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Time-resolved cryogenic modulation for targeted multidimensional capillary gas chromatography analysis

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Abstract

Multidimensional gas chromatography (MDGC) is performed in a new manner, described in this paper. The method incorporates two directly coupled columns and employs a longitudinally modulated cryogenic trap located between the columns. No heartcutting process is used, but rather a method better termed selected zone compression pulsing is used. Compared with normal MDGC, where primary column effluent has to be temporarily diverted either to a monitor detector or to the second dimension column, the new procedure in its simplest mode passes all of the first column effluent to the second column. It is simply the times at which the modulation of the trap is performed that determines which target solutes will be selected for enhanced separation. This approach allows almost instantaneous separation of selected zones on the second column, and has the potential to significantly simplify the MDGC method. Since data are presented in a time–response format, and do not require transformation as previously described for comprehensive GC when using the longitudinal modulator, quantitation and report generation are essentially the same as in any GC method and data system. Advantages also include significant sensitivity improvement. By using cryofocussing, and benefiting from the zone compression effects along with fast GC conditions on the second dimension, new possibilities for MDGC can be realised. The method is demonstrated by using a mixture of semi-volatile aromatic hydrocarbons.

Keywords: Gas chromatography; Cryogenic trapping; Coupled columns; Hydrocarbons, aromatic

1. Introduction

1.1. Multidimensional gas chromatography

Multidimensional gas chromatography (MDGC) has long been acknowledged as providing an opportunity for improved separation in GC [1]. However, this recognition has usually been qualified by the practicalities of the method with respect to setting up and maintaining the system. Often users quote the belief that MDGC is much more time-consuming, complicated, and expensive compared with single-column GC. Thus MDGC is routinely used in very few laboratories.

Conventional MDGC only selects key components from the first column for heartcutting to the second column [2,3], where they should be better resolved on a more selective phase [i.e., the second column phase separates the packet(s) of compounds that are transferred in the heartcut event]. When the heartcut operation is not invoked, all the other solutes in the first column effluent will then normally pass to the monitor detector. The selected or target components are analysed in the normal manner on the second (analytical) column. Heartcut bands may be cryofocussed at the start of the second column [4,5],

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which introduces a further step in the procedure. Thus the oven must be cooled, the cryofluid turned off, then the heartcut species eluted in a second oven program (note that most analyses will use temperature programmed conditions). A more complicated variation on the MDGC theme is that of Krock et al. [6], who described a system with multiple parallel traps to which selected heartcuts or contiguous fractions of first column effluent could be sent, awaiting subsequent separate elution and analysis on a second column. In most instances of conventional MDGC, timing of heartcuts is a critical decision for the analyst, since exclusion of certain bands is often as important as selecting the required component peaks.

Whilst this is only a cursory and selected overview of conventional MDGC (further operational modes can be referred to in the text by Cortes [7]), the position of MDGC in the chromatographer's toolbox can be appreciated.

Recently the whole concept of MDGC has undergone a major technological advance through introduction of the comprehensive gas chromatography (GC×GC) method [8–12] and related methods which also deliver superior separations in a two-dimensional (2D) mode [13]. This now overcomes the need for careful timing of heartcuts, but importantly applies the multidimensional separation analysis advantage to all solutes in the GC analysis. The new presentation format demands a new approach to solute quantitation since a two-dimensional separation space is now employed, and also must stand the test of analyst acceptance before becoming widespread in analytical laboratories.

1.2. The role of cryogenic modulation

In a study to investigate the scope of the longitudinally modulated cryogenic system (LMCS) recently introduced by these researchers [11,14–17], we evaluate here the role of selected zone compression during GC analysis, and endeavour to demonstrate that it can be employed in a mode that gives data comparable with that of conventional MDGC, offering simplified access to routine MDGC analysis. Of particular interest is to develop a method that permits target component analysis at high sensitivity, and allows data to be handled in a manner equivalent to normal GC data processing, where a report at the conclusion of the analysis simply lists each recorded peak and its related analytical properties (retention time, area, height etc). The LMCS procedure has a novel and elegant role to play in comprehensive GC×GC, where peaks are produced in a two-dimensional space and are presented as contour plots representing their heights within this space. However data handling of the GC×GC method is not trivial, with automated peak presentation not yet available. We have recently reported the use of selective peak enhancement where the cryofluid is turned on/off at predetermined section of the chromatogram [18]. That report was essentially intended to demonstrate the flexibility of the LMCS approach, giving rise to a range of unusual modalities rather than to propose a universally applicable method. By keeping the cryofluid on for the total analysis, new considerations must be contemplated and operational mechanisms developed, as described herein.

The cryogenic focussing process gives many times greater peak heights due to zone compression. Peak width reduction corresponds to height increase. Columns are placed in the GC and are connected by using direct zero dead volume couplings, so that there is continuous fluid connection between both columns. The only modification is the presence of the cryogenic region which essentially acts as a barrier to solute passing from one column to the next. Once solute is focussed in the trap, its migration is stopped until the trap is moved along the column to expose the cryotrapped solute to the oven heat. Since the LMCS may give instantaneous re-mobilisation of trapped solutes, it can effectively re-inject complete bands into the second column at any chosen time. Bands then proceed to travel towards the detector. Since the first and second column are orthogonal with respect to separation mechanisms, then provided the solutes have a sufficiently different interaction energy with the second column phase, there is a potential for increased separation.

1.3. Expansion of separation space

Greater resolution in MDGC methods is believed to rely on the manner in which separation space is expanded, thus allowing more resolved peaks to be

fitted into the chromatogram. In the normal directly coupled dual column experiment, separation space is not expanded, rather peaks are just shifted around in the given space. In GC×GC, all peaks are subjected to the two-dimension space, so capacity (i.e., number of separable peaks) is increased many-fold (the total capacity is now the capacity of one column multiplied by the capacity of the other column). In conventional MDGC, the capacity is increased only for the region of first column that is heartcut to the second column, and then only by the degree that the second column provides increased capacity for that heartcut section. In this manner, the total capacity will be the sum of the capacity on the first column, and the small capacity increase for each selected heartcut transferred to the second column. At the maximum, the total system capacity could not exceed the sum of capacities of the two columns, but for various reasons, this maximum cannot possibly be achieved. Thus only a modest increase is realised. In the present method it should be possible to obtain greater capacity than can be achieved in regular heartcutting MDGC since each heartcut is analysed under very fast conditions and more individual heartcuts can be incorporated into the analysis. This point will be further developed in a subsequent paper.

This paper will report studies on a new MDGC method designed to offer analysts a convenient first entry into multidimensional separations leading to both increased resolution of target solutes and increased analysis sensitivity.

2. Experimental

2.1. Instrumentation

A HP6890 gas chromatograph (Hewlett-Packard, Wilmington, DE, USA) was used throughout this study, fitted with a split/splitless injector, flame ionization detection (FID) system and a HP7683 series automatic liquid sampler. The injector was operated in the split mode (40 ml/min) at 250°C, and the FID system was operated at 300°C at an acquisition rate of 100 Hz with a 10 ml/min N_2 makeup gas. For analysis of the semi-volatile samples, an oven temperature program of 40°C (1 min hold), 20°C/min to 150°C then 2°C/min to 230°C was used. Carrier gas was operated in the constant flow mode.

2.2. Multidimensional/comprehensive chromatography parameters

An LMCS as reported elsewhere [17,19] was used to achieve the multidimensional and comprehensive chromatography modes. Essentially, the second capillary column of the directly connected two-column ensemble is inserted trough a small tubular trap which is cooled by CO_2. The trap effectively collects or focuses solute as it travels along the column, and by moving the trap towards the inlet direction, the collected band of solute is exposed to the oven temperature and then rapidly continues its migration in the second column. Thus we can effect pulses of solutes into column 2. The way the trap is moved (e.g., the timing of movement) determines what effect we produce for the chromatographic analysis. For comprehensive GC×GC conditions, different modulation frequencies were used according to the peak widths generated by first column conditions, and were usually one modulation every 4 or 5 s, with a cryogenic trap rest time of 1 s in the position that allows compressed zones to be remobilised. This was controlled through an external timing system. We use a nomenclature of [*x*,*y*] for total modulation time *x* and hold time for remobilisation of *y* (in units of s). For time-resolved analysis, the cryogenic trap was moved at times predetermined by the peak positions of target peaks to be resolved during the analysis. In this case, movement of the trap was controlled through the HP6890 Chemstation software and external event outputs. As reported previously [18] for our study of multi-mode operation of the cryogenic system, the column set 1 consisted of a first dimension of 30 m×0.25 mm I.D., 1.0 μm d_f BPX5 phase column with an 80 cm×0.10 mm I.D., 0.20 μm d_f BPX50 phase column second dimension. The short second column is required for comprehensive gas chromatography, where rapid elution is critical and should be completed on the time scale of the modulation frequency (e.g., 5 s). However since successive ''heartcuts'' in the time-resolved method are temporally separated on the scale of minutes, the second column need not be so short, and a longer column giving better separation may be employed.

Thus column set 2 comprised a 30 m×0.25 mm I.D., 0.25 μm d_f BPX5 column coupled to a 2.0 m×0.10 mm I.D., 0.1 μm d_f BPX50 column. Column set 3 was the same as column set 2, except a 5 m BPX50 second dimension column was used. Carrier gas (He for column set 1, H_2 for sets 2 and 3) flow-rates were approximately 1–2 ml/min. All columns were provided by SGE International (Ringwood, Australia). The use of a longer column has implications for the extent of peak broadening between the modulator and detector, and hence peak sensitivity of detection.

2.3. Standards

For demonstration of the principle of time-resolved cryogenic modulation, a semi-volatile aromatic mix (part No.: SVM-124-1) from Ultra Scientific (North Kingstown, RI, USA) was used, diluted in pesticide-grade dichloromethane to a suitable concentration. In this paper, peaks will be numbered in elution order in Fig. 3, and will not be separately identified. Identification may be found in a previous paper [18].

3. Results and discussion

3.1. General concepts

The experimental arrangement of the columns and modulating trap is shown in Fig. 1. Rapid analysis should be achieved on the second column, since this assures that successive pulsing events do not result in overlapping elution zones which would potentially interfere with resolution quality. Thus small retention factors will usually characterise the elution of solutes on the second column, although further study is required to understand how they may be optimised to produce best separation under fast GC conditions. Typical conditions leading to fast elution include one or a combination of short column length, thin stationary phase film and narrow inner diameter column for the second column.

Fig. 2 illustrates schematically the conceptual development of the time-resolved modulation method. We have previously demonstrated [18] the approach that we termed selective peak enhancement, where an individual peak or unresolved set of peaks

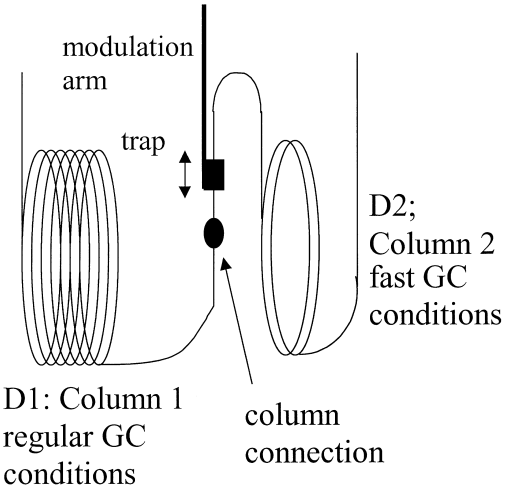

Fig. 1. Schematic diagram of the longitudinally modulated cryogenic system. The modulator consists of a pneumatic operated movement, with CO_2 provided to the trap. More complete details will be presented elsewhere [19].

– well separated from others – was selected for cryogenic focussing and ''re-injection''. In that case, the CO_2 could be switched on before, and switched off just after, each step. During this time, the selected peak was completely trapped, and the trap was then moved to remobilise the peak. Thus, peaks not targeted for enhancement just passed through the trap in a usual fashion without retardation or focussing. In the method described here, the cryogen is kept on for the whole analysis.

In Fig. 2A, the process shows all four normal (broad) peaks in the upper trace being individually collected, and the enhanced peaks, produced by rapidly pulsing them to the fast elution second column, are shown in the lower trace. Fig. 2B extends this to show two overlapping peaks, b, being collected/focussed then separated on the second column. Likewise peaks marked d are well resolved. Peaks marked d are drawn to show a reversal of relative elution on the second column, indicative of different phase selectivities on the two columns. This selectivity difference is important if overlapping peaks on column 1 are to exhibit enhanced separation.

Fig. 2C is intended to show that if many peaks are simultaneously collected such as group c, it is possible that the phase selectivity and column

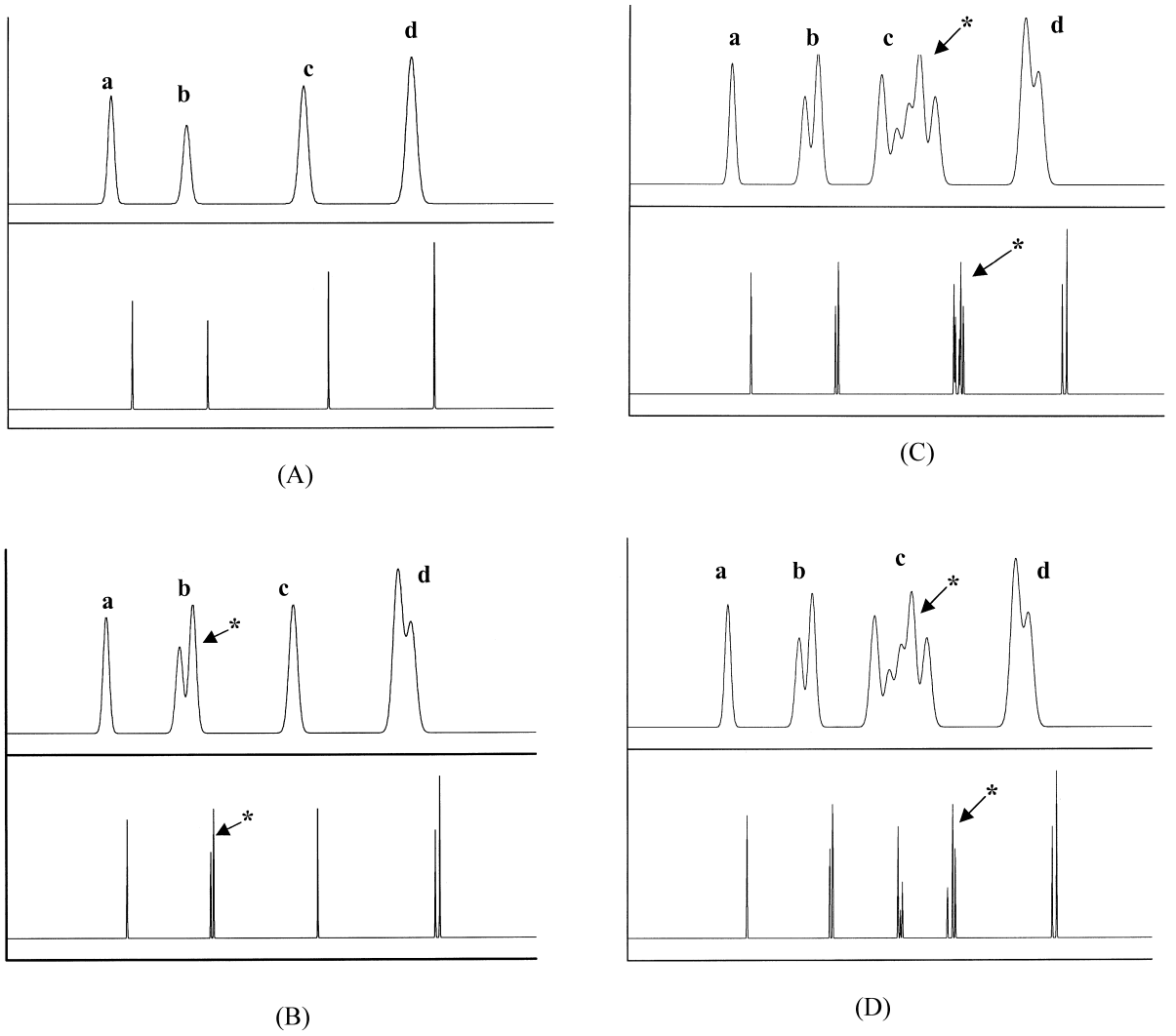

Fig. 2. Hypothetical chromatograms demonstrating various modes for collection and remobilisation of selected peak situations. The lower traces will in all cases have a response scale many times greater than that of the upper traces. For details and specific comments on each case, refer to text.

efficiency of column 2 is insufficient to adequately resolve them all. Since we prefer fast separation on the second column, and so use a short column for this, the peak capacity is small and this gives limited separation capability for a pulsed group. A longer second dimension column could be used if required to increase separation of the coeluting first column peaks. However, if a target is known to be within this group (and its retention time is known from standards), such as given for peak marked * in group c in Fig. 2D, then we can separate away early peaks in this set by trapping and eluting them separately. While they are being eluted, we collect peak * and most likely some small amounts (or all) of some peaks neighbouring the target peak. This simplifies the total band composition collected with peak * and increases the potential for subsequent separation. It is advisable that additional peaks following peak * are retained in the trap so that if any of them could potentially interfere with the elution of peak * on

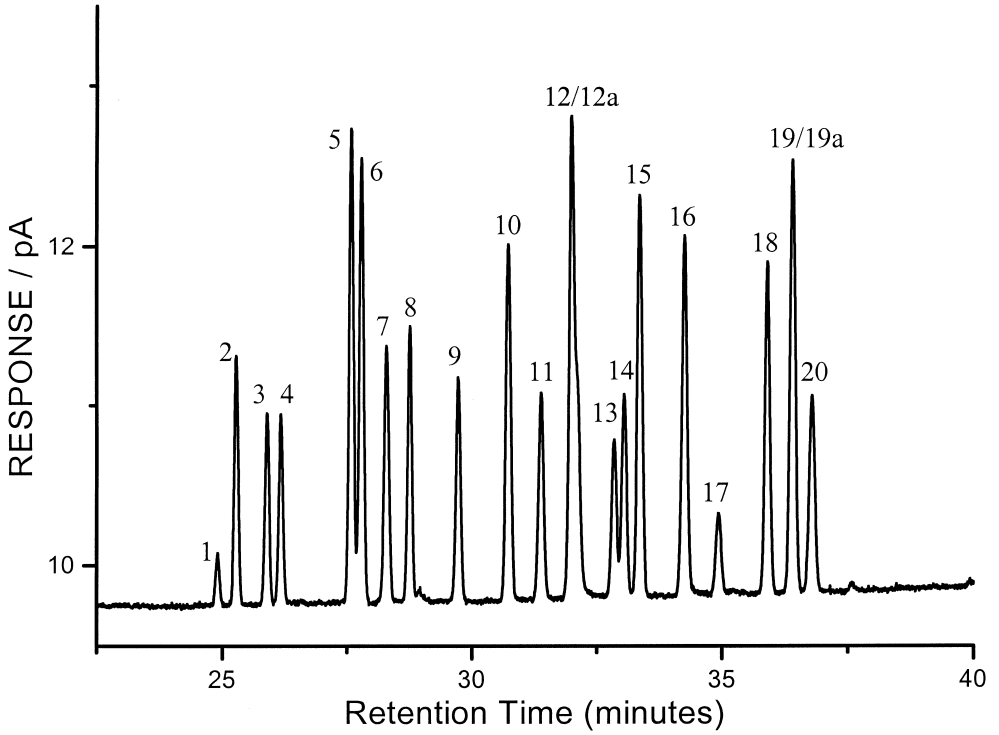

Fig. 3. Normal GC analysis of the semi-volatiles aromatics sample on column set 1. Note that peak heights are about 0.5–3 pA, and that peak widths are about 10 s. In this case the compounds pass through the column set without hindrance from cryogenic conditions since the CO_2 is not applied.

column 2, they are kept in the trap for a sufficient period. This is easily achieved in the system described here. It will be best to then clear them out of the trapping zone by performing a modulation before peaks indicated by d are collected.

The final result, shown in Fig. 2D, will be a series of hopefully well-separated target peaks. This process can be performed any number of times during an analysis and collected packets of first column effluent can be as narrow as required, with only the proviso that collected bands should be separated from their contiguous or neighbouring collected bands when analysed on column 2. There are a number of precautions or comments that must be kept in mind with this method.

(i) Any peaks which may potentially co-elute with the peak of interest should be excluded from being collected in the same event with the required target peak. If not, then maybe a different column set should be chosen in order to manipulate phase selectivities.

(ii) Timing will need to be taken from a GC screening run report, so that modulation event times are properly defined. There will be a small offset for the exact times when compounds are expected to enter the trap, because the times when components elute during the screening run are for elution over the two columns, whilst the time they enter the trap is a little less. This can be estimated easily.

(iii) Minor constituents not identified in the screening run, used for event timing, may be missed by not allocating separate modulation events to them, however the extra sensitivity of the method, combined with enhanced resolution offers the possibility of recognising otherwise unidentified solutes.

(iv) With electronic pressure control, there is

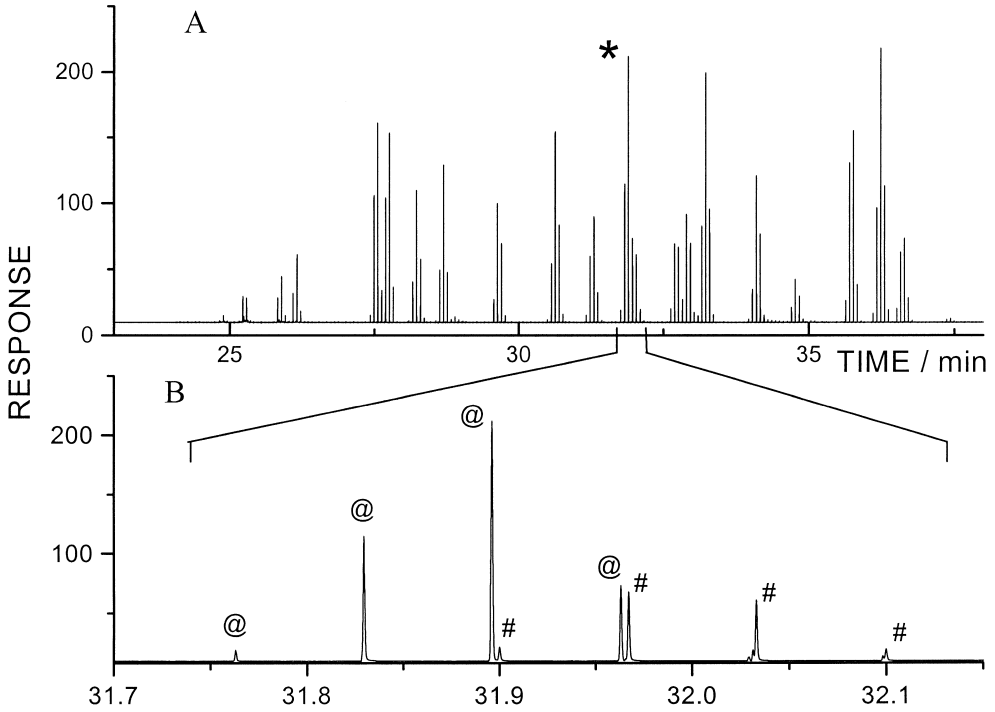

Fig. 4. Comprehensive GC×GC of the same sample as in Fig. 3, with [4,1] timing. (A) Direct output of data, and (B) expansion of the peaks at about 32 min, showing that where two solutes are collected in the one event then they are resolvable on the second column. Note the improved separations in the second dimension for these two peaks, which are not resolved in the first dimension (shown by the overlapping peaks 12/12a in Fig. 3). Peak response for the largest peak is ca. 200 pA.

excellent chromatographic reproducibility in retention times, so once a method is established it should be very precisely reproducible.

3.2. Example of a semi-volatile mixture analysis

The above conceptual approach to time resolved MDGC has been applied to a semi-volatile sample, previously used for a comprehensive gas chromatography study [18]. In that study, since multiple second dimension analyses were required in order to generate the two-dimensional peak profile or contour, the first column was operated in a manner that gave slow elution and broader peaks than might normally be wanted. The second dimension was fast.

Here, there is no need for transformation of data and peak contour generation, hence the first dimension can be used in a faster separation mode, however for comparison purposes, conditions were set up to allow a GC×GC run to be also conducted on the peaks using column set 1. The second dimension can be operated in a similar fashion to that of the prior study. The only requirement is to decide what are the solutes of interest, and how to suitably set up the timing according to the general approach shown in Fig. 2. The primary principles will be that all target analytes are to be presented to the detector as completely resolved peaks, and for those solutes not of interest we will not be concerned if they coelute with other non-critical solutes. Regardless, many of the solutes will still be well separated and quantifiable.

Fig. 3 illustrates the normal GC analysis of the semi-volatiles aromatics sample. In this case, all compounds pass through both columns, with the cryofluid not supplied to the trap. Peaks are about

10 s wide, and are of reasonably low response (ca. 0.5–3 pA). When this sample is subjected to GC×GC, using [4,1] modulation, the result of Fig. 4A was obtained. The peaks can still be discerned but each is now a sequence of sharp pulses due to zone compression of part of each peak and then its rapid travel through the second column. In some cases, we can see that overlapping peaks give two separable peaks in the second dimension pulse. Fig. 4B is an expansion of part of the chromatogram showing that excellent peak shapes are obtained and the separation of components is achieved. Peak heights are about 60–70-fold larger than those in the regular GC result of Fig. 3. Note that when peak labelled * in Fig. 4A is expanded in Fig. 4B, two separate sets of peaks, marked @ and #, are discernable. Each of these sets of peaks are the same component, but occur in successive modulation events.

The GC×GC result is also presented in a two-dimensional contour plot as shown in Fig. 5. First column retention (^1t_R) is given on the horizontal axis, second column retention (^2t_R) on the vertical. The separation of components based on the improved selectivity of column 2 is readily evident here, and provides additional retention-correlated chemical data in the second dimension. A small peak 16a is obscured by the large peak 16, and is not separately identified in subsequent chromatograms. Using this result, we can now predict which contiguous components may be collected together in the one trapping event and resolved on the second. For instance, circled peaks marked ''X'' are well separated on column 2 and elute adjacent on column 1, so may be co-collected and pulsed to column 2 as one event. The experimental result of discrete collection of peak(s) within a chromatogram is illustrated in Fig. 6A, with the time-resolved modulation process based on the timing events listed in Table 1. On the time-frame of the GC analysis each modulation pulse appears as a single peak, but consists of each of the

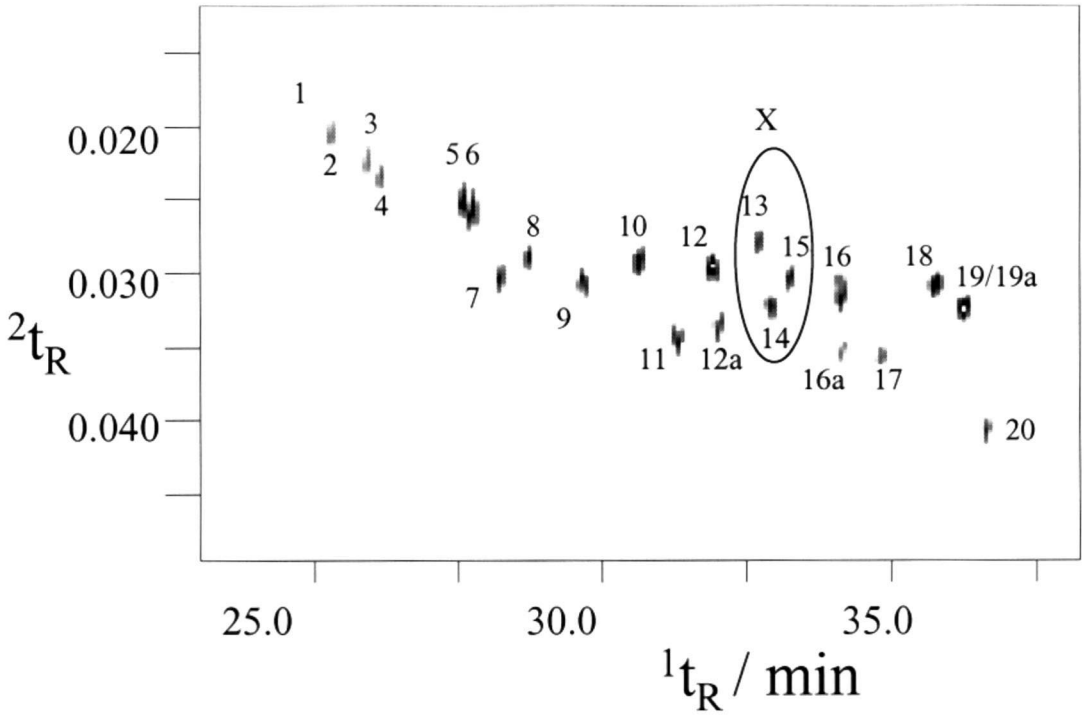

Fig. 5. Data from Fig. 4 presented in GC×GC form as a two-dimensional separation contour plot. Peaks marked X may be collected in the one cryofocussing event as described in the text.

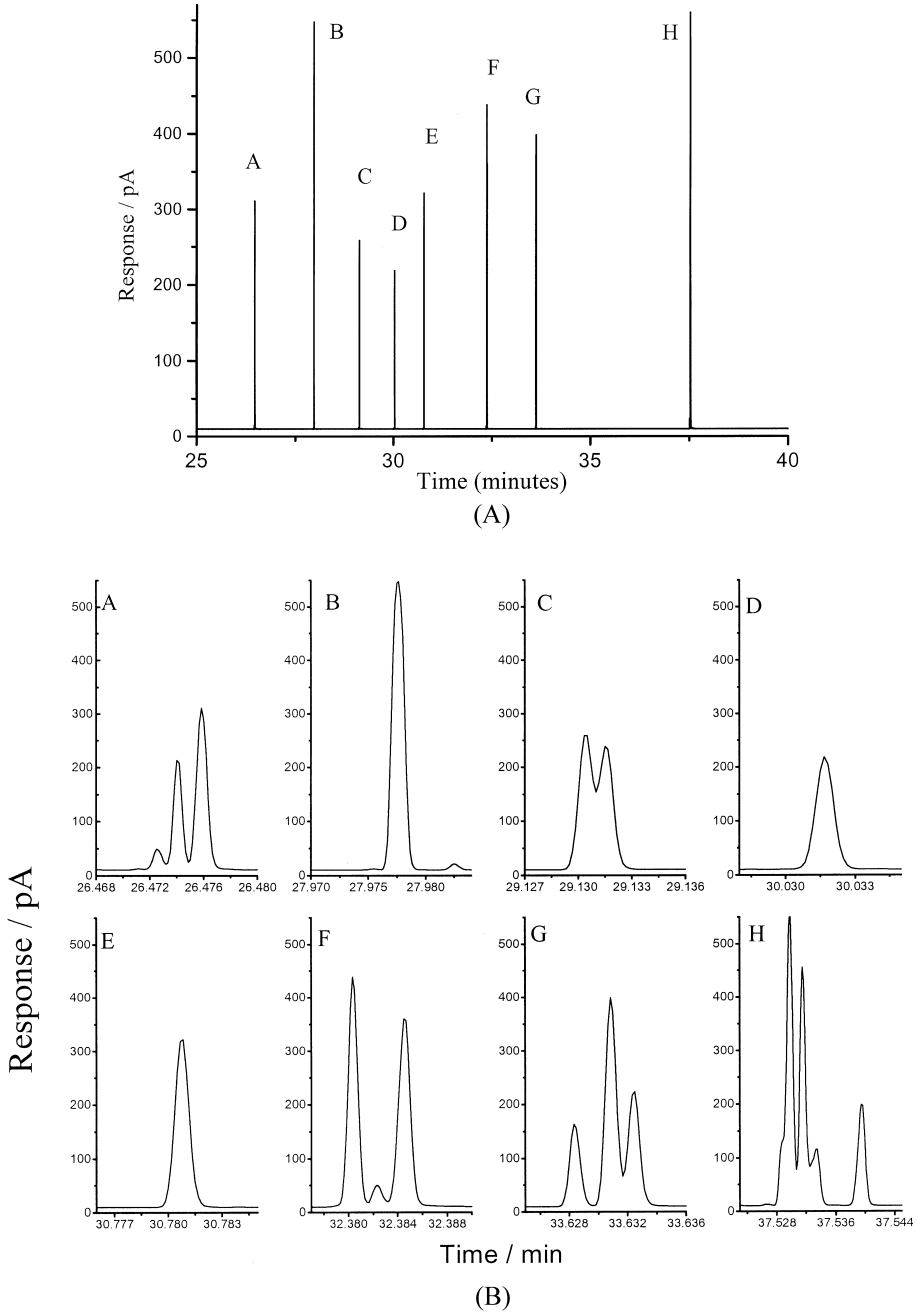

Fig. 6. (A) Chromatogram of the result obtained for trap movement according to the sequence of event times presented in Table 1 for column set 1. Since eight timed release movements are used, there are eight sharp pulse regions produced on this chromatogram. (B) Expansion of each of the eight pulsed zones shown in (A). Again, note that peaks are very tall due to whole-of-peak trapping and rapid remobilisation.

Table 1
Schedule of valve operations for each of the column sets[a]

Event	Trap position[b]	D2=0.8 m BPX50		D2=2.0 m BPX50		D2=5.0 m BPX50	
		Event time	Peaks trapped	Event time	Peaks trapped	Event time	Peaks trapped
1	T	20.00		10.00		13.00	
2	R	26.45	1, 2, 3, 4	16.25	1, 2, 3, 4	20.33	1, 2, 3, 4
3	T	26.60		16.65		20.70	
4	R	27.95	5, 6	17.10	5, 6	21.60	5, 6
5	T	28.05		17.25		21.80	
6	R	29.10	7, 8	18.20	7, 8	23.05	7, 8
7	T	29.25		18.53		23.35	
8	R	30.00	9	18.80	9, 10	24.00	9, 10
9	T	30.10		19.20		24.45	
10	R	30.75	10	19.75	11, 12, 12a	25.05	11, 12, 12a
11	T	30.80		20.00		25.55	
12	R	32.35	11, 12, 12a	21.05	13, 14, 15	26.75	13, 14, 15
13	T	32.50		21.15		27.00	
14	R	33.60	13, 14, 15	22.38	16, 17, 18	28.20	16, 17, 18
15	T	33.75		22.65		28.70	
16	R	37.50	16, 17, 18, 19, 19a, 20	23.25	19, 19a, *20*[c]	29.10	19, 19a
17	T			23.45		29.60	
18	R			24.00	20	30.30	20

[a] The groups of peaks trapped are numbered A, B, C ... sequentially in their respective Figs. 6, 7 and 8.
[b] T refers to trap in its home position; R refers to trap moved to release the trapped components.
[c] Some of component 20 was trapped during this event.

co-trapped components. For instance, expanded trace identified as zone G on Fig. 6B is the result for the peaks marked X in Fig. 5. Fig. 6B includes expansions of all the collected zones, A–H. Peak heights in the modulation process are now up to 500 pA, corresponding to about a 150-fold signal height increase.

Fig. 7 is a repeat of the above experiment, but under column set 2 and timing conditions listed in Table 1. These two results can be considered to be reasonably general and representative of any chromatography sample that might be advantageously analysed by this method. Since column 2 is now 2 m long, better resolution is seen on the expanded plots. For example compare zone F, Fig. 6B, with zone E, Fig. 7B, for the same pair of peaks. Table 2 lists the properties of these peaks. Likewise, Fig. 8 is the analogous result for column set 3. The 5 m BPX50 column now gives excellent resolution as shown in the expanded peak plots in Fig. 8C. Peak heights are not enhanced as much here due to the greater dispersion and broader peaks which result from their passage through the longer second dimension column.

3.3. Quantitative aspects

Relative peak areas may be used to identify various peaks in the second dimension analysis, by comparison with the first dimension result. Thus for the pulsed peak G in Fig. 6, we collect the three peaks numbered 13, 14 and 15 in Fig. 3. Comparison of the two respective chromatograms shows that the three peaks' relative peak areas are preserved, but the elution order on the second column is now 13, 15 then 14. By referring to the GC×GC result, 15 has a shorter retention time than peak 14 on the second column, however since it had a later elution time in the first dimension, its 2D time was at a higher temperature. In the Fig. 6 experiment, all three peaks were retained in the trap and then pulsed at the same time – and hence same temperature – to column 2, and so peaks 13 and 14 will now have shorter times than they had in the Fig. 3 experiment, and shift in a manner that they now bracket peak 15.

3.4. Sensitivity of detection

This additional advantage arises from the benefit

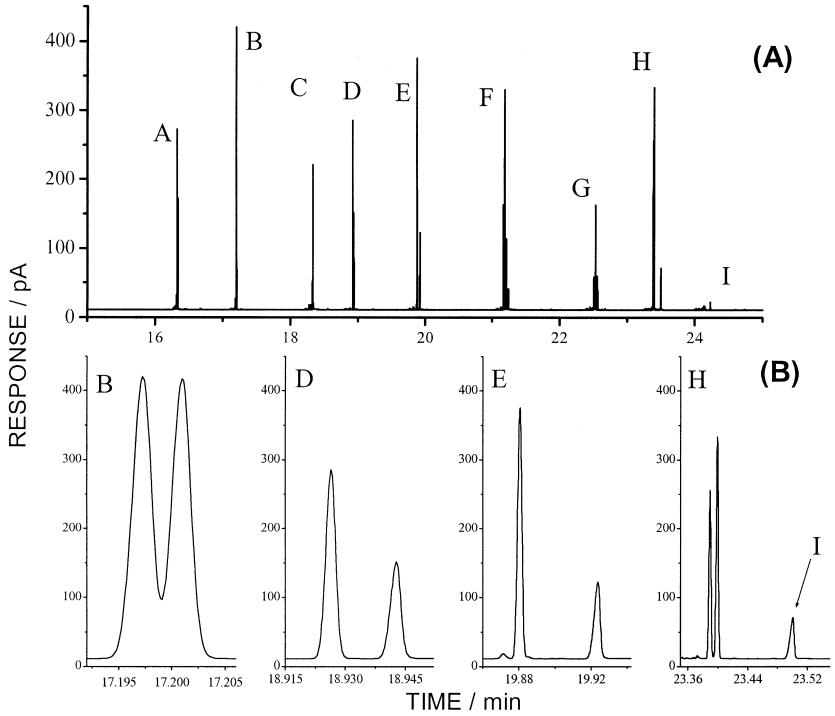

Fig. 7. Repeat of the experiment shown in Fig. 6, but with altered timing for trap movement given in Table 1, and using column set 2. Only a selection of expanded zones are included.

that zone compression has on peak detectivity. Forming bands into peaks as narrow as w_b=100–150 ms at the detector, compared with 5–10 s broad at the end of a single column analysis, gives peak height increases of maybe 30–60 times. Here, the only broadening to consider is that occurring on the short, fast second column. If the modulator is capable of introducing peaks of the order of 10–20 ms pulsed into the second column, then peak broadening on column 2 will exceed this by many-fold. For instance a 1 m column with 5000 plates/m, having a solute with a 3 s elution time will give a peak of w_b~170 ms. Since we do see peaks of this dimension in our rapid second dimension, then the broadening generated by the ''re-injection'' step is not too significant. Second dimension chromatograms also have a small phase bleed component at temperatures approaching 220°C or more, as can be seen on Fig. 8B. These peak are little retained, and so have narrow peak widths (ca. 60 ms) and elute before the analyte peaks. As peaks are retained longer, they are more broadened, and so for instance in Fig. 8C, zone E peak halfwidths for the 2 peaks are 330 and 390 ms, respectively (Table 2). Peak

Table 2
Peak widths and resolutions observed for components 12 and 12a with each column set

Parameter	D2=0.8 m BPX50		D2=2.0 m BPX50		D2=5.0 m BPX50	
	Peak 12	Peak 12a	Peak 12	Peak 12a	Peak 12	Peak 12a
t_R (min)	32.380	32.385	19.880	19.923	25.459	25.581
t_R after release event (min)	0.0300	0.0350	0.130	0.173	0.409	0.531
Peak w_h (min)	0.00162	0.00128	0.0031	0.00398	0.00528	0.00652
R_s	2.03		7.15		12.2	

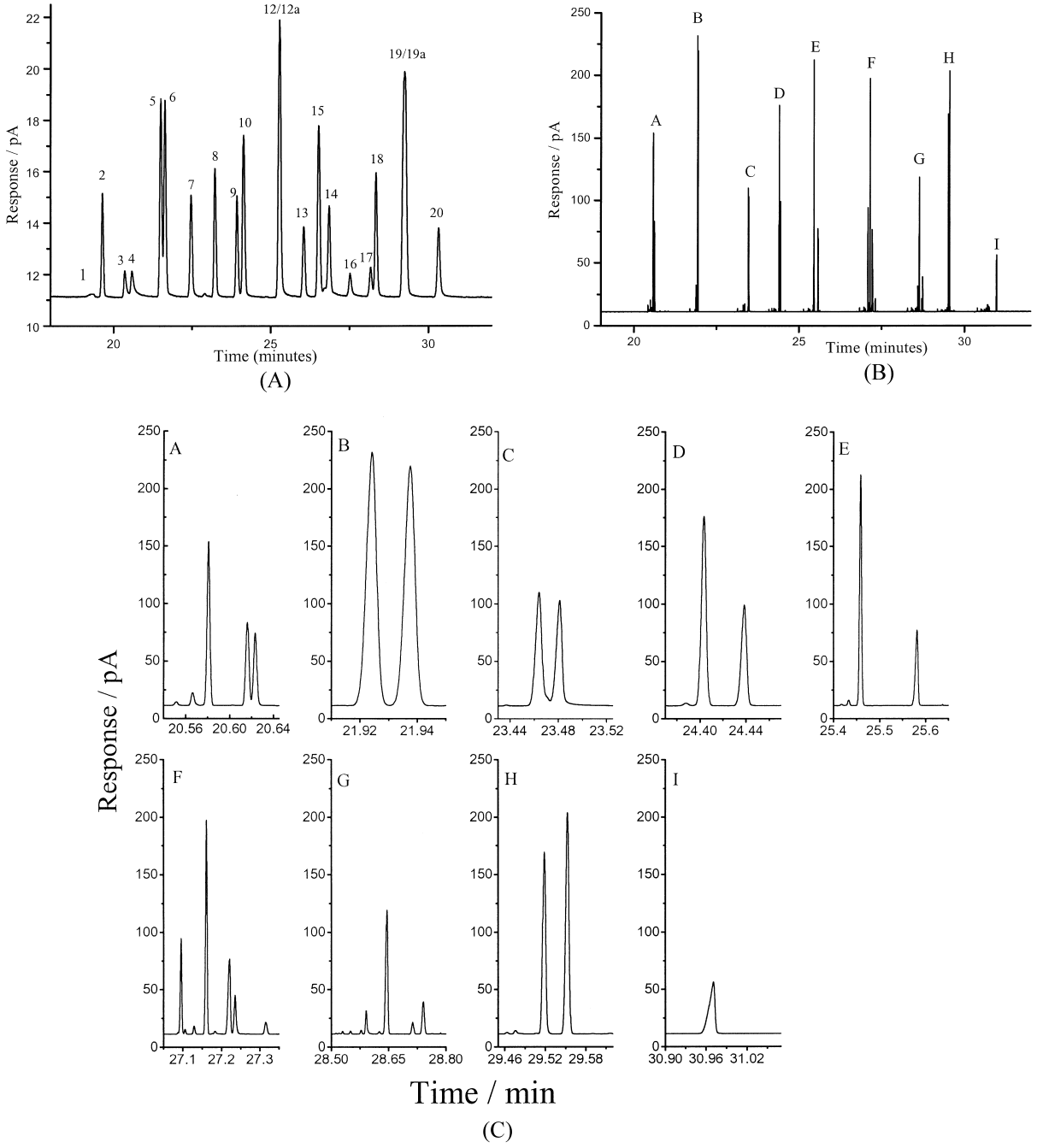

Fig. 8. (A) Normal GC analysis of the semi-volatiles aromatics sample on column set 3. (B) Repeat of the experiment shown in Fig. 6 but with a 5 m second column, and timings given in Table 1. (C) Expansion of each of the nine pulsed zones shown in (B).

height enhancements are better for the faster eluting peaks on the second dimension.

For instance peaks 13 and 14 in Fig. 8A correspond to peaks a and d in Fig. 9 (an expanded region of Zone F from Fig. 8C), but peak a is larger than peak d whereas 13 was shorter than 14. Peak B in Fig. 9 is a bleed peak, and sets of peaks marked S we call system peaks. Their origin is not known, but may be due to bleed, or trace carrier gas organics. Peak halfwidths of the labelled peaks a–f are: 156, 270, 258, 300, 420, 330 and 420 ms, respectively. This second dimension chromatogram was produced from a modulation event at time 26.75 min. If we take the bleed peaks as an estimate of the unretained peak, then the efficiency (effective plates) for peak f is 5400 plates/m, which is an acceptable value for the 0.1 mm I.D. capillary.

3.5. Example hypothetical case study for time-resolved targeted MDGC: polychlorinated biphenyl (PCB) specific congener analysis

PCB specific congener analysis may target either an abbreviated seven congener set, or an expanded set of about 19 or more PCBs. One report using MDGC [5] showed almost complete baseline separation of the set of seven congeners from a range of arochlors. The only incomplete separation was for congener CB138, which had an overlap problem with CB160/161/163. This study used a BPX5-HT8 column combination, but also used conventional heartcut with a suitable flow switching mechanism. Cryofocussing the heartcut zones meant that at the conclusion of the first column elution, the oven had to be cooled, the cryofluid turned off, and the oven temperature program then repeated. One analysis can take up to 2 h.

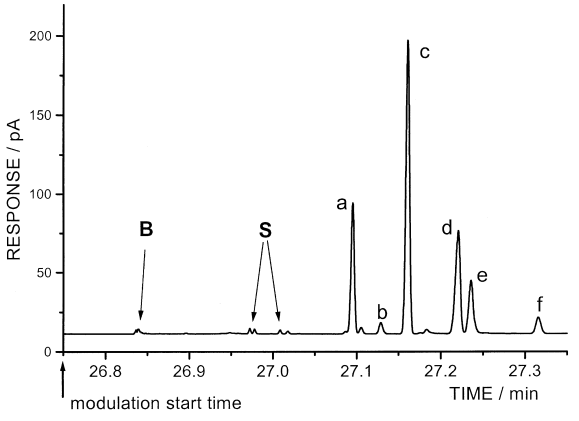

Fig. 9. Expansion of zone F from Fig. 8B. Peaks labelled B are bleed peaks, and S are termed system peaks. This second dimension chromatogram commences at the time when the modulation event occurs for this trapped zone (26.75 min).

Since MDGC requires careful adjustment of not only the timing of heartcuts but careful balancing of the heartcut and analytical columns, method set-up is more convoluted than using a single column. But the single column cannot reliably provide the specific congener information. The recommended approach with time-resolved target analysis will be to prepare a mixture of the specific congeners, obtain their retentions on the two-column set-up, make an appropriate retention time adjustment due to the extra second column (of the order of a few seconds), test the timing event program on a specific congener standard mixture, then perform the analysis. The correct column combination needs to be considered, and checking of the purity of peaks by suitable means. We previously found that the BPX5-HT8 column combination was a good choice for conventional MDGC, and so would be the first choice for the time-resolved cryogenic method described in this paper. Again, most probably a slightly longer second column would be beneficial. For PCBs electron-capture detection (ECD) is usually recommended. Since the present approach generates very fast peaks arising from zone compression, of superior sensitivity, then either regular fast responding FID can be used, or micro-ECD with rapid data acquisition, of at least 50 Hz, would be advised. Note that now ECD should be able to give detection to below ppb levels. The specificity advantages of ECD may be a consideration in the method.

4. Conclusion

The principles outlined in this paper demonstrate a new operational mechanism for multidimensional gas chromatography. Effective trapping of particular zones of a primary separation, followed by rapid introduction to a second column, can lead to improved separation performance. The method appears to incorporate most of the features of traditional

MDGC, but can produce fast analysis and significant response sensitivity increases. This is achieved by the manner in which the cryogenic trap is moved (modulated), which has not previously been described in this way. Clearly any GC analysis can incorporate the mechanism proposed, and could be used with for example chiral second dimension columns, or any other analysis which can benefit from the advantages that the method delivers. With electronic pressure control, peak retention precision and proper implementation of timing of the trap movement events should permit excellent selection of required peaks so that the first dimension resolution is not diminished by the collection of bands within the trap. Further experimentation will illustrate and expand upon the initial studies reported herein.

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