



# Accelerant Identification in Fire Debris by TCT–GC–MS

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The chemical detection of ignitable fuel traces in fire debris is a challenge requiring highly sensitive, hyphenated analytical systems. One coupled system suitable for the task is thermal desorption cold trap injection–gas chromatography–mass spectrometry (TCT–GC–MS). In this study, thermal desorption and cryogenic trapping were optimized to eliminate matrix interferences and to enrich target compounds in fire debris. Subsequent GC–MS provided chromatographic profiles of target ionic species required for the unequivocal identification of accelerants.

## Introduction

The chemical analysis of fire debris for traces of ignitable fuels is both problematic and complex.<sup>1–9</sup> Arson investigators have proposed various solutions based on identification of the accelerant,<sup>3,10</sup> matrix effects,<sup>11,12</sup> interferences of pyrolytic products,<sup>13,14</sup> a comparison with inadequate standard chromatograms,<sup>15,16</sup> the low content of target compounds, the tedious preliminary sample manipulation<sup>17</sup> and the time-dependant modification of the accelerant chromatographic profile.<sup>18</sup>

Many extraction techniques have been used to minimize the negative effects mentioned above, including passive adsorption/thermal desorption and solvent extraction,<sup>17</sup> headspace<sup>19</sup> and solid-phase micro-extraction.<sup>20–22</sup> All of these extraction techniques when coupled with gas chromatography (GC)–mass spectrometry (MS) give results that, in the majority of instances, are sufficient to identify the original accelerant.<sup>23</sup> Further improvements applied to certain method phases or components increase the performance of the method.<sup>24–31</sup>

The aim of this study was to optimize the thermal desorption cold trap (TCT) extraction process, followed by the recovery of specific chromatographic profiles and digital parameters by GC–MS, so as to verify the sensitivity and specificity of the accelerant analysis method. A flow chart pathway made identifying the nature and conditions of any studied accelerant easier.

## Experimental

**Reference samples and standards:** For gasoline identification, the characterization of specific peaks and the ratios of five pairs of isomers were determined using 50% and 80% evaporated fuel. Such standard accelerants were obtained by leaving fresh gasoline to evaporate, under normal conditions, up to the planned loss. Two series of five vials containing 3.5 g of white quartz, –50 +70 mesh (Aldrich Chimica, Milan, Italy) were spiked with 5  $\mu$ L of weathered gasoline. The vials, hermetically sealed, were shaken overnight so as to produce a homogeneous distribution of gasoline. An aliquot was withdrawn from each vial and subjected to TCT–GC–MS analysis. The analysed amounts, expressed as nL of evaporated gasoline, are reported in Table 1.

Twenty-five target components from gasoline were identified using their respective authenticated standards from Aldrich Chimica.

**TCT–GC–MS:** All identification of accelerants on reference samples was performed using a TCT–GC–MS system comprising a CP 4010 thermal desorption cold trap injector (Varian, Bergen op Zoom, Belgium), coupled on-line with an HP 5890 II gas chromatograph and a quadrupole HP 5971 A mass spectrometer (both Agilent Technologies, Waldbronn, Germany).

Each sample was subjected to on-line thermal desorption with cryofocusing using the TCT device. The desorber was

programmed for an extraction under helium flow at 120 °C for 4 min, cryofocalization at –100 °C and injection at 250 °C.

The chromatographic separation of analytes was obtained by means of an HP 50+ capillary column (Agilent Technologies) with the following dimensions: length 30 m; internal diameter 0.25 mm and film thickness 0.5 µm. The column was subjected to a head pressure of 50 KPa and to the following temperature programme: 50 °C for 1 min, followed by 10 °C/min up to 220 °C and hold for 25 min.

The mass spectrometer was used in SCAN mode to detect ions produced by electron ionization (70 eV) at an ion source temperature of 184 °C, in the mass range 50–270 daltons.

## Results and Discussion

**Thermal cold trap injector performance:** The results for reference and real samples from the more common ignitable liquids (gasoline, diesel fuel, kerosene and solvents) demonstrate the potential of this technique.

The application of this technique did not require any preliminary sample manipulation, with the exception of drying wet samples overnight on anhydrous calcium chloride. It was essential to avoid blocking of the cryotrap. During the drying of wet samples no appreciable loss of accelerant was observed.

At the temperature and time desorption used (120 °C for 4 min), the most representative and diagnostic components of all studied accelerants were extracted. For example, from samples containing traces of gasoline, aromatic compounds ranging from benzene (78 uma) to alkyl-biphenyls (196 uma), depending on the degree of accelerant evaporation, were desorbed and detected.

Moreover, thermal treatment reduced interferences and contamination caused by the matrix and eliminated any solvent effect. Time consumption in the extraction phase was drastically reduced, as was the cost and disposal of the solvents used.

By combining the time and temperature extraction with the high efficiency of cold trap enrichment, a small amount of sample (100–150 mg), was sufficient to allow detection of the target compounds (Figure 1).

**Accelerant identification:** In spite of thermal extraction selectivity, the complexity of the resulting chromatogram often does not permit ready identification of an accelerant in traces.

This is, however, facilitated by a mass spectral analysis of the accelerant components. By extracting the specific ions from each class of target component, a fingerprint for each accelerant was obtained.<sup>32</sup>

Gasoline is identified by its aromatic components (Figure 3(a); extracting the ion currents corresponding to the fragments at  $m/z$  91 for toluene and xylenes,  $m/z$  105 and 119 for C3- and C4-alkyl-benzenes, respectively (Figure 3(b)). In addition, the ion currents of species at  $m/z$  128, 142 and 156 can be extracted to verify the naphthalenic component of gasoline (Figure 3(c)). The aromatic targets, xylenes, alkyl-benzenes, naphthalene and alkyl-naphthalenes, do not represent the most abundant classes of gasoline components, but they are the most persistent to the high temperatures generated by fire. Consequently, they might be highly concentrated and easily detected. In particular, for conditions in which a high degree of evaporation occurred, the investigation of alkyl-biphenyls may be successfully performed. The ions at  $m/z$  168, 182 and 196 are representative of this class of high-boiling components.

On the basis of this preliminary information, the correct identification of gasoline was obtained by following the left path of the flow chart in Figure 2.

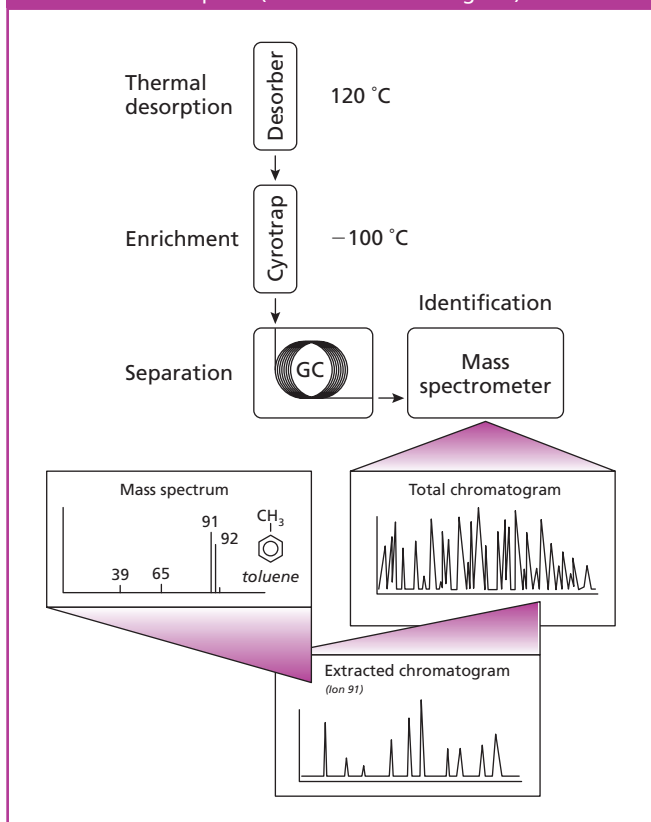
The first step in the path is the analysis of the ratios between three pairs of isomers: xylenes, pseudocumene versus mesitylene and isodurene versus durene. The determined values of these ratios are reported in Table 1 for 50% evaporated gasoline. Similar results were obtained for 80% evaporated gasoline. Values reported in Table 1 were obtained by calculating the ratio between the areas of two contiguous peak compounds having the same chemical properties, such as structure or molecular weight. If correct ratios were confirmed, the second step involving the examination of ratios of two pairs of methyl- and dimethyl-naphthalenes, was performed. The similarity of these values with respect to the ones reported in Table 1, was enough to confirm the final identification of gasoline. The correct ratio between 2-methyl- and 1-methyl-naphthalene is essential for gasoline confirmation, according to recent literature.<sup>3</sup>

Only in highly evaporated gasoline, do alkyl-biphenyls become detectable.

**Table 1:** Area ratios for five couples of diagnostic peaks in 50% evaporated gasoline.

Gasoline (nL abs.)	xylenes		<i>pseudo-cumene</i> versus <i>mesitylene</i>		<i>iso-durene</i> versus <i>durene</i>		<i>2-Met-naphthalene</i> versus <i>1-Met-naphthalene</i>		<i>1,3- + 1,6-diMet-naphthalene</i> versus <i>2,6- + 2,7-diMet-naphthalene</i>	
	$m/z = 91$		$m/z = 105$		$m/z = 119$		$m/z = 142$		$m/z = 156$	
	<b>Retention time (min)</b>									
	6.20	6.81	8.47	7.85	10.77	10.63	14.79	15.26	16.66	16.26
	<b>Ratios (average and standard deviation)</b>									
5.5	1.85		1.43		3.29		1.18		1.71	
13.5	2.23		1.18		2.63		1.91		1.46	
20.8	2.03		1.26		2.92		1.81		1.56	
38.7	2.15		1.26		2.23		2.00		1.54	
71.8	2.56		1.34		2.18		2.06		1.41	
	2.16 ± 0.26		1.29 ± 0.09		2.65 ± 0.47		1.79 ± 0.35		1.54 ± 0.11	

**Figure 1:** TCT–GC–MS system used for accelerant identification in fire debris, instrumental responses (total chromatogram) and elaborated reports (extracted chromatogram).



## Only in highly evaporated gasoline, do alkyl-biphenyls become detectable.

Ignitable liquids, mainly composed of aliphatic hydrocarbons, such as kerosene, diesel fuel (Figure 4(a)) and aviation gasoline, were identified following the central path reported in Figure 2. Characteristic fragments of this accelerant family are the ions at  $m/z$  57 and 71. Kerosene and diesel fuel show a specific ratio value of 1.5–1.6 for the ions at  $m/z$  57 versus 71 (Figure 4(b)). Differentiation occurs on the basis of their different hydrocarbon chain lengths (kerosene  $C_{12}$ – $C_{15}$ , diesel fuel  $C_{12}$ – $C_{18}$ ).

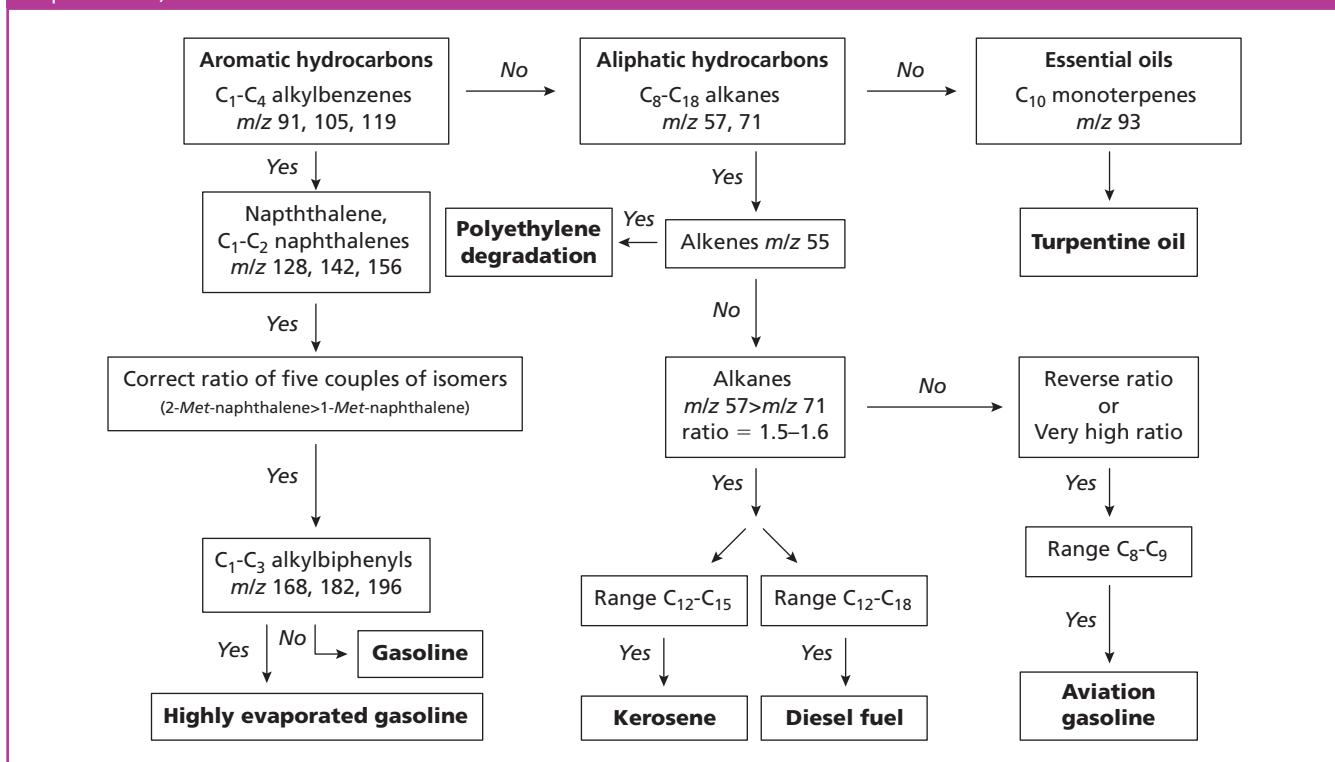
When a hydrocarbon chain ranges from  $C_8$  to  $C_9$  and the ratio  $m/z$  57 versus 71 assumes a value lower than 1 or higher than 1.6, the accelerant is identified as aviation gasoline.

In this examination, calculated ratios for all observed accelerants in real samples became significant only when they fell inside the interval  $\pm 20\%$  of corresponding reference values.

Some unusual families of accelerants including turpentine oil and petroleum solvents may also be found. The first family is characterized by the ion at  $m/z$  93, a typical fragment of the monoterpenoid components, as reported in the right-hand path of Figure 2.

The other family is represented by solvents, such as Exxon 100, 150 and 200, identifiable by their different aromatic compositions. C3- and C4-alkylbenzenes predominate in Exxon 100 and 150, respectively, and diagnostic ion fragments are extracted at  $m/z$  105 and 119. The major components of Exxon 200 are naphthalene, methyl- and dimethyl-naphthalenes, corresponding to ionic species at  $m/z$  128, 142 and 156.

**Figure 2:** Flow chart for identification of frequently used accelerants (gasoline, kerosene, diesel fuel, aviation gasoline and turpentine oil).



**Accelerant quantification:** Quantification is not usually necessary but an indication of the smallest detectable amount of an accelerant is sometimes considered important. Certain real situations hold back the effective concentration of a specific accelerant. The biggest problem is the unfeasibility to obtain the reference accelerant in the same evaporation state. The main reason is the impossibility to produce the same conditions of a real fire in the laboratory. The temperature, its increase and decrease rate; the oxygen level; evaporation and condensation phenomena and so on may have a drastic effect on the peak final distribution and abundances. The sampling site, together with the nature of collected debris, deeply influences the content of an accelerant.

By taking these evaluations into account, the TCT-GC-MS system is able to detect amounts of 50% evaporated standard gasoline above 3 nL spiked on an inert matrix such as sand.

**Real samples:** During the five years that this approach has been applied, many cases had independent confirmation. Two of these cases are exemplary.

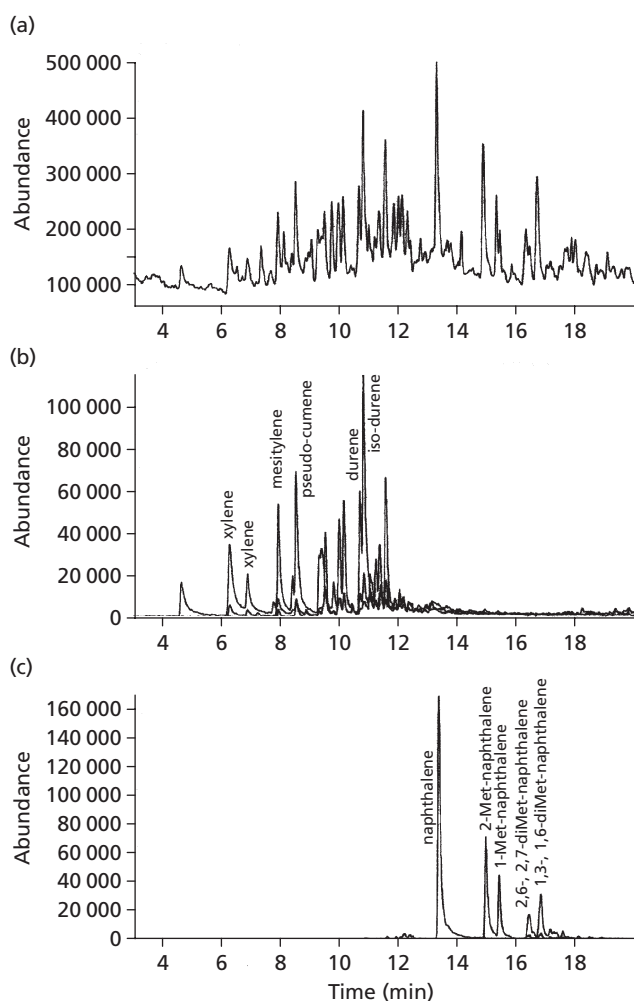
A fire destroyed a shoe manufacturer. Debris samples were collected inside the building from sites believed interesting by the fire investigator. Analysed debris were materials that had caught fire (shoes and raw materials) and soot covering the walls and plaster. Some analysed debris gave the typical chromatographic profile of gasoline, together with the aliphatic hydrocarbons of diesel fuel. Positive samples were those collected around the proposed ignition point of the fire and the line from this site to the exit. Some smoke-damaged plaster collected far from the previous sites, on the perimeter walls, were also positive, probably because of vapour condensation of its cold surface. On first analysis, the cause of the fire might have been attributed to the products and machinery commonly used in the building. However, a more detailed analysis of peak abundance, ratios and distribution suggested the use of fuels as a fire accelerant. Subsequently, a sample of pink liquid was found in a plastic container outside the burned building. This, the owners claimed, was not present before the fire. Analysing a sample of this liquid provided results very similar to those obtained from the fire debris, confirming the second hypothesis.

The second case concerned a fire in an ironworks shed. Likewise, in this instance gasoline was identified and confirmed by a second series of sampling and analyses. In addition, after several months of investigation, a former worker admitted to being the arsonist and to having used gasoline for ignition.

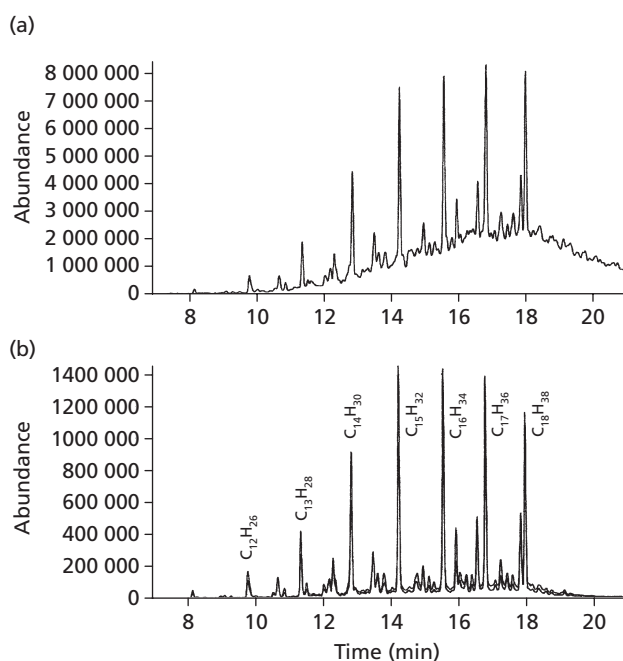
## Conclusions

Many reasons indicate the use of this method in fire investigations. Sample manipulation is reduced and solvents are completely avoided. The amount of sample required for each analysis is very low ensuring further controls and analyses.

**Figure 3:** (a) Typical TCT-GC-MS total chromatogram; (b) chromatographic profiles of alkybenzenes as ions at  $m/z$  91, 105, 119 and their identification; and (c) alkylnaphthalenes as ions at  $m/z$  128, 142, 156 and their identification, obtained through analysis of 21 nL 50% evaporated gasoline.



**Figure 4:** (a) Typical TCT-GC-MS total chromatogram; (b) chromatographic profiles of alkanes as ions at  $m/z$  57, 71 and their identification, obtained through analysis of 11 nL of fresh diesel fuel.



Recovery is usually very high and may be modulated by combining the time and temperature of thermal desorption. Desorbed compounds are enriched by efficient cryofocusing, which gives the entire system great sensitivity. High-boiling components of many fuels may be extracted from the matrix and can be fundamental for accelerant identification (e.g., alkyl-naphthalenes and alkyl-biphenyls in gasoline).

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