ELSEVIER

Journal of Chromatography A, 726 (1996) 167–178

JOURNAL OF CHROMATOGRAPHY A

Qualitative analysis of contaminated environmental extracts by multidimensional gas chromatography with infrared and mass spectral detection (MDGC–IR–MS)

Kevin A. Krock, Charles L. Wilkins*

Department of Chemistry, University of California, Riverside, Riverside, CA 92521-0403, USA

Received 20 June 1995; revised 20 September 1995; accepted 21 September 1995

Abstract

The use of capillary gas chromatography in conjunction with spectral detection has been utilized for several years for both quantitative and qualitative analyses of environmental extracts. Unfortunately, in some extreme cases, chromatographic peak overlap precludes the accurate identification of many of the components, and alternative separation strategies employing multidimensional techniques must be utilized to improve the qualitative information. This study presents the application of a valve-based, multiple parallel trap, multi-stage multidimensional gas chromatography–infrared spectroscopy–mass spectrometry system to qualitative analysis of extracts from water, clay and soil samples contaminated by decades of old agricultural product dumping. The water and clay extracts were found to be fairly simple and required only a single chromatographic stage for analysis. Water and clay contaminants identified by both infrared (IR) and mass spectra included 1-chloro-4-methylsulfonyl-benzene, disulfoton, dieldrin, and several organophosphorus pesticides. In contrast, the soil extract required 25 heartcuts and second-stage separations to obtain higher accuracy qualitative identifications or classifications. Components identified by IR and mass spectra included 1-chlorooctane, dimethyl phthalate, phorate, 4,4′-dichlorobenzophenone, 3,4′-DDD, chlorobenzilate, 4,4′-DDD, and bis(2-ethylhexyl)phthalate. This study demonstrates the system's ability to perform equally well in both 1-D and 2-D configurations with these types of samples, and it also illustrates some of the temperature-dependent limitations of the system.

Keywords: Environmental analysis; Water analysis; Soil; Pesticides

1. Introduction

Qualitative and quantitative study of environmental contaminants has been important for several years. Investigations into atmospheric, water, and soil contamination have utilized a wide variety of chemical instrumentation but, due to the complexity of most environmental extracts, typical methods for analyzing these samples require a high resolution separation technique coupled with spectroscopic detectors. In the past, the most widely used method for unequivocal identification and quantitation of these hazardous substances has been gas chromatography–mass spectrometry (GC–MS). However, in the late 1970s to early 1980s, there was an increased interest in the development of gas chromatography–infrared spectroscopy (GC–IR) as an alternative or supplement to GC–MS methods for environmental

*Corresponding author.

0021-9673/96/$15.00
SSDI 0021-9673(95)01065-3

analysis [1–6]. With the advent of commercial linked GC–IR–MS instruments, an economically feasible method of obtaining complementary spectral information using a single instrument became available, and this subsequently led to its use in both target and non-target environmental analysis [7–10]. However, high accuracy qualitative identifications in non-target analyses are dependent upon the purity of components delivered to the detectors. In many environmental extracts, the analytes of interest are overlapped with other analytes or matrix components, so it is essential to utilize multidimensional gas chromatography (MDGC) to improve the accuracy of the identifications in non-target methods.

In the past, the application of MDGC in environmental analysis has been primarily limited to analysis of isomeric compounds, such as polychlorinated biphenyl congeners (PCBs). In these types of applications, MDGC is typically used with electron capture detectors because of the high sensitivity of the detector towards chlorinated compounds [11,12]. However, some PCB congeners are more toxic than others, and differentiation of the individual congeners is desirable. The combination of MDGC and mass spectrometry has provided the best examples of target qualitative and quantitative analysis of PCB congeners [13,14]. However, due to the inherent instrumentation restrictions of typical MDGC systems based on mechanical valves, Deans' design [15], or Schomburg's 'live-T' [16], the widespread use of MDGC in non-target analysis applications has been non-existent, and as mentioned above, applications such as PCB congener analysis are usually targeted at the differentiation of a few congeners. Therefore, the purpose of this study is to illustrate the wider applicability of MDGC to comprehensive qualitative environmental analysis by a novel MDGC–IR–MS system with multiple parallel cryogenic traps and sample recycling ability [17–20].

One area of environmental analysis which has received considerable attention over the years concerns the identification of pesticides and their metabolites or degradation products in environmental matrices, such as soil, water, and plant material. The comprehensive qualitative analysis of these types of complex mixtures is complicated by the large number of components, the wide variety of polarities, and the potentially wide range of component concentrations. However, because of the advances in MDGC–IR–MS hardware previously applied to other sample types [15,16], matrices contaminated by agricultural products or any other source can be much more easily analyzed. For the study described here, samples of soil, clay, and water contaminated by decades old experimental agricultural products were analyzed as a test of the limitations and advantages of the novel MDGC system. Before the University of California, Riverside was established in 1959, the area surrounding the current university site was a Citrus Experiment Station. From the time that the station was founded in 1906 to several decades ago, waste generated from various experiments with, for example, insecticides, herbicides and defoliants, was discarded in a small gully behind some of the station greenhouses. Years after the dumping stopped, the area was declared a US Superfund Hazardous Waste site. Unfortunately, there are very few records of the compounds or classes of compounds deposited in the dump. Therefore, this type of sample is ideal for analysis by MDGC–IR–MS because of the expected complexity and variety of components and the requirement for high accuracy component identifications.

Because no records were kept regarding the types of agricultural products in the dump, it was initially difficult to develop an analytical methodology for the analysis. However, following an examination of the general history of agricultural products [21], it was clear that the discovery of several chlorinated pesticides, such as DDT, *p*-dichlorobenzene and hexachlorocyclohexanes (BHCs), and organophosphorus (OP) pesticides, such as tetraethyl pyrophosphate (TEPP), parathion and malathion, coincided well with the developments and research at the Citrus Experimental Station. It was expected that these types of agricultural products could be present as products, metabolites, or degradation products in the dump site soil. Initial standard GC–IR–MS investigations confirmed the presence of several chlorinated and organophosphorus pesticides. Fortunately, there have been several applications of GC–MS for both qualitative and quantitative analysis of both chlorinated and OP pesticides [22–29], so there was ample analytical background to adapt to the novel multidimensional GC–IR–MS instrument for the analysis of contaminated environmental extracts.

Additionally, these reports provided critical information on identifications based strictly on EI mass spectra when IR spectra proved insufficient, which is the case with many OP pesticides.

2. Experimental section

2.1. Samples

As mentioned above, the samples of water, clay, and soil were drawn from a Superfund agricultural product dumping site located in the University's old experimental agricultural fields. The water was taken from a monitor well near the site, and it had an odor which was very similar to that of the clay. Approximately 500 g of a gray, sandy clay were taken from approximately 0.5 m below the surface of the dumpsite, and the sample was stored in a cleaned glass bottle with a Teflon-lined cap. As with the clay, approximately 250 g of dark brown soil were removed from approximately 3 m below the dump surface and stored in a cleaned glass bottle with a Teflon-lined cap. All samples were extracted within 2 days of obtaining them.

2.2. Extraction techniques

2.2.1. Water analytes

The water extraction was based on the US Environmental Protection Agency (EPA) Method 3510A [30]. This method is a simple separatory funnel extraction, and methylene chloride was used as the solvent because it was felt that it would extract a sufficiently large number of the organic analytes. The extraction was performed with 100 ml of water and three 60-ml aliquots of CH_2Cl_2. The separatory funnel was agitated for ~2 min for each aliquot with periodic venting to prevent glassware breakage or sample expulsion from the funnel. The CH_2Cl_2 aliquots were then added together and reduced to approximately 1 ml under vacuum. Because this study was mainly concerned with the qualitative analysis of the sample, no surrogate or matrix standards were added, so no value on extraction efficiency for the water was obtained.

2.2.2. Soil and clay analytes

The clay and soil extractions were based on the US EPA Method 3550A [31]. This method utilizes sample ultrasonication, and as described above, methylene chloride was used as the solvent for identical reasons. Clay extraction was performed with 100 g of clay mixed with 100 g of dried Na_2SO_4 and three 100-ml aliquots of CH_2Cl_2, and the soil extraction was performed with 30 g of clay mixed with 60 g of dried Na_2SO_4 and three 100-ml aliquots of CH_2Cl_2. Na_2SO_4 was added to each sample to break up the clay and increase the surface area of the sample exposed to the solvent and to aid in the removal of excess water from the sample. Each aliquot was sonicated in a bath at 100% for 3 min. For each sample, the CH_2Cl_2 aliquots were then added together and reduced to approximately 1 ml under vacuum. As with the water extraction, no surrogate or matrix standards were added, so no values on the extraction efficiencies for the solid samples were obtained.

2.3. Instrumentation

A commercially available Hewlett-Packard (HP, Palo Alto, CA, USA) GC–IR–MS system was modified for multidimensional gas chromatography. The system consisted of an HP 5890 Series II gas chromatograph coupled in parallel with an HP 5965B infrared detector and a HP 5970B mass selective detector (Fig. 1). Details of the modification can be found in previous reports [17–20]. Effluent output from the lightpipe infrared detector was either vented or collected into one of the five parallel cryogenic traps. For the second stage of analysis, trapped effluents were re-injected onto the higher-stage column by turning off the liquid nitrogen flow to the selected trap, allowing the trap to achieve thermal equilibrium with the external trap oven, and finally, routing carrier gas flow to the trap with the selection valves. In this configuration, the mechanical valve switching and carrier gas pressure adjustments required for multistage experiments were accomplished manually. Using the arrangement depicted in Fig. 1, the parallel cryogenic trapping multidimensional system did not interfere with normal operation of the GC–IR–MS system, so both infrared and mass

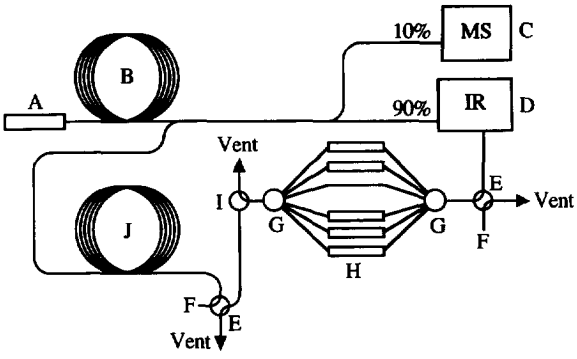

Fig. 1. Schematic diagram of the parallel cryogenic trap MDGC–IR–MS system: A, splitless injection port; B, Rt_x-5 non-polar first-stage separation column; C, HP 5970B MSD; D, HP 5965B IRD; E, four-port two-way valve (300°C maximum temperature); F, external auxiliary carrier gas; G, six-port selection valve (300°C maximum temperature); H, stainless-steel cryogenic traps; I, three-port two-way valve (300°C maximum temperature); J, Rt_x-1701 intermediate polarity column.

spectral data were obtainable for eluting components resulting from any GC separation stage.

2.4. Mechanical valving system

Five mechanical valves were incorporated into the design of the system. The two valves used for cryogenic trap selection were Rheodyne Model 7060 selection valves with Vespel rotor seals (Rheodyne, Cotati, CA, USA; 300°C maximum temperature), and these valves resided in the external trap oven. Each valve provides one common input/output line and six selectable trap lines. 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 (Valco Instruments Co. Houston, TX, USA; 350°C maximum temperature) was used to switch flow from the traps to either a vent or the higher-stage separation columns. The last two valves in the system were four-port two-position Valco Model 4C6WT valves (Valco Instruments Co.; 350°C maximum temperature). The first of these valves was used to direct flow from the lightpipe to either a vent or the cryogenic trap array. The other valve was used to control flow to either of the two higher-stage separation columns. These remaining three valves were placed inside the GC oven.

2.5. External trap oven heating system

The cryogenic trapping array [17–20] was situated inside a small oven on top of the gas chromatographic oven, and a 0.75 m × 0.53 mm I.D. deactivated MXT column (Restek Corp., Bellefonte, PA, USA) was used as a transfer line to carry sample from the valves in the GC oven to the external trap array. Heating of the external trap oven was accomplished by three lengths of heating tape and variable voltage regulators. The temperatures at the tips of the valves were maintained at 280°C to help reduce component condensation in the valve, and the transfer line temperature was also maintained at 280°C for identical reasons.

2.6. Chromatography

For separations, initial injections were 1.0-μl splitless injections followed by an injection port purge 55 s after injection. Two columns were installed in the chromatograph: one first-stage separation column and one higher-stage separation column. The first-stage column was a Restek Rt_x-5 non-polar column (5% diphenyl–95% dimethyl polysiloxane, 30 m × 0.32 mm, 1.0 μm film thickness), and the higher-stage separation column was a Restek intermediate polarity Rt_x-1701 column (14% cyanopropylphenyl–86% dimethyl polysiloxane, 30 m × 0.32 mm, 1.0 μm film thickness). This configuration differs from that used in previous MDGC–IR–MS studies [17,18,20] because the boiling point range for the soil sample was expected to go above the maximum oven temperature of the Restek Stabilwax column (Carbowax 20M, 240°C maximum temperature, so the column was removed. The oven temperature program used was 45°C then 4°C/min to 260°C for 30 min. Carrier gas linear velocities used in all parts of the study were approximately 30 cm/s at 70°C.

2.7. Spectroscopy

Infrared spectra were collected by the HP 5965B infrared detector at a rate of 10 scans per spectrum

with 16 cm^{-1} optical resolution, corresponding to a rate of one spectrum per second. An HP infrared vapor phase library with ~5100 spectra was used for component identifications from the GC–IR data. Mass spectra were recorded with the HP 5970B mass selective detector in full scan mode scanning between m/z 40 and 350, corresponding to an acquisition rate of approximately one spectrum per second. Two different methods were used for the analysis of the GC–MS data. The first method used the HP Pascal ChemStation probability-based matching (PBM) searching algorithm [32–36] with ~41 000 electron ionization (EI) mass spectra, and the second method used the program MassLib (Chemical Concepts, Weinheim, Germany) running on a VAXstation II computer (Digital Equipment Corporation, Maynard, MA, USA). MassLib uses the SISCOM searching algorithm [37–40], and approximately 71 000 EI mass spectra were used in the data analysis. All identifications made in this study were supported by both the infrared and mass spectral data.

3. Results and discussion

The first of the three samples analyzed was the water extract. Fig. 2 is the total ion chromatogram of the first-stage separation. It is clear that either there were very few organic compounds present in the water or the methylene chloride did not extract as many components as anticipated. However, following the extraction step, the water lost its distinctive smell, and the methylene chloride extract had a very strong odor similar to that of the original water. Therefore, it was believed that the components of interest were indeed extracted. After analyzing the infrared and mass spectral data for the six main components, the identifications or classifications listed in the caption of Fig. 2 were made. The main organic component of the water extract was 1-chloro-4-methylsulfonyl-benzene, and the other minor components were phosphorodithioate pesticide and phenol derivatives. Because of the apparently small (<50 ng) quantity of material in the extract, accurate identifications of the phosphorodithioate derivatives could not be made, and no attempt to perform an on-column enrichment step was made because classification was sufficient for this extract. On account of the extract simplicity, it should be noted that only a single chromatographic stage was required for the separation and identification of these components.

The clay extract was the second sample to be analyzed, and as shown in Fig. 3, this extract was also fairly simple, with over 35 major and minor components. Compared with the MS response shown

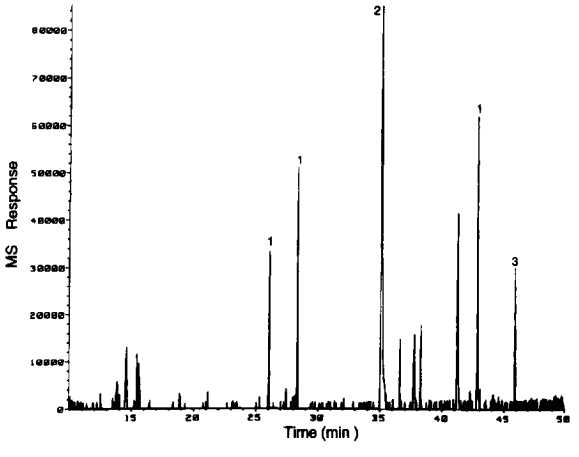

Fig. 2. First-stage total-ion chromatogram of the water–methylene chloride extract. Peaks: 1=phosphorodithioate derivatives; 2=1-chloro-4-methylsulfonyl-benzene; 3=phenol derivative.

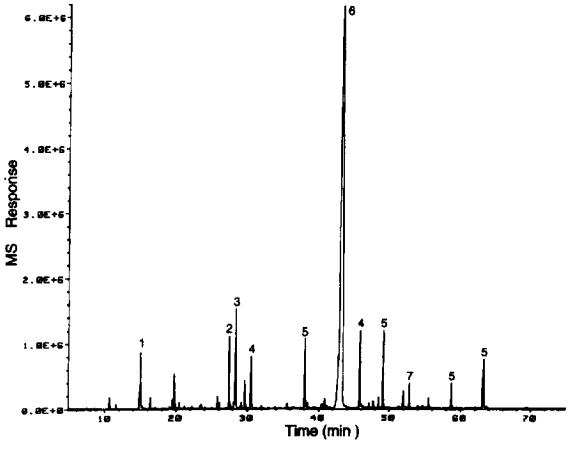

Fig. 3. First-stage total-ion chromatogram of the clay–methylene chloride extract. Peaks: 1=1,1-bis(methylthio)ethane; 2=*O,O*-diethyl-*S*-vinyl phosphorodithioate; 3=*O,O,S*-triethyl phosphorodithioate; 4=ethylthioethane isomer; 5=phosphorodithioate derivative; 6=disulfoton; 7=dieldrin.

in Fig. 2, it is obvious that the concentrations of organic components are much higher in the clay extract than the water extract. As with the water sample, the strong characteristic odor of the clay was completely absent from the extracted material following the extraction step and apparent in the extract. The main organic component of the clay is the organophosphorus pesticide *O,O*-diethyl-*S*-[2-(ethylthio)ethyl]phosphorodithioate or disulfoton. With regard to the odor similarity between the water and clay, disulfoton and 1-chloro-4-methylsulfonylbenzene do indeed have similar smells, but it is obvious from the identifications that the source of the water contamination is not due to the clay components leaching into the soil. Several other components in this extract were identified by their infrared and mass spectra, and their identifications are given in the caption of Fig. 3. The majority of the components appear to be phosphorodithioate pesticides or their degradation products.

The soil extract was expected to be the most complex of the analyzed samples and, as shown in Fig. 4, there are many more components in a wider concentration distribution than either of the two previous samples. Upon examination of the infrared and mass spectral data and chromatographic data, it was obvious that an additional separation stage would be required to improve the qualitative identifications. The peak labels in Fig. 4 correspond to several of the identifications shown in Table 1. These components were identified so that they could be used as heartcut markers, and with them, the accuracy of the heartcuts could be monitored. Because the MDGC system was equipped with five cryogenic traps, the chromatogram in Fig. 4 was broken up into several areas of five heartcuts each. Fig. 5 shows the heartcut map on an expanded first-stage chromato-

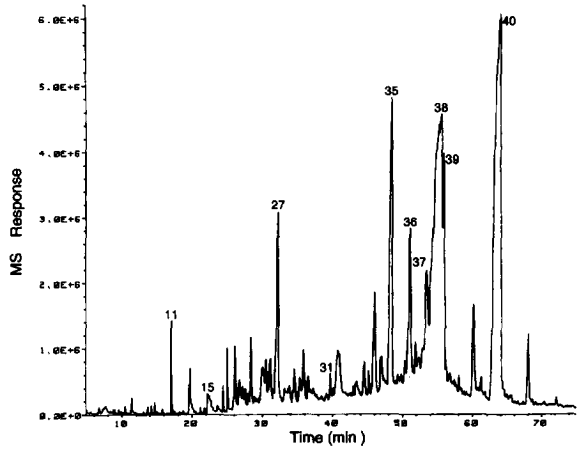

Fig. 4. First-stage total-ion chromatogram of the soil–methylene chloride extract. Peak numbers correspond to the identifications in Table 1.

Table 1
Soil extract component identifications by infrared and mass spectral analysis

Peak number	Identification
1	1,4-Dioxane
2	1-Octene
3	1-Chlorohexane
4	1-Chlorobenzene
5	Butyric acid
6	1,3-Dimethylbenzene
7	Cyclohexanone
8	Sulfonyl-bis-methane
9	1-Decene
10	2-Ethyl-1-hexanol
11	1-Chlorooctane
12	Heptanol
13	Phosphoric acid, triethyl ester
14	Triethyl phosphorothioate
15	2,4-Dichlorophenol
16	1-Chlorodecane
17	Phosphorothiolate derivative
18	3-Methyl-5-propyl-nonane
19	*O,O*-Diethyl-*S*-methyl phosphorodithioate
20	*O,O,S*-Triethyl phosphorothiolate
21	4-Chloro-2-methyl benzenamine
22	4-(1,1-Dimethylethyl)-phenol
23	*O,O,S*-Triethyl phosphorodithioate
24	2,6-Dimethyl naphthalene
25	2,4,5-Trichlorophenol
26	Dimethylnaphthalene isomer
27	Dimethyl phthalate
28	Trimethylnaphthalene isomer
29	Cyclohexanone
30	1-[4-(1,1-Dimethylethyl)- phenoxy]-2-propanol
31	Phorate
32	α-Hexachlorocyclohexane
33	Bis(*p*-chlorophenyl)-methane
34	Phosphorodithioate derivative
35	4,4′-Dichloro-benzophenone
36	1,1′-(Chloroethenylidene)-bis[*p*-chlorobenzene]
37	3,4′-DDD
38	Chlorobenzilate
39	4,4′-DDD
40	Bis(2-ethylhexyl)phthalate
41	Chlorodiphenylmethanol derivatives
42	Chlorodiphenylmethane derivatives

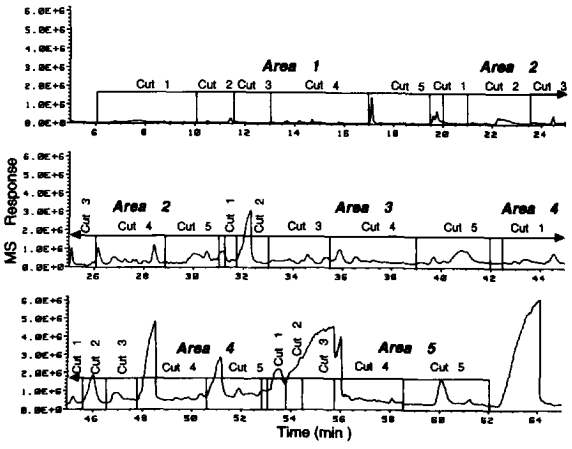

Fig. 5. Expanded first-stage total-ion chromatogram of the soil–methylene chloride extract showing the five heartcut areas as well as the individual heartcuts. Heartcut overlap between the experimental areas was done to ensure comprehensive heartcutting.

gram of the soil extract. Initially, five areas of five heartcuts were taken from the first-stage separation, but difficulties were encountered in the last two areas and will be addressed later. Additionally, a slight overlap between the first and last heartcut of an area was performed to ensure comprehensive heartcutting of the sample.

The five second-stage total ion chromatograms for Area 1 are shown in Fig. 6. These cuts primarily contain smaller molecules which are probably metabolites or degradation products of the pesticides identified in the later heartcuts. One interesting feature that the multi-trap system has is providing the ability to identify possible chromatographic problems in the first-stage separation. Notice how butyric acid (peak 5) was detected in all five of the heartcuts at the same retention time as the main peak in Cut 1. The appearance of these five peaks leads to the conclusion that either the butyric acid tailed in the first stage or deleteriously interacted with the valve system, or it could be due to a combination of the two. As mentioned above, several first-stage chromatographic components were identified for marker purposes, and the marker compound 1-chlorooctane (peak 11) appears in Cut 5. From Fig. 4 and Fig. 5 it is clear that the marker is eluting in the expected area and heartcut, so for Area 1, it appears that all of the intended heartcuts were obtained.

As shown in Fig. 7, the second-stage separations of the five heartcuts are well resolved and provide much better spectra than the first-stage separation. However, it is also in this region that a significant problem with the system was first encountered. Two large broad peaks can be seen in Cut 3 after 30 min, and these two peaks appeared to have IR and mass spectra indicative of some of the late eluting components. Additionally, it was not clear why these broad peaks would appear in the second-stage separation of one cut and not the others. Inspection of the other second-stage chromatograms in Fig. 10 and

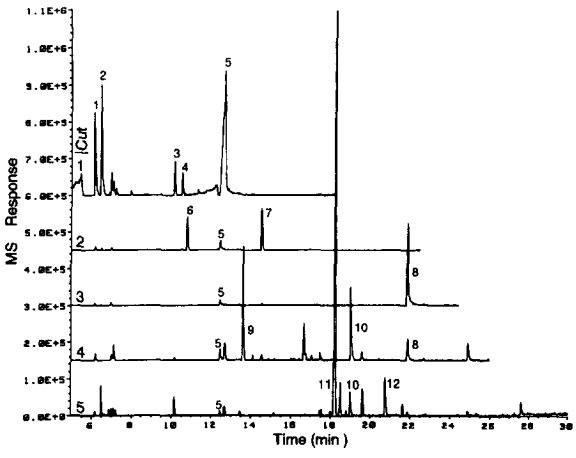

Fig. 6. Second-stage total-ion chromatograms for Area 1 of the soil–methylene chloride extract. Peak numbers correspond to the identifications in Table 1.

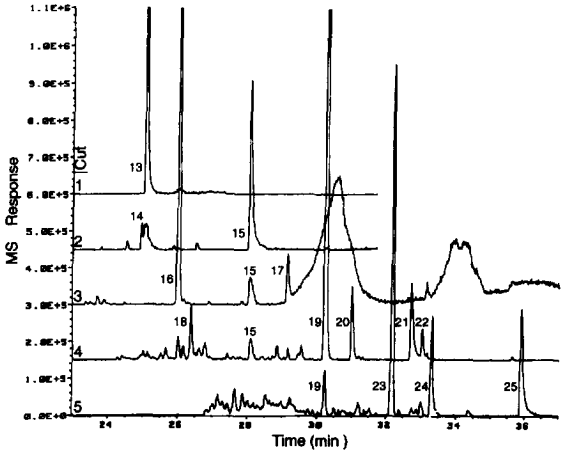

Fig. 7. Second-stage total-ion chromatograms for Area 2 of the soil–methylene chloride extract. Peak numbers correspond to the identifications in Table 1.

Fig. 11 shows similar large broad peaks with spectra similar to the late eluting components. However, in Fig. 10 and Fig. 11, the peaks appear in Cut 1 rather than Cut 3, so it can be inferred that the broad peaks are not due to heartcutting problems. After examining the system depicted in Fig. 1, it became clear that this phenomenon was caused by the lack of flow balancing at the junction between the higher-stage column (J) and the first-stage column (B). Because the flows were initially balanced at 100°C and the temperature program went up to 260°C, the change in helium viscosity at the higher temperature was enough to allow the late eluting compounds to accumulate in the end of the higher-stage column. When the oven was cooled down for the second-stage separations, the late eluting components stayed in the end of the column until the second-stage temperature program reached a temperature which was high enough to volatilize these components. Therefore, in the case of Fig. 7, the temperature program reached its critical temperature during the separation of Cut 3. In Fig. 10 and Fig. 11, this temperature was reached during the second-stage separation of Cut 1. One way to overcome this problem is to equilibrate the second-stage column at 260°C for several minutes before initiating the second-stage separations. However, a less primitive and more time-saving method involves the use of computer pressure or flow control which can compensate for the viscosity change as a function of temperature and can more accurately balance the flows at this junction. Unfortunately, the latter method is considerably more expensive than the former, which is the primary reason for the lack of its implementation in this system.

Area 2 also contains a good example of why it is necessary to have both infrared and mass spectral detection. Cuts 4 and 5 in Fig. 7 have a few organophosphate pesticides present (peaks 19, 20, and 23), but after the initial computer-based spectral searches of both the IR and MS data, the classification as OP pesticides was the only identification that could be obtained. Fig. 8 shows the infrared spectra taken from these three peaks, and it is clear that their structures are all very similar. The spectra indicate the presence of aliphatic C–H stretching modes from the bands at 2800–3000 cm^{-1} and strong CH_2–O–(P or S) stretching modes from the bands at 900–

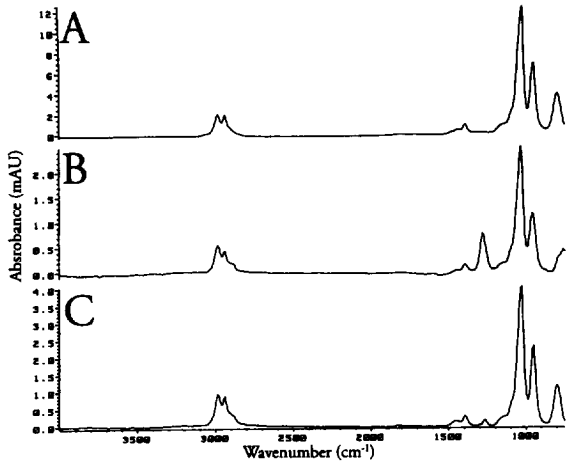

Fig. 8. Infrared spectra taken from heartcuts 4 and 5 in Area 2. All spectra show the common C–H stretching bands at 2800–3000 cm^{-1}, and all three also have a strong CH_2–O–(P or S) stretching bands at 900–1100 cm^{-1}. A: 30.3 min in both cut 4 and cut 5 (Peak 20); B: 31.0 min in cut 4 (Peak 21); C: 32.2 min in cut 5 (Peak 22).

1100 cm^{-1}, but other than those bands, there is very little specific structural information available. One exception is the P=O stretch at approximately 1250–1300 cm^{-1} in Fig. 8B which indicates the possibility of a phosphorothiolate rather than a phosphorodithioate. The mass spectra shown in Fig. 9 have much more structural information than the IR spectra, and structural confirmations could be made by

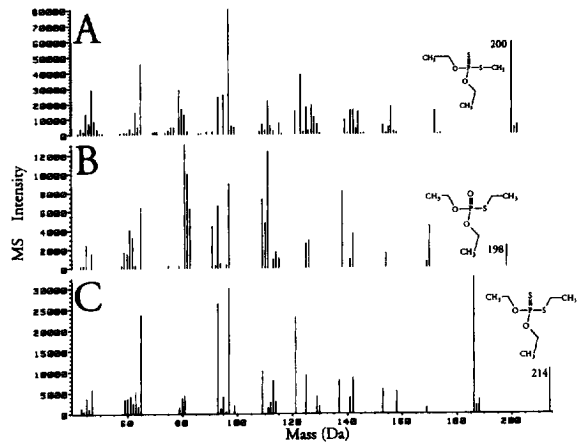

Fig. 9. Mass spectra taken from heartcuts 4 and 5 in Area 2. A: 30.3 min in both cut 4 and cut 5 (Peak 20); B: 31.0 min in cut 4 (Peak 21); C: 32.2 min in cut 5 (Peak 22). Mass labels and molecular structures are shown for several fragment ions.

comparing the molecular and fragment ions with known fragmentation pathways of these pesticides [41]. The mass spectra and the corresponding molecular structures for the molecular ions are shown in Fig. 9. It was only after utilizing the complementary information of both the IR and the mass spectra that the identification of these three components could be made. Additionally, this illustrates the well-known limitations of library search methods, and it is clear that either very specific libraries must be constructed for each compound class or alternative computer analysis methods must be devised.

Fig. 10 shows the five second-stage total ion chromatograms for Area 3. It is obvious from this figure that the second-stage resolution was much better than that obtained in the first stage, but the identifications were primarily limited to general classifications due to the lack of requisite library spectra. Additionally, the large, broad peaks visible at the end of the Cut 1 chromatogram were due to the previously described flow imbalance. Another curious problem with the system hardware is also evident in this series of chromatograms. Dimethyl phthalate (peak 27) was identified in the first three heartcuts, but the retention time of the dimethyl phthalate peak in Cut 1 is approximately 1.5 min less than the other peaks. This phenomenon can also be seen in Fig. 11, but it is not apparent in either of the first two areas. The reasons for this are not fully understood. However, it may be related either to GC

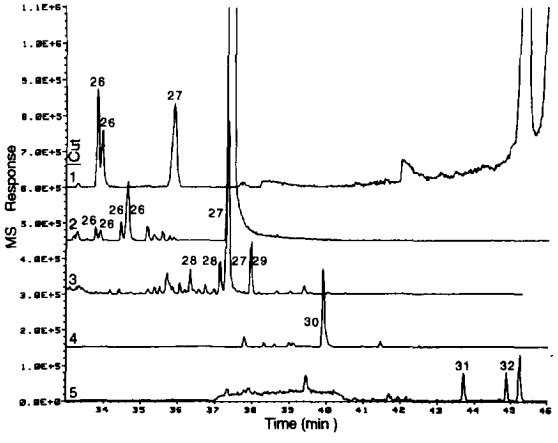

Fig. 10. Second-stage total-ion chromatograms for Area 3 of the soil–methylene chloride extract. Peak numbers correspond to the identifications in Table 1.

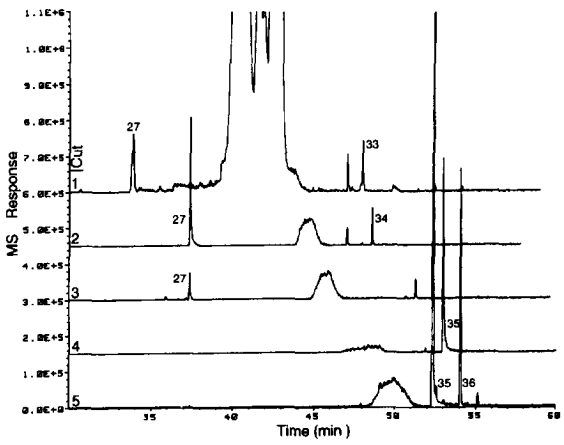

Fig. 11. Second-stage total-ion chromatograms for Area 4 of the soil–methylene chloride extract. Peak numbers correspond to the identifications in Table 1.

oven temperature or column flow differences between the first-stage separation and the initial second-stage separation of less volatile components or to second-stage column inefficiency due to overloading by the high concentration components. Nevertheless, the IR and mass spectra can be used to identify the presence of shifted peaks and minimize inaccurate identifications based strictly on retention times.

All of the previous problems associated with the system are again apparent in Fig. 11, and it should also be noted that there are far fewer components in these heartcuts compared with the previous cuts. However, it is in these late eluting areas that the true evidence of the pesticide contamination become apparent. Two of the metabolites of DDT were detected and identified in Cuts 4 and 5 (peaks 35 and 36). Unfortunately, in comparison with the first-stage chromatogram heartcuts in Fig. 5, the concentration of the components present in the second-stage chromatograms was significantly less than was expected. The reason for this, as will be discussed in more depth shortly, was cold-spot formation in the transfer line of the external trapping oven. The increasing peak areas of the 4,4′-dichlorobenzophenone (peak 35) in Cuts 4 and 5 were indicative of peak fronting in the first-stage separation, and the peak shape of peak 35 in Fig. 4 confirmed that assessment. Nonetheless, the differences between the expected and actual peak areas were much greater than they should have been, and the differences could not be com-

pletely attributed to fronting or cycle-to-cycle sample loss. Furthermore, this problem was found to be more pronounced in the heartcuts taken from Area 5.

The original five heartcuts taken from Area 5 had peak areas much smaller than expected, but there was a continuous increase in the areas as the heartcut second-stage separations progressed from the first to the fifth. It was clear from this observation that there was a possible problem with the transfer of low volatility components from the GC oven to the cryogenic traps. The external trap oven air temperature was maintained at 280°C, but because the transfer line before the first trap selection valve passed near cooled traps, some localized cold spots along the line may have been formed. If this were the case, low volatility effluents would partially condense in the cold spots and be transferred to the traps at a slow rate. Fig. 12 shows the results of the experiment that confirmed the hypothesis. Fig. 12A is the first-stage chromatogram of Area 5 with three extended heartcuts shown, and Fig. 12B shows the three second-stage chromatograms obtained from the three heartcuts. The second-stage separation of Cut 1 shows evidence of a large amount of 4,4′-dichlorobenzophenone (peak 35), which was expected, but the concentration of chlorobenzilate (peak 38) was much lower than it should have been, had there been no transfer problems. The second-stage separations

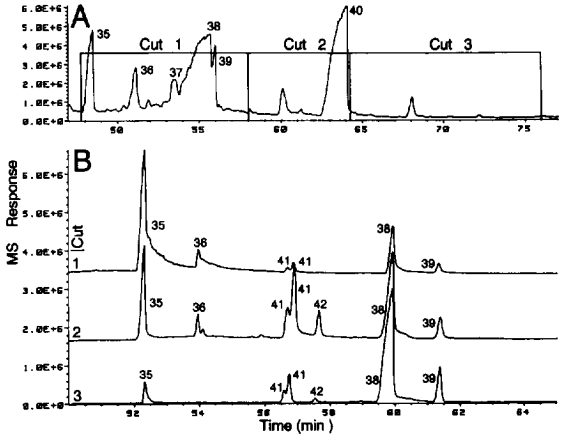

Fig. 12. First- and second-stage total ion chromatograms for Area 5 of the soil–methylene chloride extract. A: First-stage separation showing the three selected heartcut regions. B: Three second-stage separations for each of the heartcuts in A. Peak numbers correspond to the identifications in Table 1.

of Cuts 2 and 3 show the slow decrease in the amount of 4,4′-dichlorobenzophenone (peak 35) while the amount of chlorobenzilate (peak 38) continues to increase into Cut 3. Another piece of evidence which supports the hypothesis was the complete lack of the bis(2-ethylhexyl) phthalate (peak 40) in the second-stage heartcuts. Because the chlorobenzilate peak area was still increasing after approximately 28 min of trapping and none of the bis(2-ethylhexyl) phthalate appeared in any of the cuts after approximately 12 min of trapping, it appeared that the cold spot problem was quite significant for low volatility components. Possible system improvements to overcome this problem include a single high temperature trapping valve with a new cryogenic trap design and heating arrangement or a stainless steel clad fused silica capillary which is resistively heated. Regardless, it was clear that not many more components were revealed by a second stage of chromatography on this area, and the detected components were easily identified or classified.

With regard to all of the components identified in the soil extract, several of the expected OP and chlorinated pesticides were identified, along with many of their possible metabolites and degradation products. In addition to the anticipated components, several other components were identified, including a high concentration of bis(2-ethylhexyl) phthalate. The presence of this component in the soil was attributed to its leaching from many of the plastic carboys used to store the waste, before it was eventually buried. As for the other components, it is difficult to determine the precise source of contamination. Some of the components may indeed be metabolites while others may be the original agricultural products. Nevertheless, as an initial study of a sample taken from one small area of the site, the data helped to identify some of the possible original and current contaminants.

4. Conclusions

Due to the range of components, volatilities, and concentrations, this 'real-world' study was one of the most stringent tests of the advantages and limitations of the MDGC–IR–MS system. It is clear from the results that the system can operate equally well in

both 1-D and 2-D configurations by simply switching valves, and, as expected, accurate identifications or classifications of many components could be made from the various sets of IR and mass spectral data. Although the retention times of the early eluting components could be used for an initial qualitative identification, it is clear that the system was more amenable to the analysis of volatile and semi-volatile extracts than the later eluting low volatility components, but with the changes suggested above, the temperature limitations may be removed. In spite of the limitations recognized in the study, the system was able to detect and accurately identify several environmental contaminants in extracts from several sample matrices, and this clearly demonstrates the potential qualitative power of the novel multi-trap, recycling MDGC–IR–MS system for these types of analyses. These results also provide much more than proof of the system's utility; it is anticipated that the information generated from these experiments as well as any future experiments could be used to help with possible remediation and disposal efforts. Additionally, it is information such as that obtained here, that may help to both correct past and identify further contamination of the environment, and with the future improvements in analytical hardware and software, this high accuracy information may be generated easier and faster than previously thought possible.

Acknowledgments

We gratefully acknowledge financial support from the National Science Foundation under grant CHE-92-01277. The Society of Analytical Chemists of Pittsburgh is also appreciated for their funding of a 1994 American Chemical Society Division of Analytical Chemistry Graduate Student Summer Fellowship.

References

[1] L.H. Keith, Environ. Sci. Technol., 10 (1976) 555.
[2] M.D. Erickson, D.L. Newton, E.D. Pellizzari and K.B. Tomer, J. Chromatogr. Sci., 17 (1979) 449.
[3] K.H. Shafer, S.V. Lucas and R.J. Jakobson, J. Chromatogr. Sci., 17 (1979) 464.
[4] L.V. Azarraga and C.A. Potter, J. High Resolution Chromatogr. Chromatogr. Commun., 4 (1981) 61.
[5] D.F. Gurka, P.R. Laska and R. Titus, J. Chromatogr. Sci., 20 (1982) 145.
[6] D.F. Gurka, L.D. Betowski, Anal. Chem., 54 (1982) 1819.
[7] D.F. Gurka, M. Hiatt and R. Titus, Anal. Chem., 56 (1984) 1102.
[8] K.H. Shafer, T.L. Hayes, J.W. Brasch and R.J. Jakobsen, Anal. Chem., 56 (1984) 237.
[9] D.F. Gurka and R. Titus, Anal. Chem., 58 (1986) 2189.
[10] D.F. Gurka, L.D. Betowski, T.L. Jones, S.M. Pyle, R. Titus, J.M. Ballard, Y. Tondeur and W. Niederhut, J. Chromatogr. Sci., 26 (1988) 301.
[11] M.S. Rahman, S. Bøwadt and B. Larsen, J. High Resolution Chromatogr., 16 (1993) 731.
[12] E. Sippola, K. Himberg, F. David and P. Sandra, J. Chromatogr. A, 683 (1994) 45.
[13] F.R. Guenther, S.N. Chesler and R.E. Rebbert, J. High Resolution Chromatogr., 12 (1989) 821.
[14] K.K. Himberg and E. Sippola, Chemosphere, 27 (1993) 17.
[15] D.R. Deans, Chromatographia, 1 (1968) 18.
[16] G. Schomburg, F. Weeke, F. Muller and M. Oreans, Chromatographia, 16 (1982) 87.
[17] K.A. Krock, N. Ragunathan and C.L. Wilkins, Anal. Chem., 66 (1994) 425.
[18] K.A. Krock, N. Ragunathan, C. Klawun, T. Sasaki and C.L. Wilkins, Analyst, 119 (1994) 483.
[19] C.L. Wilkins, Anal. Chem., 66 (1994) 295A.
[20] K.A. Krock and C.L. Wilkins, J. Chromatogr. A, 678 (1994) 265.
[21] G.W. Ware, The Pesticide Book, 3rd Edition, Thomson Publications, Fresno, CA, 1989, Ch. 1.
[22] R. Massé, D. Lalanne, F. Messier and M. Sylvestre, Biomed. Environ. Mass Spectrosc., 18 (1989) 741.
[23] E. Benfenati, P. Tremolada, L. Chiappetta, R. Frassanito, G. Bassi, N. DiToro, R. Fanelli and G. Stella, Chemosphere, 21 (1990) 1411.
[24] G. Durand and D. Barceló, Anal. Chim. Acta, 243 (1991) 259.
[25] G. Durand, P. Gille, D. Fraisse and D. Barceló, J. Chromatogr., 603 (1992) 175.
[26] S. Lacorte, C. Molina and D. Barceló, Anal. Chim. Acta, 281 (1993) 71.
[27] J. Hong, Y. Eo, J. Rhee, T. Kim and K. Kim, J. Chromatogr., 639 (1993) 261.
[28] M. Psathaki, E. Manoussaridou and E.G. Stephanou, J. Chromatogr. A, 667 (1994) 241.
[29] C. Crespo, R.M. Marcé and F. Borrull, J. Chromatogr. A, 670 (1994) 135.
[30] US Environmental Protection Agency, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Ed., Rev. 1, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1990, Vol II, Method 3510A.
[31] US Environmental Protection Agency, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Ed., Rev. 1, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1990, Vol II, Method 3550A.

[32] F.W. McLafferty, R.H. Hertel and R.D. Villwock, Org. Mass Spectr., 9 (1974) 690.
[33] G.M. Pesyna, F.W. McLafferty, R. Venkataraghavan and H.E. Dayringer, Anal. Chem., 47 (1975) 1161.
[34] G.M. Pesyna, R. Venkataraghavan, H.E. Dayringer and F.W. McLafferty, Anal. Chem., 48 (1976) 1362.
[35] B.L. Atwater, D.B. Stauffer, F.W. McLafferty and D.W. Peterson, Anal. Chem., 57 (1985) 899.
[36] D.B. Stauffer, F.W. McLafferty, R.D. Ellis and D.W. Peterson, Anal. Chem., 57 (1985) 1056.
[37] H. Damen, D. Henneburg and B. Weimann, Anal. Chim. Acta, 103 (1978) 289.
[38] L. Domokos, D. Henneburg and B. Weimann, Anal. Chim. Acta, 150 (1983) 37.
[39] L. Domokos, D. Henneburg and B. Weimann, Anal. Chim. Acta, 165 (1984) 61.
[40] L. Domokos and D. Henneburg, Anal. Chim. Acta, 165 (1984) 75.
[41] S. Safe and O. Hutzinger, Mass Spectrometry of Pesticides and Pollutants, CRC Press, Cleveland, OH, 1973, Ch. 21.