

Utilization of a benchtop mass spectrometer with capillary supercritical fluid chromatography

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ABSTRACT

Direct coupling of a capillary supercritical fluid chromatograph to a benchtop electron ionization (EI) mass spectrometer using a GC–MS interface with minor modification is described. The SFC–EI–MS of the thermally labile pesticides aldicarb, diuron, methio-carb, alachlor, bendiocarb, and carbaryl plus other analytes have been obtained with good chromatographic integrity and sensitivity. This system routinely provided low nanogram level detection in the full scan mode for the pesticides as well as picogram levels for some selected analytes. The highest %R.S.D. for repeated injections of naphthalene over a two-week period using this benchtop SFC–EI–MS system was 6.4. The EI-mass spectra have been successfully searched using conventional mass spectral libraries.

INTRODUCTION

The viability of supercritical fluid chromatography with mass spectrometry (SFC–MS) has been demonstrated by many researchers [1–15]. These investigations have produced reliable methods for conducting chemical ionization (CI), atmospheric pressure ionization (API) and electron ionization (EI) with both capillary and packed-column SFC. A majority of these investigators have employed CI since it generally provided lower detection limits than EI at high source pressures typical for SFC. Most of the mass spectrometers used for these studies have been research grade instruments.

The use of benchtop mass spectrometers in conjunction with gas chromatography has made GC–MS accessible to most laboratories. These instruments have not been applied to SFC primarily because of their pumping limitations, low mass range,

and integrated design. The mass range limitation is critical for analysis of high-molecular-mass compounds, but does not limit the use of benchtop instruments for the analysis of lower-molecular-mass thermally labile or highly polar compounds. The sophistication involved in the reported interfacing techniques is also a problem and is often too complex to implement in a routine analytical instrument.

There are only three papers thus far cited in the literature on SFC with a benchtop mass spectrometer. Two of these research groups resorted to chemical ionization to accommodate the high source pressures of SFC. One, by Lee and Henion [16], described the marriage of capillary SFC to a HP 5970 mass selective detector modified with the addition of 330 L/s turbo pump and a HP 5995 CI ion source. This system detected low nanogram levels of some selected volatile compounds. The CI mass spectra of these compounds showed an abundance of (M + 1) ions, but lacked the structurally

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important fragmentation ions typical of EI conditions. This same instrument was later successfully used to generate pseudo-electron ionization spectra by charge exchange ionization [17]. Saunders *et al.* [18] on the other hand showed the feasibility of coupling micro-packed columns to a benchtop thermospray mass spectrometer. These authors utilized a HP 5970 mass-selective detector equipped with a Vestec 101 thermospray unit and a modified ion source designed to operate at higher pressures. Good chromatographic separation and CI mass spectra for a mixture of ureas were reported. Todd *et al.* [19] have reported the use of an EI-ion trap detector; however, the sensitivity was in the microgram range for a butylbenzene standard.

The ideal SFC–MS interface for routine analytical use should be as simple as the GC–MS interface and also capable of operating with electron ionization to provide spectra that are reproducible and can be searched against existing EI libraries. The present paper describes the development and evaluation of such a benchtop SFC–MS system employing electron ionization. The mass spectrometer used in this study was a commercially available Leybold Inficon benchtop MS equipped with an EI source. Minor modifications were made to the original stainless steel GC–MS interface to convert it into a SFC–MS interface. The compounds investigated were primarily thermally labile; however, other analytes commonly reported in other SFC–MS papers are also described.

EXPERIMENTAL

Samples

Aldicarb, diuron, methiocarb, alachlor, bendiocarb and carbaryl pesticide reference standards

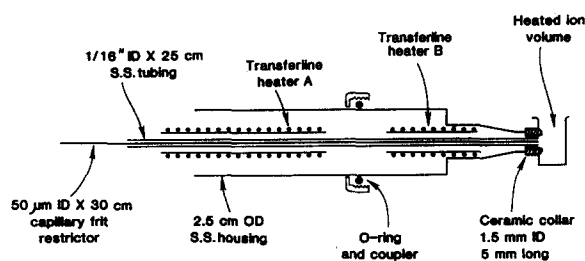


Fig. 1. Schematic diagram of the SFC–MS Interface. " = Inch; S.S. = stainless steel.

were obtained from the Environmental Protection Agency (Research Triangle Park, NC, USA). Other chemicals were purchased from Aldrich (Milwaukee, WI, USA).

Instrumentation

A Leybold Inficon (E. Syracuse, NY, USA) benchtop quadrupole mass spectrometer was modified for SFC work by altering the standard GC interface and adding increased pumping. This instrument comes from the manufacturer with an open heated EI source, a 50 L/s turbo pump and a scan range of 10–650 u. Fig. 1 shows the modified interface as used for SFC applications. The major change to the original interface was the introduction of an extra heater and thermocouple to allow for differential heating of the transfer line.

The principal modification to the mass spectrometer involved removing the existing pumping manifold from the integrated system and replacing it with a new larger diameter manifold with a 4-in. (1 in. = 2.54 cm) flange for the pump. A new 150 L/s Leybold (Export, PA, USA) turbo pump replaced the existing 50 L/s pump. This turbo pump provides adequate vacuum to allow use of the SFC in the pressure range of 100–350 atm (1 atm = 101 325 Pa). Although not tested, it is expected that the system can handle the effluents to the syringe pump's upper range of 400 atm. One additional modification involved adding a 1-in. Cajon fitting to the new vacuum manifold which allowed the addition of an ion gauge. Fig. 2 presents a drawing of the manifold. Because of the added size of the pump, an external stand was constructed to hold the manifold, pump, and pump controller. The existing ionizer and rod assembly were used with no modifications; no changes were made to the electronics.

A Lee Scientific (Salt Lake City, UT, USA) Model 600 syringe pump with a dedicated pump controller and a Hewlett-Packard (Palo Alto, CA, USA) Model 5720A gas chromatograph were used as the basic supercritical fluid chromatograph. A Valco (Houston, TX, USA) Model C14W.1 injection valve with an internal volume of 0.06 µl allowed for direct injection of samples. Both a 1.5 m × 0.05 mm I.D. SB-Biphenyl 30 and a 1.5 m × 0.05 mm I.D. SB-Octyl 30 column, purchased from Lee Scientific, were used for the study. The pressures were maintained in the column by a Lee Scientific

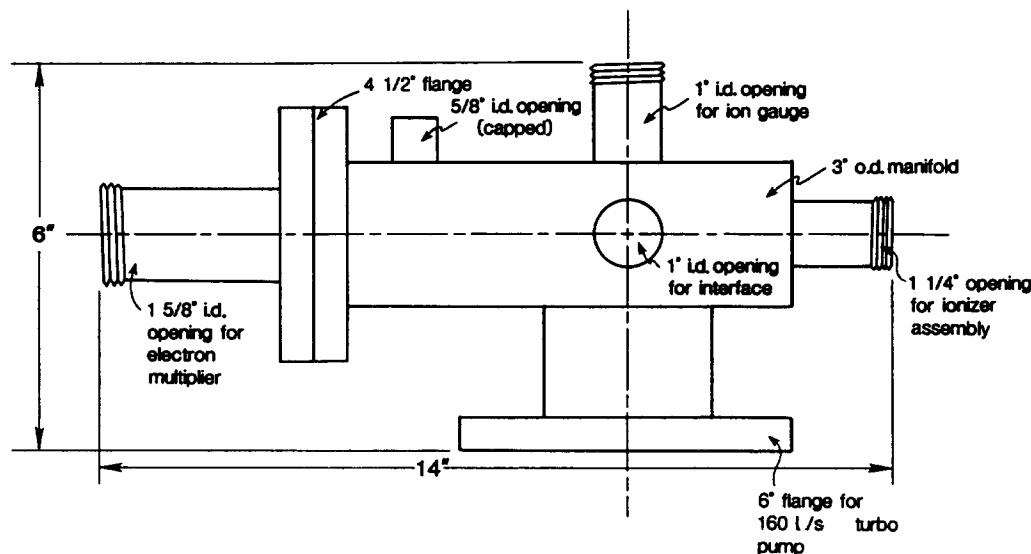


Fig. 2. Schematic diagram of the pumping manifold.

frit restrictor (rated at 0.5 cm/s at 102 atm) cut to allow for an approximate 1 ml/min gas equivalent flow (measured by allowing the carbon dioxide to expand into a bubble meter) at a head pressure of 102 atm into the mass spectrometer. Carbon dioxide was used as the mobile phase throughout this study, while the SFC conditions varied according to the analytes being analyzed. Conditions are listed under each chromatogram.

Interface design

The interface shown in Fig. 1 consists of a 30 cm \times 1/16 in. I.D. stainless-steel differentially heated transfer line and a 40 cm \times 50 μ m I.D. capillary frit restrictor, all contained in a 1 in. O.D. stainless-steel tube. The tip of the probe was heated by the ion volume via the ceramic collar which also prevented shorting of the ion volume and the interface. The transfer line heater A was maintained at the SFC oven temperature while heater B was maintained at about 155°C. The ion volume was maintained at 290°C. The connection of the frit restrictor to the analytical column was accomplished using a fused-silica coupler obtained from Lee Scientific. The restrictor tip was positioned flush with the tip of the transfer line to allow the supercritical fluid to expand inside the ion volume. Nominal flow at the restrictor was about 1 ml/min of carbon dioxide gas

at a head pressure of 102 atm. The pressure in the manifold ranged from $2 \cdot 10^{-5}$ Torr (1 Torr = 133.322 Pa) at a SFC pressure of 100 atm to about $8 \cdot 10^{-5}$ Torr at 250 atm.

RESULTS AND DISCUSSION

The primary objective of this study was to develop an inexpensive benchtop electron ionization mass spectrometer as a detector for an on-line supercritical flow system that was previously developed for the trace analysis of pesticides in complex sample matrices [20]. The initial studies were focused on coupling the SFC apparatus to the benchtop mass spectrometer using a simple interface. The existing stainless steel GC-MS interface that came with the mass spectrometer was ideal for use with SFC. Initially, this interface was used without any modification. An integral tapered restrictor [21] was attached to the analytical column to obtain desired flow-rates of the decompressed gas (typically 1–5 ml/min). A few problems were encountered with this early system. One of the problems was the differences in sensitivity between solid and liquid analytes (at room temperature and pressure). Liquid samples could be detected at low nanogram levels while reproducible spectra for solid analytes were unattainable at these levels. Varying parameters

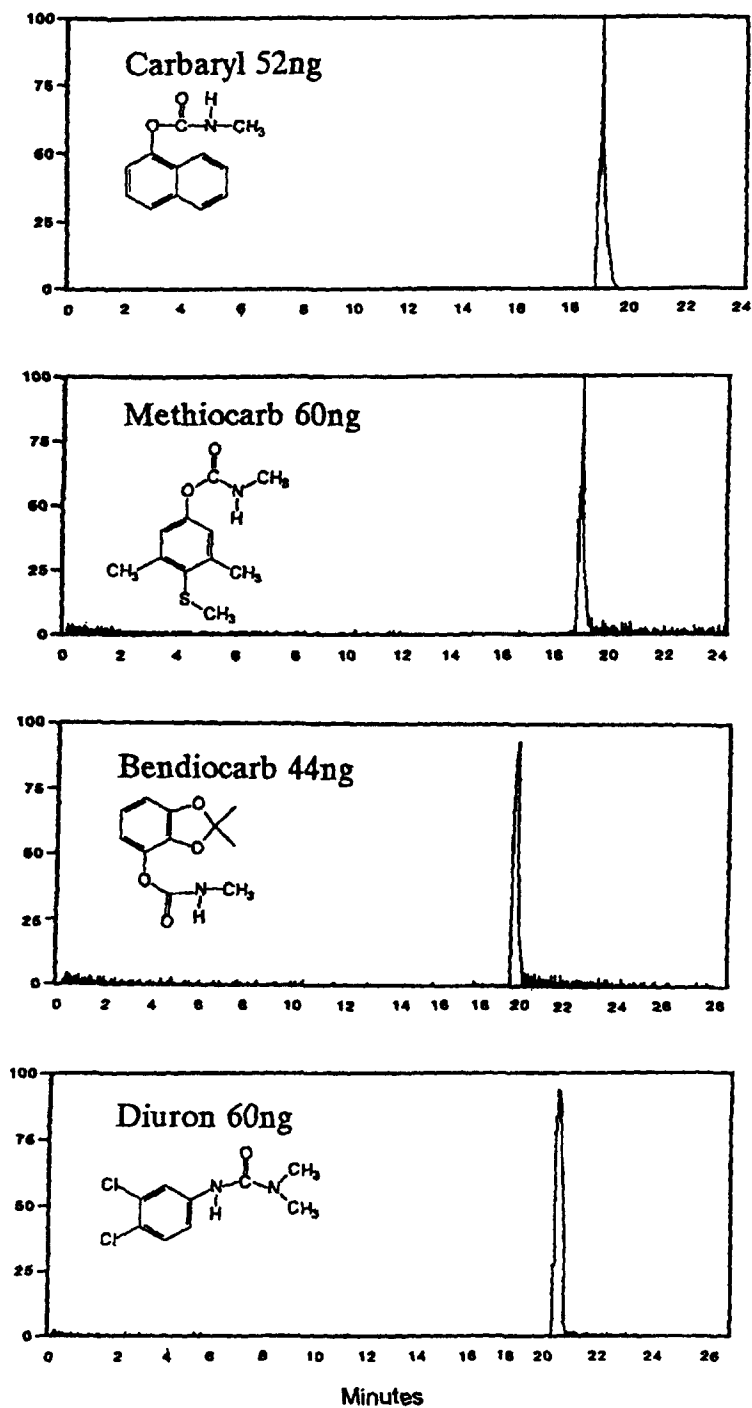


Fig. 3. The SFC-EI-MS total ion chromatograms of four thermally labile pesticides using a 1.5 m × 0.05 mm I.D. SB-octyl 30 column at 90°C and 0.45 g/ml.

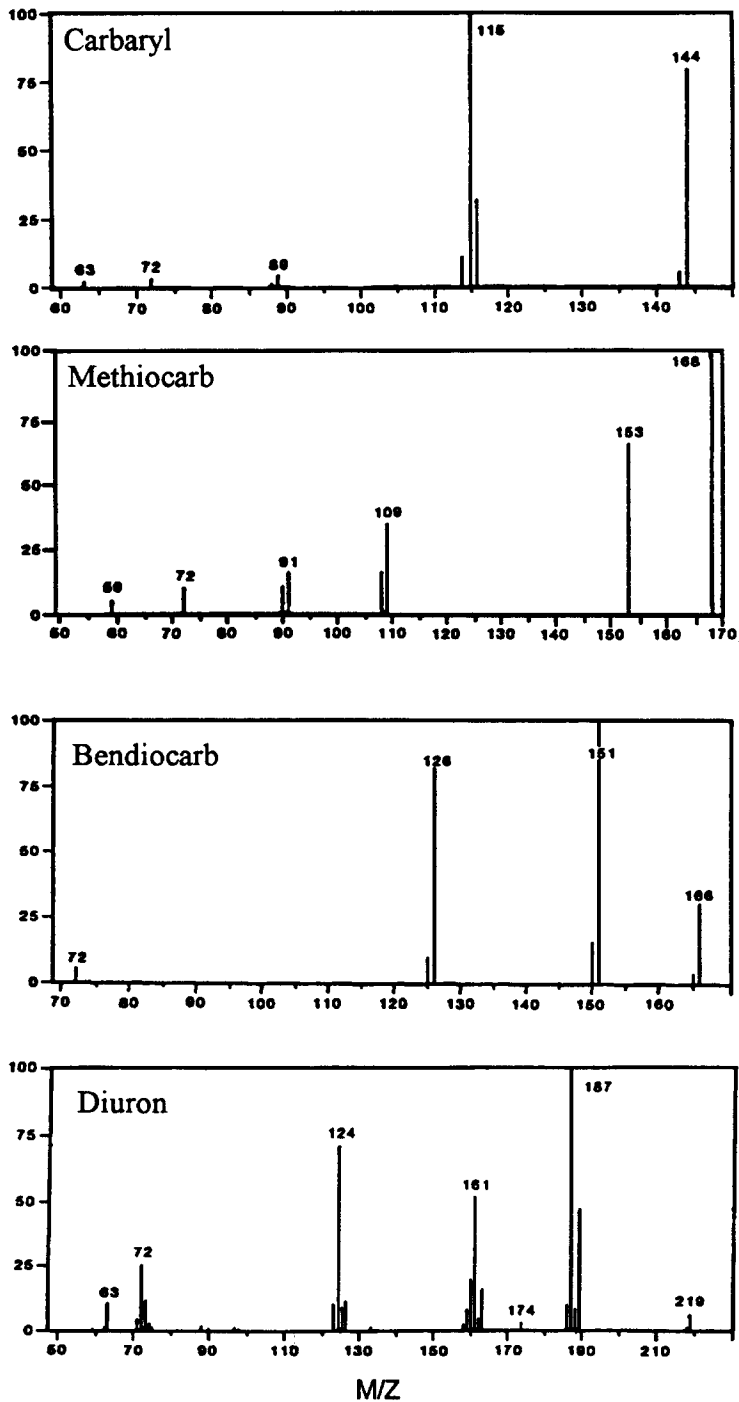


Fig. 4. The EI-mass spectra of the four pesticides in Fig. 3.

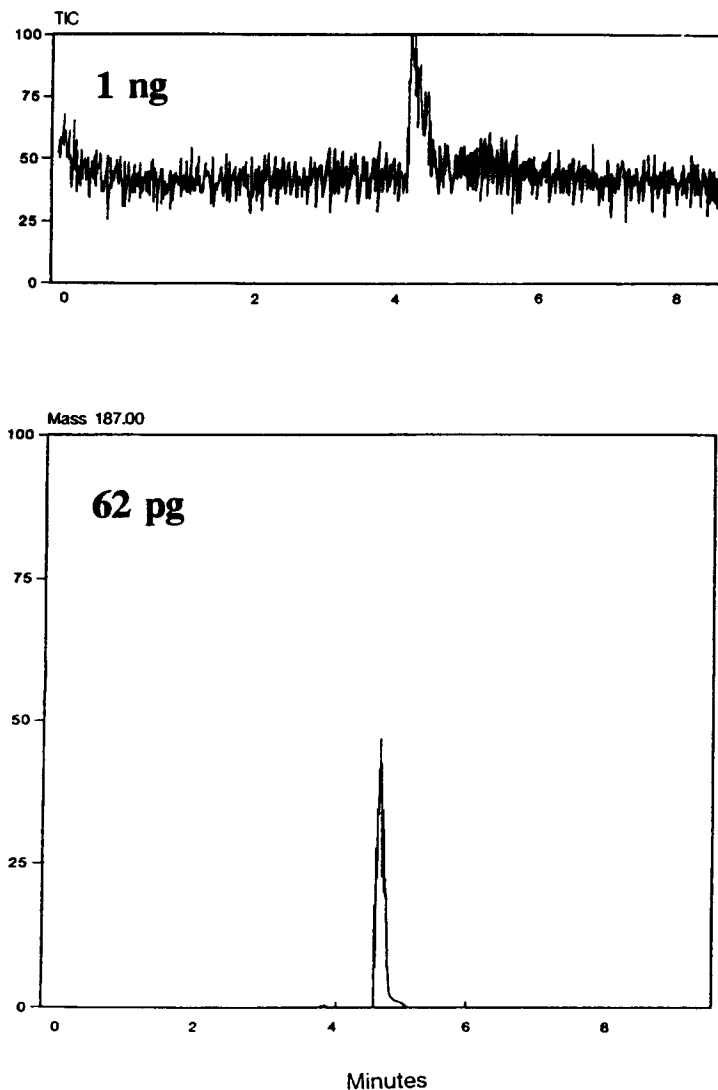


Fig. 5. Full-scan detection of 1 ng diuron and 62 pg in the selected-ion mode using a 1.5 m \times 0.05 mm I.D. SB-octyl 30 column at 100°C and 0.6 g/ml.

such as the temperatures of the transfer line and ion volume, flow-rate, and the position of the tip of the restrictor had no effect. Modifying the interface to allow differential heating of the transfer line also had no effect. The problem was solved by adjusting the temperature of the probe tip and ion source to 290°C. Two other shortcomings of the SFC-MS apparatus were the short life of the thoriated tungsten filament in the ionizer and clogging of the tapered restrictor tip. These problems were eliminated by

replacing the tungsten filament with a rhenium filament and using a capillary frit restrictor in place of the integral restrictor. The design and evaluation of the interface and mass spectrometer are presented in the following discussion.

Evaluation of the SFC-MS apparatus

Capillary SFC-MS is an attractive tool for polar thermally labile compounds such as carbamate pesticides [22–25] that are not amenable to GC-MS

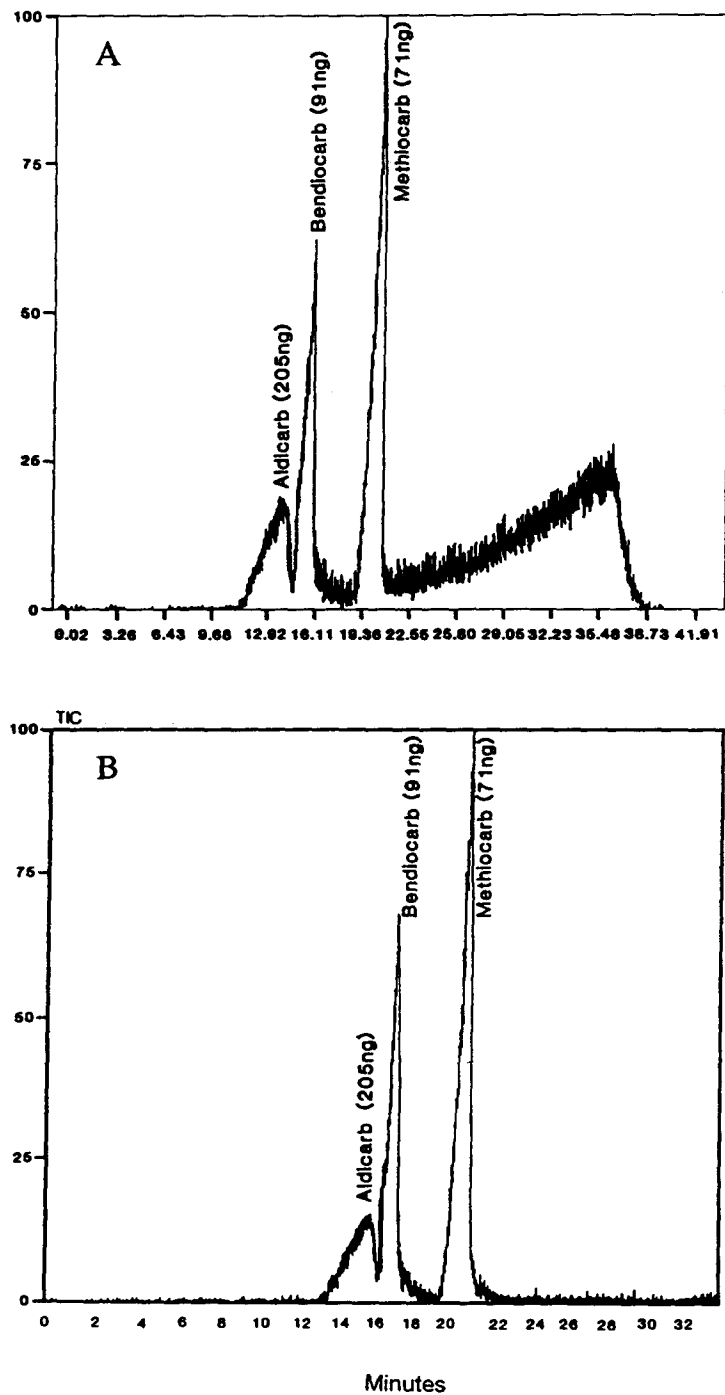


Fig. 6. The total ion chromatograms of a mixture of three carbamate pesticides obtained at different scan ranges using a 1.5 m × 0.05 mm I.D. SB-octyl 30 column at 80°C with density programming of carbon dioxide from 0.1 g/ml to 0.6 g/ml at 0.012 g/ml per min. (A) Scan range 50–250 u; (B) scan range 75–250 u.

methods. The SFC–EI–MS total ion chromatograms of four thermally labile pesticides including carbaryl (52 ng), methiocarb (60 ng), bendiocarb (44 ng) and diuron (60 ng) are shown in Fig. 3. Typical EI mass spectra of these pesticides are shown in Fig. 4 which compared favorably with the reference EI spectra obtained by other introduction methods. The chromatograms in Fig. 5 show the detection of 1 ng of diuron in the full scan mode ($S/N = 5$) and 63 pg of diuron in the selected-ion mode ($S/N > 100$), demonstrating the detection capability of this system. Separation and detection of a standard solution containing three carbamate pes-

ticides using density programming are shown in Fig. 6. The two chromatograms A and B were obtained under identical conditions except for the scan range. Chromatogram A was obtained by scanning between 50 and 250 u, while chromatogram B was obtained between 75 and 250 u. There is a substantial reduction in the noise and baseline drift in the TIC scanned above m/z 75, since predominant ions in the noise part of the TIC in Fig. 6A were m/z 71 and 72. The poor peak shape for the aldicarb in these figures was due to the stationary phase employed. The chromatograms shown in Fig. 7 are another example of the detection capability of

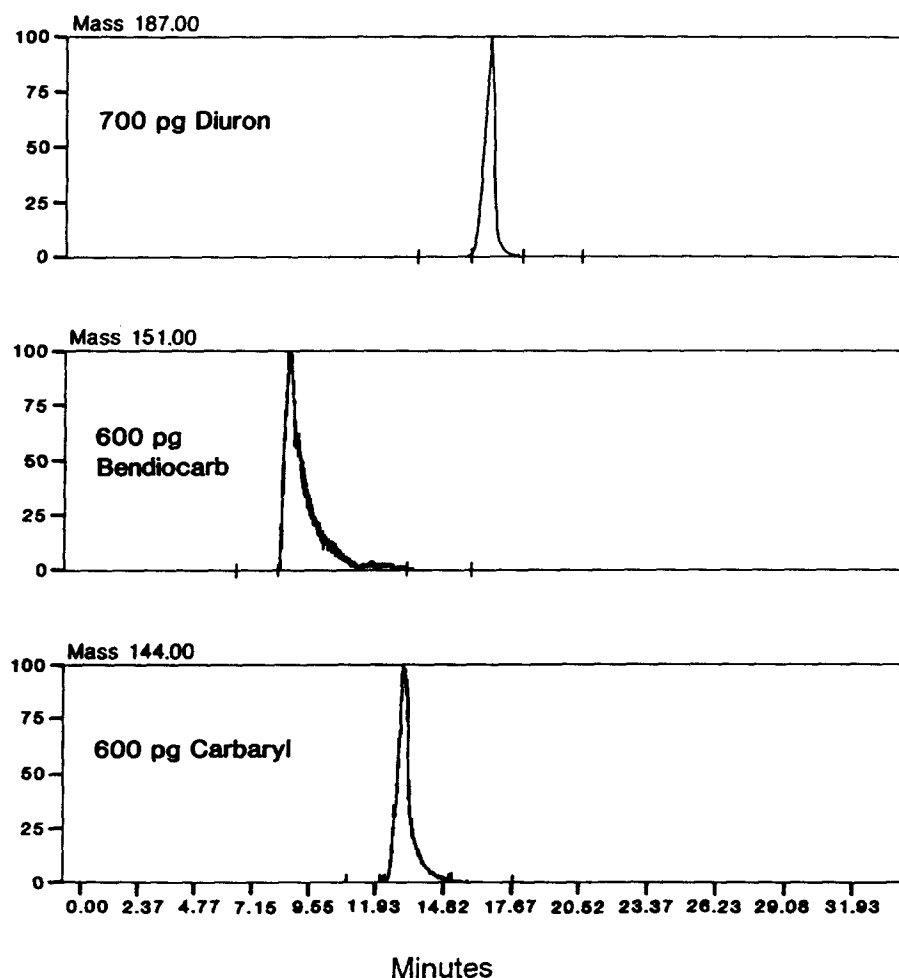


Fig. 7. Separation and detection of a pesticide mixture containing picogram levels of three thermally labile pesticides in the selected-ion mode. SFC conditions: 1.5 m \times 0.05 mm I.D. SB-biphenyl 30 column at 100°C with density programming of carbon dioxide from 0.1 to 0.6 g/ml at 0.012 g/ml per min.

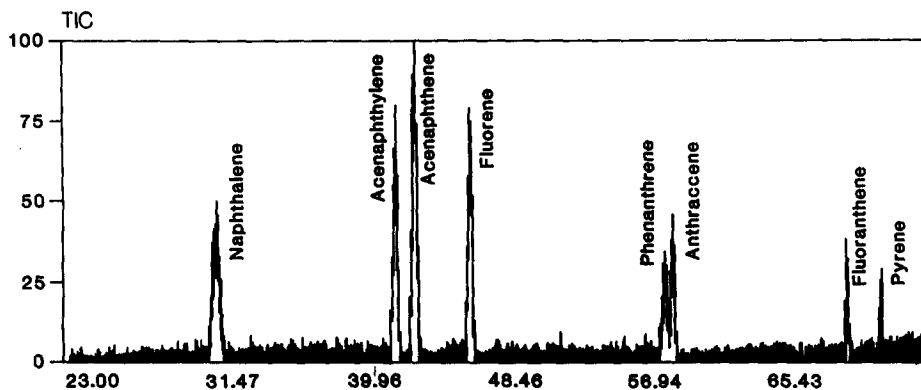


Fig. 8. Total ion chromatograms of a mixture containing eight polynuclear aromatic hydrocarbons using 5 m × 0.05 mm I.D. SB-biphenyl 30 column at 100°C with density programming from 0.2 to 0.3 g/ml at 0.01 g/ml per min then to 0.7 g/ml at 0.015 g/ml per min.

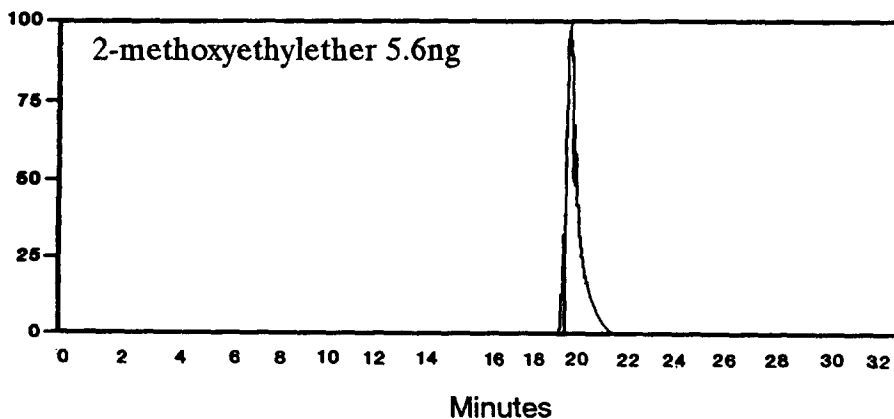
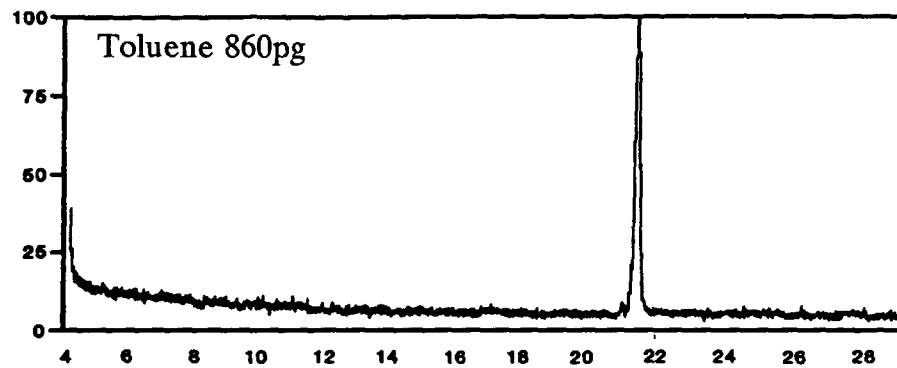


Fig. 9. Total ion chromatograms of 860 pg of toluene and 5.6 ng of 2-methoxyethyl ether using a 5 m × 0.05 mm I.D. SE-52 column at 100°C at 0.2 g/ml of carbon dioxide.

this system as a routine analytical tool. These chromatograms were obtained in the selected-ion monitoring mode for a standard pesticide solution containing diuron (700 pg), bendiocarb (600 pg), and carbaryl (600 pg) in methanol. The *S/N* ratios for these selected ion peaks were calculated to be 2700, 297, and 606 for diuron, bendiocarb and carbaryl, respectively.

The application of SFC–EI–MS to polynuclear aromatic hydrocarbons (PAHs) is shown in Fig. 8. The total ion chromatogram shows the separation and detection of a standard solution containing 15 ng each of eight PAHs.

Fig. 9 shows the total ion chromatogram for 860 pg of toluene and 5.6 ng of 2-methoxyethyl ether. Toluene has shown the lowest detectable level. There remains a significant difference in sensitivity and chromatographic peak shape between the solid pesticide and polynuclear aromatic compounds and the liquid analytes such as toluene and 2-methoxyethyl ether. Our best explanation for the observed differences is the insufficient atomization of the solid analytes at the restrictor end.

The SFC–EI–MS system has been evaluated for reproducibility and linearity of the detector response. Repeated injections of different standard naphthalene solutions were analyzed over a period of two weeks. The peak area results are shown in Fig. 10 for samples ranging from 50.7 ng to 126 ng.

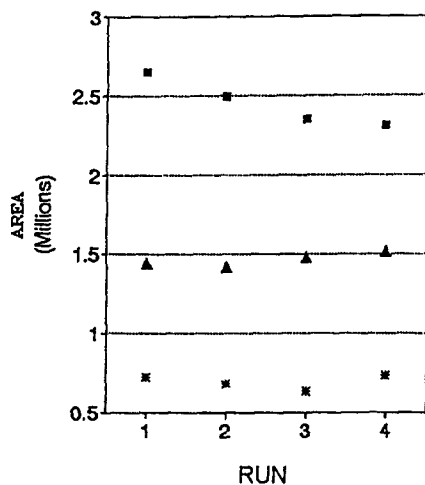


Fig. 10. The reproducibility of peak areas from the SFC–EI–MS for various amounts of naphthalene in methanol injected over two weeks. Symbols: ■ = 126 ng, ▲ = 76 ng, * = 50.7 ng.

The calculated %R.S.D. (5 replicates for each point) was from 2.9 to 6.4. It is evident from this graph that the response of this system is quite consistent.

The effect of the SFC column pressure on sensitivity and the signal-to-noise ratio has been evaluated using hexachlorobenzene as a standard. For column pressure between 219 and 347 atm, the chromatographic peak area of *m/z* 284 for a 100-ng injection of hexachlorobenzene changed from 50 841 to 10 750 for a decrease in sensitivity of 4.7. The *S/N* ratio decreased from 16 to 6 with the increase in pressure. Table I summarizes the peak areas and *S/N* for *m/z* 284 for three replicate 100-ng hexachlorobenzene injections at four different pressures. The best sensitivity is obtained at low pressure. The mass spectra obtained from the SFC–MS scanned above *m/z* 75 have been computer searched against the NIST/EPA/MSDC Version 3.02 Mass Spectral Database. For spectra that contained a low number of peaks below *m/z* 75, similarity indexes greater than 75 (perfect match = 100) have been obtained for comparison against the full library. Compounds which produce mass spectra with major peaks below *m/z* 75 do not provide good matches. Improved searching results have been achieved using an in-house library containing SFC mass spectra (start mass *m/z* 75). Similarity indexes of greater than 75 are common for spectra searched against this library.

CONCLUSIONS

The data presented in this paper clearly demonstrate the ease and feasibility of converting a commercially available benchtop GC–MS system into a SFC–EI–MS system for routine analytical work. The described instrument represents the most sensitive SFC–EI–MS reported yet. Traditional GC–MS techniques are not suitable for thermally labile pesticides, for which HPLC is the recommended analytical technique. The preliminary results reported here show that the analysis of these compounds are possible using SFC–MS with carbon dioxide as the mobile phase. The EI mass spectra can be searched against the conventional mass spectral library for compound identification. Further work is in progress in optimizing the detection capabilities of this system.

TABLE I

PEAK AREAS (m/z 284) AND SIGNAL-TO-NOISE RATIOS FOR A 100-ng HEXACHLOROBENZENE INJECTION AS A FUNCTION OF COLUMN PRESSURE

Values for the peak areas and S/N ratios are averages from three measurements.

Pressure (atm)	Peak area	S/N	R.S.D. (%)
219	50 841	16	1.4
250	28 804	22	2.2
305	14 088	10	5.6
347	10 750	6	2.1

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