

Applying the Technology of the TurboMatrix 650 ATD to the Analysis of Liquid Accelerants in Arson Investigation

Introduction

Fire investigation involves many different types of analyses – from crime scene investigation through analytical chemistry. If a fire's ignition is suspicious, the analysis will include gas chromatography (GC) as a means to detect the presence of a liquid accelerant; this analysis may include mass spectrometry (MS) as the initial detector or as confirmatory analysis. Gas chromatography mass spectrometry (GC/MS) provides a means to identify the accelerant through its chromatographic fingerprint; mass spectral data confirms this determination by identifying marker components of this fingerprint and their fragmentation.

The ASTM classification table (Table 1 - Page 2) breaks liquid accelerants into 6 major classes. This table is a useful tool to assist the analyst in the identification of an accelerant. Each class of accelerants is described across a row of the table; included in this description are characteristic compounds and ion fragments. Relating the detected ion fragments of the analysis to specific compounds will link the experimental data to an ASTM classification of the accelerant¹.

Prior to GC/MS analysis, fire-debris samples require sample collection and sample preparation to acquire a representative sample and transform the matrix of this sample into one which is appropriate for GC analysis. Recommendations for sample-matrix type, sample collection, storage containers, and sample preparation methods are found throughout literature and within methods developed by the American Society for Testing and Materials (ASTM International). The sample preparation methods found in these sources generally fall into 3 classes: headspace, solvent extraction, and steam distillation. Sample preparation for GC/MS analysis is typically performed by headspace or solvent extraction.

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Dynamic headspace with automated thermal desorption (ATD) sample collection is discussed in the article “Sample preparation for the chemical analysis of debris in suspect arson cases” by Bertsch and Zhang². This article presents the advantages and disadvantages of the common types of sample preparation. In this article, dynamic headspace and thermal desorption are described as very sensitive and clean methods. The only disadvantage is the inability to perform multiple analyses on a single sample tube.

The goal of this study is to eliminate the use of solvents for sample preparation and to implement sample re-collection on the ATD, allowing multiple analyses of a single sample tube. The discussion will include sample matrix, sample collection and storage, sample containers, sample introduction and analysis by GC/MS using the unique solutions provided by the technology of the TurboMatrix™ 650 ATD and Clarus® GC/MS system.

Experimental

Sample Collection – For this study, test samples of lumber were burned with and without an added liquid accelerant – gasoline – on a clean, concrete surface. The samples were extinguished with water and stored in a 0.5-L glass jar.

Sample Preparation – In preparation for GC/MS analysis, a dynamic headspace extraction was performed on the debris samples. This procedure consisted of heating the

jar of debris to 80 °C and equilibrating it at this temperature for 20 minutes. The contents of the jar were purged onto a metal ATD sample-collection tube packed with Tenax TA with a flow of clean, dry air at 50 mL/min. The sample collection time was 2 minutes; during this time the ATD sample tube remained at room temperature (21 °C), outside the oven. Tenax TA was used as the adsorbent throughout this study; arson samples often contain a large amount of water – Tenax was selected for its hydrophobic properties so that less water would be introduced into the analytical system. Standards were obtained from Restek (Bellefonte, PA). The weathered gasoline kit was used here; this included un-weathered, as well as 25, 50, 75 and 99% weathered standards. 5 µL of the liquid standard, diluted in methanol, was spiked directly onto an ATD tube; the tube was then purged with clean, dry air at 50 mL/min for 5 minutes at room temperature to remove the methanol.

Instrumental Analysis – The instrumental platform used in this study was the PerkinElmer® TurboMatrix 650 ATD coupled to the PerkinElmer Clarus 600 T GC/MS – this system offers the laboratory an analytical platform for the analysis of liquid accelerants.

The heated zones of the TurboMatrix 650 ATD were set to 250 °C to prevent condensation of high-molecular-weight compounds. A dual-stage desorption with re-collection of the secondary split allows for re-analysis and/or for archival purposes. The pneumatics operated in constant-flow mode, utilizing an auxiliary temperature sensor in the GC oven (Table 2 - Page 3).

Table 1: ASTM Accelerant Classification Table – ASTM Method E1387-01.

Class Number	Class Name	Hydrocarbon Range	Dominant Component Classes	Diagnostic Ions (m/z)
1	Light Petroleum Distillates	C ₄ - C ₈	Alkanes	43,57,71
2	Gasoline	C ₄ - C ₁₂	Alkanes Alkylbenzenes Naphthalene	43,57,71 91,106,120 128,142,156
3	Medium Petroleum Distillates	C ₈ - C ₁₂	Alkanes Alkylbenzenes	43,57,71 91,106,120
4	Kerosene	C ₉ - C ₁₆	Alkanes Alkylbenzenes	43,57,71 91,106,120
5	Heavy Petroleum Distillates	C ₁₀ - C ₂₃	Alkanes Alkylbenzenes Naphthalenes	43,57,71 91,106,120 128,142,156
0	Miscellaneous	Variable	Alkanes	43,57,71
0.1	Oxygenated Solvents		Alkylbenzenes	91,106,120
0.2	Isoparaffins		Alcohols	31,45
0.3	Normal Alkanes		Ketones	43,58
0.4	Aromatic Solvents		Esters	43,73
0.5	Naphthenic/paraffinic solvents		Terpenes	93,136

Adapted from the American Society for Testing and Materials Methods

As indicated on Table 3, a 0.32- μm diameter fused-silica transfer line connected the ATD to the Elite-1MS capillary column. The GC oven program began at 35 °C and was ramped at 15 °C/min to 280 °C; the total GC run time was 20 min. The mass spectrometer cycled at 4 scans per second across a range of m/z 30-500; the heated zones of the MS were maintained at 280 °C. The instrument was controlled by and the data was reported with TurboMass™ GC/MS software.

Table 2: Detailed Operating Parameters for TurboMatrix 650 ATD Instrument.

Thermal Desorption Unit:	PerkinElmer TurboMatrix 650 ATD
Transfer-Line Temperature:	250 °C
Valve Temperature:	250 °C
Tube Temperature:	250 °C
Trap Temperature (Low):	-25 °C
Trap Temperature (High):	250 °C
Trap Heating Rate:	Ballistic
Trap Hold Time:	10 min
Desorb Time:	1 min
Desorb Flow Time:	1 min
GC Cycle Time:	30 min
Inlet Split:	On
Outlet Split:	On
Injections Per Tube:	Multiple
Split Mode:	Flow
Thermal Desorption Mode:	2-Stage Desorb & Re-collect
Dry Purge:	Off
Carrier Mode:	Flow
Column:	1 mL/min
Re-collect Flow:	50 mL/min
Desorb:	1 mL/min
Column Setting During Desorb:	1 mL/min
Transfer-Line Type:	Short
Trap-Packing Type:	Tenax TA
Tube Type:	Metal
Tube-Packing Type:	Tenax TA

Table 3: Detailed Operating Parameters for GC/MS System.

Gas Chromatograph: PerkinElmer Clarus 600 GC			
Analytical Column:	Elite - 1MS (15 m x 0.25 mm x 0.1 μm)		
Carrier Gas Type:	He		
Oven Program:	Temp	Hold Time	Rate
	35 °C	1 min	15 °C/min
	280 °C	3 min	END
Detector Type:	Mass Spectrometer		
Mass Spectrometer: PerkinElmer Clarus 600 MS			
GC Inlet Line Temp:	280 °C		
Ion Source Temperature:	280 °C		
Function Type:	Full Scan		
Full-Scan Range:	m/z 30-500		
Full-Scan Time:	0.2 sec		
InterScan Delay:	0.05 sec		

Results

In preparation for the analysis of an arson sample, a series of weathered-gasoline standards were analyzed. Pictured in Figure 1 is the weathered gasoline series – as you can see, the total ion fingerprint of gasoline vs. 99% weathered gasoline is quite different. In Figures 2 through 4 (Page 4), each of the characteristic compound classes identified by the ASTM are displayed in detail.

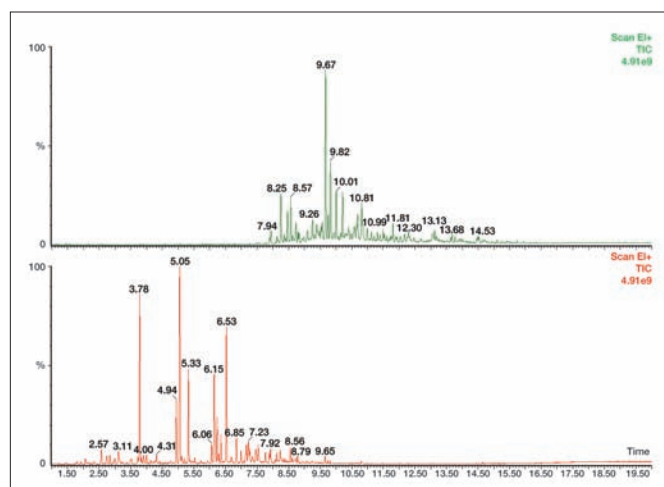


Figure 1. Total ion chromatograms of un-weathered (bottom) and 99% weathered (top) gasoline standards.

Figure 2 displays the alkylbenzene or BTEX (benzene, toluene, ethylbenzene, xylene) compounds – as you can see, these are the primary components of un-weathered gasoline. Resulting from their low molecular weight and high volatility, the alkylbenzenes are first to evaporate and comprise a very low percentage of 99% weathered gasoline. Conversely, the naphthalenes (Figure 3) comprise a small percentage of un-weathered gasoline, are much less volatile, and represent the majority of the 99% weathered gasoline fingerprint. The alkanes in gasoline (Figure 4) span a wide volatility range – this results in high mass discrimination in the highly-weathered standards.

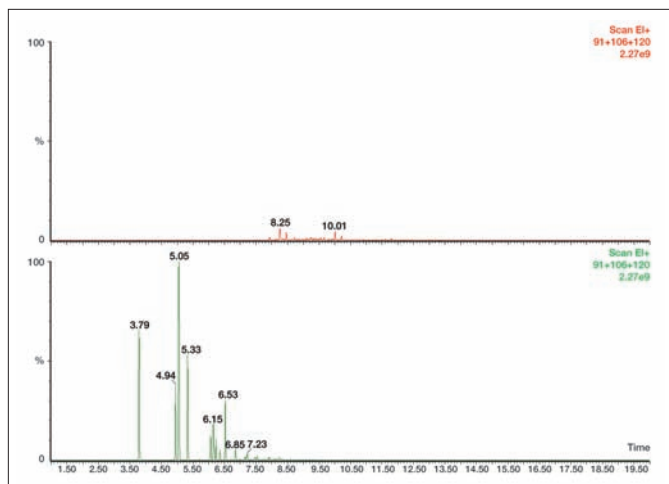


Figure 2. The comparison of the extracted ion chromatogram of alkylbenzenes (m/z 91,106,120) in un-weathered (bottom) and 99% weathered (top) gasoline.

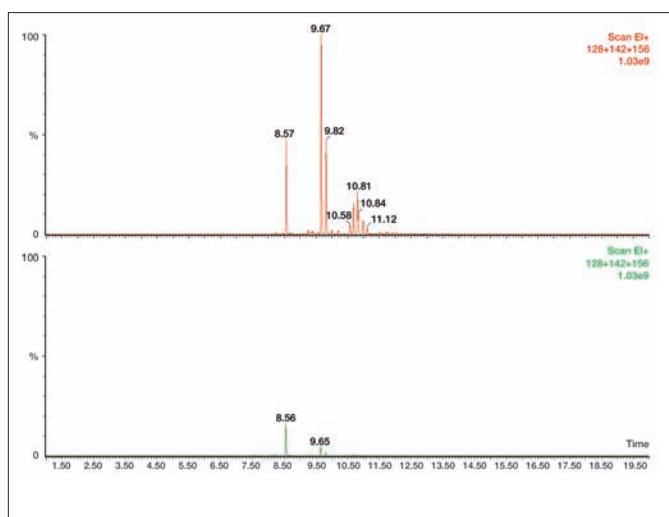


Figure 3. The comparison of the extracted ion chromatogram of naphthalenes (m/z 128, 142, 156) in un-weathered (bottom) and 99% weathered (top) gasoline.

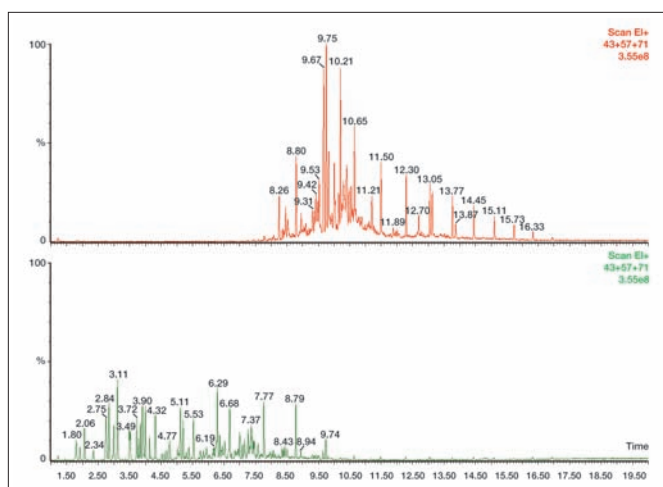


Figure 4. The comparison of the extracted ion chromatogram of alkanes (m/z 43, 57, 71) in un-weathered (bottom) and 99% weathered (top) gasoline.

Depending on the heat and duration of the fire and the volume of accelerant used, the fingerprint of an arson sample with a particular accelerant will vary across the range of weathering. Each of the compound classes which make up a particular accelerant should be monitored in both reference material and sample analysis to ensure correct identification. This study includes the analysis of samples from a test fire burned with and without gasoline as the accelerant. Chromatograms from this analysis are presented in Figure 5 – in this case, presence of an accelerant is quite obvious.

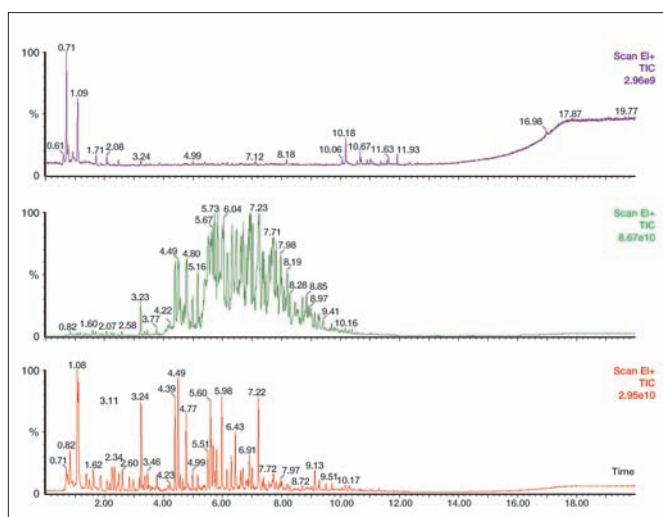


Figure 5. The comparison of the analysis of a test sample of wood burned without gasoline (top) with a low split (center) and high split (bottom) run of a wood sample burned with gasoline.

Throughout the study, the ATD was operated in sample re-collection mode – sample re-collection, as implemented in the TurboMatrix 650 ATD system, is activated during the second stage of thermal desorption. The effluent desorbing from the ATD cold trap is split before entering the GC transfer line, in this case 50:1. This split results in 49 mL/min flowing back onto the sample tube (re-collected), and 1 mL/min down the analytical column; approximately 98% of the sample is available for re-analysis and archival.

In the test sample, the amount of gasoline was so high that it was necessary to re-analyze the sample tube at a significantly higher split ratio to obtain a chromatogram with useful fingerprint data (Figure 5). Once adequate split-ratio conditions were achieved, the sample was re-analyzed 15 consecutive times under identical conditions, each time splitting 50:1 – this is demonstrated in Figure 6. The fingerprint of the arson sample can be reproduced time after time, for confirmatory analyses.

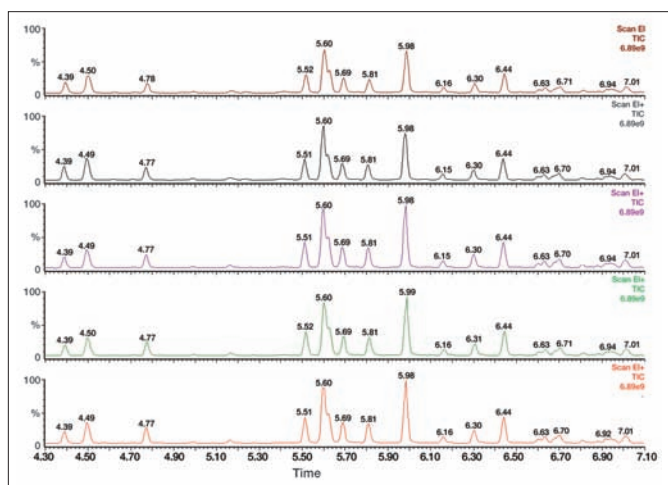


Figure 6. The analysis, re-collection and re-analysis of a single ATD sample tube – 5 times, under sample re-collection mode of operation.

Conclusion

As with all forensic analyses, the data generated in arson investigation must be legally defensible, creating the need for duplicate analyses and sample archival. Sample re-collection allows laboratories to perform multiple analyses of the same sample in addition to preserving both the instrument sample (thermal desorption tube) as well as the bulk debris sample.

Thermal extraction combined with dynamic headspace and automated thermal desorption is clearly a clean and very sensitive sampling technique in arson investigation. Additionally, this sample preparation technique eliminates the need for solvent extraction, reducing the use of carbon and eliminating solvent-disposal costs, analyst's preparation time and solvent exposure hazard.

References

1. American Society of Testing and Materials. ASTM Method E1387-01 Standard test method for ignitable liquid residues in extracts from fire debris samples by Gas Chromatography. In: Annual Book of ASTM Standards. Philadelphia, PA: ASTM, 2002:543-53.
2. Bertsch W., Zhang Q. Sample preparation for the chemical analysis of debris in suspect arson cases. Anal Chim Acta 1990; 236:183-95.