

Rapid Identification of Accelerants in Arson Analysis Using GC/TOF-MS and Automated Chromatogram Matching

Karen Fleisher¹, Scott J. Harrison², Nick Bukowski², Lu Lin², Mary Blackburn³ ● ¹Miami Dade County Crime Laboratory, Miami FL., ²Thermo Finnigan, Manchester M23 9BE, UK,

³Thermo Finnigan Training Institute, Northpointe Blvd, West Palm Beach, FL

Introduction

The investigation of suspected arson cases is both a time and labor-intensive operation; not only is the work highly repetitive in nature, but very large volumes of data are generated which need to be reviewed. The characterization of pure flammable liquids is a relatively simple task. However, real samples are complex mixtures containing both artifacts and pyrolysis products in addition to the masked accelerant; collectively complicating the identification process. In the process of analyzing these complex samples the analyst is required to engage in exhaustive reviews of complex GC/MS chromatograms. (A typical Total Ion Chromatogram (TIC) is shown in Figure 1).

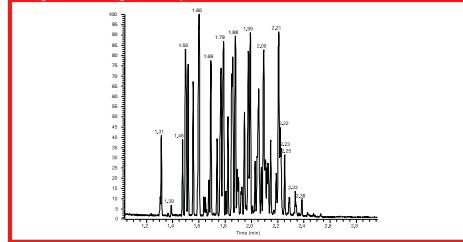
A skilled arson investigator can often identify an accelerant hidden in complex chromatographic data by recognizing patterns formed by the relative abundance of key compounds. The specialized skills of an experienced analyst can be significantly augmented by the use of a sophisticated data collection and analysis system, relieving many of the more tedious aspects of the work and delivering a rapid identification.

Historically, arson analysis has consisted of long GC/MS run times followed by the review of the mass chromatographic data. The application of GC/TOF-MS using fast GC techniques can greatly reduce the data acquisition period and when coupled with an automated processing method ultimately reduce the total analysis time. The data presented here describes the rapid analysis of arson samples using GC/TOF-MS and automated chromatogram matching.

Material and Methods

Arson samples were analyzed as follows; arson debris was incubated at 70 °C, in a stainless steel can containing a 15 x 3 mm carbon strip suspended from the lid. The strip was then placed in a standard 1.8 ml vial and 1 mL of carbon disulfide was added to desorb the entrained material. Injections of 1 µL were made directly from the vial using an autosampler. The GC conditions were as follows: injector temperature 200 °C, oven initially 50 °C, ramped at 50 °C/minute to 300 °C, and held for 1 minute, Split injection, with a split flow of 100 mL/min and a constant column flow of 2.0 mL/min. The column used for analysis was a 30m DB-5, 0.18 mm ID, 0.18 µm film. Data acquisition was performed at a rate of 20 spectra per second over the mass range 40-440 amu using a solvent delay of 0.5 minutes, giving a total run time of 6 minutes. Data processing and results were automatically generated using Xaminer software.

FIGURE 1. Total Ion Chromatogram of Complex Arson Sample Acquired on Using a Time-of-Flight Mass Spectrometer.



Results

The chromatograms acquired during the analysis of arson cases can be complex (Figure 1) and typically require lengthy oven programs to sufficiently resolve components to allow for accurate identification of the accelerant in question. When arson samples are analyzed with a high speed Time-of-Flight (TOF) instrument (as shown in Figure 1) we are able to reduce run times drastically whilst retaining resolution, with sensitivity approaching that of SIM mode, and benefiting from the improved information offered by full scan spectra. The data in Figure 2A compare similar samples analyzed on the Tempus GC/TOF-MS and a conventional quadrupole GC/MS. With the higher data acquisition rate of the TOF we are able to utilize fast GC techniques, reducing the run time to approximately one quarter of the time required for the conventional quadrupole analysis. While reducing the run time, the chromatographic resolution of the TOF data is still maintained (Figure 2B).

The ability to acquire data rapidly on the one hand still leaves the analyst with the perhaps more daunting task of interpreting the data. When arson data is analyzed by traditional methods the process is labor intensive and time consuming, therefore the use of an automated system would be beneficial. Any automated approach undertaken, must be validated with suitable examples. The chromatograms in Figure 3A represent a 4-component blend of flammable liquid containing dicarboxylic acid methyl esters. The actual arson sample is the top trace and the bottom trace is an authentic reference standard. The traces shown in Figure 3b are an expansion of the chromatograms shown in Figure 3a and depict the 4 peaks of the authentic standard, and the fact that the relative

FIGURE 2a. Comparison of Time-of-Flight Data with Conventional Quadrupole analysis using the same time scale.

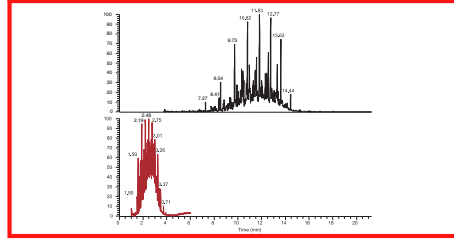
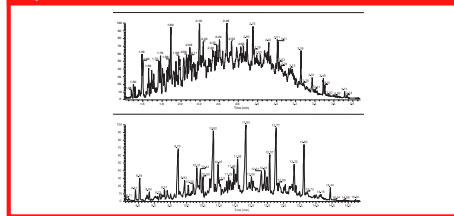


FIGURE 2b. Comparison of Time-of-Flight Data with Conventional Quadrupole analysis with consistent resolution.



amounts of the corresponding peaks in the arson sample are consistent with the standard. Thus we have an automated processing method that indicates the accelerant in this case is "Prep-Eez Sandpaper".

Whilst we have shown that we can easily analyze and process a simple mixture, most arson samples are of a more complex nature. Figure 4a shows the trace of a complex arson sample matched with a 25% Weathered Gasoline authentic reference standard. The first page of the Xaminer Sample Identification Report is shown in Figure 4b. The Identification Report depicts the TIC and 4 summed ion chromatograms defined by the user. These summed ions represent individual compound classes. For additional visual confirmation each of the summed ion chromatograms can be split out into individual ion chromatograms and may be reported also. The print out of the Aromatics Profile is shown in Figure 4c. Hence, we have a method that automatically matches a sample to a known standard and provides the analyst with an easily reviewed visual confirmation of the derived match.

FIGURE 3a. Matching of an arson sample containing a simple mixture of compounds.

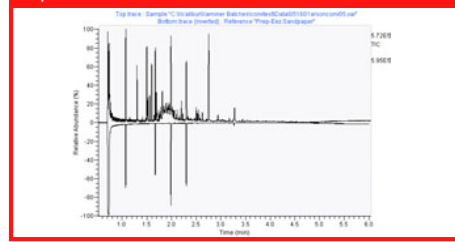


FIGURE 3b. Expanded view of Figure 3a depicting peaks of importance.

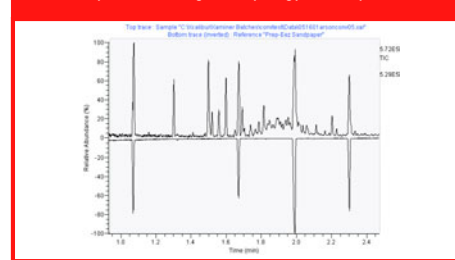


FIGURE 4a. Matching of an arson sample containing a complex mixture of compounds.

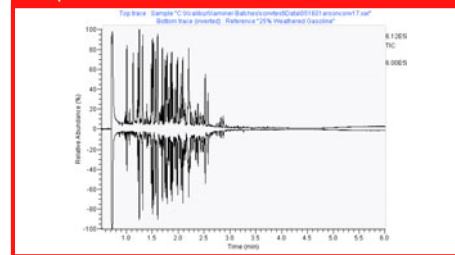


FIGURE 4b. Identification Report from Matching Results Showing TIC and Summed Ion Chromatograms.

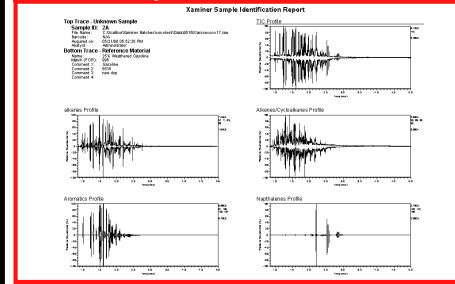


FIGURE 4c. Identification Report from Matching Results Showing Summed Ion Chromatogram and Individual Selected Ion Chromatograms.

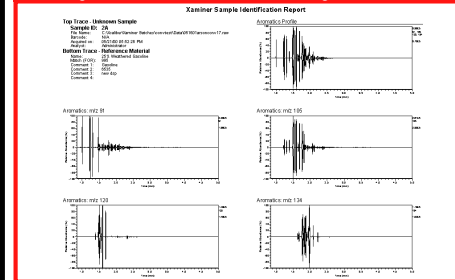


FIGURE 5a. TIC of Extremely Low Level Arson Sample.

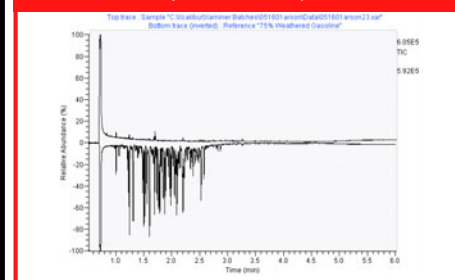
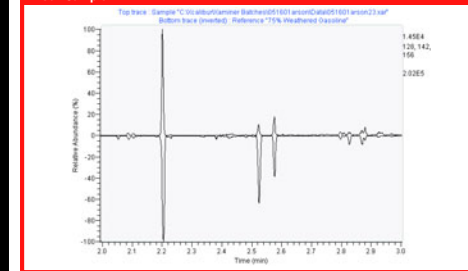


FIGURE 5b. Xaminer Results Displaying the Napthalene Profile of Low Level Arson Sample.



In addition to rapid analysis the TOF is extremely sensitive thus enabling identification of arson samples containing minute amounts of residual accelerant. Figure 5a depicts the analysis of an arson sample that contains extremely low levels of accelerant. The basis for identification of this sample as gasoline is only obvious when the summed ion chromatograms and individual extracted ion chromatograms are reviewed as shown in Figure 5b.

Conclusions

Currently the analysis of arson samples is laborious and time consuming. This fact is due to both the actual data acquisition and the subsequent manual data analysis. We have shown that through the use of GC/TOF-MS analysis and automated pattern matching software (Xaminer™) that arson cases can be rapidly and accurately analyzed. Actual time of analysis is reduced by the fact that the high-speed acquisition rate of the TOF enables us to employ fast GC techniques without loss of resolution or sensitivity. The application of automated chromatogram pattern matching software resulted in accurate and rapid identification of actual arson samples and further reduced time spent per sample. This reduction of both run-time and data processing/review time increases sample throughput and productivity. Finally, a repetitive and subjective burden is lifted from the analyst while the analyst's confidence is increased in the ultimate identification of the accelerant.

Acknowledgements

Contributions made by the following people are greatly appreciated. Dick Webber- Thermo Finnigan, John Lucey- Michigan State Police, Colleen Carbine- Miami Dade County Police, Carl Chasteen- Florida Fire and Arson Laboratory, Carl Lugville- Florida Fire and Arson Laboratory