

# The Investigation of Arson Samples by GCxGC-TOFMS

LECO Corporation; South Africa • LECO Corporation; Saint Joseph, Michigan USA

Key Words: TOFMS, GCxGC, Forensics

## 1. Introduction

The crime of arson is a worldwide problem. It is defined as the willful and malicious burning of a person's property, and can be used (amongst other possibilities) to institute fraudulent insurance claims and destroy evidence of other crime or malpractice. It is extremely difficult to investigate as the crime itself destroys the physical evidence at its origin.

Investigation of the crime is complicated by many factors. Some of the most important are: 1) only small amounts of accelerant remains after a fire; 2) the accelerant itself undergoes changes as a result of exposure to extreme heat; 3) pyrolysis of matrix materials generates volatiles which interfere with the determination of accelerant components surviving after a fire.

As a result of the above considerations, the identification of individual compounds in an arson sample becomes less significant. For this reason no Peak Tables have been included in this Application Note. Pattern recognition plays a much greater role, and the screening of accelerant residues by MS requires selection of diagnostic ions typical of a particular accelerant. These can be molecular or fragment ions, showing a characteristic isomer pattern for the accelerant. Some ions which are typically used in arson investigations are shown in Table 1 below.

Table 1. Identified compounds and unique ions

Compound	m/z
Saturated aliphatics (straight chain and branched)	57, 71, 85, 99
Alicyclics and olefinics	55, 69, 83, 97
C1 to C4 alkylbenzenes	91, 105, 119
Benzene and C1 to C3 alkylbenzenes	78, 92, 106, 120
C4 alkylbenzenes	119, 134
C5 and C6 alkylbenzenes	148, 162
Alkyl naphthalenes	128, 142, 156, 170
Alkylstyrenes and dihydroindenes	104, 118, 132, 146
Alkylanthracenes	178, 192, 206
Alkylbiphenyls and acenaphthenes	154, 168, 182, 196
Monoterpenes (C10H16)	93, 136

Using ion profiles makes it possible to reduce matrix interference, and obtain a better picture of the arson sample. Diagnostic patterns can be seen which are characteristic of the presence of accelerants, and a more confident prediction of the presence or absence of an accelerant can be made. One-dimensional GC, coupled with MS/FID has been used for many years to investigate arson samples. This approach is complicated by the considerable amounts of matrix components present in arson samples, and the overlap of numerous interfering compounds. GCxGC should provide a better tool for arson investigation. The increased peak capacity of GCxGC will

give improved separation of matrix interference from components of interest, and the patterns characteristic of the use of an accelerant should be more simple to discern.

We have investigated this possibility in arson samples containing gasoline as an accelerant. These samples were supplied by Ms. B-J de Vos and Ms. L Lebelo of the National Metrology Laboratory; Pretoria, South Africa.

## 2. Instruments and Methods

LECO Pegasus® 4D GCxGC-TOFMS

GC Conditions

Column 1: 30 m x 0.25 mm x 0.25  $\mu$ m Rtx-5 Sil MS

Column 2: 2 m x 0.18 mm x 0.20  $\mu$ m Rtx-200

Inlet: Split (1:100) at 200°C

Oven

Primary: 35°C (2 minutes), 2°/minute to 175°

Secondary: 50°C (2 minutes), 2°/minute to 190°

Modulator Offset: 20°C

Modulation Period: 6 seconds

Transfer Line: 200°C

Injection: 1  $\mu$ l

Carrier Gas: Helium, 1.0 mL/minute constant flow

TOFMS Conditions

Source Temperature: 200°C

Acquisition Rate: 100 spectra/sec

Stored Mass Range: 45 to 350 u

## 3. Results

A gasoline standard sample was run under the conditions described above. This was followed by the sample provided by the NML. This sample was from a genuine arson case, in which gasoline was known to have been used as an accelerant. The sample results were then compared with one another, by first examining the TIC and then using three sets of extracted ions, chosen from Table 1 above. The sets of extracted ions used were: 1) 57 + 71 + 85; 2) 91 + 105 + 134; and 3) 128 + 142 + 156 + 170.

The first set is used to highlight the alkanes present in the samples; the second set to highlight the substituted benzene aromatics; and the third set to highlight naphthalene and the mono-, di-, and tri- substituted naphthalenes. In this way it was possible to visualize the compounds present in both samples and compare the patterns of these components very easily. GCxGC is a powerful tool for visual fingerprinting (far better than 1D GC). Partial chromatograms follow (see Figures 1-8).

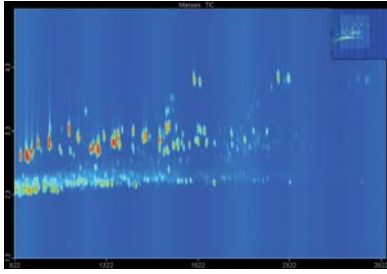


Figure 1. Gasoline standard sample showing the TIC.

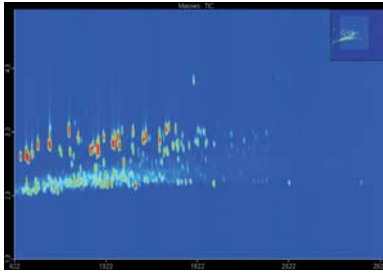


Figure 2. Arson sample showing the TIC.

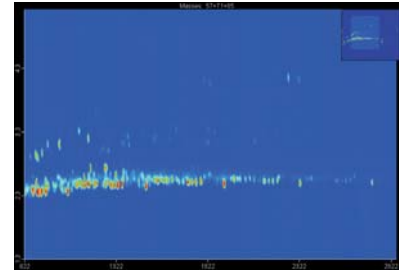


Figure 3. Gasoline standard sample showing 57+71+85 extracted ions.

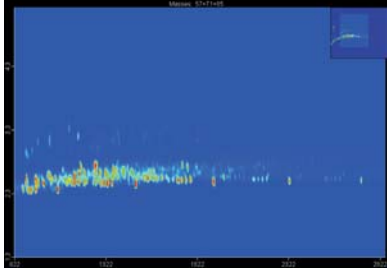


Figure 4. Arson sample showing 57+71+85 extracted ions.

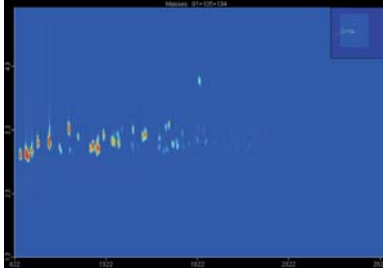


Figure 5. Gasoline standard sample showing 91+105+134 extracted ions.

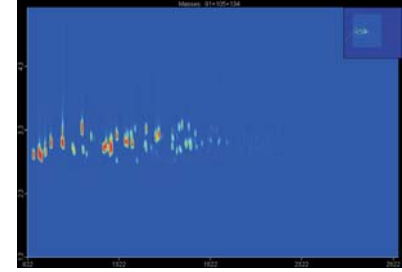


Figure 6. Arson sample showing 91+105+134 extracted ions.

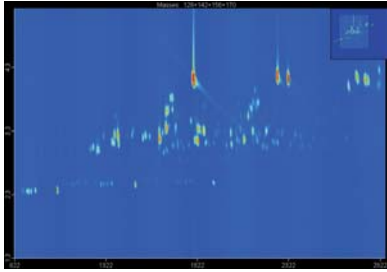


Figure 7. Gasoline standard sample showing 128+142+156+170 extracted ions.

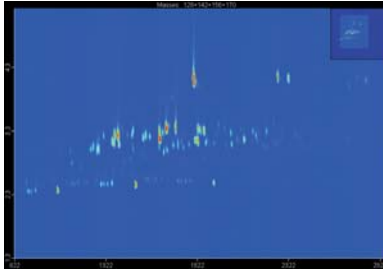


Figure 8. Arson sample showing 128+142+156+170 extracted ions.

#### 4. Conclusions

In all of the four sets of results shown above, it can be seen that the chromatograms are highly similar. It has to be borne in mind that the one sample is a neat gasoline standard, whereas the other is an actual sample collected at the scene of an arson crime. As such it has been subjected to intense heat. It is also possible that arson samples may be damaged by inexperienced investigators during the crime scene investigation, and also by the agents which could have been used to extinguish the fire (e.g. water, sand, CO<sub>2</sub> foam).

Consequently, there will always be differences in relative concentrations of components in the samples. Some components in the accelerant may be consumed by the fire more readily than others, so differences in patterns between standards and arson samples will be visible.

However, the overall similarity between the sets of chromatograms provides conclusive proof that gasoline was used as an accelerant. The use of GCxGC coupled to a Time-of-Flight Mass Spectrometer allows highly characteristic chromatograms of the important components in the gasoline standard and the arson sample to be compared easily, and a positive confirmation of the use of gasoline as an accelerant can be made.

Although the work described is only a first step in the investigation of arson samples by GCxGC-TOFMS, it shows the tremendous potential of the method for this type of analysis. In a subsequent Application Note—to appear on the LECO Africa website ([lecoafrica.co.za](http://lecoafrica.co.za))—the use of paraffin (kerosene) and diesel (diesel fuel #2) as arson accelerants will be described.

#### 5. References

B-J de Vos; Thesis submitted for the degree of Master of Science, Chemistry, University of Pretoria, Pretoria, South Africa, February 2005; and the references cited therein.

