Detection of Gasoline in Fire Debris by GC/MS/MS

GC/MS

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Introduction

Samples of debris from fires are routinely analyzed for traces of hydrocarbon accelerants[1]. The method of analysis has been by gas chromatography with FID, once sample work-up is complete. More recently, mass spectrometry has been the method of detection used[2]. The switch to MS, instead of FID, was undertaken in order to eliminate the problems caused by the interference of pyrolysis products in the chromatograms obtained. The method of determination of hydrocarbon distillate type was by comparison of the sample chromatogram to that of standards. Individual mass chromatograms of key ions are typically plotted to make this comparison. However, a good comparison is not always possible as in many cases the sample is well burned, leading to residues of distillate and large amounts of pyrolysis products.

Discussion

In order to overcome the pyrolysis product interference and improve detection levels, MS/MS was utilized as the method of detection. As gasoline is one of the more common distillates used by arsonists, the identification of gasoline in fire debris samples was undertaken. Initially the ion of m/z 91, either as a parent, or daughter ion, was isolated and the MS/MS chromatograms for a variety of hydrocarbon distillates were obtained. The same analysis was then performed on fire debris samples. Initial results were successful and thus it was decided to improve the technique by isolating the masses as set out in Table 1. These masses are the molecular weights of the more abundant aromatic compounds found in the gasoline.

As gasoline is a distillate, the ratios of the isomers for each molecular weight are characteristic, and were thus compared. It was decided to compare the aromatic compounds, as these are the more characteristic compounds contained in gasoline.

The initial experimentation with m/z 91 showed that the use of resonance excitation did not provide enough fragmentation ions; therefore, non-resonance excitation was used throughout the mass ranges isolated. This method proved to be sufficient for all masses analyzed. The Toolkit Automated Method Development (AMD) feature was used to determine the CID voltage for each mass. Standards for the common aromatic compounds in gasoline were injected for this purpose.

Figure 1 shows a typical gasoline sample chromatogram using electron ionization GC/MS and a carpet sampled burned with gasoline as the accelerant. The difference in correlation of the two
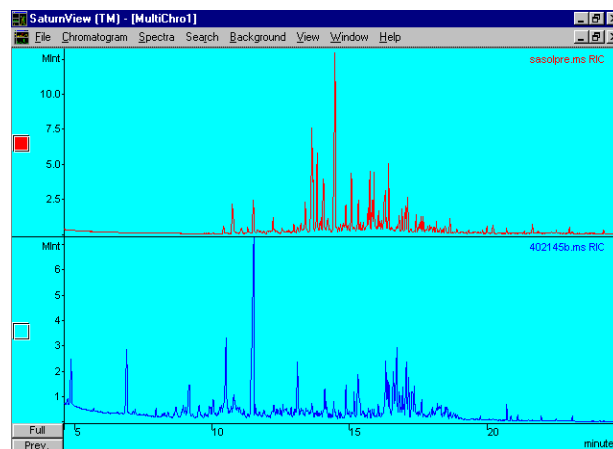

Figure 1: (Top) GC/MS analysis of gasoline sample. (Bottom) GC/MS analysis of carpet sample burned with gasoline.

samples is such that no positive conclusion that gasoline was used as an accelerant can be made. The pyrolysis products from the burned carpet contribute heavily to the chromatogram, as the gasoline residue is minute.

Gasoline contains many compounds that are aromatic and are alkylbenzenes. These compounds contain a predominant ion at m/z 91 and they can be screened by the presence of this ion from the rest of the aliphatic hydrocarbons. By choosing this ion as the parent ion for MS/MS analysis, a chromatographic pattern can be obtained for the gasoline and burned carpet samples. Figure 2 shows these chromatograms.
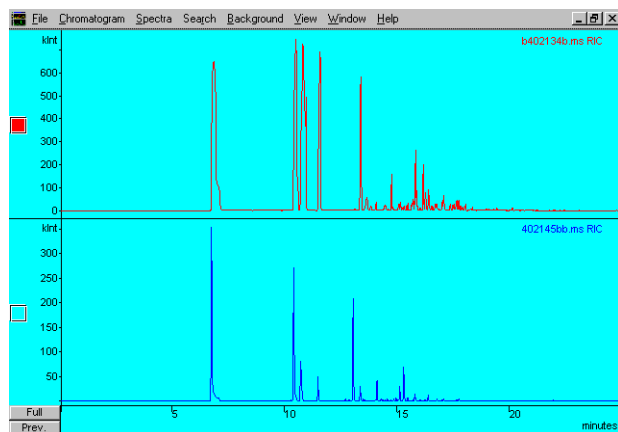

Figure 2: (Top) GC/MS/MS analysis of a gasoline sample using m/z 91 as the parent ion. (Bottom) GC/MS/MS analysis of a burned carpet sample using m/z 91 as the parent ion.

Note that the correlation is much better than that obtained using GC/MS, as in Figure 1.By taking this one step further, an even better correlation can be obtained. MS/MS is a time programmable feature throughout the chromatogram. This allows us to choose certain key compounds such as alkylbenzenes and alkyl substituted PAH's and analyze for these compounds and exclude all other matrix ions. In Figure 3 we can see that the correlation for this GC/MS/MS analysis is excellent and that the carpet was burned with gasoline.
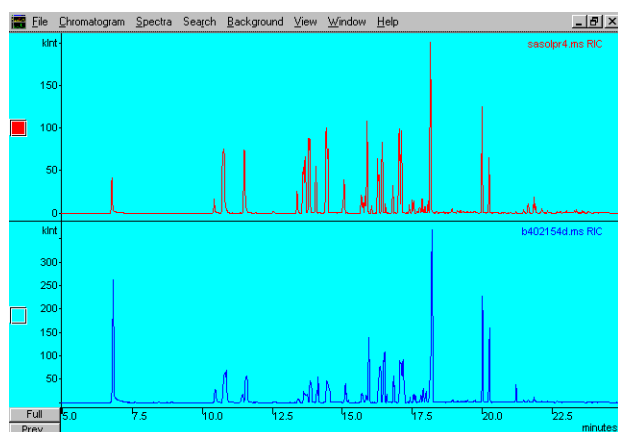

Figure 3: (top) Time programmed GC/MS/MS analysis of gasoline for aromatic compounds. (Bottom) Time programmed GC/MS/MS analysis of carpet sample burned with gasoline.

Experimental
Samples of fire debris were placed in oven bags with a charcoal absorbent strip. The bags were sealed and then heated to 60°C and maintained for 8 hours. After removal from the oven, the absorbent strip is removed, desorbed with carbon disulfide and the solution analyzed.

Gas Chromatograph
Column: DB-1 30M x 0.32mm ID x 0.25μm
Oven Program: 30°C for 6 minutes, program to 70°C at 7°C/min., program to 230°C at 10°C/min. and hold for 13 minutes.
Injector: 180°C

Mass Spectrometer
Scan range: 40-300
Scan rate: 0.71 Sec/Scan
Background mass: 35 u
Ion trap temperature: 120°C
Manifold temperature: 45°C
Transfer line temperature: 280°C
Window: 2 AMU for all compounds
RF level: 48 AMU for all compounds

Table 1: MS/MS Conditions		
Mass	**Non-Resonant Voltage**	**Compound**
91	50	C1-Benzene
106	35	C2-Benzene
120	40	C3-Benzene
134	35	C4-Benzene
148	40	C5-Benzene
162	30	C6-Benzene
128	30	Naphthalene
142	30	C1-Naphthalene
156	30	C2-Naphthalene
170	30	C3-Naphthalene
178	30	Anthracene
192	30	C1-Anthracene
206	85	C2-Anthracene

Conclusion
The use of GC/MS/MS allows a direct comparison of standard compounds to burned material, in order to determine the type of accelerant used in a fire. An excellent correlation can be obtained, since the matrix compounds of the sample can be eliminated due to the high selectivity of GC/MS/MS. GC/MS/MS is an invaluable analytical technique in suspected arson cases.

Acknowledgement

References
1. Smith, RM, *Anal. Chem.,* 1982, 1410A.
2. Bertsch, W, *Anal. Chem.,* 1996, 540A.