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AS205

Wellbrook Court I Girton Road I Cambridge I CB3 0NA I
I tel: +44 (0) 1223 279210 I fax: +44 (0) 1223 279253
I email: enquiries@anatune.co.uk I anatune.co.uk

ANALYSIS OF FIRE DEBRIS SAMPLES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND CHEMOMETRICS

Jamie Minaeian, Eleanor Miller, Phine Banks and Camilla Liscio, Anatune Ltd., Girton, Cambridgeshire (UK).
Karen Robertson, Scottish Police Authority Forensic Services, Gartcosh, Scotland.

INTRODUCTION

The use of biofuels as an accelerant in arson attacks has increased over recent years. This can be challenging for the Forensic Chemist tasked with analysing the debris to determine the location and nature of the fire.

Biofuels, in particular biodiesels, incorporate long chain methyl esters from vegetable and animal fats, together with the range of hydrocarbon components.

This application note showcases the power of chemometrics using Agilent Mass Profiler Professional (MPP) software to highlight small differences in chromatograms taken from fire debris samples, which would be extremely challenging to conduct manually.

INTRUMENTATION

- SPME Analysis:
- GC – Agilent 7890B
- MS – Agilent MSD 5975B
- Autosampler – Gerstel MPS XT with Agitator and SPME capabilities
- SPME – 20 mm fibre with DVB, Carboxin and PDMS

Figure 1: Agilent 7890B/5975B GC/MS used for this analysis. The GERSTEL MPS XT has been equipped with an Agitator and SPME capabilities.

SCENARIO

Samples were set to mirror what could be received as a case. The 'scene' samples were prepared by SPA Forensic Services and included:

- A liquid sample of diesel
- A liquid sample of biodiesel
- A piece of burnt cloth spiked with one of the fuels (this was conducted as a 'blind' experiment)
- A control nylon bag as per normal casework procedures to ensure no cross contamination

METHODS

The liquid samples were injected six times each, interspersed with blanks. A preliminary analysis of the data showed two very similar sets of chromatograms. The differences were difficult to determine by manually inspecting the chromatograms. Figure 2 shows the chromatograms of diesel (top) and biodiesel (bottom).

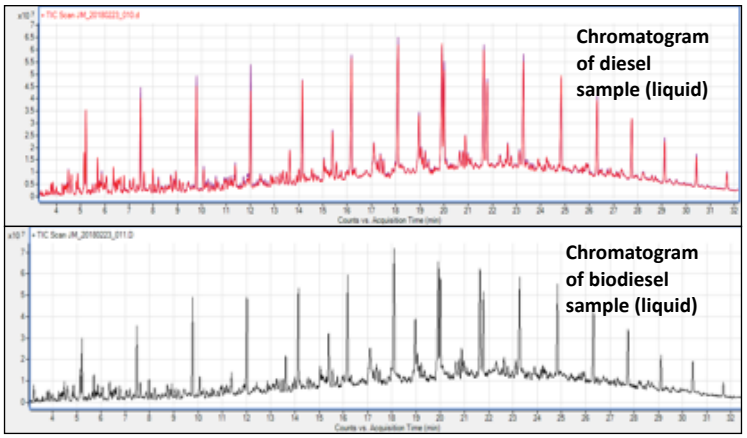

Figure 2: TIC of two samples, one of diesel (top), one of biodiesel (bottom).

Acquired data were processed using Agilent Mass Hunter Unknowns Analysis software to deconvolute the complex chromatographic information, extract and library search relevant components. Deconvoluted data were converted to Compound Exchange Format files (CEF) to be exported to Agilent Mass Profiler Professional (MPP) software for statistical interpretation of the data.

RESULTS AND DISCUSSION

MPP data processing performs the following: experiment grouping, filtering according to abundance, retention time and mass, retention time alignment, baselining, significance testing and fold change. This process allows to recognise what in MPP software are called *entities*. An entity (aka compound or component) is a molecular species for which retention time, mass and abundance have been detected. Entities can be identified or unidentified.

Significance analysis combines a statistical significance test (t-test or ANOVA) with a fold change filter and visualises the results in a volcano plot. A volcano plot shows statistically significant differences between sets of samples, based on a number of entities. Figure 3 shows the volcano plot obtained for the liquid injection replicates. Compounds showed above the green horizontal line (p-value cut-off) and the two vertical lines (fold change cut-off) passed the significance analysis. The blue dots represent the biodiesel, with the red dots representing the diesel. Table 1 lists the suggested compounds.

As highlighted in Table 1, the chemometrics approach allowed the determination of fatty acid methyl esters (FAMEs) as statistically different in the two investigated samples.

Furthermore, Principal Components Analysis (PCA) is a very effective visual way to explore the variance in the data set and it helps with the identification of patterns. Figure 4 shows the Principal Component Analysis graphs for the investigated samples. The two samples separated nicely in different clusters, with yellow dots indicating the biodiesel, and red dots indicating the diesel samples.

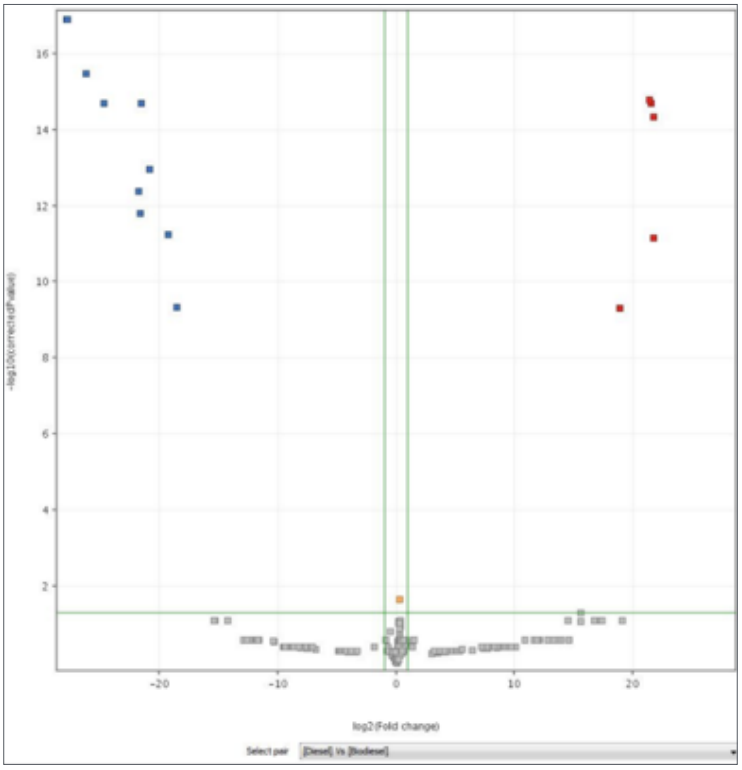

Figure 3: Volcano plot for the significance analysis of the replicate liquid injections

Compounds	Retention Time	Formula	CAS Number
Hexadecanoic acid, methyl ester	23.830	C17H34O2	112-39-0
9-Octadecenoic acid (Z)-, methyl ester	26.536	C19H36O2	112-62-9
Methyl stearate	26.854	C19H38O2	112-61-8
9,11-Octadecadienoic acid, methyl ester, (E,E)-	26.440	C19H34O2	13038-47-6
Eicosanoic acid, methyl ester	29.618	C21H42O2	1120-28-1
Methyl 20-methyl-heneicosanoate	32.181	C23H46O2	1000336-47-4

Table 1: List of compounds highlighted as significant by the Volcano plot in the liquid injection samples.

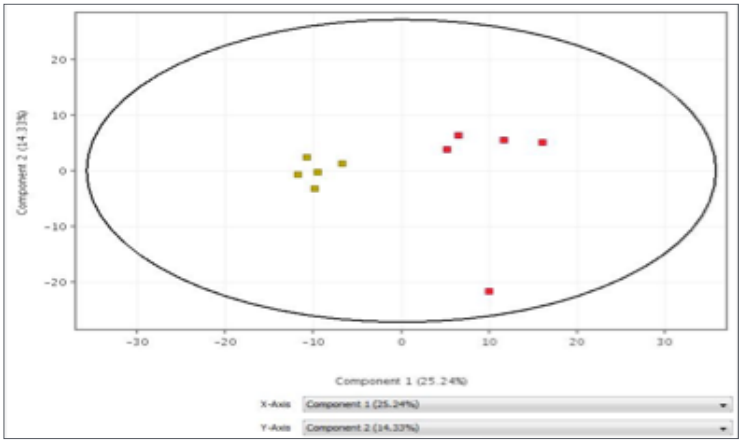

Figure 4: PCA obtained for the analysis of liquid samples by GC-MS

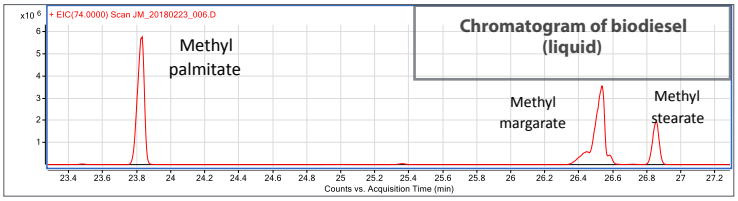

Figure 5: EIC of the biodiesel liquid injections. The shown peaks are from the left methyl palmitate, methyl margarate and methyl stearate, respectively. This is overlaid with a blank in black.

The biodiesel sample was then analysed by SPME-GC-MS using the same GC-MS conditions. As the SPME analysis requires compounds to be in the headspace, the observed peaks are smaller than those obtained by liquid injection. However, they still present an acceptable signal-to-noise ratio of 3.6. Figure 7 shows the overlaid EICs for the SPME analysis.

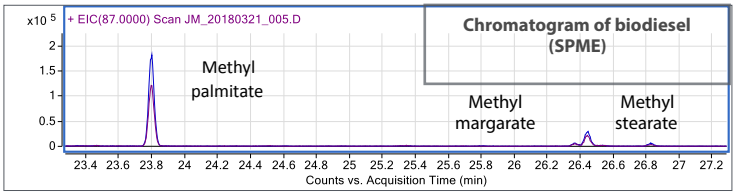

Figure 6: Overlaid EICs for the repeated SPME injections. The shown peaks are, from the left methyl palmitate, methyl margarate and methyl stearate. A blank has been overlaid in black.

The analysis of the fabric sample revealed the same peaks at lower intensity, nevertheless, methyl palmitate and methyl stearate could still be detected, leading to the conclusion that biodiesel was the used fire accelerant

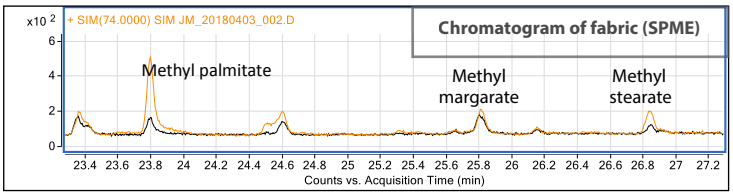

Figure 7: Overlaid EICs of burnt fabric sample suggesting the presence of methyl palmitate, methyl margarate and methyl stearate. Overlaid is a blank in black.

CONCLUSIONS

This short study demonstrates the power of chemometrics to allow the identification of small differences between samples looking similar by visual inspection.

PCA plots clearly separates the sample in two distinctive clusters. The Volcano plot allowed the identification of entities statistically different between the samples. This difference was confirmed by the inspection of the EICs of the two samples.

Furthermore, SPME analysis showed a capability to detect the target compounds offering better selectivity when compared to the liquid injections.

This work was done in collaboration with the Scottish Police Authority Forensic Services.