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Quantitative aspects of a valve-based, multi-stage multidimensional gas chromatography–infrared spectroscopy–mass spectrometry system

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Abstract

Use of high-resolution capillary gas chromatography coupled with infrared and mass spectral detectors is a very powerful qualitative analytical technique. However, accurate qualitative analyses with spectroscopic detection requires that the separation system provide the detectors with pure components. Unfortunately, in very complex mixtures, this is virtually impossible when single-stage separations are employed. This paper describes the sample recycling capabilities of a valve-based multidimensional gas chromatography system equipped with both infrared and mass spectral detectors. Sample recycle efficiencies, valve adsorption effects and cycle-to-cycle reproducibility are considered. Mixtures including the Grob test mixture were analyzed and it was found that 35 out of the 40 total components examined could be recycled six times or more following injection of 500 ng or less of each component. Additionally, the first demonstration of a 23-stage recycling experiment with several components of a chlorinated hydrocarbon mixture is shown. This demonstrates the plausibility of performing GC^n experiments, where n is the number of separation stages, with values of n up to 23 for these components. It is also shown that mechanical valves generally do not have deleterious effects on the majority of these components. The main limitations of the system appear to be the design of the heating system and the manual control of the pressure and flow switching systems. The applicability of the present results to qualitative analyses are discussed.

1. Introduction

For over a decade, it has been established that the combination of capillary gas chromatography (GC) with infrared (IR) and mass spectral (MS) detectors can provide highly accurate qualitative information [1,2]. However, statistical examinations of complex chromatograms by Davis and Giddings [3] demonstrate that the probability of completely isolating every component of even relatively simple mixtures using a single-column separation is very low. In terms of the spectroscopic detection of effluents, incomplete separation yields IR and mass spectra of mixtures rather than pure components. Ultimately, the quality of the library search or spectral interpretation is compromised. Methods of improving the chromatographic resolution to provide the detectors with single-component peaks include use of longer capillary columns, smaller inner

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diameter (I.D.) capillary columns, and multidimensional techniques.

Unfortunately, because of inherent restrictions on the chromatography imposed the sample size and flow requirements of IR lightpipe detectors, small I.D. capillary columns (≤ 300 μm) cannot be used. Although detection limits of IR detectors are in the low nanogram range, samples with a wide range of component concentrations require sample dilution to reduce chromatographic column overloading. Such dilutions reduce the amount of minor components and, if they are to be detected, critical minor components may have been diluted below the minimum identifiable quantity. Thus, smaller I.D. capillaries are incompatible with the requirements of the IR detector. On the other hand, long capillary columns with inner diameters compatible with a lightpipe can be used to improve the separation resolution, but the carrier gas pressure requirements for a column long enough to provide a sufficient number of theoretical plates to completely separate a mixture containing several hundred components would preclude the use of common injection techniques. As a consequence, methods other than column dimension adjustments must be employed to achieve improved separations.

Another option for improving chromatographic resolution while observing the constraints imposed by the detection system is multidimensional (MD) GC. This technique generates its improved chromatographic resolution by utilizing columns with different stationary phase selectivities between two or more stages of separation and by reducing the number of components separated in the higher order separations through selective sample transfer. Samples can be transferred from the first-stage column to a subsequent analytical column by utilizing either mechanical valves or a valveless pressure switching technique based on Deans' original design [4]. Both methods have positive and negative aspects, as previously discussed in detail by Bertsch [5]. However, it is generally accepted is that valveless switching is the best method for MD-GC sample transfer, even though several reports have shown that mechanical valve-based systems function just as well as their valveless counterparts [6–9].

The two main problems attributed to mechanical valves are their activity towards polar compounds at trace levels and band broadening. During the past several years, there have been numerous conflicting reports regarding the activity of mechanical valves in capillary GC [6–14]. In most of the reports, the activity of the valves was assessed by analysis of a Grob test mixture [15], but in other reports, subsets of the components of a Grob mixture were used. Several reports over the last 15 years have shown mild to severe activity of mechanical valves towards 2-ethylhexanoic acid [10], 2,3-butanediol [11], 2,6-dimethylaniline [11], dicyclohexylamine [11,12], octanoic acid [13], trichlorophenol [13], nitrophenol [13], 2-methoxyethanol [14], 2-ethoxyethanol [14] and 2-isopropylethanol [15]. On the other hand, others have reported a lack of activity towards the compounds previously listed [6–9]. Unfortunately, the reason for these differences is not obvious. The other difficulty, peak broadening, can result from the combined valve and transfer volumes being greater than that of the column, so that in effect, a mixing volume is created within the valve. This problem can be alleviated by approximately matching the capillary column I.D. with the valve passage diameter. For conventional-size capillaries (ca. 320 μm I.D.) and valves with internal volumes of 1–2 μl, the effect from peak broadening is insignificant [5].

The primary advantages mechanical valves have over valveless systems are their simplicity and lower cost. Fig. 1 shows a schematic diagram of the mechanical valve-based system utilized in the study. Here, a total of five mechanical valves were incorporated into the design in order to achieve the desired chromatographic flexibility. Equivalent chromatographic systems based upon valveless switching technology would be extremely complex and cost prohibitive. Previous research utilizing instrumentation similar to that shown in Fig. 1 revealed that the qualitative information generated is not affected by use of mechanical valves [16–18]. Additionally, two recent studies demonstrated the use of the sys-

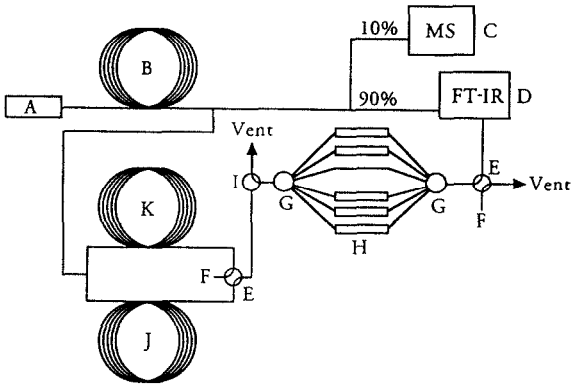

Fig. 1. Schematic diagram of the parallel cryogenic trap MD-GC–Fourier transform (FT) IR–MS system. A = Splitless injection port; B = Rt_x-1701 intermediate-polarity first separation stage column; C = HP 5970B mass-selective detector; D = HP 5965B IR detector; E = four-port, two-way valve (300°C maximum temperature); F = external auxilliary carrier gas; G = six-port selection valve (300°C maximum temperature); H = stainless-steel cryogenic traps; I = three-port, two-way valve (300°C maximum temperature); J = Stabilwax polar column; K = Rt_x-5 non-polar column.

tem for sample recycling to improve chromatographic resolution and component identification accuracy [17,18]. Even though the previous reports demonstrated the capability of using only three sample recycles (GC^3), they were the first demonstrations of the feasibility of sample recycling and GC^n experiments with the IR lightpipe of a combined MD-GC–IR–MS system.

Sample recycling through an IR lightpipe instrument was first demonstrated by Azarraga and Potter in 1981 [19], but literature references to this technique have been non-existent until very recently [17,18]. The system diagrammed in Fig. 1 was specifically designed to accommodate sample recycling, but most of the past research has been directed towards understanding and demonstrating the qualitative advantages of the system. The purpose of the present study is to examine the sample recycling process in order to determine whether or not there are any deleterious effects due to sample adsorption or trapping inefficiencies. Furthermore, it is of interest to characterize and along with the other results, a overall recycling efficiency.

2. Experimental

2.1. Instrumentation

A commercially available Hewlett-Packard (HP, Palo Alto, CA, USA) GC–IR–MS system was modified for MD-GC. The system consists of a HP 5890 series II gas chromatograph coupled in parallel with an HP 5965B IR detector and a HP 5970B mass-selective detector (Fig. 1). Effluent output from the lightpipe IR detector is either vented or collected into one of the five parallel cryogenic traps. For second and higher stages of analysis, trapped effluents are reinjected onto one of the analytical columns by turning off the liquid nitrogen flow to the selected trap and routing carrier gas flow to the trap with the selection valves. In the present configuration, the mechanical valve switching and carrier gas pressure adjustments required for multistage experiments are accomplished manually. Using the arrangement depicted in Fig. 1, the parallel cryogenic trapping multidimensional system does not interfere with normal operation of the GC–IR–MS system, so both IR and MS data are obtainable for eluting components resulting from any GC separation stage.

2.2. Samples

Five standard mixtures (Supelco, Bellefonte, PA, USA) were chosen to represent a broad cross-section of functionalities and reactivities. Table 1 summarizes the contents of each of the mixtures as well as the amount of material injected for each component. The Grob mixture was selected so that direct comparisons with previous reports on the activities of mechanical valves could be performed, and the other mixtures were chosen to probe the activity of the valves towards several different classes of compounds not present in the Grob mixture.

2.3. Mechanical valving system

Five mechanical valves are incorporated into the design of the system. The two valves used for cryogenic trap selection are Rheodyne Model

Table 1
Study mixture components and result summary

Mixture	Peak No.	Component	Quantity injected (ng)	Maximum number of recycles		R^2 for linear regression of 10 recycles		Slope-based recycle (%)	
				MS	IR	MS	IR	MS	IR
Grob Mixture	1	2,3-Butanediol	530	11	12	0.991	0.950	64	66
	2	Decane	280	18	18	0.999	0.999	75	77
	3	1-Octanol	360	13	16	0.997	0.999	69	73
	4	Undecane	290	18	18	0.999	1.00	74	76
	5	Nonanal	400	10	12	0.991	0.996	60	66
	6	2,6-Dimethylphenol	320	13	12	0.993	0.999	65	69
	7	2-Ethylhexanoic acid	380	6	6	0.957	0.990	45	60
	8	2,6-Dimethylaniline	320	8	6	0.992	0.996	46	50
	9	C_{10} Acid methyl ester	420	12	11	0.991	0.993	64	65
	10	C_{11} Acid methyl ester	420	9	9	0.943	0.971	48	55
	11	Dicyclohexylamine	310	1	1	N/A	N/A	N/A	N/A
	12	C_{12} Acid methyl ester	410	6	5	0.993	0.993	32	37
Hazardous substances mixture	13	Aniline	500	10	10	0.989	0.989	60	58
	14	Benzyl alcohol	500	11	10	0.990	0.991	61	62
	15	*p*-Chloroaniline	500	6	8	0.993	0.970	45	50
	16	2-Methylnaphthalene	500	11	8	0.971	0.972	59	68
	17	*m*-Nitroaniline	500	2	6	1.00	0.959	17	45
	18	Dibenzofuran	500	4	2	0.956	1.00	25	46
Phenol mixture	19	2-Chlorophenol	500	16	16	0.991	0.983	73	73
	20	2-Methylphenol	500	15	9	0.980	0.995	70	71
	21	4-Methylphenol	500	13	12	0.981	0.988	64	66
	22	2,4-Dimethylphenol	500	13	12	0.972	0.992	66	68
	23	2,6-Dichlorophenol	500	11	10	0.938	0.976	57	61
	24	2,4,5-Trichlorophenol	500	5	5	0.990	0.981	33	40
	25	2,3,4,6-Tetrachlorophenol	500	2	3	1.00	0.981	49	22
Base–neutrals mixture	26	N-Nitrosodimethylamine	500	12	11	0.993	0.989	70	69
	27	Di-2-chloroethyl ether	500	14	14	0.998	0.988	78	79
	28	Di-2-chloroisopropyl ether	500	14	14	0.970	0.999	80	80
	29	N-Nitrosodipropylamine	500	12	12	0.988	0.998	62	65
	30	2-Chloroethoxymethane	500	14	13	0.999	0.999	72	72
	31	Dimethyl phthalate	500	10	10	0.987	0.996	52	56
	32	Diethyl phthalate	500	9	6	0.909	0.986	46	32
	33	4-Chlorophenyl phenyl ether	500	6	6	0.969	0.982	30	30
Chlorinated hydrocarbon mixture	34	1,3-Dichlorobenzene	500	23	20	0.998	0.999	78	77
	35	1,4-Dichlorobenzene	500	23	20	0.999	0.998	76	75
	36	1,2-Dichlorobenzene	500	23	19	0.998	0.999	79	78
	37	Hexachloroethane	500	15	22	0.996	0.997	75	75
	38	1,2,4-Trichlorobenzene	500	23	14	0.997	0.999	71	71
	39	Hexachlorobutadiene	500	15	16	0.996	0.999	80	79
	40	2-Chloronaphthalene	500	12	4	0.987	0.962	35	36

N/A = Not applicable.

7060 selection valves with Vespel rotor seals. Each valve provides one common input/output line and six selectable trap lines (Rheodyne, Cotati, CA, USA; 300°C maximum temperature). The internal valve passages are 0.41 mm in diameter, and the internal volume of each of the valves is less than 2 μl. A three-port, two-position Valco Model 3N3WT valve (Houston, TX, USA; 350°C maximum temperature) is used to switch flow from the traps to either a vent or the higher separation stage columns. The last two valves in the system are four-port, two-position Valco Model 4C6WT valves (350°C maximum temperature). The first of these valves is used to direct flow from the lightpipe to either a vent or the cryogenic trap array. The other valve is used to control flow to either of the two higher separation stage columns.

2.4. External trap oven heating system

The cryogenic trapping array is situated inside a small oven on top of the GC oven, and a 0.75 m × 0.53 mm I.D. MXT-5 column (Restek, Bellefonte, PA, USA) carries sample from the valves in the GC oven to the trap array. Heating of the external trap oven is accomplished by three lengths of heating tape and variable-voltage regulators. Fig. 2 shows a top view scale drawing of the external trap oven on top of the GC oven. The boxed and lined areas show the heater placement, and the circles show where the resistive thermal devices (RTD) are placed in order to monitor the oven temperatures. The temperatures at the tips of the valves are maintained at 250°C to help reduce component condensation in the valve, and the transfer line temperature is also maintained at 250°C for identical reasons.

2.5. Chromatography

For separations, initial injections were 1.0-μl splitless injections followed by an injection port purge 55 s after injection. The amount of sample delivered to the first stage column was at the column's approximate sample capacity of 500 ng per component. This was done to provide

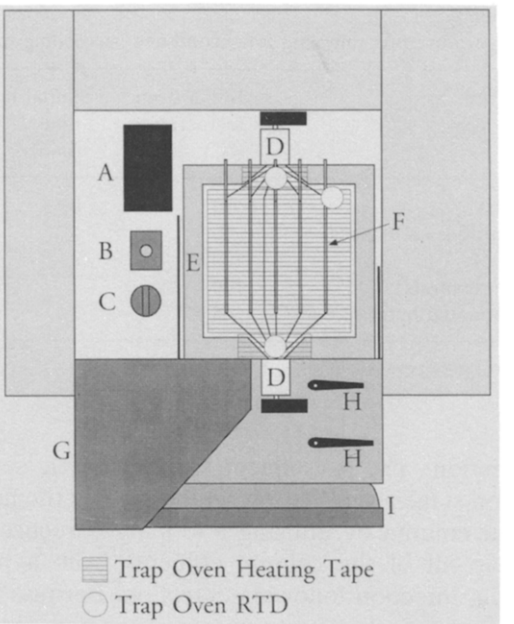

Fig. 2. Top view scale drawing of the GC oven and external trap oven. A = Injection port cooling fan; B = splitless injection port; C = three-port, two-way valve (300°C maximum temperature); D = six-port selection valve (300°C maximum temperature); E = external trap oven ceramic insulation; F = stainless-steel cryogenic traps; G = GC oven extension and bracket; H = four-port, two-way valve (300°C maximum temperature); I = GC oven door.

enough sample to obtain several recycles without grossly overloading the analytical column, in order to obtain a high number of sample recycles. Three columns were installed in the chromatograph: one first-stage separation column and two higher separation stage columns. The first-stage column was a Restek Rt_x-1701 intermediate polarity column (30 m × 0.32 mm, 1.0 μm film thickness), and the two higher separation stage columns were Restek polar Stabilwax and non-polar Rt_x-5 columns (both 30 m × 0.32 mm, 1.0 μm film thickness). Temperature programs utilized for the second and succeeding stages of separation for each of the standards are summarized in Table 2. Carrier gas linear velocities used in all parts of the study were approximately 30 cm/s at 70°c. Each standard was first separated on the intermediate-polarity column, and the entire sample was refocussed into a single cryogenic trap after

Table 2
Temperature programming for second and succeeding stage separations

Mixture	Initial oven temperature (°C)	Initial hold time (min)	Temperature ramp rate (°C/min)	Final oven temperature (°C)	Final hold time (min)	Infrared SWC range[a] (cm^{-1})
Grob	50	0	4	210	0.00	1000–3100
Hazardous substances	60	4	15	230	9.67	1300–1800
Phenol	100	2	15	230	14.33	1200–1600
Base–neutrals	100	2	15	230	14.33	1000–1600
Chlorinated hydrocarbons	45	7	10	190	1.50	779–1600

[a] SWC = Selective wavelength chromatogram.

detection. The subsequent sample recycle separation stages were performed using only the nonpolar column by utilizing a looping sequence to retrap all of the column effluents from a particular injection following detection. Because the purpose of the study was to examine valve interactions with mixture components, only one analytical column was used.

2.6. Spectrometry

IR spectra were collected by the HP 5965B IR detector at a rate of 10 scans per spectrum with 16 cm^{-1} optical resolution, corresponding to a rate of one spectrum per second. IR reconstructed chromatograms were produced using a second-derivative selective-wavelength reconstruction with the wavenumber ranges shown in Table 2. Mass spectra were recorded with the HP 5970B mass-selective detector in full scan mode scanning between 20 and 275 u, corresponding to an acquisition rate of approximately 1.3 spectra per second.

3. Results and discussion

As mentioned above, most of the previous research performed with the system diagrammed in Fig. 1 was focused on qualitative analysis applications. This is the first comprehensive report on the quantitative aspects of the system with regard to sample recycling and valve adsorption. Studies using initial versions of the MD-GC system [16–20] resulted in a number of improvements which are incorporated in the present design. As a consequence, it is possible to demonstrate a level of recycling performance previously not obtained.

The MD-GC system used in this study was developed with the intention of reducing the reported deleterious effects upon the chromatography due to the presence of mechanical valves while retaining the desired chromatographic flexibility. As can be seen in Fig. 1, the valves have been placed either after detection or immediately before the higher separation stage columns. By doing this, peak broadening at the detector due to the valve rotor mixing volume is dramatically reduced. Additional reduction of peak broadening is achieved by using 0.32 mm I.D. capillary columns and transfer lines throughout the system. Generally, the measured peak widths at half height for most components in the valve-based system are comparable to widths measured in a system without the valves.

Valve temperature effects and reactivity were also taken into account when developing the design, but neither of those effects were examined until this study. The temperatures of the trap selection valves and transfer line in the external trap oven were maintained at 250°C by use of heating tape. However, as Fig. 2 shows, the switching valves are placed inside the GC oven and their temperatures vary with the temperature GC oven programming. Valves inside of temperature-programmed GC ovens have been previously shown to have temperature lag problems when oven temperature ramps are greater than 2°C/min [9,11]. It is this lag that is expected

to cause an approximate loss of 2% of the sample per valve passage. Additionally, component condensation in the trap selection valves was designed to be minimized but, due to GC column (230°C) and trap selection valve temperature limits (300°C), high boiling point and late-eluting components were experimentally determined to be less efficiently transferred to the cryogenic traps. It is possible to differentiate between component reactivity towards the valves and component transfer inefficiencies due to condensation by comparing peak areas, valve temperature, and the maximum number of recycles for a particular component. A component was considered to have some activity towards valve surfaces if its elution temperature was below 230°C and it had a maximum recycle number of less than ten. On the other hand, components which eluted during the 230°C isothermal portion of the temperature programs and had maximum recycle numbers less than ten were considered to be affected by condensation in the valve passages, rather than activity.

As Table 1 shows, most of the components examined in the study had maximum recycle numbers equal to or greater than ten cycles. The last recycle for each component was identified as the last chromatogram in which the component peak could be integrated and a library searchable spectrum obtained. However, several components could not be recycled through the system more than six times. This apparent shortcoming must be examined in terms of the *qualitative* analysis of a sample. The maximum number of recycles required for a particular sample depends upon the number of analytical columns present in the system and the amount of information required from the analysis. For example, a system with two analytical columns would require a primary separation and one recycle of the entire sample on each of the two analytical columns to provide a total of three independent separations with three different sets of IR and mass spectra as well as three sets of retention times. Therefore, with a single sample injection, three complementary sets of data could be obtained using only two sample recycles. With this information, a more accurate qualitative analysis can be performed. Additionally, heartcuts can be made during any of the recycles, and those cuts can subsequently be recycled on each of the analytical columns. In the end, the practical number of recycles for a qualitative analysis is roughly six cycles per component, so for 35 of the 40 examined compounds, more than adequate recycling capability is provided.

Because the chromatographic system effluent is split in parallel to the IR and MS detectors as shown in Fig. 1, a loss of approximately 10% is expected due to the destructive nature of MS detection. In addition to detector losses, Miller [9] reported typical sample losses of about 2% per valve path, so approximately 10% more of the sample is expected to be lost due to valve losses. Therefore, if the system operates without additional losses due to reactivity, condensation, or other factors, the maximum recycle efficiency of the system should be about 80% per cycle. Based upon the expected consistent loss of 20% per cycle, there is an anticipated sample consumption which can be fitted to an exponential regression. That theoretical consumption curve is shown in Fig. 3. However, such an exponential fitting procedure does not provide easy access to information regarding the efficiency of the system. A plot of the natural logarithms of the integrated chromatographic peak areas versus the recycle number should give a straight line with the slope of the line (m) related to the percent efficiency per cycle of the system by:

$$\% \text{ Efficiency} = e^{m} \cdot 100\% \quad (1)$$

Additionally, the correlation coefficient (R^2, with an expected value of 1.00) of the linear regression provides some insight into the cycle-to-cycle behavior of the system. A lower correlation coefficient can be taken to be an indication of cycle-to-cycle variation of valve adsorption, component condensation, carrier gas pressure, or inadequate detector response.

The first test mixture examined was the Grob mixture. Fig. 4 is a series of total ion chromatograms showing the sample consumption of the various components from cycle-to-cycle. All but one of the components are apparent up to the fifth recycle, but dicyclohexylamine is completely missing following the first recycle. As previously

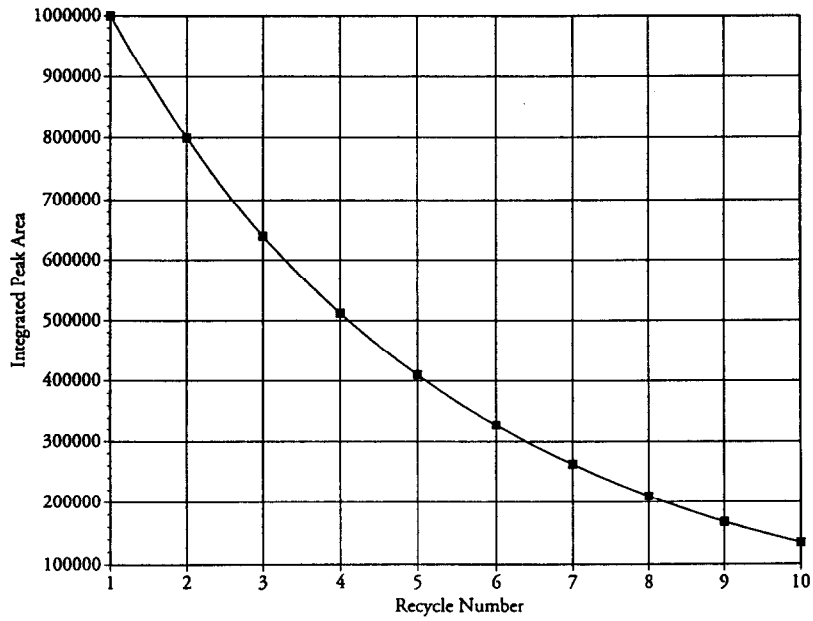

Fig. 3. Theoretical integrated peak area versus recycle number plot showing the exponential consumption of sample from cycle-to-cycle.

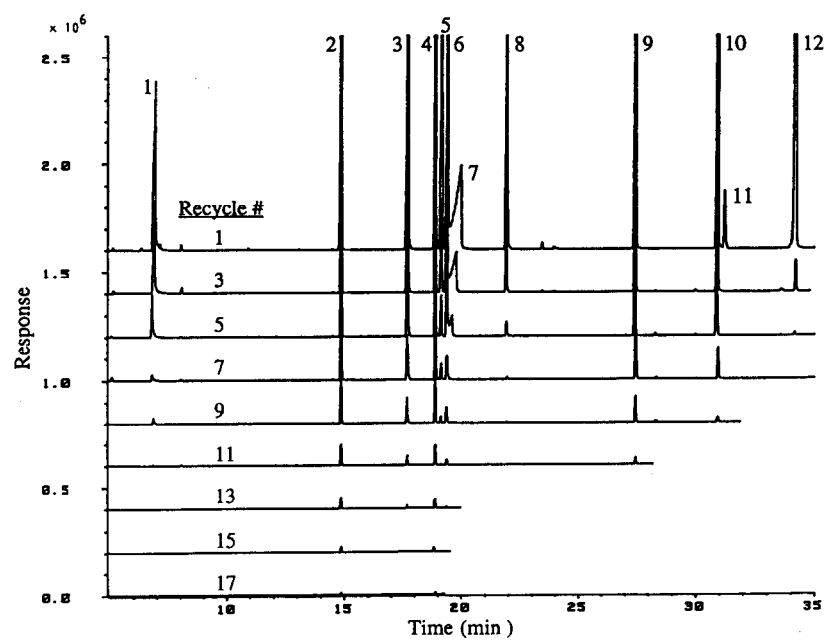

Fig. 4. MS total ion chromatograms of the Grob test mixture recycling experiments. In order to improve clarity, only every other separation is shown. Peak labels correspond to components listed in Table 1.

mentioned, there have been conflicting reports regarding interactions between mechanical valves and dicyclohexylamine. The present research is in agreement with those earlier reports demonstrating problems with the amine [11,12]. As expected, the non-polar components, decane and undecane, could be recycled most often (17 times) and, interestingly, 1-octanol could be recycled 15 times. The quantity of material in the last recycle for each of these three components is approximately 2 ng, close to the expected minimum identifiable quantities with the current configuration of the detector system. Fig. 5a and b are the recycle regression plots for the Grob mixture. The differing slopes between the IR and MS plots for the same compounds can be attributed to the differing responses of the detectors for different components. The correlation coefficients and recycle efficiencies obtained from the regression slopes are summarized in Table 1. Efficiencies for several of the components are above 50%, with a maximum of about 75% for decane. Correlation coefficients are also high, with most values between 0.95 and 1.00. For the majority of the components, the results are close to theory, but the acid methyl esters had values lower than expected. These lower values are thought to be the result of component condensation in the trap valves because elution times for these components were well into the 230°C isothermal temperature program. However, overall system performance appears to be within the expected range with the single exception of the strongly basic dicyclohexylamine.

Although the Grob mixture provides a broad spectrum of components and functionalities, there are several classes of compounds which are not included in the mixture. Therefore, four other mixtures were chosen to fill in some of the missing classes. The second mixture analyzed was a hazardous substances mixture. Regression plots similar to those in Fig. 5 were made from the integrated peak area data; Table 1 summarizes these results. The most noticeable differences between the Grob mixture and the hazardous substances mixture are the lower number of recycles achieved and the lower efficiencies per recycle. One possible reason for these lower values is that half of the compounds in this mixture have nitrogen containing groups and, like dicyclohexylamine and 2,6-dimethylaniline

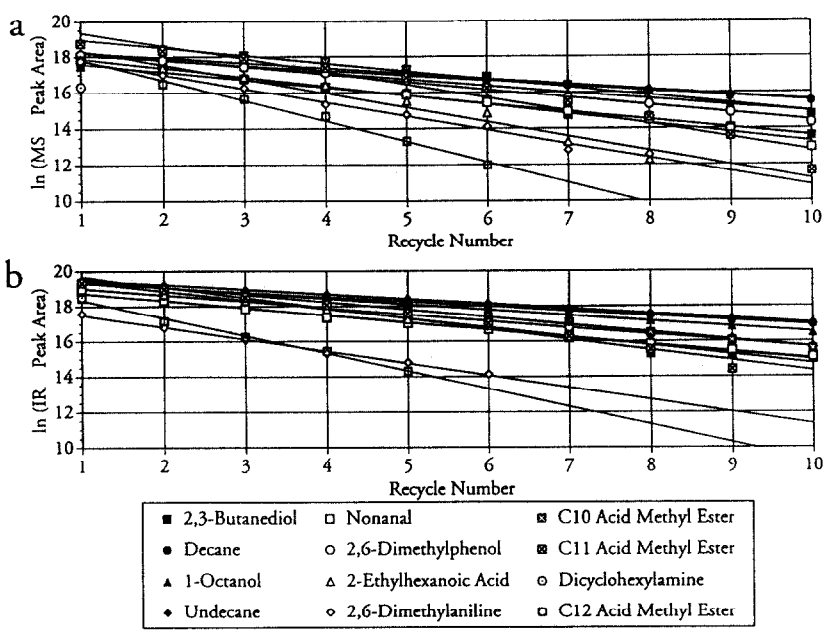

Fig. 5. Linear recycle regression plots for the Grob test mixture. (a) MS response data; (b) IR response data.

in the Grob mixture, it appears that some nitrogen-containing compounds may have lower efficiencies for reasons other than basicity. Dibenzofuran also has a low values for all three categories in Table 1, but the reason for these low values seems to be related to the valve temperature problems previously described. However, the recycling ability of the system for these types of compounds appears to be more than adequate.

A phenol mixture was the third sample analyzed. The results of the recycling were better than those of the hazardous substances mixture and, not surprisingly, similar to that obtained for 2,6-dimethylphenol in the Grob mixture. The values for the correlation coefficient and recycle efficiency summarized in Table 1 were obtained with the same data reduction methods used for the previous mixtures. A comparison of the recycle percentage results for 2,4-dimethylphenol and 2,6-dimethylphenol shows a great similarity, and their maximum number of recycles are also similar. However, because more 2,4-dimethylphenol was injected it was expected that it could be recycled more times than 2,6-dimethylphenol. The discrepancy between these two results may be due to an inaccurate estimate of injection volume which would lead to a lower amount of injected material, or it may be due to an unidentified initial loss of material between the first stage of separation and the latter stages. Phenols as a class do not appear to have serious interactions with mechanical valves. This can be seen by comparing both the maximum number of recycles and the recycle efficiencies obtained for the first five components. As for the last two components, they are high-temperature, late-eluting components that are probably hindered more by the temperature limitations of the system than by activity towards the valve surfaces.

The fourth mixture analyzed in this study was a base–neutrals mixture. The results obtained from the linear regression analysis of the results for this sample are also summarized in Table 1. It is interesting that all eight of the compounds are capable of being recycled a minimum of six times, and di-2-chloroethyl ether and di-2-chloroisopropyl ether have recycle efficiencies which are equal to or near to the expected maximum value of 80%. The two phthalates and 4-chlorophenyl phenyl ether have relatively low efficiencies, but the temperature limitations of the system seem to be the cause of the lower values for these two components. It is also interesting that the two nitrosamines present in the mixture have recycling efficiencies and recycle numbers much higher than those found for the other nitrogen- containing components in the study. The reason for this is not known, but it may be related to the relatively short retention times and low elution temperatures of the two components. This base–neutrals mixture provided the first data demonstrating that the expected maximum recycling efficiency could be reached.

Finally, the last mixture investigated in this study was a chlorinated hydrocarbon mixture. As with the other four mixtures, a summary of the linear regression analysis results appears in Table 1. Fig. 6 shows a series of IR selected-wavelength chromatograms for the first four components of the chlorinated hydrocarbon mixture. Of those first four components, only hexachloroethane is present at the 22nd cycle, where an estimated quantity of about 1 ng is detected. This amount of hexachloroethane would be expected to be present in the final cycle based on previously measured minimum identifiable quantities for these types of compounds [21]. In contrast, Fig. 7 shows a series of total ion chromatograms for the same four compounds, clearly demonstrating the difference between the IR and MS responses. Hexachloroethane appears to be completely absent by the 19th cycle in Fig. 7 as opposed to the 22nd cycle in Fig. 6. However, the three isomers of dichlorobenzene are present at the 22nd cycle in Fig. 7, yet they are gone by the 19th and 20th cycles in Fig. 6. Overall, the recycle efficiencies are very high for all but 2-chloronaphthalene, and several are equal to or close to the expected maximum efficiency. 2-Chloronaphthalene has a low recycle efficiency because of the system temperature limits and due to its high elution temperature and long retention time. The difference in the maximum number of recycles detected for this

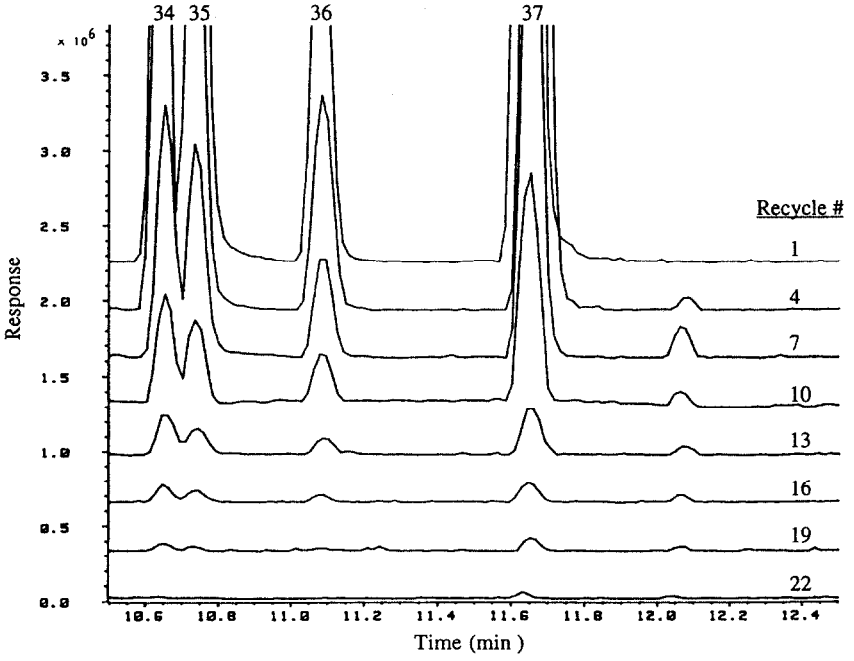

Fig. 6. IR total response chromatograms for the first four components of the chlorinated hydrocarbon mixture recycling experiments. In order to improve clarity, only every third separation is shown. Peak labels correspond to components listed in Table 1.

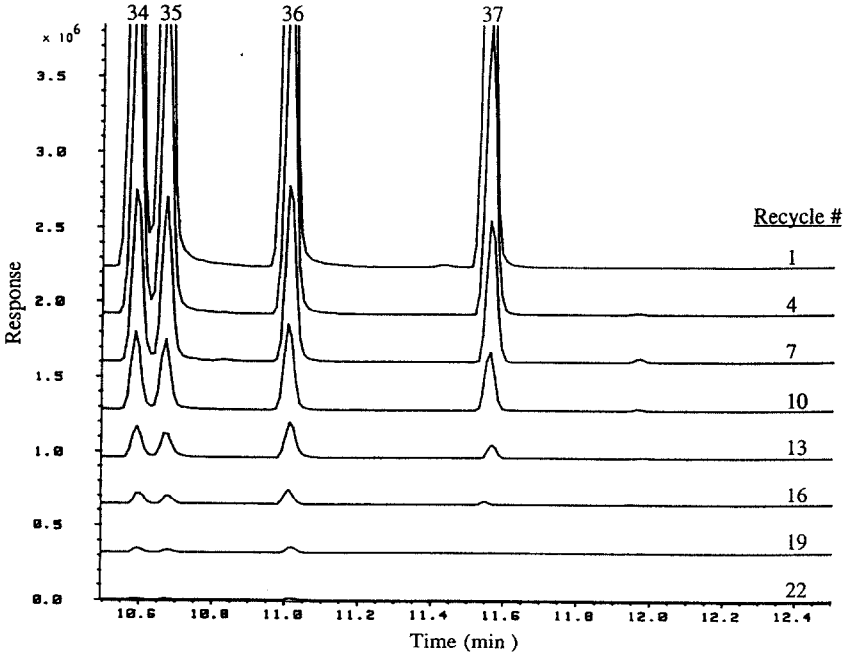

Fig. 7. MS total ion chromatograms for the first four components of the chlorinated hydrocarbon mixture recycling experiments. In order to improve clarity, only every third separation is shown. Peak labels correspond to components listed in Table 1.

compound is due to the choice of IR selected-wavelength chromatogram range used in the reconstruction. The strongest IR absorption band for 2-chloronaphthalene falls below the detector cutoff of 779 cm^{-1}, and the reconstruction range does not go high enough to incorporate the aromatic C–H stretch at approximately 3050 cm^{-1}. Out of all of the mixtures considered in this study, the chlorinated hydrocarbon mixture provides the most impressive data, demonstrating for the first time that it is possible to recycle the same components up to 23 times with a single injection, and this demonstrates the possibility of performing a GC^{23} experiment with these compounds. Additionally, five of the seven components could be recycled and detected at least 20 times using one detector or the other. For these compounds, the high correlation coefficients exhibit the fairly high cycle-to-cycle repeatability of the recycling. As these data show, chlorinated compounds appear to have the less activity towards mechanical valves than another other class of compounds studied other than alkanes.

4. Conclusions

For the first time, a comprehensive examination of component activity towards mechanical valves in a recycling MD-GC–IR–MS system has been performed. For most of the compounds in the study, very high to medium recycling efficiencies were determined and, as the correlation coefficients of the linear regressions demonstrate, most components have reasonably high cycle-to-cycle reproducibility. It therefore appears that mechanical valves do not introduce severe problems for a broad range of chemical classes, with the possible exception of certain types of nitrogen-containing compounds. In terms of recycling ability, the majority of components examined in this study can be recycled more times than should be required for typical qualitative analysis applications. This study also demonstrates the plausibility of GC^n where n is the number of stages of separation, with values of n routinely in excess of 6. Here it has been shown that a maximum of 23 recycles can be accomplished with a single injection of a mixture containing 500 ng each of 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene. In general, the MD-GC system presented here provides unprecedented separation abilities for combined spectroscopic detection systems. However, there are aspects of the system which presently limit its widespread application.

One of the main difficulties with the current design is the temperature limitations imposed by some of the valves. The data presented in this study reveal that there are problems with late-eluting, high-elution-temperature components. With improved valves the present limitations may be removed. Another problem which needs to be addressed is the manually actuated nature of the switching and pressure system. Run-to-run and cycle-to-cycle reproducibility would be greatly improved by the addition of electronic pressure control to control the various carrier gas flows, and heartcut timing reproducibility would also be improved with computer-controlled valve actuators. Nevertheless, as a feasibility study, the results are very encouraging. The range of compounds examined were intended to demonstrate the wide applicability of the instrumentation applications outside of the previously studied areas of essential oil and petroleum analysis [16–18,20]. It is expected that, with further development of the hardware along the lines discussed here, it should be possible to develop a completely flexible computer-controlled MD-GC chromatographic system with IR and MS detection at each stage of separation. Such a system would provide the ability to separate components in very complex mixtures to any required resolution. Furthermore, in concert with improved data reduction algorithms, the resulting analytical tool will greatly improve and simplify overall qualitative analysis of complex volatile mixtures.

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