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Rapid sequential heart-cut multidimensional gas chromatographic analysis

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Abstract

A method is described which allows the sequential fast analysis of heart-cuts taken during the first column elution of an essential oil sample in a multidimensional gas chromatography experiment. In this investigation, a relatively short, narrow bore capillary column is used in the second dimension, with fast cryogenic modulation permitting rapid delivery of cryofocussed heart-cuts into the second column of the multidimensional arrangement. In this implementation, the total analysis time on the second column is of the order of 30 s, which is less than the duration of the sampled heart-cuts (1 min), with peak theoretical efficiencies of about 7000 m^{-1}. Thus, the method should allow on-line heart-cutting of as many discrete heart-cuts as one may require from the first dimension chromatogram, and so two-dimensional separation can be achieved for almost the whole sample in one single analysis without the need for repeat injections or cycling of the oven temperature. The method is demonstrated by the transfer and rapid re-injection of 1 min heart-cuts taken from an initial separation stage of peppermint essential oil. The cryofocussing and fast analysis step is shown to increase signal response by up to 40-fold. Total peak capacity in the described system is measured to be of the order of 1800, with capacities of about 20–30 for each 30 s second dimension analysis. By increasing the frequency of sampling to remove excessive (unused) time to develop the ^{2}D separation, it should be possible to achieve peak capacities of 5000 or more baseline resolved peaks.

Keywords: Gas chromatography, comprehensive two-dimensional; Cryogenic trapping; Rapid remobilisation; Peppermint oil

1. Introduction

Multidimensional gas chromatography (MDGC) is the act of subjecting discrete fractions or all of a sample to two or more independent gas chromatography (GC) separation steps. In GC, the transfer of effluent to an independent separation step is known as heart-cutting and is most commonly achieved using a pneumatic pressure controlled switch (Deans switch) or a moving mechanical valve [1,2]. MDGC was first established around the late 1950s and has become a well-established technique with the motivation being the need for increasing separation power in gas chromatography [3]. In a two-part review [4,5], Bertsch summarized the history and recent developments of multidimensional gas chromatography.

A range of operational variations exist for such coupled column instruments [6,7]. For instance, the transferred heart-cut may be passed unhindered to the second column or could be focused at the start of the second dimension (normally by cryogenic means). One, or multiple, trap(s) can be used for heart-cut collection where they are stored until the secondary column is available for subsequent individual analysis. Both columns can be contained within the same oven or in separate ovens according to the demands of the method. Whilst it is recognised that the multidimensional approach gives improved separation capability, one of the difficulties in implementation is that it is often not possible or it may be tedious to apply the two-dimensional approach to the whole sample. Thus, target analysis of, e.g. specific compounds in a sample might be the more common application of MDGC.

In the investigation of a very complex tobacco flu-cured essential oil sample, Gordon et al. identified 306 components [8], 80 of which were reported in tobacco for the first time. The instrument employed two ovens, and a single trap for the collection of a single heart-cut. After the completion of each heart-cut analysis, the second oven was cooled in preparation

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for the analysis of the next heart-cut. Thus, it was feasible to only analyse one heart-cut per injection. Consequently, the total of 23 heart-cuts required 48 h of instrument time. This tempers the impressive separation performance reported.

Wilkins and coworkers discussed the potential time reduction that could be achieved using multiple parallel cryogenic trapping, rather than just a single trap as used in Gordon et al.'s work [9]. For example, a primary separation of 30 min duration could have saved at least 6 h if Gordon used a six-trap instrument [10]. Using an instrument comprising six parallel cryogenic traps, Wilkins and coworkers analysed an unleaded gasoline sample [11], taking five contiguous 72 s heart-cuts from the one injection which were released in turn onto the second column for further separation. The total time for complete analysis of the unleaded gasoline was 2 h, compared with 3–4 h if only one cryogenic trap were used. Whilst faster analysis may have been possible by using higher resolution narrow bore capillary columns, this was not demonstrated due to the practical limitations (mainly sampling speed) of the infrared detector employed.

In 1991, Liu and Phillips [12] reported a "comprehensive two-dimensional" GC technique (GC × GC) that could subject all sample components to the total separation potential of two sequential GC columns, with total analysis time determined only by the elution time of the first column. The GC × GC literature describes applications demonstrating the complexity of cigarette smoke using TOFMS detection [19], and high resolution essential oil analysis [13] including chiral analysis [14], and may be compared with the above traditional MDGC studies. These illustrate the promise and potential of GC × GC, compared with the discrete 'unit-operation' approach of MDGC. This essentially realised the proposition by Giddings [15] where maximum separation power can be achieved by comprehensively coupling the two separation dimensions. In GC × GC, a modulation process effectively collects sequential parts of the first column effluent and rapidly re-injects each to the second column. The period of collection/re-injection process should be faster than the bandwidth of an individual peak eluted from ^{1}D (the first dimension column), with about four samplings per ^{1}D peak considered acceptable [16], and so each component is now split into a number of separate sub-peaks. Elution on ^{2}D (second dimension) must therefore be very fast — of the order of the modulation period. Since this must be about 1–5 s, then ^{2}D must likewise provide very fast analysis, so typically GC × GC uses short (ca. 1 m), narrow bore (ca 0.1 mm i.d.), thin film (ca. 0.1 μm film thickness) columns as the second column separation medium. Perhaps, the only drawback of GC × GC, a technique that this group [17] and others have been developing over the past 5 years, is the need to present the data in two-dimensional format, and the consequent questions surrounding automated data processing.

The experience acquired over recent years dedicated to fast modulation processes and with an appreciation of classical MDGC goals has suggested that alternative opportunities exist for advanced separation analysis, and thus the present work revisits MDGC approaches. By using rapid microvalve switching, whilst maintaining the very effective re-injection capability achieved with the cryogenic modulation process (referred to as the longitudinally modulated cryogenic system, LMCS) developed in this laboratory [18,19], the role of fast ^{2}D separations combined with heart-cutting MDGC can be further studied. In a recent study [20], the use of the proposed system described here using a column geometry very similar to that used in comprehensive two-dimensional gas chromatography was described. However, the separation capacity of ^{2}D was limited. That study suggests that a longer ^{2}D column would provide considerably improved separation, and that with fast elution on ^{2}D combined with rapid remobilisation, a new way to perform multiple fast MDGC throughout a considerable portion of a primary column separation might be possible. The recent study of MacNamara [21], of pesticides in lemon oil using a conventional MDGC system with normal column dimensions, reported target analysis of a small number of pesticides and produced peaks of normal capillary GC dimensions. Such an approach will still not be conducive to significant expansion of total peak capacity. The length of the ^{2}D is now only limited by the time taken for the ^{2}D analysis to be completed before the next heart-cut is delivered to the second column. This paper describes initial experiments and observations using this approach.

2. Experimental

2.1. Gas chromatography system

All analyses were performed using an Agilent Technologies 6890 model gas chromatograph equipped two flame ionisation detectors, 7683 series auto sampler, two injection modules, and Chemstation software. The GC was retrofitted with an Everest model longitudinally modulated cryogenic system (Chromatography Concepts, Doncaster, Australia), and a 10-port microswitching valve (model EH6C10WT, VICI Valco Instruments, Houston, TX). The GC was equipped with a split/splitless injector, operated at 250 °C; an injection volume of 1.0 μL was employed in split mode (20:1, 20.0 mL/min) unless otherwise stated. The carrier gas was hydrogen, and the column head pressure was 35.19 psi. The schematic diagram of this equipment is based on that reported earlier [20], and is shown in Fig. 1, incorporating the longer ^{2}D column. The switching valve may be replaced with a Deans switch if required, should activity of a valve be of concern. In the present study, over a period of 1 year and routine operation up to 250 °C, there was no apparent deterioration in valve performance.

2.2. Separation columns

The column set consisted of a ^{1}D fused silica capillary column of 95% methyl–5% phenyl polysilphenylene-siloxane

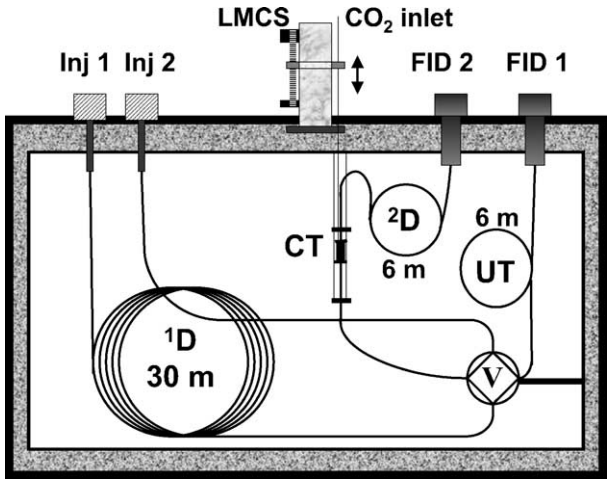

Fig. 1. Schematic diagram of the experimental set-up. FID1 reports the normal single column GC result, or a sample with the heart-cuts absent. FID2 reports the chromatogram(s) arising from each heart-cut event, either with or without cryofocussing and remobilisation. Valve V is used to select heart-cuts to transfer to column ^{2}D.

(BPX5) phase (0.25 μm film thickness, d_f) with dimensions 30 m × 0.25 mm i.d., as the first column, terminating at the switching valve. Two columns lead from the valve to the detectors. The first is a segment of uncoated, deactivated fused silica capillary (5.9 m × 0.10 mm i.d.) connected to FID1. The second is the ^{2}D separation column, with polyethylene glycol (BP20) phase (0.10 μm d_f) of dimensions 6.6 m × 0.10 mm i.d. and is fed through the cryotrap, and then is connected to FID2. The ^{2}D distance from the cryotrap to the detector is slightly shorter than this, at about ∼6.45 m. All columns were from SGE International (Ringwood, Australia).

2.3. GC conditions

All experiments reported were programmed at a rate of 3.0 °C/min beginning at 1 min, the oven temperature rose from an initial temperature of 60 °C to a final temperature of 246 °C with a total analysis time of 63 min.

2.4. Samples

As a reasonably complex application sample, peppermint essential oil was used where 1 min heart-cuts were taken through the most convoluted area of the separation. The peppermint essential oil was obtained from Auroma Pty. Ltd. (Hallam, Australia). The peppermint oil sample was prepared for analysis by diluting 25 μL of peppermint oil in 975 μL of hexane. This sample was then injected by split mode (20:1 split ratio) into the GC column.

2.5. Description of operation

2.5.1. Operation 1

Heart-cuts of 1 min duration were taken throughout the most convoluted area of the single dimension chromatogram, which comprises both major and minor components. This area ranged from 20 to 30 min with the five 1 min heart-cuts taken at 20–21, 22–23, 24–25, 26–27 and 28–29 min, respectively. The heart-cuts and remobilisation times when the cryotrap is simply moved down (towards the incoming carrier gas flow, see Fig. 1) are listed in Table 1. Heart-cutting diverts the selected zone away from the uncoated capillary tube and to the ^{2}D column. Clearly, chromatographic regions 21–22, 23–24, 25–26 and 27–28 travel through the uncoated tube to FID1.

Table 1
Chromatographic data and efficiencies calculated for selected components in cryotrapped heart-cut 4 event, with remobilisation at 27.2 min

t_R (min)	^2t_R (s)	w_h (s)	N (theoretical plates)	N (effective plates)
27.368	10.08	0.1098	46690	10070
27.377	10.62	0.108	53570	12940
27.413	12.78	0.1344	50090	16700
27.423	13.38	0.1536	42040	14950
27.43	13.8	0.1608	40800	15120
27.446	14.76	0.1434	58690	23600
27.502	18.12	0.1986	46120	22730
27.514	18.84	0.1944	52030	26480

t_R is the total time taken for the solute to reach the detector, ^2t_R the time the solute takes to traverse the second column, w_h the peak half width, and N the efficiency. For the 6 m second dimension column, it is estimated that the unretained peak will be about $^2t_M \sim 5.5$ s.

2.5.2. Operation 2

Operation 1 may also be performed with cryotrapping of each of the five 1 min heart-cuts at the head of the ^{2}D column. Each of the heart-cut fractions will be separately remobilised or re-injected into ^{2}D and eluted before the next heart-cut is sent to ^{2}D. Remobilisation occurs by moving the cryotrap along the column to expose the trapped solute, and is done at 21.2, 23.2, 25.2, 27.2 and 29.2 min. In this instance, resolution of specific components on ^{2}D may be calculated to compare with resolution obtained on the total column set. It is possible to collect more than one heart-cut in the one trapping event, but there is little justification for this operation apart from demonstrating that collecting too much of a heart-cut zone will complicate the subsequent ^{2}D chromatogram. It is important to ensure that column separation capacity is not compromised by introducing too many components into the short ^{2}D column during each heart-cut event [22].

3. Results and discussion

Fig. 2A is the original chromatogram of peppermint oil, which wholly passes through the uncoated tube (UT) and to FID1. In common with many essential oils, this sample contains a number of major components (here, they are off-scale with responses ca. 400 and 700 pA, so that the minor peaks can be seen), and many minor components. The

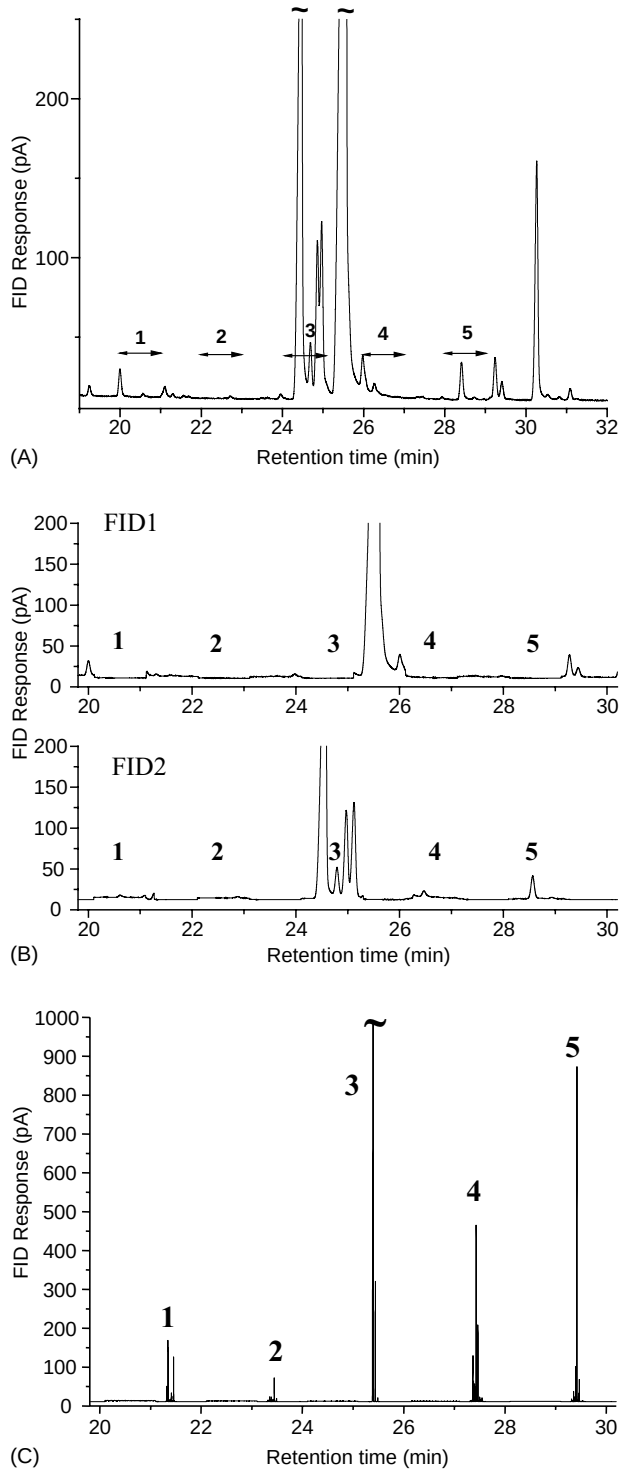

Fig. 2. (A) Expanded gas chromatogram of peppermint essential oil showing the selected heart-cuts and trace components. The two major peaks have response maxima of 400 and 700 pA, respectively, and both exhibit overloading. (B) FID1: peppermint GC trace on FID1 with heart-cuts (denoted 1–5) absent (only non-heart-cut sections pass to the FID1). FID2: heart-cut sections 1–5 recorded at FID2, after passage through ^{2}D column, but without cryotrapping. (C) The five heart-cuts shown in (B) (FID2) are separately sequential cryotrapped and rapidly remobilised, to produce fast GC analysis on ^{2}D with good efficiency and response. Heart-cuts and remobilisation times given in Section 2.

five heart-cut events are shown on this chromatogram. There is no particular reason for choice of the heart-cut times, but for convenience are conducted at 1 min intervals, over a total time of 10 min (times are listed in Section 2). The total number of events in this case is controlled by the events table in the software, and for the system here is rather limited. A more liberal events table will allow a more extensive number of heart-cuts, which in principle can be limitless. Fig. 2B is a display of the total sample with the heart-cutting implemented. Thus, Fig. 2B (FID1) shows that regions 1–5 are absent (i.e. the FID1 result) and the lower trace (Fig. 2B, FID2) is the corresponding heart-cuts that travel through the cryotrap (here, without cryogen supplied) to FID2. It should be apparent that the arithmetic summation of Fig. 2B (FID1 and FID) should be equivalent to Fig. 2A. Since ^{2}D is a retaining column, there is a small finite retention increment (and in this case also a possible small shift in retention) of the components, which would have to be taken into account if a direct comparison of the FID2 result with the selected heart-cut zones originally seen on FID1 is required.

The effect of cryotrapping on each of the heart-cut zones can be seen in Fig. 2C. The major peak, in heart-cut zone 3, is significantly off scale (response 8000 pA, but is also significantly overloaded, for the 400 pA peak in Fig. 2A). For a non-overloaded peak comparison, the peak at 28.5 min in Fig. 2A has a response of 30 pA, compared with its corresponding response in Fig. 2C of 800 pA (almost 30-fold increase). The extent of response increase depends upon the extent of zone compression (peak widths) in the first dimension, and the time that a peak elutes on ^{2}D — the earlier eluting solutes have narrower peaks, and proportionally greater response increase. Note that compared to a normal GC analysis, the fast elution reported here requires a faster data acquisition rate, which does increase detector noise marginally.

The narrow peaks in Fig. 2C cannot be readily displayed unless an expanded scale is used. Fig. 3 is an expansion of each of the five heart-cuts, where time zero for each plot is the time that the trap is moved to permit the cryofocussed solutes to heat up and travel to the ^{2}D separation column. Again, to permit the small peaks to be seen, the vertical response scale is also expanded. The vertical comparison also allows some appreciation of the breadth of the separated zones or windows on the second column. This should correspond, to a first approximation, to the polarity range of the solutes in each of the heart-cut zones, where low polarity solutes are expected to be the least retained on the polar polyethylene glycol phase. The proper interpretation would be arrived at if the individual identities of each of the peaks was known, so that this correlation might be better rationalised.

Since the oven temperature increments by about 6 °C between successive heart-cuts, it may be asked whether the isolation of the separate heart-cuts serves an improved separation purpose, if the more volatile compounds can be isolated from the later peaks if a single narrow bore capillary analysis were performed. First, Fig. 3 suggests that there is

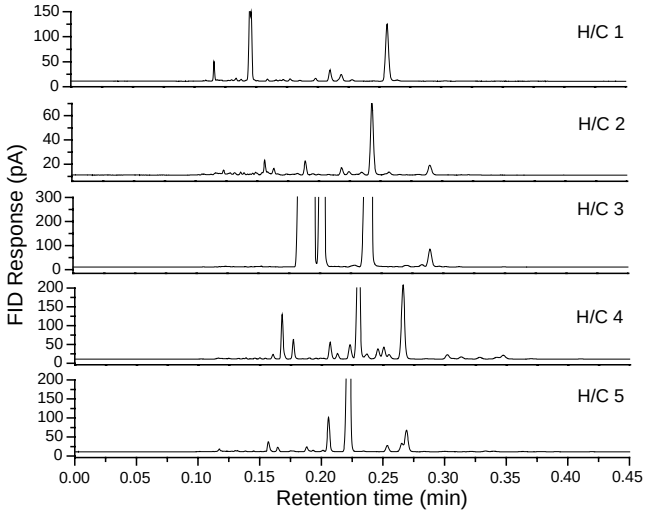

Fig. 3. Vertical alignment of each heart-cut (time = 0 corresponds to the remobilisation time of each heart-cut) to demonstrate the component elution (separation) window for each heart-cut. Vertical scale expanded to show detail of smaller components.

little spare separation capacity to fit in more components before the separation window in subsequent heart-cuts. But to test this, two neighbouring heart-cut events were collected together, and only after the second, was the cryotrap moved. This result is compared with the selection and trapping of each heart-cut in separate analyses, but remobilisation at the later heart-cut trap movement time. Fig. 4 is the result of this trial. In Fig. 4A, the dotted trace is the peak-rich result for heart-cut 1, held until the remobilisation step of heart-cut 2 (i.e. 23.2 min), whilst the solid line is the result for heart-cut 2. There is considerable peak overlap, so if too wide a heart-cut is taken, separation performance will deteriorate. Fig. 4B shows the result when both heart-cuts 1 and 2 are collected together in one single trapping event and remobilised at 23.2 min. Clearly, effective separation requires heart-cuts of limited duration.

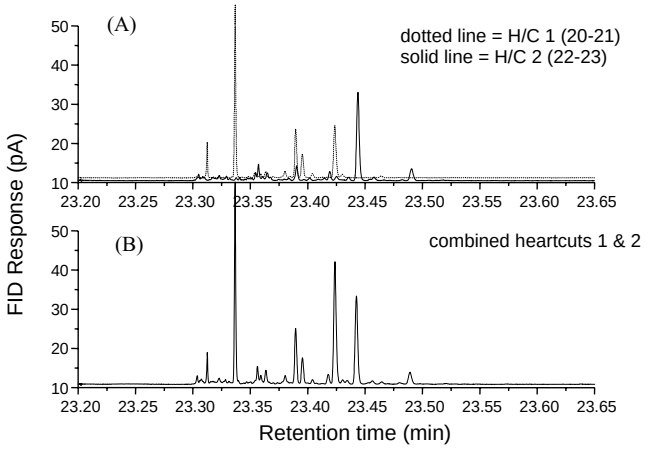

Fig. 4. Comparison of separate collection of heart-cuts 1 and 2, each remobilised at 23.2 min (A), with collection of heart-cuts 1 and 2 together, and both remobilised at 23.2 min (B).

As a confirmation of enhanced separation performance of the heart-cut/cryotrap process, the result of Fig. 3 (H/C2) can be contrasted with the corresponding normal GC result (Fig. 2A, heart-cut 2) and the heart-cut without cryotrapping result (Fig. 2B, heart-cut 2). As stated earlier, there is a slight difference between the result of the passage of the zone through the uncoated tubing, and the same zone passed through the ^{2}D column (see minor differences between Fig. 2A (heart-cut 2) and Fig. 2B (heart-cut 2)), but one might think that there are only one, or maybe two peaks in this chromatogram. However, for this equivalent heart-cut region, Fig. 3 (H/C2) shows many well separated, good response peaks, that one can only imagine would be undetected in normal GC analysis. Note that in Fig. 3 (H/C2), a step response is seen above chromatographic detector baseline when no sample is introduced into the ^{2}D column. This corresponds to either chemical response (unresolved peaks), and/or column bleed from the long primary column. This step response arises at about 22.1 min, which should approximate the unretained peak time (or void time) on ^{2}D, i.e. about 6 s. A similar value of 5.5 s is found by calculation.

Since the cryotrap collects all effluent from the end of the primary column in each of the trapping events, it is important to conduct blank injections to confirm that the peaks are not artifacts of, for example, phase bleed. In Fig. 5, the dotted line is the blank injection result for the region equivalent to heart-cut 4. The solid line indicates that a large number of peaks arise from the essential oil, and are authentic components from the sample injection. Many of these peaks will not be seen in the original GC trace.

Fig. 5 data have been interpreted on the basis of peak widths and retention times on the second column (time taken from the movement of the cryotrap) in order to evaluate column efficiency for selected peaks A–E, and peak capacity. Table 1 reports the widths and efficiencies (theoretical plates) of these peaks in this chromatogram. Generally theo-

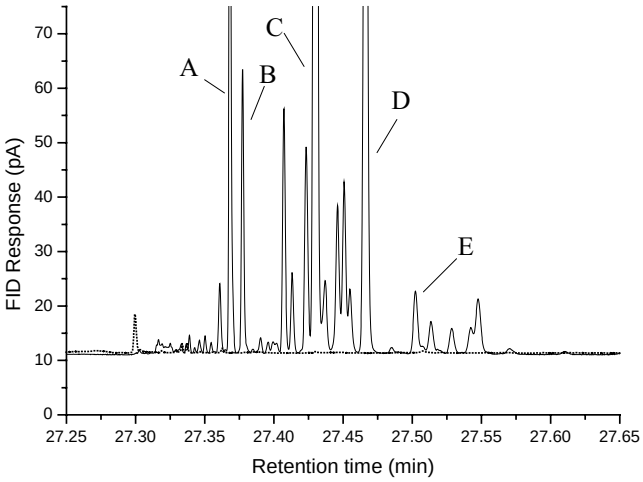

Fig. 5. Heart-cut 4 chromatogram showing overlay of the peppermint injection with a separate trace of a blank injection (dotted line). Quantitative data for identified peaks A–E are given in Table 2.

Table 2
Quantitative data for selected peaks in heart-cut 4

Peak	Replicate 1		Replicate 2		Replicate 3		Overall peak area (%R.S.D.)
	Solute t_R (min)	Peak area (pA s)	Solute t_R (min)	Peak area (pA s)	Solute t_R (min)	Peak area (pA s)	
A	27.368	13.37	27.368	13.32	27.369	13.34	0.2
B	27.378	6.18	27.377	6.12	27.378	6.19	0.6
C	27.431	76.55	27.430	76.43	27.431	75.28	0.9
D	27.467	36.1	27.466	36.09	27.467	36.11	0.1
E	27.503	2.67	27.502	2.74	27.502	2.81	2.6

Remobilisation time = 27.2 min. Refer to Fig. 5 for peak identification.

retical plates of the order of 40,000–50,000 are obtained. In the absence of a direct measure of the unretained peak in this experiment for each heart-cut, if a t_M of 5.5 s (giving a carrier flow velocity of 110 cm/s) is taken for heart-cut 4, then effective plates of 10,000–20,000 are obtained for selected peaks in Fig. 5. Thus, theoretical and effective plates of about 7000 and 4000 m^{-1}, respectively, are obtained for the 100 μm i.d. ^{2}D capillary. These data are less than the theoretical value for a capillary column of these dimensions, and this may be due to a higher carrier flow than optimum, and a lower coating efficiency for the polar polyethylene glycol phase. The peak capacity of the second dimension can be estimated by taking an average peak width for a second dimension peak, and calculating the total number of resolved peaks that can be placed in the separation window. By using a peak width definition of 6σ, about 30 equally resolved peaks can be separated within about 24 s on the second column (note that no peaks eluted later than about 30 s on the second column). In a total analysis time of 60 min, this equates to a peak capacity of about 1800. Since only 40% of the separation space is used in the present case, the sampling frequency could be increased, or a longer ^{2}D column used, to get even greater separation capacity. Taking the value of 40% as the start point, it can be estimated that the total analytical peak capacity might be about 5000 or more. This is considerably more than a normal (or even a narrow bore) capillary, and supports the notion that the present method provides expanded peak capacity, as well as improved response.

Finally, the analysis of the sample was performed in triplicate, and the same heart-cut compared across the three chromatograms by both overlaying the expanded heart-cut results, and by calculation of statistical data. Chromatograms (not shown) indicate that the responses are well preserved from run to run in this experiment. Table 2 reports selected data for five components (A–E) in heart-cut fraction 4, including their total retention times and areas. Note that the recorded retention times differ by no more than 0.001 min, and that quantitative response data vary by no more than R.S.D. of 1.0% for the replicate injection, except for the smallest of the selected peaks. Thus, excellent reproducibility is obtained.

There are a few additional points to be recognised in the present work. First, it is possible to split peaks between two different trapping events, and so quantitative analysis in this instance would require addition of each of the peaks of a solute. Second, holding the solutes in the trap requires them to be effectively immobilised at the trapping temperature. For highly volatile solutes, the trap will require effective supply of cryogen. Note that heart-cut 1 has been held in the cryotrap for up to 3 min, without any breakthrough noted. Being only 3 cm long, the trap must perform very well in order to hold the more volatile solutes. Note that the solvent tail here is not held for a full 1 min trapping period, and suffers breakthrough. For less volatile solutes, the trap performs reproducibly and reliably. Placement of the system into a GC–mass spectrometer instrument will allow mass spectra for all solutes to be obtained, and this is the next objective of this work. Note that since these peaks are broader than those encountered in comprehensive two-dimensional gas chromatography, the quadrupole mass spectrometer should be suitable for such work, as opposed to the time-of-flight instrument normally recommended in GC × GC.

4. Conclusions

This work has described a relatively simple process for performing heart-cutting in an MDGC approach with cryotrapping and rapid re-injection of the heart-cuts into a short, narrow ID capillary column to allow complete, high resolution separation of each heart-cut within the sampling time of the primary column effluent. The system is more complex than a single column GC set-up, requiring two injectors and detectors, a switching valve and the cryotrapping unit, however, in respect of multidimensional systems, it is not complex. It should be possible to implement this approach for almost a complete sample, with contiguous heart-cuts taken over the whole primary column elution of the sample, to give a complete multidimensional gas chromatography result for all components of the sample. This method offers considerable time savings, improved resolution and considerable response increase over conventional MDGC. The principles employed here derive from the considerations of comprehensive two-dimensional gas chromatography, where high performance modulation and fast second dimension analysis is critical.

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