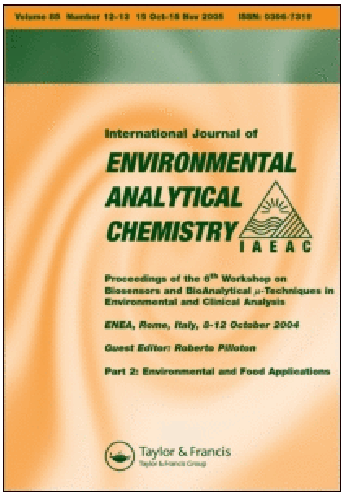

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APPLICATIONS OF MASS SPECTROMETRY TO ENVIRONMENTAL SAMPLES

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A variety of mass spectrometric techniques including electron impact ionization, positive and negative chemical ionization, low and high mass resolution and MS/MS are applied to samples of environmental interest. Examples of real data are given to demonstrate some of the applications of this methodology to several different sample matrices and the high degree of sensitivity and specificity made possible with modern instrumentation.

KEY WORDS: High resolution, MS/MS, positive CI, negative CI.

INTRODUCTION

Mass spectrometry(MS) is probably the most widely used technique at present for the identification and quantitation of trace levels of organic compounds. This is largely due to the very high degree of both sensitivity and specificity inherent in the instrumentation available.

The following data show examples of real life samples where methodologies utilize high resolution MS, positive and negative chemical ionization MS and MS/MS. These techniques were used to identify unknown components of complex mixtures and to eliminate analytical interferences which would otherwise cause incorrect quantitation. Classes of toxic chemicals analyzed include chlorinated dioxins and furans in pulp and paper mill effluents and sewage sludge, nitro-PAH in diesel exhaust, halogenated compounds in incinerator ash and pesticides in soil. All of the data shown were obtained from a VG Autospec Q hybrid mass spectrometer.

EXPERIMENTAL

Sample preparation and extraction

Pulp and paper mill effluents, sewage sludge samples and incinerator ash were processed using the sample handling and workup procedures given in Reference Method EPS 1/RM/19[1]. Diesel exhaust samples were prepared following the method given in Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions[2]. Soil samples for pesticide contamination were extracted with dichloromethane/hexane.

GC-MS system

All analysis were carried out using a VG ANALYTICAL Autospec Q hybrid mass spectrometer interfaced to a HP 5890 (Series II) gas chromatograph and equipped with a DIGITAL VAX4000 model 60 workstation using OPUS software. GC separations were performed on a J&W 30 m × 0.25 mm i.d. DB-5 fused silica capillary column with 0.25 um film thickness. Samples were injected onto the GC using the split/splitless injector in the splitless mode with a purge delay of 1.0 min. The column temperature program varied depending on the nature of the sample. UHP Helium was used as carrier gas and UHP methane or anhydrous ammonia as reagent gases for chemical ionization. Xenon was used as collision gas for MS/MS experiments.

RESULTS AND DISCUSSION

Chlorofurans in pulp and paper mill effluent

The top two traces of Figure 1 show mass chromatograms of a pulp and paper mill effluent monitoring the molecular ion for tetrachlorodibenzofurans at a mass spectral resolution of 10000. The 2378 isomer peak results from 5 pg of TCDF which is equivalent to 100 pg/l in the effluent.

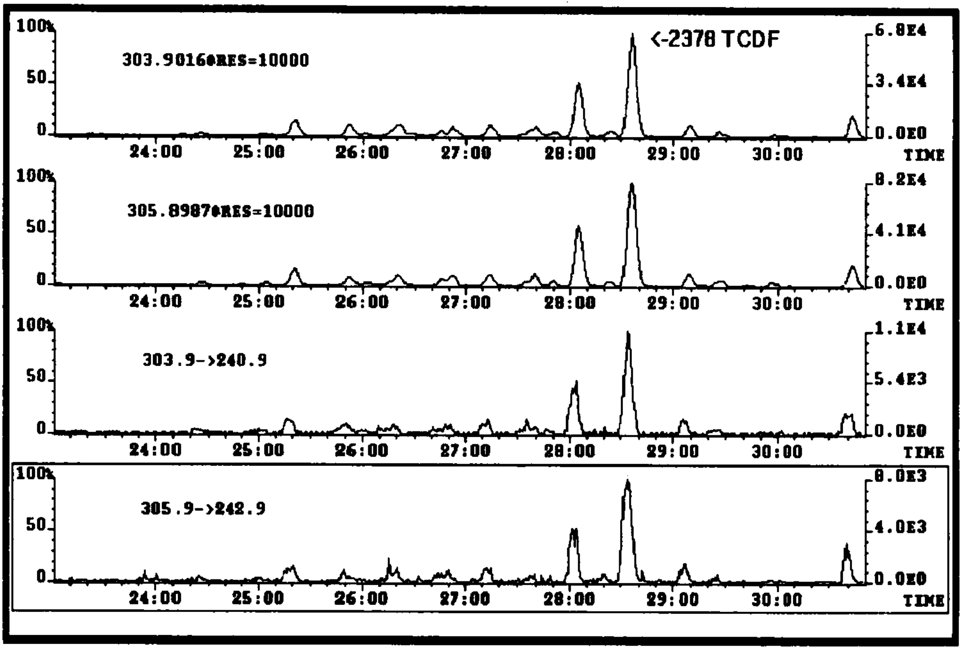

Figure 1 HRMS and MS/MS chromatograms of a pulp mill effluent.

The bottom two traces show the MS/MS chromatograms monitoring the loss of COCl from the molecular ion of tetrachlorodibenzofurans with the parent ion resolution set at 1000 and the daughter ion at unit resolution. The MS/MS analysis is less sensitive than high resolution selective ion recording (SIR) but is useful as a confirmation technique.

Nitro-PAH in diesel exhaust

Figure 2 shows mass chromatograms of a diesel exhaust extract for the molecular ion of C16 nitro-PAH isomers (N-fluoranthene/N-pyrene) under different operating conditions. The selectivity of analysis increases from low resolution electron impact (EI), high resolution EI, low resolution negative chemical ionization (NCI) and finally high resolution NCI showing that only one peak is really a nitro-PAH. This Figure also demonstrates a significant increase in sensitivity when NCI is used.

Figure 3 shows mass chromatograms of a diesel exhaust extract for the molecular ion of C13 nitro-PAH isomers (N-fluorene) utilizing high resolution SIR and MS/MS in the NCI mode. It is evident that in this case MS/MS is more specific than high resolution MS.

Figure 4 shows the signal to noise calculations for 15 pg of 2-nitrofluorene run by high resolution MS and by MS/MS in the NCI mode. The slightly lower sensitivity of the MS/MS result is more than compensated by its greater selectivity as seen in Figure 3. It is also noteworthy that the absolute signal intensity is two orders of magnitude lower for MS/MS but the noise is also much lower than for high resolution MS.

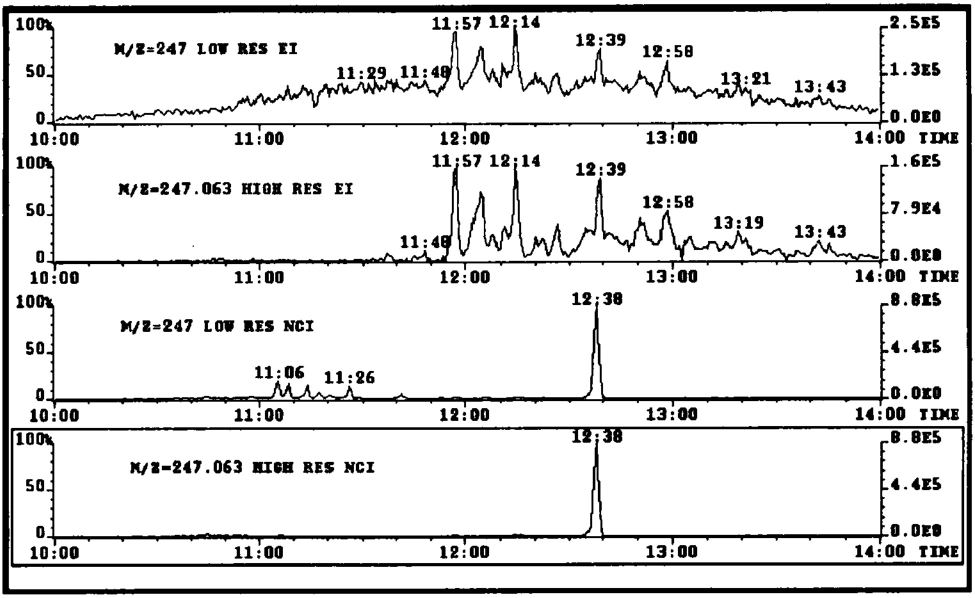

Figure 2 Mass chromatograms of nitro-PAH in diesel exhaust using EI and NCI modes.

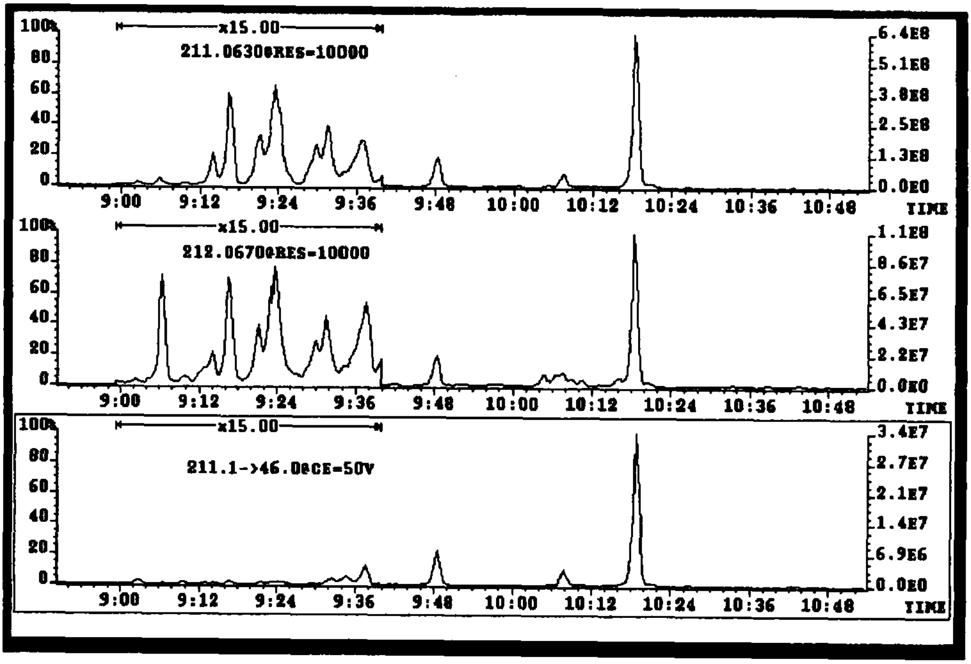

Figure 3 HRMS and MS/MS chromatograms of nitro-PAH in diesel exhaust.

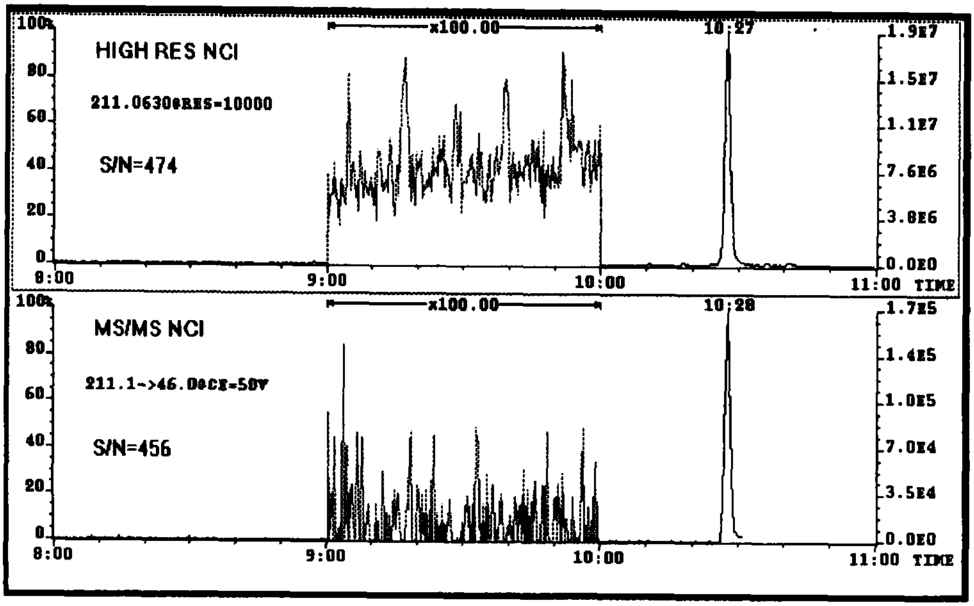

Figure 4 Comparison of signal to noise for HRMS and MS/MS for nitro-PAH.

Halogenated compounds in sewage sludge

Figure 5 shows mass chromatograms of a sewage sludge extract analyzed by electron impact and negative CI. The NCI trace shows electron capturing components at greater sensitivity than the EI trace and the mass traces of 35 and 79 allow the identification of chlorine and bromine containing compounds.

Figure 6 shows the EI spectrum of the peak marked with an asterisk in Figure 5. High resolution analysis gave the empirical formula shown confirming the compound to be a pentabromodiphenylether isomer.

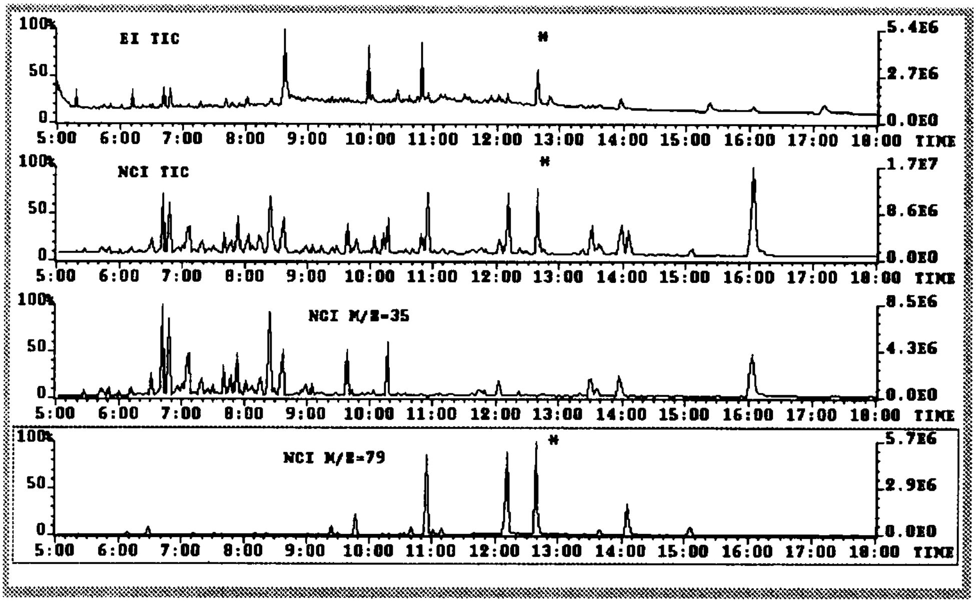

Figure 5 Full scan and ion chromatograms of a sludge extract in EI and NCI modes.

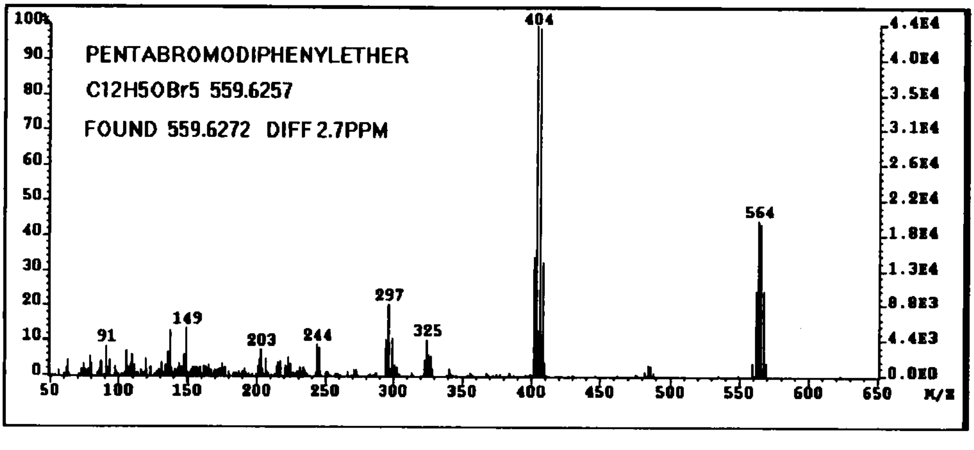

Figure 6 EI spectrum of a brominated compound in sludge extract.

Incinerator ash

Figure 7 shows the electron impact total ion current for an extract of bottom ash from the incineration of pentachlorophenol contaminated waste. The largest peak is due to octachlorodibenzofuran and dioxin but there are later eluting peaks. Figure 8 shows the EI spectrum of the peak marked with an asterisk along with the empirical formula from high resolution analysis indicating it to be a hexachloropyrene isomer.

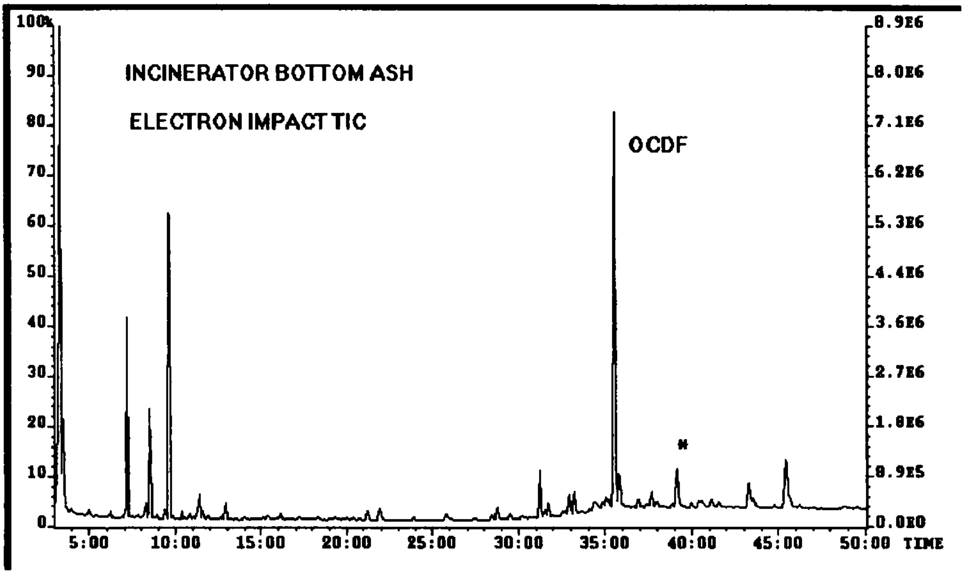

Figure 7 Total ion chromatogram of incinerator bottom ash.

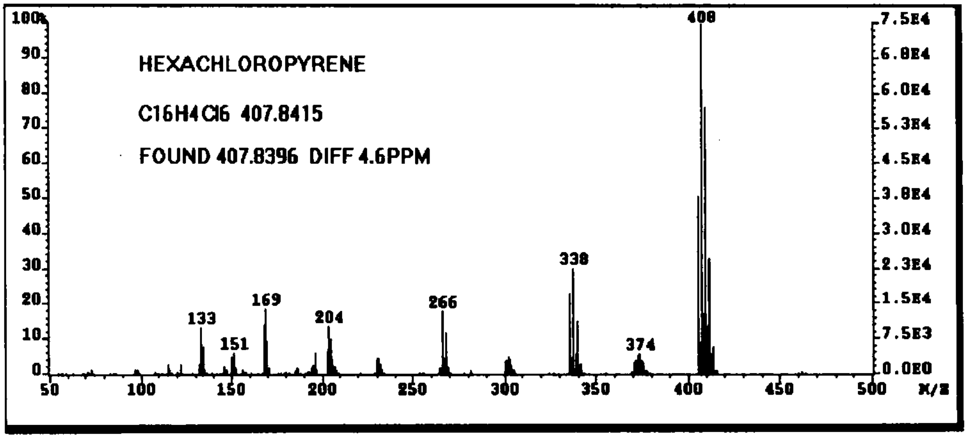

Figure 8 EI spectrum of compound in incinerator ash.

Pesticides in soil

Figures 9, 10 and 11 show the mass spectra of the pesticide parathion detected in soil from an old storage site, analysed by three different ionization modes. As can be seen, the spectra are totally different and these techniques can be used as a confirmation of identity if high resolution or MS/MS capability is not available.

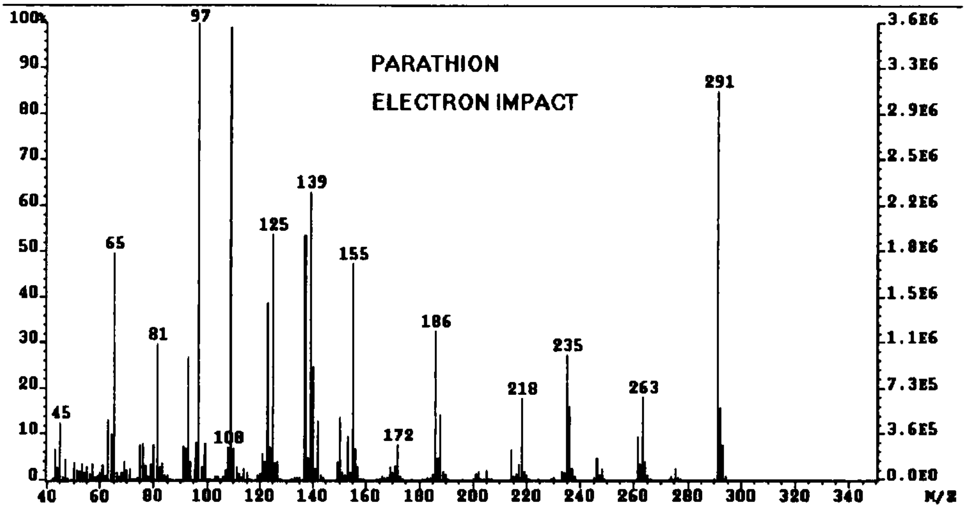

Figure 9 EI spectrum of Parathion.

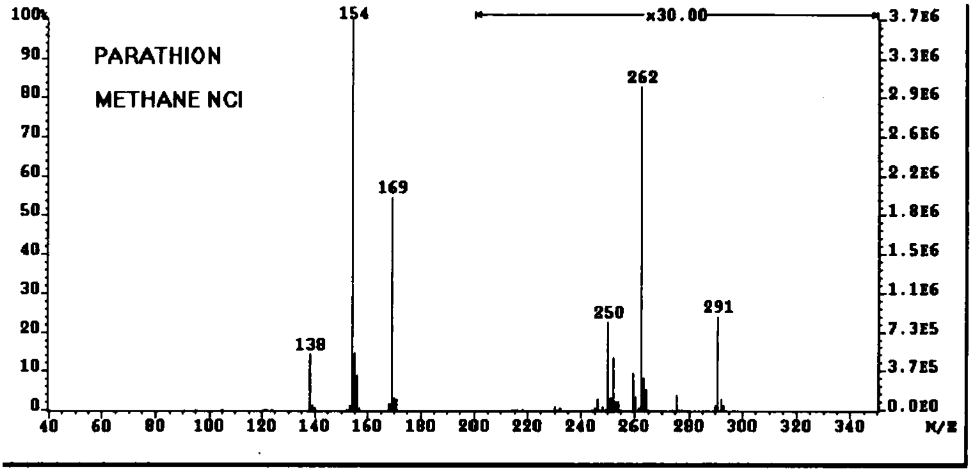

Figure 10 Methane NCI spectrum of Parathion.

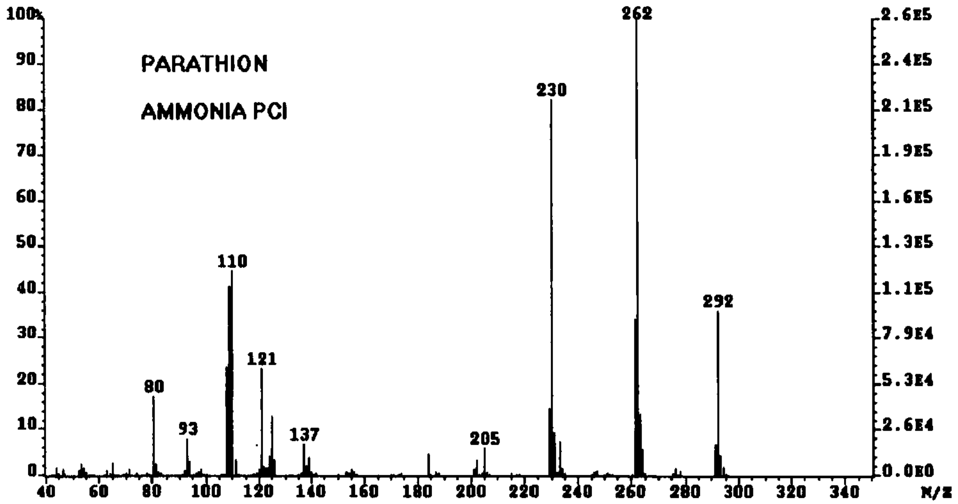

Figure 11 Ammonia PCI spectrum of Parathion.

CONCLUSIONS

These results demonstrate the wide variety of techniques available on modern mass spectrometers as well as the sensitivity, selectivity and capacity for identification of unknown materials inherent in the instrumentation. These examples were restricted to GC-MS but the use of LC-MS and ionization methods such as electrospray and fast atom bombardment (FAB) greatly extends the classes of compounds which can be analysed by MS.

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