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Detection of Semivolatile Pesticides using a Transportable GC/MS/MS

ABSTRACT

This application note discusses the analysis of two classes of pesticides— chlorinated species and organophosphate compounds. The Griffin 450 GC/MS/MS 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 system in analyzing relatively non-volatile compounds of interest.

INTRODUCTION

Sensitive and 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 (CW) agents, explosives, environmental pollutants, and other toxic industrial compounds and materials (TICs/TIMs). Field-deployable sensors are preferred in many instances, 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. Griffin's 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 (see Figure 1). 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 instrument 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, the LTM-GC, and the mass spectrometer.

Figure 1. The Griffin 450 - Mobile GC/MS/MS



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 μ L.

The samples were separated into their components using a Rtx-5MS column, 30 m x 0.25 mm i.d. x 0.25 μ m 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 1 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 3 minutes.

RESULTS / DISCUSSION

The total ion chromatogram (TIC) obtained for a 1 μ L injection of 1000 pg/ μ L organophosphorus pesticides solution is shown in Figure 2. The component peaks are separated from the solvent peak and are easily discernable from the baseline and from other components. Figure 3 shows a mass spectrum obtained from the methyl parathion peak. Also included in Figure 3 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.

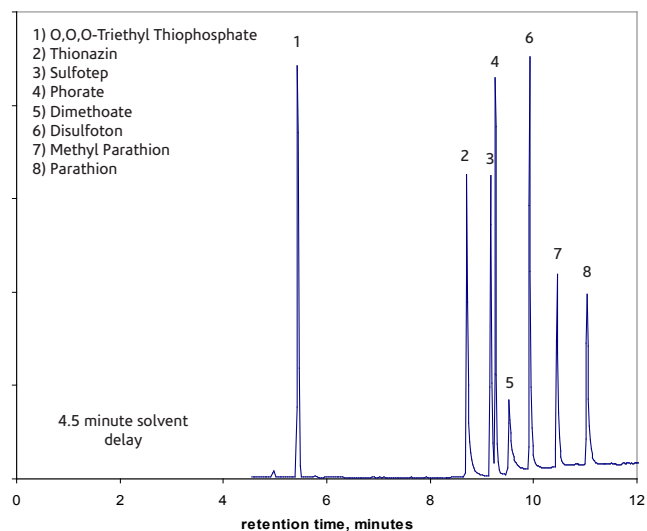


Figure 2. Total ion chromatogram trace for organophosphorus pesticides.

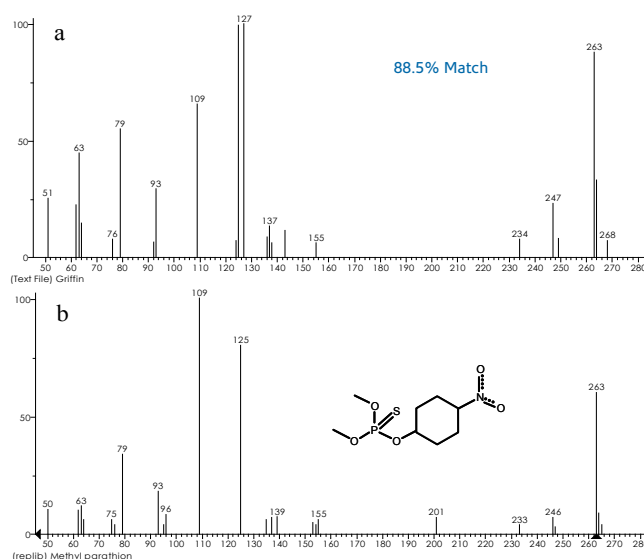


Figure 3. Methyl parathion spectrum from (a) Griffin GC/MS and (b) the NIST database.

Figure 4 shows the total ion chromatogram for the chlorinated pesticide species at 1000 pg/ μ 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 5 shows a screen capture of the Griffin software displaying the heptachlor spectrum compared to the NIST spectrum for heptachlor (in red).

In addition to performing GC/MS analyses, the Griffin 450 instrument by virtue of its being equipped with an ion trap mass analyzer is capable of tandem mass spectrometric analysis (MS/MS). Tandem MS experiments allow for enhanced sensitivity and selectivity which are particularly useful when analyzing complex mixtures such as environmental samples.

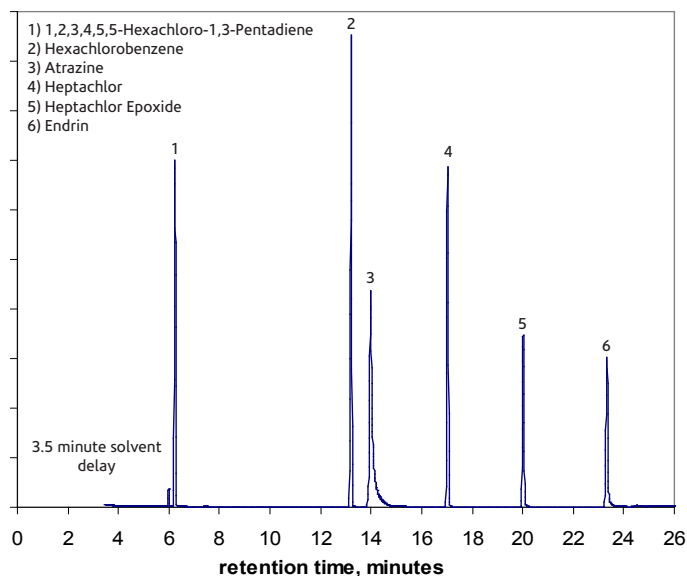


Figure 4. Total ion chromatogram trace for the chlorinated pesticide mixture.

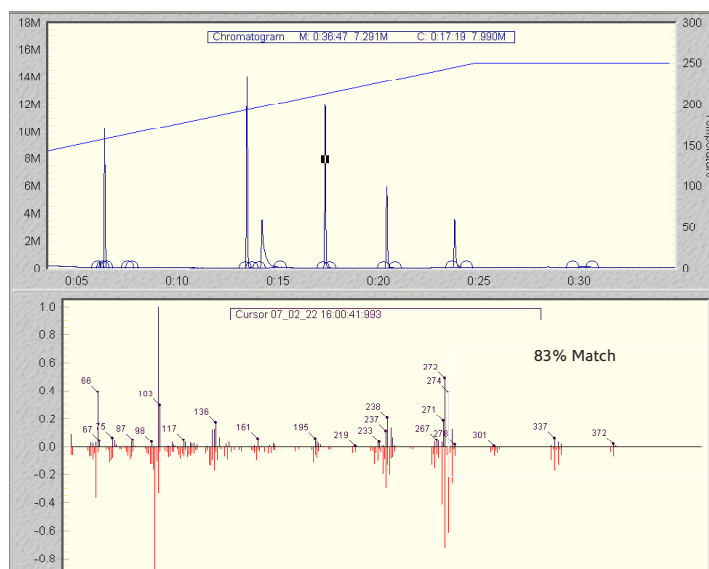


Figure 5. Software screen capture showing heptachlor mass spectrum compared with that of NIST.

For two phosphonated compounds, O,O,O-triethyl thiophosphate and sulfotep, MS/MS analyses were performed and the data are shown in Figures 6 and 7. 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.

CONCLUSIONS

As these performance data illustrate, the combination of Griffin 450 LTM-GC/MS/MS platform 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, onsite analysis of samples.

These data represent typical results.

REFERENCES

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- (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.

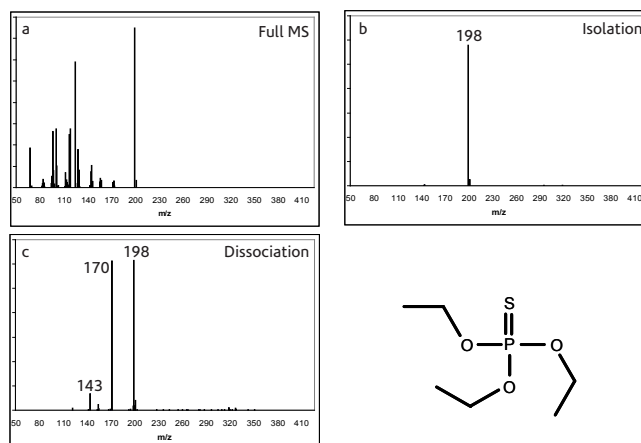


Figure 6. MS/MS data for showing full MS spectra (a), isolated precursor ion (b), and dissociation spectra (c) for O,O,O-triethyl thiophosphate.

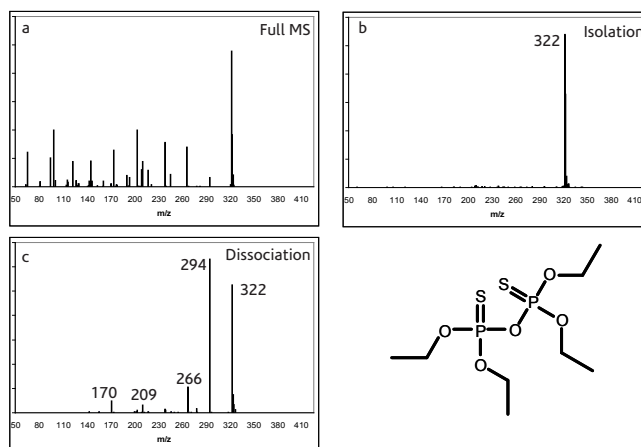


Figure 7. MS/MS data for showing full MS spectra (a), isolated precursor ion (b), and dissociation spectra (c) for sulfotep.