

ABSTRACT

This application note discusses the analysis of two classes of pesticides – chlorinated species and organophosphate compounds. The Griffin™ 450 was used to analyze pesticide samples in GC/MS and GC/MS/MS modes. The Griffin™ 400 may also be used to perform the same analysis. The resulting chromatograms demonstrate the capability of the Griffin 450 in analyzing relatively nonvolatile compounds of interest.

INTRODUCTION

Sensitive, selective detection, identification and confirmation of a wide variety of chemical species has become a necessity in many applications including the quantitation of chemical warfare agents (CWAs), explosives, environmental pollutants and other toxic industrial compounds and materials (TICs/TIMs). In many instances, field-deployable sensors are preferred because valuable time, resources and chemical information are conserved by performing analyses directly in the field, rather than retrieving samples to be studied at a later time in the laboratory. The ICx line of compact, portable tandem mass spectrometers based on the Cylindrical Ion Trap (CIT) mass analyzer^{1,2} has been developed to fulfill this need. The importance of testing for pesticides is illustrated by the need to analyze for pesticides in water supplies, including ground water, and the structural similarity of pesticides to chemical warfare agents, specifically the nerve agents. Since these compounds are semivolatile, they provide a significant analytical challenge.

EXPERIMENTAL

One widely applicable analysis method supported by the Griffin 450 is the liquid-phase analysis. This is illustrated by analyzing the EPA 8270 organophosphorus pesticide mix and the chlorinated pesticide mixture B both available from Supelco (Bellefonte, PA). The pesticides supplied in the former include O,O,O -Triethyl Thiophosphate, Thionazin, Sulfotep, Phorate, Dimethoate, Disulfoton, Methyl Parathion and Parathion. Standard samples of the pesticide mix were prepared at various concentrations in cyclohexane. The chlorinated species included 1,2,3,4,5,5-Hexachloro-1,3-Pentadiene, Hexachlorobenzene, Atrazine, Heptachlor, Heptachlor Epoxide and Endrin. Dilutions of this mixture were also made in cyclohexane.

In these analyses, the instrument was equipped with a Low Thermal Mass Gas Chromatograph (LTM-GC), which provides rapid separation and introduction of the sample to the analyzer. The complete system included a split/splitless injector, LTM-GC and a mass spectrometer.

The system used helium as the carrier gas. The injector was set in split mode, with a split ratio of 20:1 and a temperature of 250°C. All guard column lines were set at 250°C. All samples were injected using a volume of 1 µL.

The samples were separated into their components using an Rtx-5MS column, 30 m x 0.25 mm i.d. x 0.25 µm df (Restek, Bellefonte, PA), with a column flow of 1 mL/min. The separation used a temperature ramp that started at 75°C, held for one minute and increased at 30°C per minute to 135°C. From 135°C it increased at 5°C per minute to the final temperature of 275°C and held for three minutes.

The total ion current plot obtained for 1 µL injection of Grob mix standard is shown in Figure 1. The blue total ion chromatogram (bottom) shows the results of a separation of the Grob mixture components using a conventional temperature program, i.e. with a column temperature ramp of 6°C/min. It is clear that the column is performing well in that all the components are present and the individual peaks are sharp and symmetrical. The only peak that is not sharply defined is that of 2-ethylhexanoic acid which is to be expected due to the non-polar nature of the Rtx-1MS column. The hydrocarbon and FAMES peaks show the column is properly installed and the peaks resulting from the alcohol components indicate that there are no significant active sites within the injector or column.

RESULTS/DISCUSSION

The total ion chromatogram (TIC) obtained for a 1 μL injection of 1000 $\text{pg}/\mu\text{L}$ organophosphorus pesticides solution is shown in Figure 1. The component peaks are separated from the solvent peak and are easily discernible from the baseline and from other components. Figure 2 shows a mass spectrum obtained from the methyl parathion peak. Also included in Figure 2 is a spectrum for the same compound found in the NIST mass spectral database. The Griffin software was used to search acquired spectra against the database, and, in the case of methyl parathion, resulted in a match probability of 88.5% based on automated mass spectral comparison.

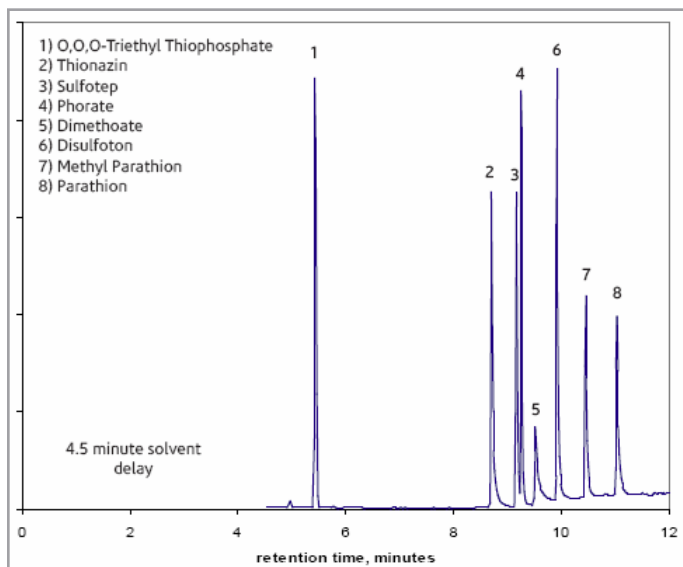


Figure 1: Total ion chromatogram trace for organophosphorus pesticides

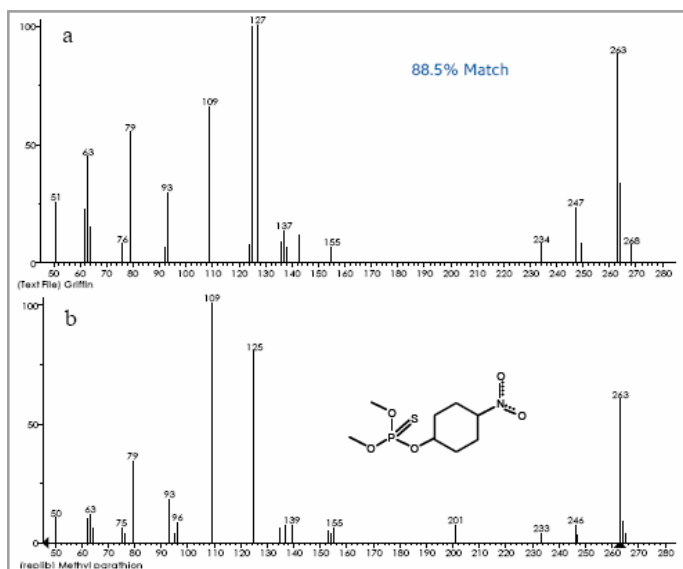


Figure 2: Methyl parathion spectrum from (a) Griffin GC/MS and (b) the NIST database

Figure 3 shows the total ion chromatogram for the chlorinated pesticide species at 1000 $\text{pg}/\mu\text{L}$ each. As with the organophosphate pesticides, searches against the NIST database resulted in the top matches being the compounds of interest, generally with match probabilities greater than 70. Figure 4 shows a screen capture of the ICx software displaying the heptachlor spectrum compared to the NIST spectrum for heptachlor (in red).

In addition to performing GC/MS analyses, the Griffin 450 is capable of tandem mass spectrometric analysis (MS/MS). Tandem MS experiments allow for enhanced sensitivity and selectivity when analyzing complex mixtures such as environmental samples.

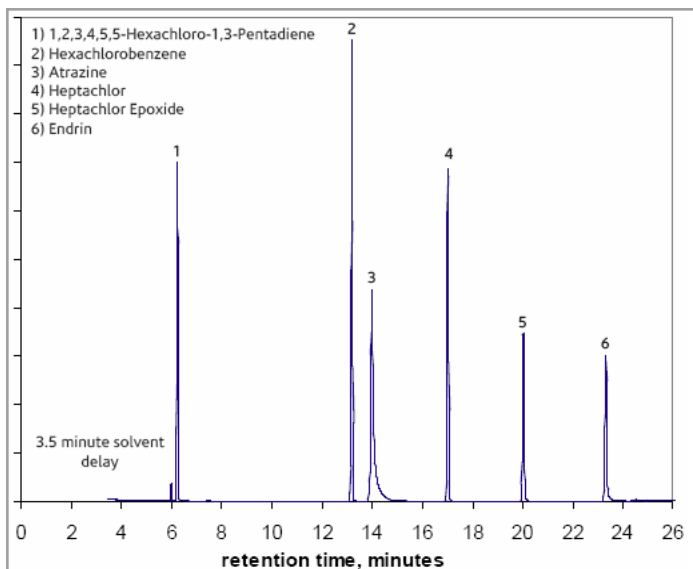


Figure 3: Total ion chromatogram trace for the chlorinated pesticide mixture

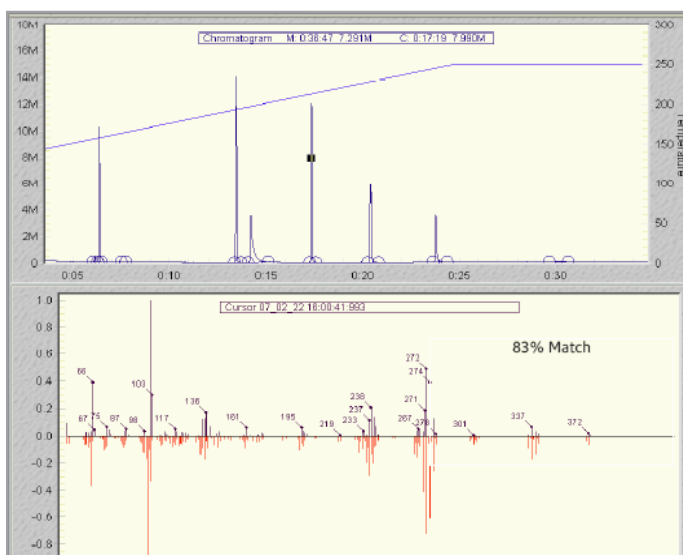


Figure 4: Software screen capture showing heptachlor mass spectrum compared with that of NIST

For two phosphonated compounds, O,O,O -triethyl thiophosphate and sulfotep, MS/MS analyses were performed and the data are shown in Figures 5 and 6. For each compound, a full MS mass spectrum (a) is shown which includes characteristic molecular ion and fragments, an isolation spectrum b) obtained from isolation of the molecular ion as the precursor (parent) ion, and the product ion mass spectrum (c) resulting from the collisionally-induced dissociation (CID) of the isolated precursor ion.

The Griffin software allowed for relatively simple selection of precursor ions and automatically sets dissociation parameters.

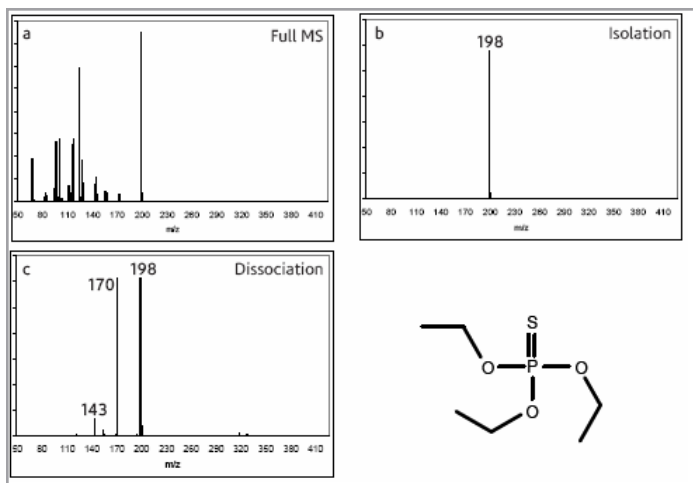


Figure 5: MS/MS data for showing full MS spectra (a) isolated precursor ion, (b) dissociation spectra, (c) for O,O,O -triethyl thiophosphate

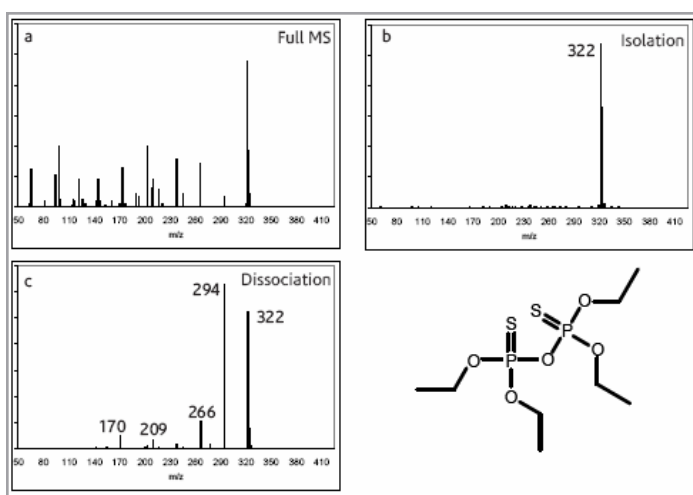


Figure 6: MS/MS data for showing full MS spectra (a) isolated precursor ion, (b) dissociation spectra, (c) for sulfotep

CONCLUSIONS

As these performance data illustrate, the combination of Griffin 450 and the Griffin software allowed for analysis and identification of mixtures of semivolatile pesticides. Combining sensitivity and the selectivity afforded by tandem mass spectrometry with the ruggedized form factor of the Griffin 450 creates a solution that can be used in varying areas and conditions for rapid, on-site analysis of samples.

These data represent typical results.

References

1. Wells, J.M.; Badman, E.R.; Cooks, R.G. *Anal. Chem.* 1998, 70, 438-444.
2. Patterson, G.E.; Guymon, A.J.; Riter, L.S.; Everly, M.; Griep-Raming, J.; Laughlin, B.C.; Ouyang, Z.; Cooks, R.G. *Anal. Chem.* 2002, 74, 6145-6153.

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