection methods of MS and flame photometric detection (FPD) to simultaneously analyze VOCs and phosphine (a widely used fumigant), respectively [29].

Although the comprehensive GC × GC technique has emerged as a powerful tool for VOC analysis with incomparable resolution, it has not reached the level to be employed as a field instrument or to be widely adopted by average laboratories for routine analysis of ambient target VOCs [30–33].

In this current study, our objective is to modify the conventional dual-detection heart-cut technique based on the Deans switch to only use a single MS for both channels. The novelty of this study lies in the modification of the Deans switch, the innovated designs in the flow control and the trapping method. Our ultimate goal is to apply a Deans switch and a thermal desorption (TD) unit to a GC/MS to analyze a full range of VOCs in ambient air.

2. Experimental

2.1. Instrumentation

The complete system consisted of a self-made TD unit, a Deans switch assembly, and a commercial GC/MS (Varian CP-3800 with a Saturn 2200 mass detector in electron impact (EI) mode). The GC was equipped with two electronic flow controllers (EFCs) for controlling the carrier gas and the auxiliary gas using a prescribed pressure program. Data treatment and operation conditions were performed using Saturn GC/MS Workstation version 5.52. The TD and Deans switch action sequences were controlled using automation software/hardware (Advantech GeniDAQ 4.0, Taiwan).

2.2. Pre-concentration by TD

The construction of the TD device is described in our previous studies [26,34]. Fig. 2 shows the schematic of the TD device. In this device, the sorption trap, packed with several carbon sorbents in a stainless steel tube, was resistively flash-heated for thermal desorption. The dimensions of the trapping tube were

Table 1
Asymmetry factors (As), peak widths, and resolution of C_6–C_7 species for both hold-up and back-flush methods.

Compound name	Hold-up			Back-flash and trap		
	Width (min)	As	Resolution[a]	Width (min)	As	Resolution
Benzene	0.770	2.656		0.375	1.592	
			0.576			0.740
Cyclohexane	0.595	2.265		0.268	1.486	
			0.429			0.623
2-Methylhexane	–	–		0.203	1.447	
			–			0.418
2,3-Dimethylpentane	–	–		0.282	1.390	
			0.439			0.603
3-Methylhexane	0.644	1.335		0.368	1.331	
			0.866			1.013
2,2-Trimethylhexane	0.643	1.342		0.382	1.333	
			0.620			0.740
n-Heptane	0.700	1.320		0.385	1.335	
			0.922			1.850
Methylcyclohexane	1.084	1.512		0.326	1.603	

(–): Compounds only barely separated.
[a] Resolution is assessed in compound pair.

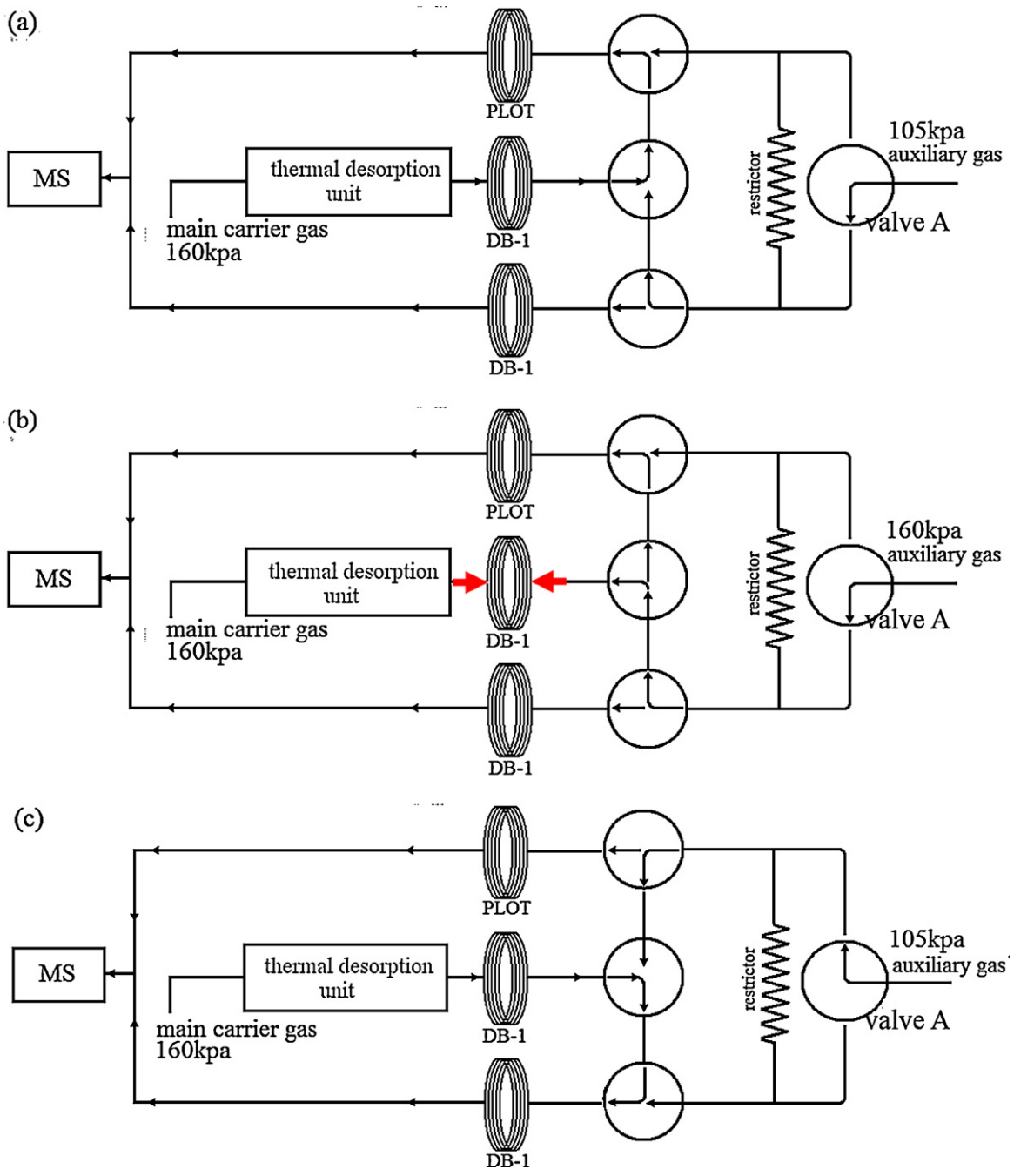

Fig. 4. Coupling of the auxiliary pressure settings with valve actions for the hold-up method. (a) Cutting light VOCs from the ^{1}D DB-1 column into the ^{2}D PLOT column. (b) Holding heavy VOCs within the ^{1}D DB-1 column. (c) Releasing heavy VOCs into the ^{2}D DB-1 column.

100 mm × 1.0 mm I.D. (1.6 mm O.D.). Three sorbents, i.e., Carboxen 1003, Carboxen 1000, and Carbotrap (Supelco, Bellefonte, PA, USA), were packed in the stated order into the trapping tube at a length of 1 cm each with glass wool plugs at both ends and between sorbents to immobilize the packing material in the tube. At the trapping stage (as shown in Fig. 2), the air sample was drawn through the trap at a flow rate of 40 mL/min, regulated by a mass flow controller, for the required time period while maintaining the trapping tube at 30 °C with a temperature controller. During injection, the 6-port valve was turned, and the trapping tube was flash-heated to 250 °C for 5 min for desorption into the GC/MS; the 6-port valve was then switched back, and the trapping tube was heated to 300 °C to bake off residues in the presence of high-purity nitrogen (99.9995%) for 30 min.

2.3. Chromatographic and MS conditions

The schematic of the Deans switch assembly used in this study is shown in Fig. 3. Separation of the C_3–C_{12} VOCs was performed using three columns. A 30 m DB-1 silica capillary column (30 m × 0.25 mm I.D. × 1 μm; J&W Scientific) was employed as the primary column (^{1}D DB-1) for pre-separation. Two additional secondary columns, a shorter DB-1 column (^{2}D DB-1) (12 m × 0.32 mm I.D. × 1 μm; J&W Scientific) and a PLOT column

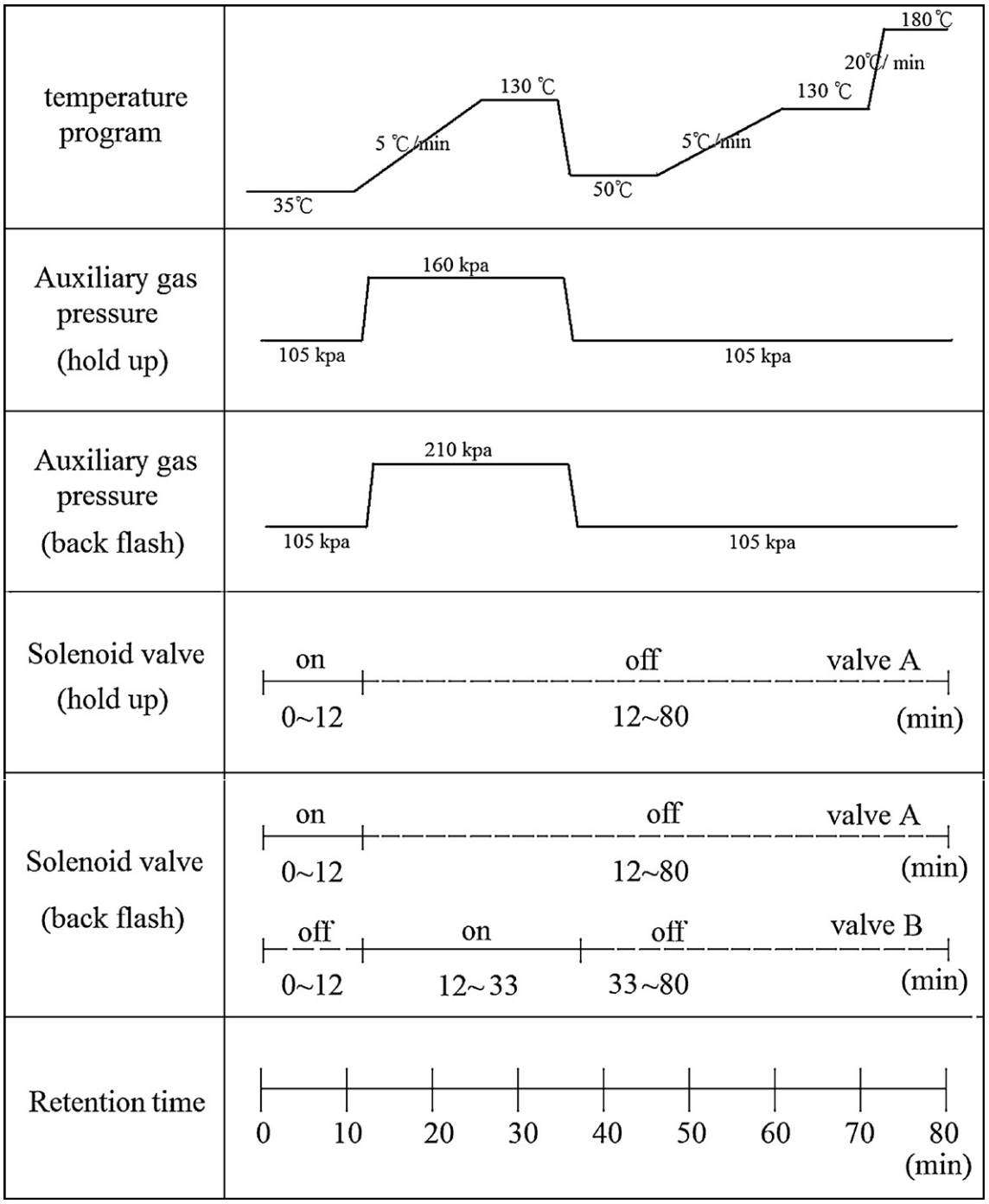

Fig. 5. Programs for oven temperature, auxiliary pressure, and valve action for both the hold-up and back-flush methods.

(^{2}D PLOT) (12 m × 0.32 mm I.D. × 8 μm; J&W Scientific), were connected to the primary column via the Deans switch. The ^{2}D PLOT column, receiving the light VOCs (smaller than C_6) from the primary column, permits superb resolution at room temperatures. The shorter ^{2}D DB-1 column was used not only to balance the resistance of the ^{2}D PLOT channel, which is necessary for operating the Deans switch, but also to provide additional theoretical plates to the ^{1}D DB-1 column for proper separation of the heavier VOCs (larger than C_5). The two column flows were merged using a micro-tee connector (ZT1M, Valco, USA) and channeled into the MS via a deactivated, uncoated capillary column (50 cm × 0.25 mm I.D.).

The GC oven was initially set at 35 °C, held for 10 min, and then ramped at 5 °C/min to 130 °C. After the last peak (1-hexene) from the ^{2}D PLOT column was eluted, the GC oven was immediately cooled to 50 °C, held for 10 min, ramped at 5 °C/min to 130 °C for 10 min, and finally ramped at 20 °C/min to 180 °C for 13.7 min.

All MS measurements were performed in total ion count (TIC) mode with a 35–200 amu scan range and 1.5 min solvent delay.

A commercial VOC standard mixture (Spectra, USA) consisting of 56 compounds from C_2 to C_{12} that includes alkanes, alkenes, and single-ring aromatics at sub-ppbv levels was used for method testing. These compounds were chosen for the target species

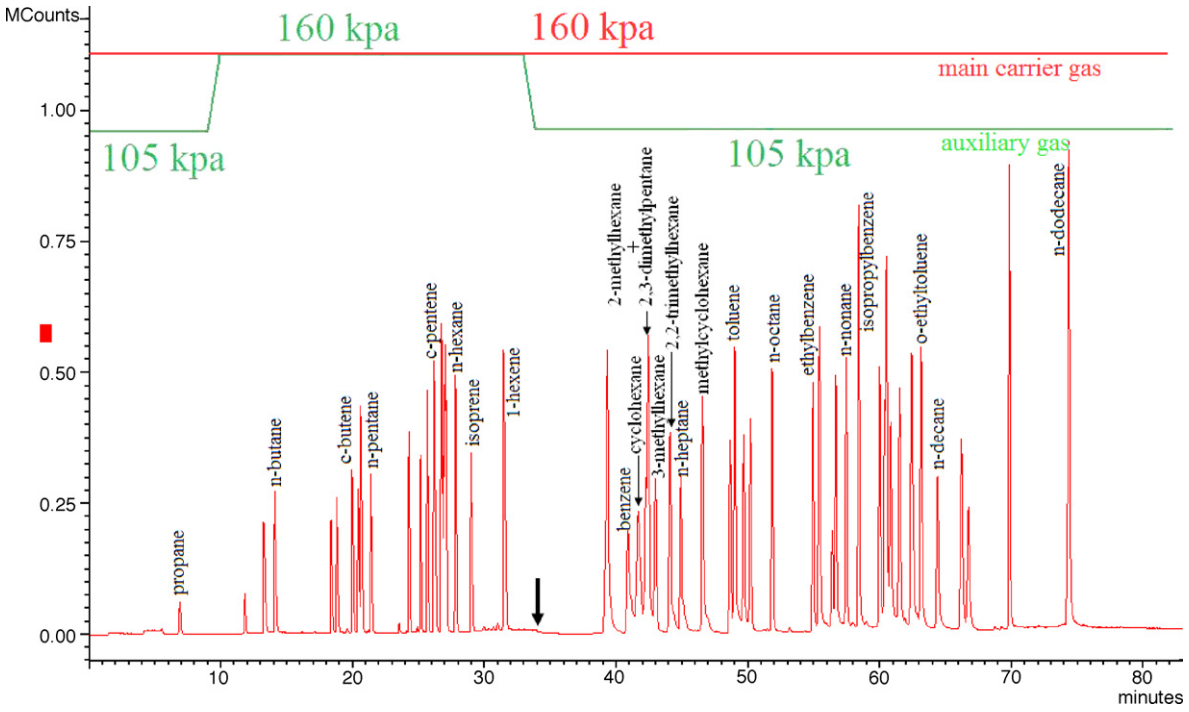

Fig. 6. Chromatogram of the hold-up method for analysis of a standard mixture. Peaks ahead of the arrow are separated by PLOT, and peaks behind the arrow are separated by DB-1.

due to their high abundance and reactivity in surface ozone formation [5].

2.4. Deans switch device

As shown in Fig. 3, the Deans switch manifold was constructed from three low dead-volume micro-tee connectors (ZT1C, Valco, USA) placed inside the GC oven, and the 3-way solenoid valve (091-0094-900, Parker, USA) was placed outside the GC oven. Surface-treated stainless-steel (s.s.) tubing (1/16 in O.D./0.04 in I.D.; Silcosteel, Restek, USA) connected these components to form a complete Deans switch. A shunt restrictor (0.01 in I.D. s.s. tubing), shown in Fig. 3, prevented backflow and subsequent peak broadening. By controlling the direction of the auxiliary flow of the Deans switch, selected peaks from the ^{1}D DB-1 column could either be cut to the ^{2}D DB-1 or to the ^{2}D PLOT columns. For example, if the solenoid valve A is in the "off" position, the auxiliary gas (going upward) pushes the ^{1}D DB-1 column effluent to the ^{2}D DB-1 column (Fig. 3). Conversely, if the solenoid valve A is in the "on" position, the auxiliary gas (going downward) pushes the ^{1}D DB-1 effluent to the ^{2}D PLOT column. As mentioned earlier, combining the two carrier flows at the ends of the columns and feeding this stream into MS will inevitably result in re-convergence of the already resolved peaks. Thus, a way to circumvent this problem must be engineered. Very few studies have combined GC/MS with the heart-cutting technique because of the restriction in the maximum allowable gas flow entering the MS. For non-MS detection, the maximum allowable flow is more lenient, which makes heart-cutting relatively easier [26,28]. Hence, delicate control of the combined flow to avoid exceeding the flow limit is pivotal to the success of this work. The manipulation of either the carrier gas or the auxiliary gas flow became reasonably easy through the use of the micro-fluidic pneumatic controllers available on commercial GCs.

3. Results and discussion

3.1. Hold-up method

In this study, the Deans switch manifold is modified by merging two carrier flows into one at the ends of the two columns and feeding the single stream into the MS. A flow program was engineered to allow a time delay between the elution of the two types of VOCs, i.e., light ($<C_6$) vs. heavy ($\geq C_6$) peaks, so that the resulting chromatogram is presented as a single chromatogram with the high boiling peaks tracing behind the low boiling peaks.

Manipulation of the resolved peaks from the two columns to avoid peak re-convergence has been successfully achieved for non-MS GC detection [23]. However, the vacuum condition of the MS made the similar peak manipulation more difficult to implement, and a new method was consequently developed. Two different approaches were attempted to avoid post-column peak re-convergence. The first approach is termed the "hold-up" method. In this method, the total flow rate into the MS was maintained below 3.5 mL/min. Pressures for the main carrier gas and the auxiliary gas were set at 160 kPa and 105 kPa, respectively, by the two EFCs. Fig. 4 shows the coupling of the auxiliary pressure settings and valve actions for the hold-up method. To execute a complete injection cycle, sample injection was first performed by TD, and the solenoid valve was switched on to direct the light VOCs from the ^{1}D DB-1 column into the ^{2}D PLOT column (Fig. 4a). After a prescribed time period, the solenoid valve was switched off, and the pressure of the auxiliary gas increased rapidly from 105 kPa to 160 kPa to prevent the heavier C_6–C_{12} compounds from eluting out of the ^{1}D DB-1 column (Fig. 4b). As soon as the final light compound (1-hexene) eluted from the ^{2}D PLOT column, the GC oven was cooled down rapidly to 50 °C. Then, the auxiliary gas pressure was rapidly returned to 105 kPa to release the heavy VOCs from the ^{1}D DB-1 column into the ^{2}D DB-1 column (Fig. 4c). Fig. 5 summarizes the programs for oven temperature, auxiliary pressure, and

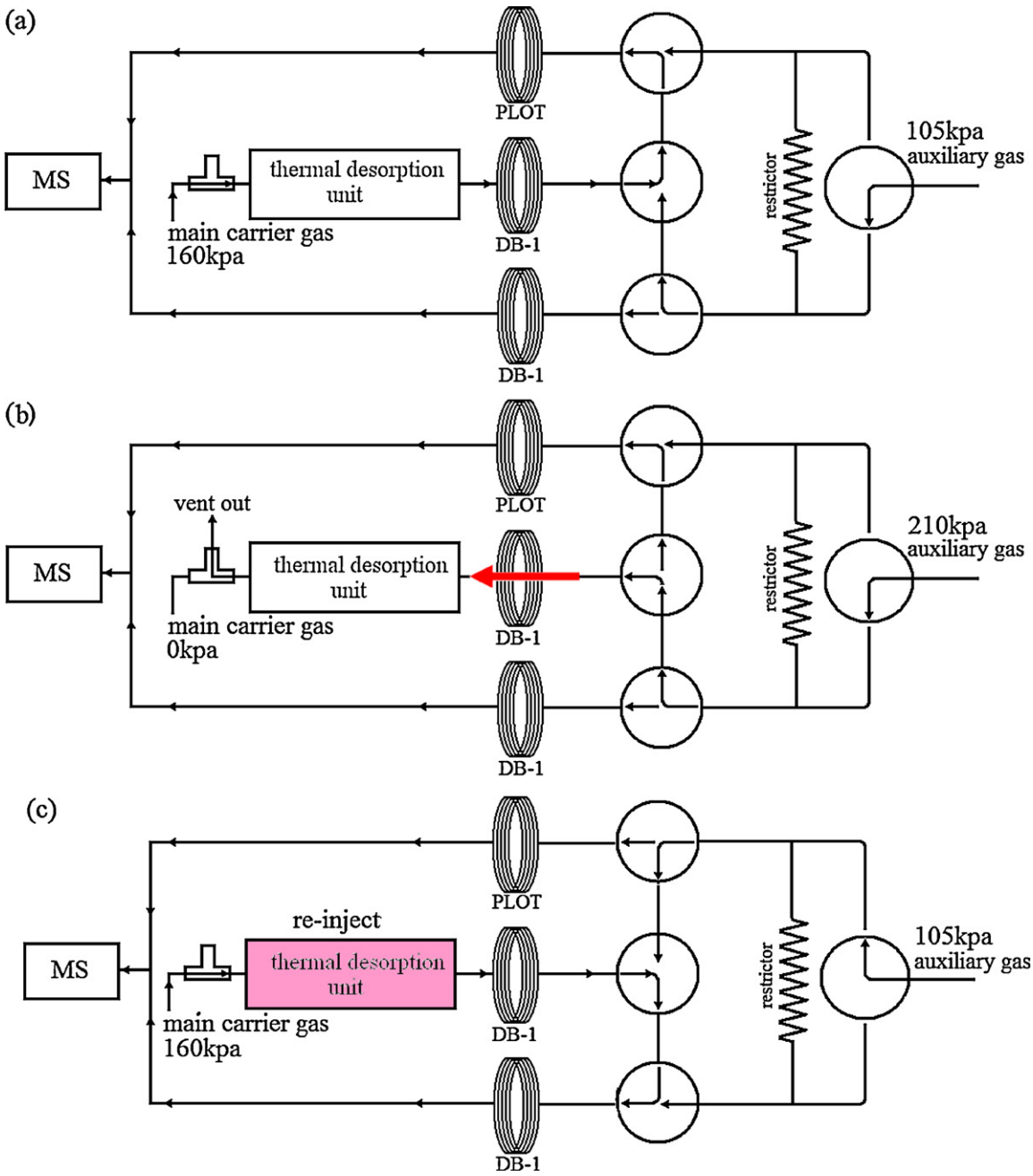

Fig. 7. Sequence of auxiliary pressure settings and valve actions for the back-flush method. (a) Cutting light VOCs from the ^{1}D DB-1 column into the ^{2}D PLOT column. (b) Back-flushing heavy VOCs into the trap. (c) Desorbing heavy VOCs into the ^{2}D DB-1 column.

valve action for the hold-up method for a typical analysis cycle. Note that although the combined flow of the main carrier and auxiliary gases may be feasible for regular GC detectors, such as the flame ionization detector (FID), the combined flow often becomes too excessive for the MS to maintain low vacuum. Thus, care must be taken to optimize the total flow to below 3.5 mL/min.

The chromatogram resulting from VOC analysis using the hold-up method under an optimized temperature program (see Fig. 5) is shown in Fig. 6, demonstrating that using one mass detector to accomplish full-range VOC analysis within one injection is feasible. However, closer examination of the chromatogram revealed that the resolution for the high boiling VOCs was compromised due to severe longitudinal diffusion in the ^{1}D DB-1 column during the hold-up stage, resulting in peak broadening. The broadening and peak tailing were more severe for the early-eluting peaks, such as benzene and heptane, than for the later peaks, such as *n*-octane and ethylbenzene, because diffusion was more pronounced for lighter molecules than for heavier molecules (Fig. 6). In light of this issue, further modifications were made to reduce the peak broadening that occurred while waiting for the light VOC section to completely elute.

3.2. Back-flush method

To alleviate peak broadening, a refocusing step was added to the hold-up configuration without changing the hardware. The major difference between the hold-up and back-flush methods is that this modified method re-collects the C_6–C_{12} portion by back-flushing it into the sorbent trap for re-focusing instead of temporarily holding the heavy compounds inside the ^{1}D DB-1 column. Subsequently,

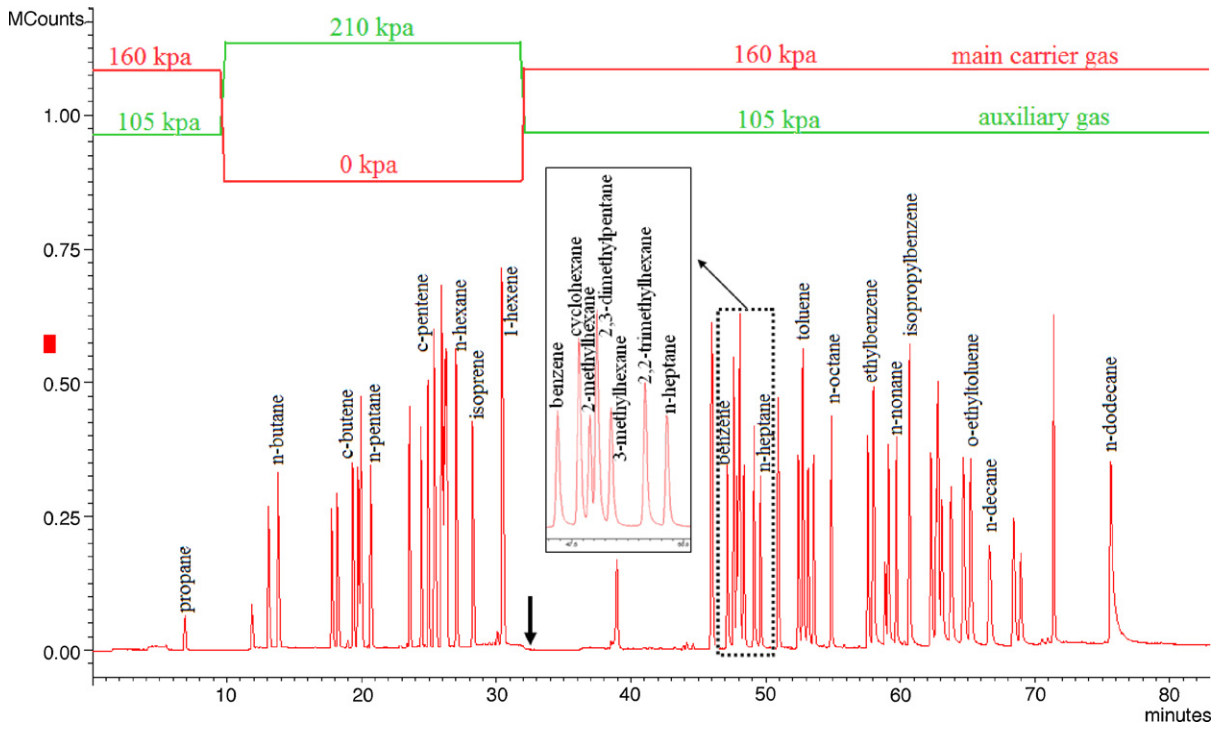

Fig. 8. Chromatogram of the back-flush method for analysis of a standard mixture. Peaks ahead of the arrow are separated by PLOT, and peaks behind the arrow are separated by DB-1. The C_6–C_7 section is enlarged to show details.

this portion is re-desorbed into the ^{1}D DB-1 column and continues to the ^{2}D DB-1 column for separation of the C_6-C_{12} compounds when the separation of light VOCs is nearly complete in the ^{2}D PLOT column. Hereafter, this method is referred to as the "back-flush" method. A slight change was made in the TD unit to accommodate the modified method; a 3-way solenoid valve (valve B) was installed upstream of the TD unit (Figs. 3 and 7) to either pass the carrier gas forward into the TD unit for injection or to vent the backward flow from the ^{1}D DB-1 column for re-collection. To carry out a complete injection cycle, VOC trapping and TD injection was performed, and then the solenoid valve A was switched on to allow the auxiliary gas to flush the light VOCs into the ^{2}D PLOT column (Fig. 7a), similar to the hold-up method shown in Fig. 4a. Subsequently, the solenoid valves A and B were shut off to stop the main carrier gas and to change the path of the auxiliary flow. Meanwhile, the auxiliary gas pressure was increased rapidly to 210 kPa to push the light VOCs into the MS and to simultaneously back-flush all of the heavier VOCs inside the ^{1}D DB-1 column back into the trapping tube (Fig. 7b). Thus, all heavier VOCs were re-focused in the trap by venting out the back-flush flow through solenoid valve B. Immediately after the separation of light VOCs was completed by the ^{2}D PLOT column, the GC oven was cooled to 50 °C, and solenoid valve B was switched back on to allow the main carrier gas to proceed into the TD unit and columns. At this time, the pressures of both the main carrier gas and the auxiliary gas decreased to the original pressure settings, and the heavier portion of VOCs was thermally desorbed again into the ^{1}D DB-1 column and continued to the ^{2}D DB-1 column (Fig. 7c). The temperature and pressure programs as well as the valve action sequences for the back-flush method are summarized in Fig. 5. A typical chromatogram for this method is shown in Fig. 8 that used an oven temperature program identical to that used for the hold-up method (Figs. 5 and 6). Note that trapping and injection were executed twice with the back-flush method for a complete analysis cycle. In addition, the peak shape for the early-eluting C_6–C_7 compounds from the ^{2}D DB-1 column improved more noticeably than those for the higher boiling compounds because diffusion is more severe for lighter molecules.

3.3. Peak symmetry and resolution

The quality of the back-flush method was quantitatively assessed on the basis of peak symmetry. An ideal peak should exhibit Gaussian features with a symmetric peak shape. Peak tailing is the most common form of peak asymmetry [35]. Here, the degree of peak tailing is defined by the asymmetry factor (As):

$$\mathrm{As} = \frac{b}{a}$$

where a and b denote peak widths of the front half and the rear half, respectively, at 10% of the peak height. If $a = b$, the asymmetry factor is unity to represent a fully symmetric peak. The parameters relevant to peak symmetry for the C_6–C_7 species (from benzene to methylcyclohexane) are shown in Table 1 for the hold-up and back-flush methods using and identical oven temperature program. For example, the As values were 2.655 and 2.264 for benzene and cyclohexane, respectively, for the hold-up method; they improved to 1.591 and 1.486 for the back-flush method. Separation of the two C_7 compounds, 2-methylhexane and 2,3-dimethylpentane was also possible with the back-flush method; these two VOCs were barely separated when the hold-up method was used. Although improvement in the As values for heavier species, e.g., 3-methylhexane, 2,2-dimethylhexane, heptane, and methylcyclohexane was less obvious, the decreases in peak width were still noticeable. The improvement in peak shape led to a significant improvement in resolution (Table 1), which also reduces the likelihood of co-elution and the uncertainty in compound identification and quantification by MS.

Table 2
Linearity and precision for C_3–C_{12} target compounds.

Compound name	Hold-up		Back-flash	
	Linearity	RSD (n = 24)	Linearity	RSD (n = 24)
Propane	0.5748	4.39%	0.6793	4.62%
Propylene	0.3026	5.15%	0.7555	4.17%
Isobutane	0.9993	2.22%	0.9995	3.14%
n-Butane	0.9991	2.37%	0.9968	2.94%
t-2-Butene	0.9983	1.49%	0.9987	1.87%
1-Butene	0.9992	1.73%	0.9992	2.05%
c-2-Butene	0.9991	2.04%	0.9980	2.26%
2-Methylbutane	0.9988	1.65%	0.9989	2.06%
n-Pentane	0.9993	1.54%	0.9997	1.71%
t-2-Pentene	0.9993	1.83%	0.9994	2.91%
1-Pentene	0.9992	1.65%	0.9991	1.85%
c-2-Pentene	0.9982	1.90%	0.9996	2.86%
2,2-Dimethylbutane	0.9979	1.86%	0.9994	2.07%
2,3-Dimethylbutane	0.9979	2.27%	0.9993	2.07%
2-Methylpentane	0.9944	3.55%	0.9939	6.34%
3-Methylpentane	0.9986	2.21%	0.9958	5.09%
n-Hexane	0.9933	3.13%	0.9954	2.74%
Isoprene	0.9931	2.81%	0.9982	3.15%
1-Hexene	0.9971	2.99%	0.9972	1.71%
Benzene	0.9731	7.19%	0.9994	2.80%
Cyclohexane	0.9754	6.14%	0.9997	2.66%
2-Methylhexane	0.9673	7.06%	0.9990	2.16%
2,3-Dimethylpentane	0.9898	4.94%	0.9997	2.25%
3-Methylhexane	0.9901	4.72%	0.9993	1.99%
2,2-Dimethylhexane	0.9989	1.69%	0.9994	1.90%
n-Heptane	0.9990	1.57%	0.9997	2.70%
Methylcyclohexane	0.9942	2.36%	0.9994	1.37%
2,3,4-Trimathylpentane	0.9975	2.43%	0.9994	1.62%
Toluene	0.9992	2.38%	0.9997	1.88%
2-Methylheptane	0.9985	3.57%	0.9998	1.94%
3-Methylheptane	0.9983	2.82%	0.9996	2.32%
n-Octane	0.9997	2.09%	0.9998	1.97%
Ethylbenzene	0.9964	2.91%	0.9998	2.54%
m,p-Xylene	0.9859	2.63%	0.9993	2.76%
Styrene	0.9962	4.10%	0.9998	2.27%
o-Xylene	0.9857	3.66%	0.9998	2.98%
n-Nonane	0.9873	2.99%	0.9991	2.18%
Isopropylbenzene	0.9991	3.15%	0.9998	2.98%
n-Propylbenzene	0.9977	3.42%	0.9999	2.43%
m-Ethyltoluene	0.9957	3.77%	0.9968	3.50%
p-Ethyltoluene	0.9972	2.50%	0.9998	2.04%
1,3,5-Trimethylbenzene	0.9859	3.59%	0.9984	4.12%
o-Ethyltoluene	0.9887	4.44%	0.9992	2.41%
1,2,4-Trimethylbenzene	0.9964	3.36%	0.9998	2.56%
n-Decane	0.9952	3.63%	0.9988	3.38%
1,2,3-Trimethylbenzene	0.9952	5.50%	0.9995	3.52%
m-Diethylbenzene	0.9902	3.60%	0.9993	3.42%
p-Diethylbenzene	0.9994	3.83%	0.9989	4.39%
Undecane	0.9768	3.35%	0.9956	3.34%
Dodecane	0.9830	7.70%	0.8318	19.15%

3.4. Precision and linearity

The applicability of both the hold-up and back-flush methods was assessed for two important quality assurance properties: precision and linearity. Both the hold-up and the back-flush method were tested by sampling the commercial VOC standard mixture. The precision test for the target compounds was performed by repeatedly injecting 300 mL aliquots of the standard mixture. The linearity test was conducted by trapping various amounts of the standard mixture (100, 200, 300, 400, and 500 mL). As shown in Table 2, poorer linearity and precision for propane and propylene were expected for both methods due to the low trapping efficiency at ambient temperatures. Decreasing the trapping temperature to sub-ambient trapping temperatures with a cooling device can effectively improve the trapping efficiency and consequently obtain better linearity and precision for compounds smaller than C_4 [34]. A cooling device was not installed in our TD unit, but it can be added when required. Under the present trapping conditions, compounds larger than C_4 can be measured quantitatively. When the hold-up method was used, the slightly poorer linearity and precision for the early-eluting species, i.e., benzene, cyclohexane, 2-methylhexane, 2,3-dimethylpentane, were the result of excessive longitudinal diffusion in the primary column due to prolonged hold-up (Table 2). When the back-flush method was used, the refocusing step eliminated this problem and greatly improved the data quality for the early-eluting C_6–C_7 compounds; better linearity ($R^2 > 0.9990$) and precision (RSD < 2.80%) were subsequently obtained. While the detection limits (D.L.) for the more volatile PLOT compounds were comparable for both trapping methods, they were noticeably better for the back-flush method than the hold-up method for the DB-1 compounds (see supplementary materials). These results demonstrate that the back-flush method is the preferred choice of method to provide full-range VOC analysis using a single MS.

4. Conclusions

This study aimed to develop a method to perform full-range VOC analysis using GC/MS that was based on the Deans switch heart-cut technique. Two approaches were attempted: the hold-up method and the back-flush method. The hold-up method opened up the possibility of full-range VOC analysis within a single sample aliquot using a modified heart-cut technique. However, peak broadening for the more volatile compounds of the C_6–C_7 species in the primary column inevitably occurred.

The addition of a re-focusing step to the system produced the back-flush method. The chromatographic quality improved dramatically for the middle range VOCs in this method, as measured by the asymmetry factors and resolution. The success of the back-flush method confirmed that full-range VOC analysis with a single MS is feasible. Although this work used a PLOT and WCOT column pair as a paradigm for full-range VOC analysis, the use of any two columns with different properties could also be attempted with this technique to benefit from MS detection in other applications.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.06.067.

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