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Parallel cryogenic trapping multidimensional gas chromatography with directly linked infrared and mass spectral detection

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ABSTRACT

This paper describes successful implementation of multiple trap multidimensional gas chromatography (GC) directly linked with parallel Fourier transform infrared (FT-IR) and mass spectroscopy (MS) detectors. For complex mixture separation, six parallel cryogenic traps are interposed between a first-stage GC pre-column and a second-stage GC analytical column. With proper choices of heart cut time intervals, this multiple parallel cryogenic trap approach allows expansion of the practical analytical dynamic range and accommodates the separation constraints of a combined GC–FT-IR–MS system. An unleaded gasoline sample is analyzed with respect to the degree of secondary separation and to the reproducibility of adjusted retention times. The results of cryogenically trapping heart cuts using both with 72- and 12-s trapping times are presented. Shortening the trapping times from 72 to 12 s results in a significant improvement in the analytical column separation and identification with infrared and mass spectra. Thus, use of multidimensional separation coupled with multispectral detection may provide increased reliability of complex mixture component identification.

INTRODUCTION

Combination of multiple types of spectroscopic detection with gas chromatographic separation is a powerful method for analysis of complex mixtures [1]. There have been several recent applications of GC–FT-IR–MS ranging from environmental component analyses [2–4] to essential oil [5,6], biochemical, and clinical analyses [7,8]. When combined infrared and mass spectral detection are used, the specific gas chromatographic separation method used is dictated, to some degree, by the constraints of detector dead volume and sensitivity. As a consequence, use of narrow-bore capillary GC columns is precluded and chromatographic performance is therefore limited. Thus, it is necessary to address the problem of reduced resolution that is inherent when one uses larger bore capillary columns that are compatible with these information-rich detectors. Obviously, if mixtures, rather than pure compounds reach the infrared and mass spectral detectors, the quality of combined spectroscopic library searches will be compromised and could lead to incorrect or ambiguous identification of mixture components. It is therefore clear that, in order to realize the true analytical potential of a combined separation and multi-spectral analysis system, an improved separation strategy is mandatory.

Recently, a multi-valve based multidimension-

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al gas chromatography (MDGC) system with two parallel cryogenic traps interposed between a first stage GC precolumn and a second stage GC analytical column with infrared and mass spectral detection was successfully implemented [9]. That study demonstrated the feasibility of carrying out a valve-based MDGC separation employing two parallel cryogenic traps for heart cutting. Here it is demonstrated that use of a new experimental setup, incorporating *multiple* parallel cryogenic traps, allows much improved performance for MDGC, in the context of a GC–FT-IR–MS analysis system.

Although MDGC [10–13] is a conceptually attractive method for complex mixture analysis, its applications to practical analytical problems has been relatively limited. However, it appears that use of multiple cryogenic traps allowing parallel heart cutting, combined with computer automation should obviate some of the previous difficulties. This paradigm, in the limit of short heart cut trapping times and a very large number of traps is conceptually equivalent to the approach of Phillips *et al.* [14]. The difference between the two methods is analogous to the difference between dispersive and Fourier infrared spectrometry. Depending on the nature of analysis, one can utilize a multiple parallel cryogenic trapping system to carry out heart cutting using 1–3 min trapping periods or higher resolution heart cuts employing 10–20-s trapping times. With longer heart cut times, the system behavior would be closer to a coupled column technique and, with a shorter heart cut time, the system would behave as a true multidimensional system [15]. Either approach has its advantages and disadvantages. With longer cut times an analyst can quickly estimate the approximate nature and number of components present in a complex mixture. Use of shorter trapping periods not only provides detailed information about the number and nature of the components, but can permit sample enrichment for trace components, and can reduce the required dynamic range within individual second stage chromatograms. In one sense, the choice can be described as a trade-off between increased information and longer analysis time versus less information and shorter total analysis time.

EXPERIMENTAL

Apparatus

The parallel cryogenic trap system was designed around a Hewlett-Packard GC–FT-IR–MS system, which was utilized as the basic instrument. The details of the instrument modifications and chromatographic conditions have been previously described [9]. Fig. 1 shows the schematic of the multidimensional system used in the work described here. This system employs two six-port rotary selection valves (Rheodyne, Cotati, CA, USA; 300°C maximum temperature) with one common input line and six individual output lines for routing analyte to selected traps and subsequent reinjection of trapped analytes onto the analytical column. Unlike the high performance on/off valves previously utilized for trap selection [9], the present valves allow selection of only one trap at a time. The six traps are fabricated from 1/16-in. (1 in. = 2.54 cm) stainless-steel tubing. Control of liquid nitrogen flow through the traps is accomplished by means of quick acting toggle valves (Supelco, Bellefonte, PA, USA).

Reinjection technique

Reinjection is carried out by selecting an unfilled trap to use as a trap bypass and then

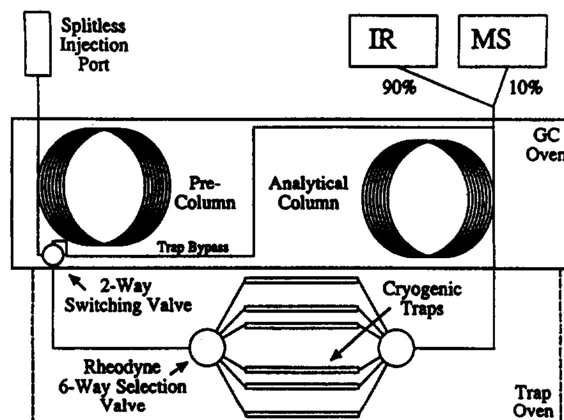

Fig. 1. Schematic diagram of the six-trap multidimensional gas chromatography system. The pre-column is a 30 m × 0.32 mm × 1.0 μm DB-1701, and the analytical column is a 30 m × 0.32 mm × 1.0 mm DB-5 column. The parallel traps are placed in an external oven located on the top of the HP 5890 gas chromatograph.

turning off the liquid nitrogen to all the traps and delaying any reinjections until the traps equilibrate to the external oven temperature (250°C).

Rotary valves

The present design significantly reduces dead volume and metal wall contact area. Valve rotors are made from an inert polymer with an internal volume of approximately 2 μl.

Sample

The sample analyzed in the present study is a unleaded gasoline sample which, for analysis, was injected using 0.5 μl splitless injections with a 50 ml/min purge at 55 s into the run. Fig. 2a shows the first 20 min of the precolumn chromatogram of this sample. The secondary separation of the segments chosen for heart cutting are shown in Fig. 2b. In the first set of experiments, five segments were chosen for heart cutting. Trapped sequentially were components eluting from the precolumn consecutive 72-s periods beginning at 6 min after sample injection. A

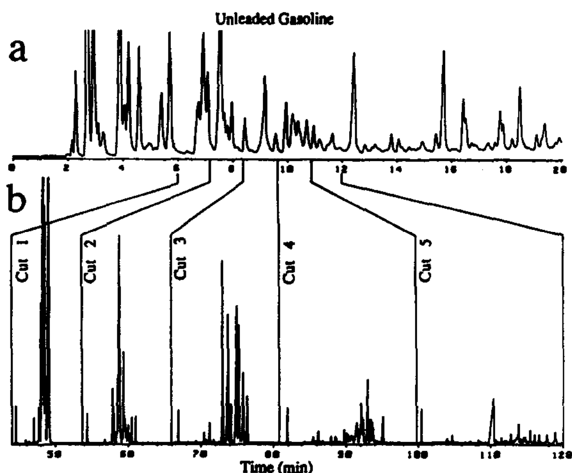

Fig. 2. (a) The first 20 min of the Gram–Schmidt reconstructed total IR response chromatogram from the precolumn separation of the unleaded gasoline sample. The areas between the lines and labeled are the 72-s heart cuts that were selected for a second stage of separation. (b) Total ion chromatogram (TIC) of the five heart cuts for run A. The five heart cuts were released to the analytical column from the traps in the sequence they were collected by the oven equilibrated method.

second set of experiments explored higher resolution analysis by sequential cryogenic trapping, for 12-s periods of precolumn eluents emerging between 7.5 and 8.5 min.

Retention time data

Two separate experiments were performed to estimate the average adjusted retention time variation. The adjusted retention time was taken as $t_R - t_M$ where t_R is the retention time of a component peak and t_M is the retention time of unretained CO_2. Both experiments were performed by making five consecutive injections and trapping the precolumn region from 8.4 min to 9.7 min in five different traps per experiment. In experiment A, the secondary separation of each of the trapped sections was performed isothermally at 30°C, and in experiment B the separations were performed isothermally at 50°C. Adjusted retention time data were derived by the Hewlett-Packard data acquisition computers from the Gram–Schmidt reconstructed chromatograms [16]. Five peaks were chosen for analysis in experiment A, and eight peaks for experiment B.

RESULTS AND DISCUSSION

The primary focus of this investigation is the design of a simple multiple parallel cryogenic trap MDGC system, the reproducibility of retention times relative to CO_2 (which served as an internal standard), and other experimental features that are unique to a multi-parallel cryogenic trap MDGC system. The unleaded gasoline sample used here for evaluation purposes is chosen because it has a conveniently large number of components and is well-suited for the experimental questions posed, rather than as a test of the qualitative analysis capabilities of the system. Because it is a hydrocarbon mixture containing primarily C_3 to C_{12} species, it does not contain components representing a wide range of polarity or functionality. Thus, the issue of qualitative analysis is secondary in this study. The first peak in each heart cut section in Fig. 2b corresponds to the unretained CO_2 peak and retention times are mea-

sured relative to that. It is interesting to note that this CO_2 is roughly the same height peak in all the cuts. This uniformity of height reveals that there are no significant leaks in the capillary–valve interface. If there were, the relative quantity of CO_2 detected when the contents of different traps were analyzed would be non-uniform. It appears that the source of CO_2 in these analyses is a minor impurity in the carrier gas which is accumulated in the traps during the trapping time. In Fig. 2a, 30 observable peaks are seen in precolumn chromatogram over the period for which heart cuts were subsequently taken. After MDGC separation using the analytical column to further separate these five cuts total approximately 93 .

Figs. 3a and b show the secondary separation of the 72-s cuts 1 and 2. The numbers above the peaks represent the cut number in which that peak appears in the series of 12-s cuts shown in Fig. 3c. Fig. 3c shows analytical column chromatograms obtained by trapping five 12-s segments from the region of the precolumn chromatogram corresponding to the second heart cut (components eluting between 6 and 7.2 min). As expected, the sum of the five chromatograms in Fig. 3c compares well with the corresponding chromatogram presented in Fig. 3b. However, when the analytical column chromatogram in Fig. 3b is compared with the individual chromatograms in Fig. 3c, it is obvious that much improved chromatographic resolution is obtained.

Qualitative infrared and mass spectral library search identification of the separated components appearing in Fig. 3c was carried out using procedures previously described [17,18]. In most cases structural classifications, rather than specific identifications, result (See Table I). A combination of factors can account for the fail-

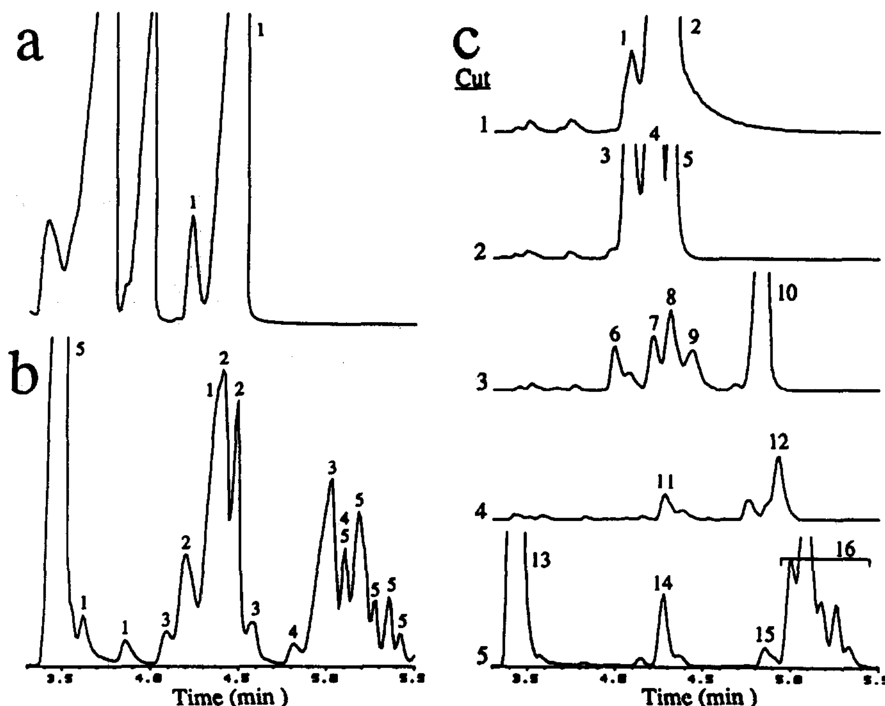

Fig. 3. An expanded view of the total ion chromatograms of the 72-s cuts 1(a) and 2(b). The peak labels represent the cut in which that particular peak appears in (c). (c) Total ion chromatograms of the five 12-s cuts over the 7.5–8.5-min range. Peak labels correspond to the component designations in Table I.

TABLE I

LIST OF COMPOUNDS IDENTIFIED IN FIG. 3 BY IR AND MS

The IR and MS libraries contain spectra of approximately 3000 and 42 000 compounds, respectively.

1	*trans*-1,3-Dimethylcyclopentane
2	2,2-Dimethylhexane
3	*trans*-1,3-Dimethylcyclopentane
4	*cis*-1,3-Dimethylcyclopentane
5	1,2-Dimethylcyclopentane
6	Cyclohexene
7	Straight-chain hydrocarbon, alkane
8	Cyclic hydrocarbon
9	Alkene
10	Heptane
11	Straight-chain hydrocarbon, alkane
12	Alkene
13	Benzene
14	Straight-chain hydrocarbon, alkane
15	Heptane isomer
16	Hexene, heptene isomers

ure to precisely identify each mixture component. Obviously, the absence of requisite library spectra could be one source of this problem. A second possibility is that inadequate chromatographic resolution, the problem addressed here, has resulted in coelution of components, thereby compromising the spectral library search approach. In any event, the demonstrably better resolution available by MDGC, which is obvious from Fig. 2, can only improve analytical reliability.

Total analysis times

As is evident from Fig. 2b, the time required to carry out complete analytical separation of the five heart cuts was 2 h. This time is significantly less than would be required if cuts were done sequentially, using multiple sample injections and a single cryogenic trap. For example, the time required for each cut, if performed sequentially, would be between 40 and 50 min to obtain both precolumn and analytical column chromatograms. Thus, complete analysis of five cuts would require between 200 and 250 min. In this example, by carrying out MDGC experiments in parallel one saves a minimum of 80 min. Although a single high-resolution narrow-bore capillary column (≤0.1 mm) could permit shorter separation times, that would be at the expense of lower dynamic range and forfeiture of the ability to use the infrared detector.

Chromatographic resolution

The results presented in Figs. 2 and 3 show that the presence of a rotary valve with a small dead volume instead of glass press-tight connectors after the traps has not degraded the chromatographic resolution through peak broadening. The peak widths, as measured as the full peak width at half height, obtained in the present investigation are comparable to those obtained previously, where glass press-tight connectors were used after the traps [9].

Retention time reproducibility

As mentioned earlier, the presence of the CO_2 peak at the beginning of each heart cut analytical chromatogram provides a convenient internal standard for the measurement of adjusted retention times. Thus, it is readily possible to cross correlate retention times between adjacent heart cuts to detect possible component carry over. Furthermore, if retention time data are accurate and precise, they can further augment the analytical information available from the infrared and mass spectra data [19]. Obviously, such use of retention time information coupled with spectroscopic detection and appropriate computer software has the potential for providing a quick and automated means of analyzing complex chromatograms generated from MDGC separations. For the experiment A data, the average variation of the adjusted retention time was 0.05 min, and for experiment B, the average was 0.02 min (see Table II). This difference in average variation may by linked to the inability of the GC oven to maintain a constant temperature near ambient, but it appears that the variations are small enough that the adjusted retention time data may be used for preliminary qualitative analysis based on retention time.

TABLE II

ADJUSTED RETENTION TIME RESULTS

Experiment A, precolumn trap from 8.4 to 9.7 min, isothermal secondary separation at 30°C; experiment B, precolumn trap from 8.4 to 9.7 min, isothermal secondary separation at 50°C. The standard deviations were obtained from five replicate runs.

Experiment	Peak No.	Average adjusted retention time (min)	Standard deviation (min)
A	1	6.73	0.04
	2	10.06	0.05
	3	12.02	0.05
	4	13.48	0.07
	5	14.23	0.05
	Average		0.05
B	1	3.24	0.01
	2	4.52	0.02
	3	5.01	0.02
	4	5.49	0.02
	5	5.71	0.02
	6	5.84	0.02
	7	6.00	0.02
	8	6.27	0.02
	Average		0.02

CONCLUSIONS

A multi-parallel cryogenic trapping scheme developed for multidimensional GC–FT-IR–MS analysis of complex mixtures has been successfully demonstrated. The system developed has the potential to analyze complex mixtures without sacrificing sample dynamic range, which is essential in environmental, essential oil and petroleum chemistry. In addition, the technique can take advantage of both the information provided by multiple retention times in addition to the infrared and mass spectra for analysis of complex mixtures. Thus, multidimensional detection combined with the multi-dimensional separation could increase the reliability of identifying of components in a complex mixture. The improvements in analysis could be further enhanced by use of multiple analytical columns with different selectivities, incorporating techniques to carry out $(GC)^n$ separations, and by performing parallel sample enrichment of different segments.

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