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Review of Analytical Techniques for Arson Residues

ABSTRACT: Arson is a serious crime that affects society through cost, property damage, and loss of life. It is important that the methods and technologies applied by fire investigators in detection of evidence and subsequent analyses have a high degree of reliability, sensitivity, and be subject to rigorous quality control and assurance. There have been considerable advances in the field of arson investigation since the 1950s. Classification of ignitable liquids has been updated to include many new categories due to developments in the petroleum industry. Techniques such as steam or vacuum distillation and gas chromatography (GC) with flame ionization detection that may have been considered acceptable—even a benchmark—40 years ago, are nowadays generally disfavored, to the extent that their implementation may almost be considered as ignorance in the field. The advent of readily available mass spectrometric techniques has revolutionized the field of fire debris analysis, increasing the degree of sensitivity and discrimination possible considerably. Multi-dimensional GC—particularly GC \times GC—while not yet widely applied, is rapidly gaining recognition as an important technique. This comprehensive review focuses on techniques and practices used in fire investigation, from scene investigation to analysis.

KEYWORDS: forensic science, arson analysis, accelerant, ignitable liquid, fire residue, smoke, solid phase microextraction, gas chromatography, mass spectrometry

Every week in the U.K., arsonists are accountable for 2100 fires, resulting in two fatalities plus 55 other casualties and a cost of £40 million (1). The crime of arson may be defined as the willful and malicious destruction of a building or other property through burning (2), and is considered one of the easiest crimes to commit and yet also one of the hardest to investigate. The number of deliberate fires has steadily increased over the last decade; however, in the year ending June 30, 2003, through government initiatives, the number of deliberate fires declined for the first time by 3% to 107,400 (1).

The crime falls under the Criminal Damages Act 1971 Section 1 (2), and in the eyes of the law, for a fire to be recorded as arson, it must encompass two intrinsic elements. It must be proven that there has been destruction of property beyond mere scorching—that is, surface burning or discoloration through heat—and that the burning was carried out through recklessness or by intent (1).

Unlike other criminal acts, much of the evidence is destroyed rather than created as the crime progresses. Also, not all property fires are deliberately set, and even the presence of ignitable liquids at a scene is not proof positive of arson, as there may well be a legitimate reason for them being there. Kerosene, for example, commonly occurs in domestic environments, either as a fuel in lamps or heaters, or as an ingredient in certain products like insecticides. The term “petroleum derivatives,” often seen on goods labels, most likely refers to kerosene or methylated spirits (3).

Accelerants

In the context of a suspicious fire, an accelerant is a substance—typically an ignitable fluid of some sort—that has been deliber-

ately introduced to a scene expressly for the purpose of facilitating the spread of a fire (4). The classifications and flammability properties of some common ignitable liquids are shown in Tables 1–3.

In 2001, the American Society for Testing and Materials (ASTM) revised the classification scheme for ignitable liquids. While the older system (Table 1) uses both names and numbers, the current system (Table 2) uses a two-dimensional approach, with more categories being defined and each category divided into three subcategories, with the exception of gasoline. This revision was necessary to accommodate the evolution of the petroleum industry with many new products being developed, products that in the old system would all have been classed in the “0” (miscellaneous) category, with the result that the number of subcategories exceeded the number of classes (7).

Many of the classification criteria in the new system are relatively straightforward, for example consisting entirely of aromatic compounds with the near absence of aliphatic components designated an aromatic product; however, the system becomes more complicated with some classes of medium-range distillate products, where differentiation is based on the relative abundances of aromatic components. Petroleum distillates and dearomatized distillates in this range will appear very similar by total ion chromatogram and flame ionization detection (FID), with the extracted ion profiles from a gas chromatography-mass spectrometry (GC-MS) necessary to make a distinction (9). This can be problematic for laboratory fire debris examiners as there are no guidelines stating the cutoff limits for aromatics for each of these groups of liquids, making it difficult to ascribe a definite identity.

While solid accelerants—candles, firelighters, magnesium, flares, and powder mixtures—are used, the most commonly used accelerants are liquids, particularly petrol, diesel, and kerosene, complex mixtures of hydrocarbons obtained from the fractional distillation of crude oil and popular due to their ready availability (10). These most commonly used ignitable liquids all have similar chemical properties; however, they differ in the boiling point ranges of their respective components (11). They are complex

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TABLE 1—Old ignitable liquid classification system.

Class Number and Name	C Range	Dominant Component Classes	Diagnostic Ions (<i>m/z</i>)
1. Light petroleum distillates	C ₄ –C ₈	Alkanes	43, 57, 71, ...
2. Gasoline	C ₄ –C ₁₂	Alkanes	43, 57, 71, ...
		Alkylbenzenes	91, 106, 120, ...
		Naphthalene	128, 142, 156, ...
3. Medium petroleum distillates	C ₈ –C ₁₂	Alkanes	43, 57, 71, ...
		Alkylbenzenes	91, 106, 120, ...
4. Kerosene	C ₉ –C ₁₆	Alkanes	43, 57, 71, ...
		Alkylbenzenes	91, 106, 120, ...
5. Heavy petroleum distillate	C ₁₀ –C ₂₃	Naphthalenes	128, 142, ...
		Alkanes	43, 57, 71, ...
		Alkylbenzenes	120, 134, 148
		Naphthalenes	128, 142, 156, ...
0. Miscellaneous	Variable	Alkanes	43, 57, 71, ...
0.1 Oxygenated solvents		Alkylbenzenes	120, 134, 148
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, ...
		Other	Variable

Adapted from American Society for Testing and Materials methods E1387-01(5) and E1618-01(6).

substances and are often hard to detect and identify, containing as they do many different components. Analyses for these ignitable liquids are exacerbated by the presence of many of these components in the pyrolysis products of many common household items like plastics and carpets.

Commonly Used Accelerants

Petrol

The most commonly encountered accelerant, petrol, is comprised of much lighter hydrocarbon components than kerosene or diesel. It has a much greater volatility and will readily form an explosive air-vapor mix to cause extensive damage upon ignition (11). Petrol has a very distinctive chromatographic pattern (Fig. 1), and unlike many other accelerants, is not characterized by equidistant *n*-alkane peaks (12). Instead, a typical petrol chromatogram as shown in Fig. 1 has many different peaks in varying proportions. Yet, while pure gasoline may have an identifiable distinctive pattern, it weathers quickly, and in its evaporated state is more difficult to recognize and can be mistaken for white spirit. In a 1993 study by Bertsch et al., out of 120 laboratories tested, only 70% correctly identified a 95% weathered gasoline sample using capillary GC-FID—the standard method at the time (13).

Studies have been carried out to determine whether or not unique “fingerprints” may be obtained for petrol from different sources, as an aid to establishing a link between a suspect and an arson scene where gasoline has been detected. This has been carried out, successfully, via tetraalkyl lead content or by examining the profiles of the more volatile components present in gasoline (14,15). However, both of these have become less feasible with the banning of leaded gasoline in the case of the former, and in the

latter the inability to differentiate samples after more than 50% evaporation due to loss of the target compounds.

Nevertheless, a more recent study in 2003 by Sandercock and Pasquier (16) has shown more promise. This study involved taking 35 randomly selected unevaporated gasolines of different grades i.e., regular unleaded, premium unleaded, and lead replacement, and then focusing on the high boiling components so that the technique may be subsequently applied to a weathered sample. The target polar compounds and poly aromatic hydrocarbons (PAHs) were isolated via a novel solid-phase micro-extraction (SPME) process incorporating activated alumina, and then analyzing by GC-MS with selected ion monitoring (SIM). The polar compounds were selected as previous studies have reported that C₀–C₄ alkylphenols exist in crude oil in varying concentrations, and have been used successfully as markers to characterize oil spills in aquatic environments due to the solubility of the phenols in water (17–19). Furthermore, a study by Mach (20) into the determination of PAHs in evaporated and burned samples of gasoline concluded that certain PAHs are unique to gasoline, while a later study by Hennig (21) demonstrated that the levels of these compounds in a sample were dependent on the refinery from which it was produced. Thatcher (22), who specified naphthalene, 1,2-dimethyl naphthalene, and phenanthrene as being viable species with which to differentiate gasoline samples, corroborated this in a 1982 study.

The Sandercock–Pasquier study (16) did not reveal significant differences between the relative ratios of the polar compounds in the samples; however, there was more success with the analysis of PAHs. This series of tests examined the two-ring C₀–C₂ naphthalenes and the three-ring C₀–C₂ fluorenes and phenanthrenes, plus C₀ anthracene. Through principal component analysis, it was found that the 35 samples could be divided into 32 unique identifiable groups, where 30 of the groups represented individual samples, with the remaining two groups comprising the five misclassified samples. Furthermore, peak area precision was superior for the two ring compounds over the three-ring compounds; thus, it was surmised that C₀–C₂ naphthalenes could be used to distinguish between different samples of gasoline via a one-step GC-MS (SIM) method (16).

Another study by Tan et al. (23) used GC-MS analysis, followed by multivariate pattern recognition techniques to identify and classify ignitable liquids in analytes, and determine maximum sampling times and detection limits for correct classification. Using a soft independent model classification analogy (SIMCA), they determined that in order to identify correctly an ignitable liquid of any class, samples need to be collected within half an hour of application at 20°C; however, samples of petrol, the most commonly encountered accelerant, can still be identified after 3 h using this model. With reference to the old classification system (Table 1), the detection limits for Class 2 and Class 5 ignitable liquids such as petrol and diesel, respectively, were found to be 0.8 µg, while for Class 3 and 4 ignitable liquids like paint thinner and kerosene they were 1.6 µg.

In instances where samples have been weathered to the extent that only heavy, low-volatility fractions remain, readily ignitable liquids, such as petrol, may become difficult to identify. Nevertheless, weathered gasoline samples have been verified by Coulombe (24) using diphenyl disulfide compounds. Using comparative GC-MS, he analyzed samples of heavily weathered petrol, evaporated diesel, creosote, evaporated gasoline from an incendiary device, and fire debris. These tests showed that the marker diphenyl disulfides were present only in the gasoline and debris samples but are not found in pyrolysate, suggesting they are

TABLE 2—Current American Society for Testing and Materials ignitable liquid classification showing group criteria and typical product categories (7).

Class	Light (C ₄ –C ₉)	Medium (C ₈ –C ₁₃)	Heavy (C ₈ –C ₂₀₊)	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics
Gasoline	Fresh gasoline generally falls in the range C ₄ –C ₁₂			Present, less abundant than aromatics	Present, less abundant than aromatics	Abundant	Present
Petroleum distillates	Petroleum ether, some cigarette lighter fluids, some camping fuels	Some charcoal starters, some paint thinners, some dry cleaning solvents	Kerosene, diesel fuel, some jet fuels, some charcoal starters	Abundant, Gaussian distribution	Present, less abundant than alkanes	Present, less abundant than alkanes	Present (depending on boiling range), less abundant than alkanes
Isoparaaffinic products	Aviation gas, specialty solvents	Some charcoal starters, some paint thinners, some copier toners	Some commercial specialty solvents	Branched alkanes abundant, <i>n</i> -alkanes absent or very diminished	Absent	Absent	Absent
Aromatic products	Some paint and varnish removers, some automotive parts cleaners, xylenes, toluene-based products	Some automotive parts cleaners, specialty cleaning solvents, some insecticide vehicles, fuel additives	Some insecticide vehicles, industrial cleaning solvents	Absent	Absent	Abundant	Abundant (depending on boiling range)
Naphthenic paraaffinic products	Cyclohexane-based solvents/products	Some charcoal starters, some insecticide vehicles, some lamp oils	Some insecticide vehicles, some lamp oils, industrial solvents	Branched alkanes abundant, <i>n</i> -alkanes absent or very diminished	Abundant	Absent	Absent
<i>n</i> -alkanes products	Solvents, pentane, hexane, heptane	Some candle oils, some copier toners	Some candle oils, carbonless forms, copier toners	Abundant	Absent	Absent	Absent
De-aromatized distillates	Some camping fuels	Some charcoal starters, some paint thinners	Some charcoal starters, odorless kerosene	Abundant, Gaussian distribution	Present, less abundant than alkanes	Absent or very diminished	Absent or very diminished
Oxygenated solvents	Alcohols, ketones, some lacquer thinners, fuel additives, surface preparation solvents	Some lacquer thinners, some industrial solvents, metal cleaners/gloss removers		Composition may vary, presence of oxygenated solvents			
Others—miscellaneous	Single component products, some blended products, some enamel reducers	Turpentine products, some blended products, various specialty products	Some blended products, various specialty products				

TABLE 3—Physical properties of selected ignitable liquids (8).

Liquid	Boiling Point (°C)	Flash Point (°C)	Ignition Temperature (°C)
Kerosene	175–260	38–74	229
Gasoline	40–190	–43	257
Diesel	190–340	69	399
Engine oil	N/A	150–230	260–371
Acetone	57	–20	465
Octane	126	13	220
Pet ether	35–60	–18	288
Spirit turpentine	135–175	35	253
Alcohol	78	13	365
White spirits	150–200	35	232

particular to gasoline, and their presence in residues as such is characteristic; however, their origin is unknown at present.

Kerosene

This is the second most popular accelerant after petrol. Although more difficult to ignite due to a lower volatility, it will burn longer and, given adequate ventilation, hotter (3). Similar to diesel, kerosene, however, contains a greater proportion of lighter hydrocarbon components, conferring it a greater volatility, and due to its relatively high boiling range (175–260°C, see Table 3) is more likely to leave a detectable residue after a fire than petrol (25). A chromatogram of unevaporated kerosene displays eight evenly spaced characteristic peaks (see Fig. 2), with many of these identifying components still visible in the weathered or burned sample (4,11). However, unlike petrol, which is almost exclusively used as motor fuel, kerosene is legitimately found in a number of common household products, from charcoal lighters to paint thinner, and is thus the most common incidental accelerant (3). Consequently, the detection of a kerosene residue at a scene must be treated with caution as it is not necessarily indicative of a

criminal act, and consideration must be given to other evidence at the scene to determine how it may have come to be there.

Diesel

Comprising the heavier components of crude oil, thus having a high boiling point with low volatility, it can be difficult to ignite (11). A diesel chromatogram has the same eight peaks characteristic of kerosene, albeit in different proportions, plus a further eight from higher boiling components (4) (see Fig. 3). Owing to its high boiling range, care should be taken during recovery that these higher boiling components are not lost, as the resultant chromatogram can resemble that of weathered kerosene (11). However, studies have found that the chromatograms of burned and weathered ignitable liquids vary in a predictable way, and hence there now exist libraries of degraded ignitable liquid patterns for comparative purposes (26).

Accelerant Detection at Scenes

In determining whether or not a scene is the result of a deliberately accelerated fire, evidence of accelerant use is often key to the investigation. While tell-tale physical markers such as intense localized burning or floor burnthrough can act as indicators of the presence of ignitable liquids (27), without the corresponding supporting laboratory evidence, any testimony is subject to debate and accusations of conjecture. Table 4 indicates some of the field methods used by scene investigators to locate traces of ignitable liquids.

To this end, odor is a key tool in detecting ignitable liquid residues at a fire scene to both human and canine investigators alike, and for many years was the standard test for ignitable liquid residues. Even at trace levels, the human nose can be trained to identify and differentiate between ignitable liquids, with a sensitivity of around 20 p.p.m. (28). However, sense of smell is subjective, varies widely with climate, and deteriorates through fatigue over the

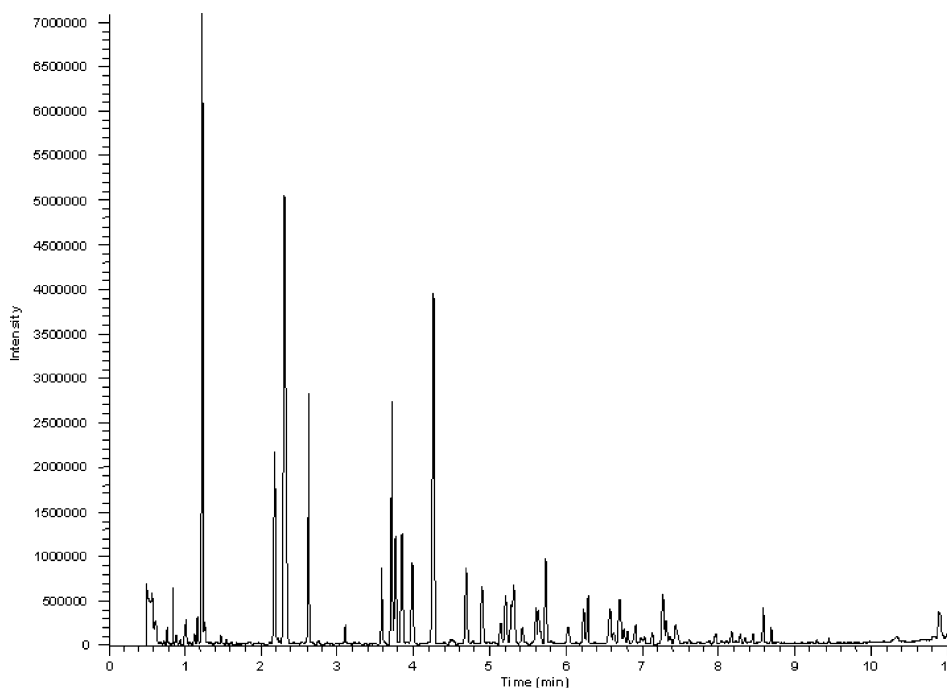


FIG. 1—Typical petrol chromatogram by gas chromatography-mass spectrometry.

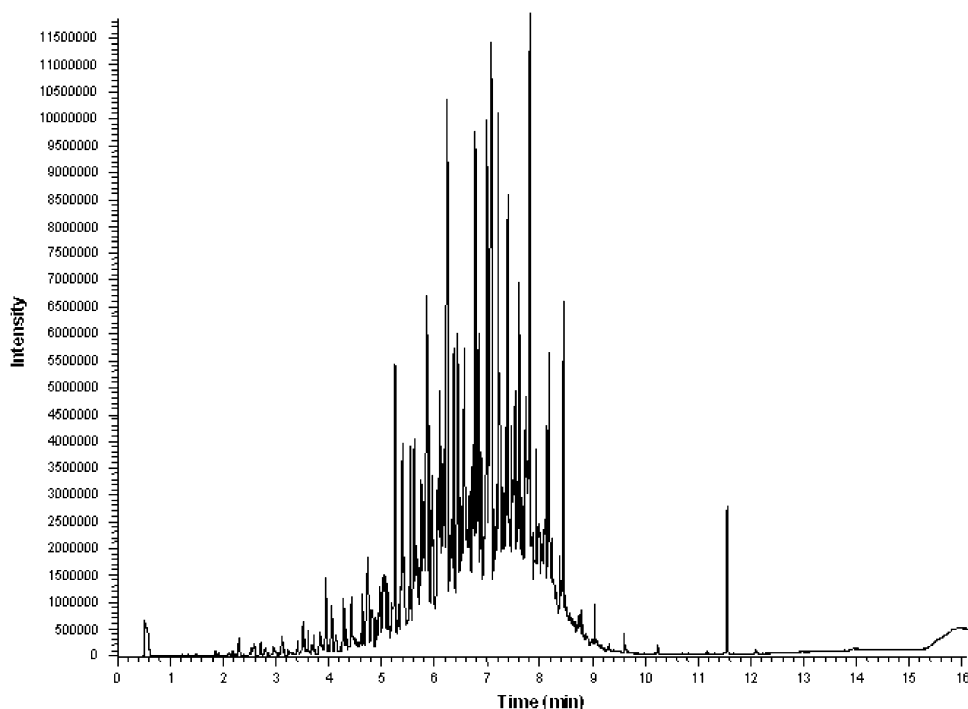


FIG. 2—Typical kerosene chromatogram by gas chromatography-mass spectrometry.

course of a day, while there is also an inherent risk involved in sniffing unknown materials (11,27). Nevertheless, many investigators still rely on their own sense of smell as the primary detector when selecting samples for subsequent analysis (11).

Canine Detection Teams

More sensitive and discriminative than the human nose, a dog's sense of smell can prove a useful asset for selecting samples with a

higher likelihood of testing positive, and there are now a number of canine accelerant detection teams in operation around the world with favorable reports of success (29). They can be trained to target certain substances specifically, and then rapidly target these scents even at large scenes (27).

Nevertheless, training and upkeep of a specialist dog is expensive, while like humans, after prolonged exposure to a scene, they can suffer olfactory fatigue and thus become less effective at detecting ignitable liquids (30). Furthermore, there have been reports

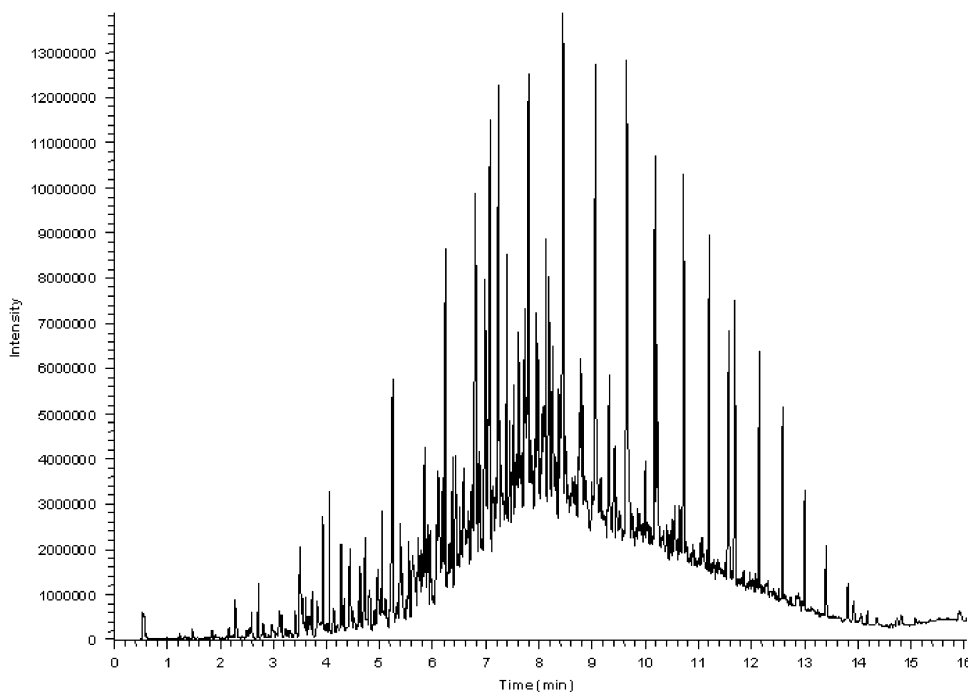


FIG. 3—Typical diesel chromatogram by gas chromatography-mass spectrometry.

TABLE 4—Field detection techniques for ignitable liquid residues.

Detection Method	Advantages	Disadvantages
Canine teams	Highly sensitive Rapid scanning of large areas Can be trained to discriminate between ignitable liquid residues and other vapors	Expensive Suffer from olfactory fatigue Cannot always discriminate between ignitable liquids and pyrolysates
Metal oxide sensor (MOS)	Cheap Small Robust Detects a wide spectrum of contaminants	Inaccurate Non-specific Reacts to moisture Prone to poisoning
Photo-ionization detector (PID)	Highly sensitive Wide operational range (10,000 p.p.m.–< 1 p.p.b.) Robust Unresponsive to moisture and inorganic vapors	Cannot distinguish between ignitable liquid residues and plastic pyrolysis products
Portable gas chromatograph	Can discriminate between ignitable liquids and burned plastic Capable of trace detection Versatile	Early models suffered from poor resolution
Portable mass spectrometer	Provides rapid at-scene information (c. 30s)	Early models somewhat bulky and heavy
Chemical tests	Quantitative Versatile sampling (air, soil, water)	Expensive Nondiscriminative Single use

that some dogs have trouble differentiating between ignitable liquid residues and pyrolysis products from burned furniture, building materials, and particularly carpets, resulting in a number of cases of false positives (29,31). Analysis of carpet samples from a 1994 Californian study (29) by pyrolysis-GC surmised that the dogs were responding to pyrolysis products from polymers like nylon 6,6 and polypropylene, among others, originating from fibers, adhesives, and backings. It should also be noted that the National Fire Protection Association has issued guidelines stating that while canines are useful tools, their alerts should not be used as evidence without proper laboratory validation (32).

Sniffers

Investigators scanning fire scenes for the best sampling areas for ignitable liquids use portable detectors, or “sniffers.” Despite being a continual source of debate, sniffers do have several advantages over dog teams, and particularly over one’s own sense of smell. While canine accelerant detection teams are expensive, portable detectors are cheap and readily available. Sniffers do not suffer from olfactory fatigue like canines or humans, so can be used for long periods without loss of sensitivity (30). In terms of safety, the use of sniffers avoids excessive exposure to toxic pyrolysis products, and are small enough to be introduced into otherwise inaccessible areas (11). Sniffers sample the headspace above debris; thus, for efficient use, the sampling area needs to be disturbed to release trapped volatiles before insertion of the probe (27). Failure to do so can lead to false negatives, commonly with soil, as found in tests carried out into sniffer responses with a variety of materials (11). A sniffer will also give positive readings when analyzing those materials that produce large amounts of pyrolysis products, such as rubber backed carpets, and may thus confuse an unskilled operator. Also, if the device is improperly calibrated or low on power, it will not function efficiently, and may give falsely negative readings (11). There are several types of commercially available sniffer, outlined in Table 4.

Portable Gas Chromatographs

Portable gas chromatographs incorporating a FID and small packed column have been developed in the last 10 years and suc-

cessfully demonstrated for the detection and analysis of ignitable liquid residues (27). Able to serve either as a sniffer by direct introduction of air samples into the detector, or as a chromatograph by prior implementation of the column, the versatile device is capable of trace detection of hydrocarbons while also being able to discriminate the source as being ignitable liquid or burned plastic. Although early trials of this potential technique suffered from poor resolution, work is ongoing, and there are expectations that this device may prove invaluable in future investigations.

Portable Mass Spectrometers

The most recent development in portable detection devices, there are now several models commercially available, including Viking Instruments’ SpectraTrack (Chantilly, VA) (33), the MM1 and EM640 from Bruker (Billerica, MA) (34), and the Kore MS-200 (35).

In 2004, Makas and Troshkov (36) studied the techniques and capabilities of field GC-MS for fast analysis, using a system incorporating a concentrator-thermodesorber unit (CTD), multiple-module GC system, and a compact magnetic mass-spectrometer with a two-stage vacuum and multicollector ion detector. They found that a high degree of sensitivity and reliability was obtained with a rapid rate of analysis, citing the detection of tributyl phosphate at 45 p.p.t. in a 1 min sampling time.

Smith et al. (37) proposed that both the size and the mass of portable instruments could be substantially reduced by the implementation of a dedicated resistive column heating system.

A system was proposed by Diaz et al. (38) to address issues relating to miniature MS instruments, such as speed, mass range sensitivity, size, resolution, and cost. They proposed utilizing the mass separation capabilities of a 90° cylindrical double-focusing mass analyzer using superimposed electric and magnetic fields with an orthogonal direction (ExB), termed CDFMS. However, in tests, they found three limitations of the technology—namely scan speed, mass range, and size—but believed these could be overcome to provide a viable system.

The Kore MS-200 portable mass spectrometer is currently in use in the field by Strathclyde Fire Brigade investigators (35). Tests using the device on burned samples of petrol-soaked rubber-backed carpets immediately after extinguishing produced spectra with strong hydrocarbon characteristics that rapidly faded away

after a few minutes. This would suggest that the optimum time to detect and definitively identify ignitable liquid residues at a scene would be as soon after the fire as is possible (39). As the MS-200 is able to provide positive information directly at the scene within 30 sec, without the need to wait for laboratory confirmation, this device is ideally suited to certain situations where sampling time is limited.

Chemical Testing

Two chemical tests also exist that have been used at fire scenes to detect quantitatively traces of ignitable liquids in air, soil, or water (27). Atmospheric sampling can be carried out using Draeger tubes, glass vials filled with a species-specific reagent, and that rely on a chemical reaction to determine the nature and type of a particular chemical constituent in a sample. A measured sample of air is drawn through the tube, and if the target species are present the reagent in the tube changes color—the length of the color change indicative of the concentration. Hydrocarbon test kits can be used for the analysis of soil or water samples, with positive results again being indicated by a color change. However, these techniques are expensive and unable to discriminate between hydrocarbons originating from ignitable liquids and those from burned plastics.

Scene Investigation

What to Sample

When collecting debris samples from a fire scene, it is important to select those materials that have the highest probability of yielding appreciable levels of identifiable ignitable liquid residue. The amount that can be recovered is governed by a number of things, particularly the substrate to which the ignitable liquid was applied. Most of the common accelerants are hydrophobic (exceptions are acetone, ethanol, and methylated spirits), and hence tend not to be washed away when the fire is extinguished. They instead become sealed into porous substances by water, where they are protected from evaporation and can potentially be recovered intact up to 3 months later (11). Water-miscible ignitable liquids, on the other hand, tend to be washed away as the fire is extinguished, and those residues that do remain are rapidly lost by evaporation due to exposure, as they do not become sealed into porous substrates, and so are more difficult to detect. Figure 4 gives an indication of the types of sample materials commonly submitted to laboratories for analysis.

The type of debris sampled will generally depend on what is available at the scene; however, materials such as glass and metal should be avoided as they typically make for poor samples because they are not particularly good sorbents and can have low surface areas (4).

Ideally, the samples should be porous and composed of adsorbent or absorbent materials with a high surface area so as to retain liquid accelerant residues. In this respect, materials such as soil, paper/cardboard, cloth, carpet, and to a lesser extent concrete are popular for debris sampling (11). Some sample matrices may produce interfering compounds either through pyrolysis or degradation, which can hinder subsequent identification. This is particularly a problem with synthetic polymeric materials and the ever-increasing abundance of petroleum-based products in everyday domestic use, ranging from insecticides to tile glue (41). However, while these materials can present an analytical challenge, their ability to thermally distort and encapsulate ignitable liquid residues can make them good samples.

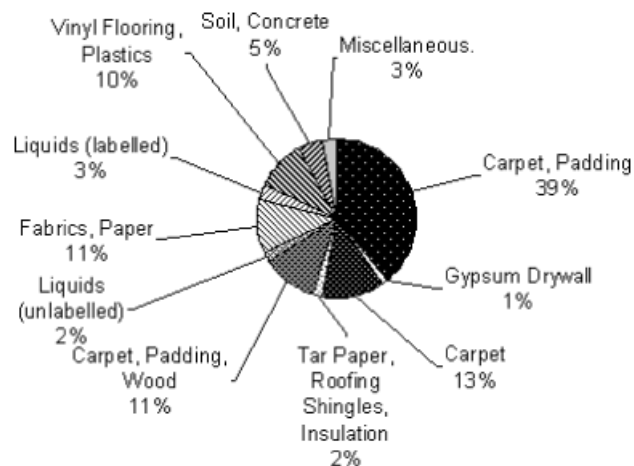


FIG. 4—Composition of commonly submitted fire debris samples (40).

Wood Samples—Timber, although absorbent and with a high surface area, tends to be disfavored as it burns easily and thus consumes much of the ignitable liquid present therein (11). In its favor, charred timber will have a surface coating of charcoal, an excellent adsorbent, particularly for volatile residues, so even if the originally applied ignitable liquid is lost, subsequent residue vapors from the extinguished scene may later become adsorbed (4).

Concrete—Concrete, although apparently disfavored due to low surface area and adsorbivity, is nevertheless sampled (11). Owing to the obvious difficulties in removing concrete for sampling, absorbents such as diatomaceous earths are sprinkled onto the surface to soak up any liquids, which are then recovered and analyzed. Flour is not a suitable absorbent in this case due to possible subsequent fermentation to produce alcohol, a major constituent of methylated spirits, with Bullington (42) suggesting calcium carbonate to be preferable.

Roofing Materials—Tar paper and roofing shingles are not recommended samples as they are typically made of asphalt, a petroleum-derived substance from the heavier components that nevertheless contains some of the lighter hydrocarbons associated with kerosene and diesel. Earlier tests on roofing shingles conducted by Lentini using direct headspace concentration and GC/FID produced chromatographic profiles resembling those of kerosene and diesel, due to fractionation of the asphalt smoke condensates in the headspace procedure. Nevertheless, later work with GC-MS revealed that differentiation between burned asphalt residues and liquid petroleum distillates could be achieved by careful examination of the olefin content (3,43,44).

Carpet Materials—By far the most commonly sampled material is carpet and carpet padding; however, as a sample matrix, it does have some inherent disadvantages. Modern carpets are typically made from synthetic fibers like nylon and are supported on a polypropylene copolymer (12). Carpet padding, on the other hand, usually comprises synthetic rubber or polyurethane with strengthening fibers. When the synthetic materials of their construct become pyrolyzed during a fire, the resultant products generated contain a number of diagnostic indicators for certain ignitable liquids, like alkylbenzenes and naphthalenes, which can trigger electronic sniffers and provoke a positive reaction from canine detection teams (11,29). There is also no characteristic profile for charred carpet, as it is very much dependent on the make-up and the conditions of pyrolysis. Studies have shown that while neither the carpet itself nor the carpet padding produce volatiles that could

be misidentified as being petroleum based, it is the carpet backing that is the prime source of interfering compounds (12). However, it was ascertained that the distribution of these compounds in the pyrolysis products differed greatly from the pattern produced by gasoline. Hence, by the implementation of GC-MS analysis and careful pattern observation by an experienced analyst, samples of gasoline in the test matrices could still be identified in the presence of these interferents, showing the necessity for subsequent laboratory-based analysis of samples.

Soot Debris

Another potential source of evidence from a fire scene comes from the smoke that is generated during the fire itself and subsequently deposited onto surfaces as soot particles. Soot is an aggregate of near-spherical particles, with subunits around 20 nm in diameter (45). They have the potential to provide useful information in cases where any traces of ignitable liquids at the seat of the fire have been destroyed or contaminated due to the ferocity of the blaze, fire suppression techniques, or environmental factors. There is a theory that the particulate carbon matter in freshly formed soot may adsorb and trap traces of ignitable liquids much like activated charcoal (46), particularly if a too rich mixture of fuel was present. Forensic laboratories are thus often requested to analyze soot from window glass or ceilings to determine the presence and identity of ignitable liquids.

After formation, soot tends to deposit itself onto cold areas such as metal surfaces or onto glass panes, or can adhere to items of fabric. In the case of window glass, subsequent thermal shattering can result in fragments being deposited outside of the fire scene where they are protected from subsequent exposure to the fire. The soot on these fragments can yield much information about the materials burnt at the fire's origin (47). For example, a fuel-rich fire will tend to produce heavy soot, while synthetic fibers and rubber materials yield an oily soot. Through analysis by pyrolysis-GC, Pinorini et al. (45) took samples of soot from various plastic materials and distinguished them from those of ignitable liquid origin, as the resultant pyrograms for the former were found to be richer and also closer to the pyrograms of the analogous unburned polymers. A disadvantage of this technique was that it typically required at least 50 µg of soot.

The use of smoke residues from fire scenes as a means of evidence is not uncommon.

A recent investigation in Essex, UK, in 2002 used smoke analysis by GC-MS for the first time to provide key evidence in a case by linking smoke from the suspect's clothing with the scene of the fire, thereby helping secure a conviction. The forensic consultant, Dr. Foster, proposed that smoke could have its own unique fingerprint. This theory was confirmed when, at his request, expert Dr. Large used GC-MS to analyze items retrieved from the suspect's car that smelled strongly of smoke, and hence determined a link between these articles and smoke from the fire scene (48–50).

It has been demonstrated that the structure of soot particles can vary depending on their origin. Palatas et al. (51) used high-resolution transmission electron microscopy (HRTEM) to study the fine structure of soots and carbon blacks. The technique used fast Fourier transform applied directly to single particles to obtain quantitative measurements of structural characteristics such as interplanar spacing, orientation, elongation, and length distribution of lattice fringes.

Pinorini et al. (45) carried out extensive work using various analytical methods to both physically and chemically characterize soot from twenty ignitable liquids and twelve plastic materials

encompassing seven polymer types. Physical studies were performed both macro- and microscopically (via tunnelling electron microscopy in the latter case), and through digitized micrographs, a detailed surface characterization was performed. Chemical composition was studied through the use of GC-MS, GC-FID, and pyrolysis-GC. In this respect, he carried out two studies—comparison of total chromatographic profiles for the FID and pyrolysis-GC, and the qualitative and quantitative analysis of 11 selected PAHs. These compounds are produced in significant amounts from the burning of crude oil and diesel (52), and have the potential to provide evidential fingerprints for ignitable liquid-generated smokes. This is because they are not only persistent, but as determined in earlier work by Pinorini himself (53), those common PAHs comprising three aromatic rings are usually present in soots of hydrocarbon-based liquid origin. Furthermore, as demonstrated by Andrasko et al. (54), PAHs appear to be produced by the burning of gasoline although not synthetic materials. However, a study by Lemieux et al. (52) would appear to contest this assertion, finding as it did that emissions of PAHs were significantly higher during the combustion of fiberglass or polymers, such as tyres, which produced almost 100 mg of benzo(a)pyrene per kg of tyre, compared with 5 mg/kg of fuel oil. Nevertheless, Pinorini found that a greater discriminating ability was achieved via the chemical analyses, particularly for soot from plastics, and by combining the physical and chemical data from the studies, it was possible to construct a dichotomic table that could be utilized for the successful classification of soot from fire scenes (45). However, he concluded that there were too many variable factors that may affect the state and composition of soot samples obtained, ranging from the conditions during combustion, to fire suppression techniques and subsequent environmental influences, not to mention the complex combination of materials combusted at a typical scene, all of which can change the deposited soot in unpredictable ways (45). Consequently, he determined that further research was necessary before this technique could be applied in a forensic context.

Sampling

Once a sample has been collected, it is essential that loss and contamination be avoided during transfer to the laboratory and subsequent storage, as this can not only effect the outcome of the analysis but may also have legal ramifications if presented as evidence in court. For this reason, the correct sampling procedure must be followed at all times with the proper documentation in order to maintain sample integrity and chain of custody (25,46), and as a part of this process, the selection of the container to be used is a far from trivial matter.

There are many types of containers available, from bags to jars and metal cans, made from a variety of materials and each with their own advantages and disadvantages, as highlighted in Table 5.

- *Plastic bags*—typically made from nylon, their use may be better suited to collection and transportation of samples, before transferring them to better containers for storage (56).
- *Rubber-sealed screw top jars.*
- *Cans*—the preferred containers of choice for most scene investigators.

Container Integrity

It is vitally important that the container used is clean and does not itself provide a source of cross-contamination. For screw top

TABLE 5—*Sampling containers for fire scene debris (11,23,55).*

Container	Advantages	Disadvantages
Plastic bags	Flexible Hold large awkward samples Convenient to carry in bulk Quickly heat sealed	Sample loss and contamination by diffusion of volatile gases through the bag Not sturdy (easily pierced)
Glass jars	Resistant to puncturing Long lifespan	Breakable Not suitable for heating during sample preparation Screw tops not particularly airtight
Plastic jars	Resistant to puncturing Long lifespan	Not suitable for heating during sample preparation Screw tops not particularly airtight
Unlined metal cans	Lack organic matter that can cause interference during analyses Very robust Excellent sealing capabilities	Tendency to rust through, whose rate is dependent upon the sample and storage conditions
Lined metal cans	Avoids rusting Very robust Excellent sealing capabilities	Some linings can cause interference during analyses

jars, the cleanliness of the lids should be assured (10). Tests have shown that many types of plastic bag contain interfering compounds (25). For these reasons, containers of unknown quality should be avoided without first performing background checks, or instead use commercially available “certified containers.”

Laboratory Sampling

Once the material has been obtained from the scene, a laboratory-based sample preparation is required in order to isolate the volatiles of interest that may be indicative of an ignitable liquid from the matrix. Ideally, this should be performed in such a way as to minimize or screen out any possible background interferents, while avoiding sample loss and maximizing detection limits. However, due to the wide range of chemical and physical properties attributable to different ignitable liquids, there is no one method that can be universally applied.

Traditional Methods

Solvent Extraction—Although generally disfavored in favor of superior methods, it is still approved by ASTM method E1386-00 (57), and useful for extracting empty containers; for very small samples; or under circumstances where the matrix holds too strong an affinity for the sample, preventing the effective use of other methods (25), as may be the case with heavily charred substrates or high boiling range sample components.

Owing to the nature and volume of solvents used, the technique suffers from a high degree of co-extraction of many unrelated matrix components, which results in complex chromatograms and poor sensitivity. A method that partially addresses this problem involves sampling the headspace above the reduced solvent extract (25). This has proved successful for lower boiling compounds, although the procedure does discriminate against obtaining higher boiling components necessary for heavily burned samples, as often these will not readily enter the headspace.

More recently, a second form of solvent extraction utilizing supercritical fluids (SFE) has been investigated, a procedure that has the advantage of avoiding subjecting samples to potentially detrimental thermal stress (58). Over a 25 min extraction, the recovery efficiency of various ignitable liquid residues from carpet was found to be in excess of 80%, with a low degree of interferent co-extraction, suggesting the potential of this technique in future analyses, although this procedure does have a tendency to co-ex-

tract unwanted components of the matrix, resulting in complex chromatographic profiles.

Steam Distillation—Steam distillation is little used today, although it is still approved by 2001 ASTM method E1385-00 (59), and is still used when large amounts of ignitable liquid residue are expected in a sample (10).

In a comparative study of distillation and adsorption techniques (60), this technique displayed superior recovery in an analysis of low to medium boiling range ignitable liquids—specifically gasoline and gas oil—using a modern protocol distillation method with *n*-hexane as the extractor solvent, proven to have high recovery efficiency.

A variation of this process, albeit less used, is vacuum distillation, and is particularly useful for fragile fire debris samples like burned documents. Recoveries for gasoline using this technique have been found to be in the order of 60% (46).

Modern Methods

These traditional methods all suffer from some major disadvantages—they are generally time consuming and require considerable work to be effective, while in many cases a high interfering background is generated or key components are lost. Improved modern methods have tried to address these issues by adopting concentration methods analogous to those used in environmental air sampling. This principally involves the adsorption and concentration of volatile analytes onto a substrate with subsequent desorption and analysis. A procedure known as direct headspace analysis may also be used on occasion, although it is generally not favored (25). This involves heating a contained sample, and then drawing of an aliquot of the vapor headspace and injecting this directly into the GC. More useful as a screening method, it has, however been effective in analyses involving highly polar substances like ethanol, if sufficiently abundant in the sample. Nevertheless, as a technique it suffers from poor sensitivity, as it does not concentrate the sample like other methods, with sensitivity limited by the low injection volume and dependent on the container size.

The preferred methods of extraction and enrichment instead use dynamic headspace sampling or passive headspace concentration.

Dynamic Headspace Sampling—This is the older of the two headspace techniques and was adapted from methods utilized in the field of environmental sampling (55). Sometimes referred to as purge and trap, the basic technique involves using an inert gas to purge continuously the heated headspace of a sample to induce the

complete removal of all the volatile components (61). The subsequent sample gas stream then passes through a cooled and/or sorbent packed trap, retaining the volatile components. These can be subsequently released by heating or solvent extraction and then quantified by GC.

The currently favored method uses the sorbent trap approach, followed by rapid thermal desorption, due mainly to the popularity and ease of use of porous sorbents such as Tenax GC, which do not require the implementation of an additional solvent extraction stage (25).

Modern methods allow the process of dynamic headspace to be fully automated, using an automatic thermal desorption system (ATD) controlled by microprocessors (62). The initial sample is obtained by drawing a large volume of the heated headspace (~ 50 mL) through a sorbent-loaded sampling tube, trapping the volatiles, and then loading into the sampling area of the apparatus. The system incorporates an initial desorption oven, followed by a secondary adsorption-desorption stage, whereby the volatile stream passes into a U-shaped cylinder loaded with an adsorbent within a temperature-controlled cold trap. Lower temperatures enhance Tenax retention capacity, as demonstrated by Brown and Purnell (63), approximately doubling per 10°C decline in temperature. The trap is flash heated at $1500^{\circ}\text{C}/\text{min}$, desorbing the analytes as a sharp band.

An inherent disadvantage in using porous sorbent, is their poor retention for identifying key components from class 1 and certain class 0 ignitable liquids (old classification system), regardless of the size of the sorbent bed used (25). Modern GC techniques can compensate for this, using concentrator technology to provide enrichment; however, in order to keep flow rates compatible, this necessitates either the implementation of sample splitting or cryogenic focusing, increasing the complexity of the analytical procedure.

An alternative is to use a sorbent with a greater sample affinity, such as activated charcoal. Owing to the strong sample interactions, thermal desorption is not usually possible, and solvent extraction is normally required, either with carbon disulfide or diethyl ether (64). Current techniques now enable this to be carried out successfully on a micro-scale using just 5 mg of charcoal, with a highly concentrated final extract volume of a few microliters that may be directly injected into the GC (65).

Nevertheless, dynamic headspace methods are still less popular than passive equilibrium methods as they are inherently labor intensive and prone to contamination via the vacuum or gas supply (66). Furthermore, due to the active nature of the process in removing as much of the residue as possible, the original sample is essentially destroyed or at least greatly reduced in efficacy, making it almost impossible for a future analyst to obtain the same results.

Passive Headspace Concentration—Passive, or static headspace analysis is a nondestructive and far simpler technique to perform than dynamic methods, and is thus generally favored (66). Essentially, the procedure involves suspending an adsorbent material, either a porous polymer or carbon, in the heated headspace of a sample, and then allowing the volatiles in the vapor to adsorb onto the surface, before extraction by solvent or thermal desorption for subsequent analysis (66–68). As with the dynamic process, the analysis of samples obtained by passive enrichment may also be automated using the same ATD technology, albeit with some slight modifications, so is ideal for rapid and batch sampling (69).

Owing to the simplicity of the technique, it is highly versatile, and can be tailored specifically to the type of debris being analy-

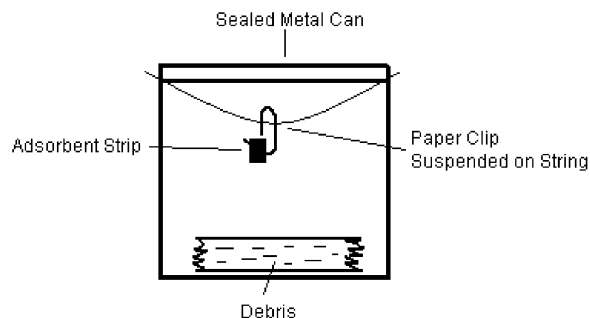


FIG. 5—Passive headspace concentration in a metal container.

zed, the sample container, and the suspected ignitable liquid used from preliminary assessments. A typical setup for passive headspace concentration is shown in Fig. 5.

An advantage of using this technique is that the original debris sample from which samples are taken can be stored for re-analysis, as unlike in the dynamic procedure, this method is performed in a closed system and avoids total depletion of the sample or introducing any potential sources of contamination.

These benefits were demonstrated in a study by Waters et al. (66), where actual debris samples containing known ignitable liquids underwent multiple sampling over time intervals of 1, 3, and 6 months for a period of a year. In each set of trials, there was no significant reduction in volatile concentration—except for some of the lighter residues—and identification was not compromised.

Recovery by passive headspace is dependent largely on temperature and time (25). Generally, temperatures above $\sim 60^{\circ}\text{C}$ are required to ensure recovery of the higher boiling diagnostic *n*-alkanes and heavy compounds; however, excessive heating, as well as longer sampling times, will result in poorer yields of the more volatile components, which become preferentially replaced by the heavier molecules (70).

Sorbents

Carbon Strips—The method most commonly applied in the field of fire investigation is currently the carbon strip technique (71), as the technology involved can be applied to virtually any ignitable liquid, including those that are water miscible (25), as the strips do not absorb water or nitrogen while having a high affinity for hydrocarbons and being resistant to oxidation (10).

The nature of the strip—adsorbent carbon impregnated upon a pliable polymer substrate—allows samples to be archived by cutting the strips in half and storing one piece for later use (25).

A drawback of this method is that the strips do not discriminate between target compounds and background compounds or pyrolysates, with resultant complex GC-MS data displaying all the compounds present (72).

Other Sorbents—Many different sorbents have been examined over the years with varying degrees of success. Clausen reported success utilizing silica as an adsorbent (73), while Baldwin favored Floricil—an activated form of magnesium silicate—finding it particularly effective for kerosenes, although gasolines suffered loss of early peaks (74).

More commonly used these days are the wide ranges of porous polymer adsorbents. Owing to their hydrophobic nature, they can reversibly adsorb volatile analytes without retaining water or low-molecular-weight permanent gases (75). There are many brands available, such as Carbowax GC, Chromosorb, Poropak Q,

Ambersorb XE340, and Tenax GC, each with their own properties and merits.

Tenax GC (2,6-diphenyl-*p*-phenylene oxide) is by far the most popular of these materials available. It is a hydrophobic material that displays a high affinity for hydrocarbons and is thermally stable up to 375°C with a fast desorption time (62,76).

The extraction procedure for Tenax GC differs from that of the carbon strip method, as it is soluble in carbon disulfide; hence, this solvent cannot be used (56). Instead, a process of thermal desorption is used to remove the trapped volatiles from the polymeric matrix directly into the GC.

SPME—Over the last decade, a technique known as SPME has emerged as a development of the passive headspace approach. Using much the same techniques as the adsorbent carbon strip (ACS) method, it benefits from greatly reduced sampling times—in the order of 10–20 min cf. up to 16 h for ACS (77)—far greater sensitivity, managing to detect gasoline in a study at levels where other passive methods failed (78), and the elimination of expensive, toxic solvents like carbon disulfide from the process (64). Furthermore, studies have shown that the process is unaffected by interferences from the pyrolysis products of wood and plastics (79).

Instead of suspending a sorbent strip in the headspace as with ACS methods, SPME technology utilizes a sorbent-coated silica fiber retracted within a hypodermic syringe (64) (see Fig. 6). The procedure follows ASTM E2154-01 (80). The needle is inserted into the sample container, before exposing the fiber for a short period of time, and then retracting it back into the needle for immediate analysis (79). The analysis may be carried out either by direct injection into the heated port of a GC where thermal desorption occurs, or into the injector port of an HPLC system where it is eluted into the mobile phase (77).

An advantage of SPME is that sampling can be performed either in a heated headspace or by insertion into an aqueous matrix, enabling sampling of aqueous fuels and water-miscible volatiles such as ethanol, methanol, and acetone (77). Extraction from aqueous solvents has also been applied to more conventional

ignitable liquids such as lighter fluid, gasoline, and diesel, displaying greatly increased sensitivity over typical solvent extraction methods (81).

Thus, there are three distinct forms of SPME sampling, referred to as the headspace method, direct method, and partial headspace method (79). The headspace method involves exposing the fiber to the headspace above a sample in the conventional way. In the direct method, the fiber is inserted fully into a sample solution, while in the partial headspace method, only part of the fiber is immersed in the solution and the remainder is exposed to the headspace above.

Each of these techniques has different recovery properties. The direct method works best for high-molecular-weight components but performs poorly with low molecular weights. Conversely, the headspace method, on the other hand, gives high recoveries for low molecular compounds but low recoveries with high molecular weights. The partial headspace method is the best of the three techniques, giving high recoveries for virtually all ignitable liquids.

The sorbent fibers used can be comprised of a number of materials and come in a variety of stationary phase thicknesses depending on the application for which they are intended. Materials used include polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene, and divinylbenzene-polydimethylsiloxane (DVB and DVB/PDMS), Carbowax[®] (CW) (Union Carbide Corp., Danbury, CT), and Carboxen[™] (Sigma-Aldrich Co., St. Louis, MO) (64). PDMS is usually considered best, having a rapid desorption time; however, the slow desorbing and hence generally disfavored Carboxen fibers have been found to be effective at recovering samples under wet conditions, particularly water-soluble alcohols (25). The results of tests by Ren and Bertsch (64) on five fibers (PA, CW/DVB, PDMS, DVB/PDMS, Carboxen/PDMS, Carboxen/DVB/PDMS) using GC-FID detection are shown in Table 6. The recovery efficiencies were performed for only three of the fibers and studied over four volatility ranges.

The thickness of the fiber stationary phase effects changes in capacity and specificity in much the same way as in a GC, with thicker phases more efficient for volatile compounds, and thinner coatings favoring large hydrophobic molecules (77).

Despite these apparent advantages, SPME has yet to be widely adopted within the forensic community beyond use as a screening test (77). This may be due to some perceived failings in the technique, namely the limited lifespan of the expensive fibers, a difficulty to integrate the process with standard automation techniques, plus the inability to archive samples. Furthermore, there is also the view that the technique may in fact be too sensitive for use with fire debris samples, able to detect, as it can, previously undetectable levels of petroleum-derived compounds in samples, which may not necessarily be of accelerant origin, thus giving false positives.

Harris and Wheeler (77) attempted to address some of these issues using a hybrid method that combined some of the various benefits of both the ACS methodology and SPME. They proposed first desorbing the SPME fiber into a significantly reduced amount of solvent (~30 µL, cf. ~700 µL) instead of direct injection into the analyzer. The reduced solvent volume makes the process safer to the analyst and generates less harmful waste than conventional ACS, while the SPME sample is now amenable to auto-sampling methods using microvial inserts. In addition, as the sample can be stored in the solvent, archiving for the purpose of future analysis becomes possible. Furthermore, as the volume of the solvent used is a variable quantity, problems caused by over-sensitivity to organic backgrounds can be addressed through simple dilution.

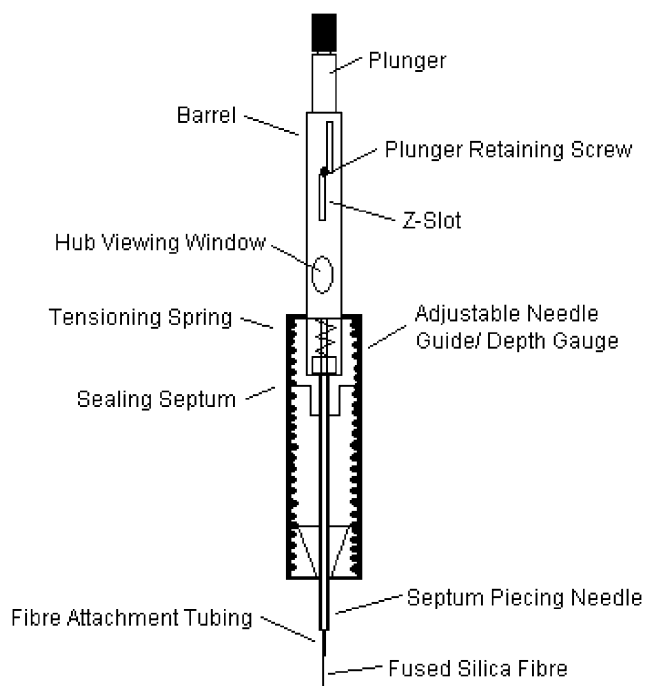


FIG. 6—Solid-phase micro-extraction assembly.

TABLE 6—Properties and applications of selected SPME fibers.

Fiber	Film Thickness (μm)	Recovery Efficiency (%)				Advantages	Disadvantages
		C ₁ –C ₅	C ₅ –C ₁₀	C ₁₀ –C ₁₅	C ₁₅ –C ₂₅		
PA	85	0.002	0.007	0.100	0.264	PDMS is preferred for medium to high M.W. ignitable liquids due to low chromatographic distortion	Poor enrichment for water-soluble compounds and low- to medium-range ignitable liquids
CW/DVB	65	—	—	—	—		
PDMS	100	0.002	0.025	0.405	0.700	Effective enrichment for high to medium volatility range distillates and water solubles	Unsuitable for enrichment of ignitable liquids above C ₁₈ such as diesel fuel
DVB/PDMS	65	—	—	—	—		
Carboxen/PDMS	75	0.027	0.064	0.298	0.457		
Carboxen/DVB/PDMS	85	—	—	—	—		

PDMS, polydimethylsiloxane; PA, polyacrylate; DVB, divinylbenzene; CW, Carbowax; SPME, solid phase micro-extraction.

In tests (77), there was a reduction in signal intensity obtained for the solvent-desorbed samples compared with the thermally desorbed and ACS samples; however, reliable interpretation of the data obtained was still possible to enable positive identification of samples.

Extraction Solvents

Traditionally, the solvent of choice in the field of forensic fire investigation has been carbon disulfide (CS₂), due in part to its high solubility and efficiency at displacing organic molecules from charcoal, and its unresponsiveness to FID detection (56).

Nevertheless, CS₂ is not a particularly desirable substance for analysts to work with due to its cost, flammability as well as its biological and environmental toxicity (77).

With the increased use of GC-MS, CS₂ has been replaced with safer solvents. Methanol, methylene chloride, diethyl ether, and pentane have all been used with varying degrees of success, albeit with greatly reduced solubility properties compared with CS₂ (73). Of these, methanol has the highest solubility next to CS₂, while a study by Lentini and Armstrong (82) cited the use of diethyl ether as being a suitable alternative if using a mass selective detector.

Analytical Techniques

GC

Most forensic fire samples utilize GC as a means of either screening samples to determine their suitability for discriminatory analysis, or for actual identification purposes (46,83).

Over the years, column technology has advanced considerably. Modern advances have now led to the development of short columns with extremely high performance and faster analysis times by utilizing high-temperature-programming rates (46).

Multi-column chromatography, wherein two columns of different selectivity are connected to the same injector, can also give improved resolution, with a single sample injection generating two chromatograms (84). However, with complex mixtures, the peak data spread over the two chromatograms are too difficult to interpret meaningfully, and is thus no more advantageous than single-column chromatography.

Another approach, termed heart-cut, is a multi-dimensional chromatographic procedure, whereby a portion of the unresolved eluent stream from the first column is transferred to a second column, again of different selectivity, giving improved resolution. A drawback is that this can overly complicate the procedure, both in

terms of the apparatus required and in operation by the analyst, and is hence not widely used (85).

Comprehensive Two-Dimensional GC

In analyses of complex mixtures, conventional GC suffers from problems of co-elution and unknown interferences. One of the most recent developments in multicolumn GC technology that has the potential to address these issues is comprehensive two-dimensional GC \times GC. It differs from other multicolumn techniques discussed previously, such as heart-cut, in that all of the analyte is transferred from the first to the second column, subjecting the entire sample to two distinct separation processes, for example by volatility and then polarity, as opposed to isolating specific target compounds, hence the term "comprehensive" (86). The data thus generated give a pattern of retention in two-dimensional space capable of providing a large amount of detailed information.

The technique was originally developed by Venkatramani and Phillips (87) for the separation of complex petroleum mixtures, and was subsequently applied in the field of environmental sampling to address the problems that conventional GC-MS techniques had in elucidating patterns with extensive co-elution from highly complex samples. By using this new approach, separation of complex mixtures was increased by an order of magnitude, resolving thousands of peaks where previously single GC gave less than 100 (86).

The key to the technology lies in the modulator—the device that connects the two columns. Its purpose is to sample periodically from the first column into the second, compressing the analyte into a narrow peak (~ 80 ms at half height) as it does so (82). When this narrow band is subsequently injected onto the second column, co-elutents are resolved by a rapid second separation, which is completed before the cycle begins again. The modulator can be thermally controlled—although cryogenic, mechanical valve, and pulsed liquid CO₂ jet variations have all been used—and comprises a short capillary column (*c.* 1 m) with a thick-film stationary phase (*c.* 0.1 μm). Analytes from the first column become momentarily adsorbed, and then desorbed and compressed as the heater rotates over the trap. This process of spatial band compression also has the effect of considerably reducing signal to noise ratio, improving detection and quantification ability (88).

The process has been successfully performed with detectors as simple as an FID. However, with the implementation of a mass-selective device instead, there is the potential to identify thousands of individual components in a matrix, with the added benefit of spectral library matching (86).

TABLE 7—Key points of detectors for GC.

Detector	Key Points and Uses
Flame ionization detector (FID)	For many years the standard detector for hydrocarbon analysis
Fourier transform infrared	Limited sensitivity
Microcells	Identifies terpenes, gasoline, and complex pyrolysis products
Photo-ionization detector (PID)	Used in tandem with FID Detailed characterization of aromatics aids confirmation Higher selectivity gives more accurate pattern recognition
Substance-specific detectors:	
Oxygen	Oxygen detectors used to identify ethanol and methyl tertiary butyl ether
Nitrogen phosphorus	Monitoring of nitrogen, phosphorus, and sulfur enables the origin of gasoline to be determined
Sulfur	Sulfur detectors are expensive and complicated
Electron capture detector	Halogenated hydrocarbons and organometallics High degree of precision for petroleum distillates

In the sphere of environmental forensics sampling, GC \times GC has been extensively applied to the analysis of crude oil and petroleum distillate samples through work on crude oil spills and contamination (86); hence, there is clearly scope for its use in forensic fire analyses and ignitable liquid detection. In tests, it was able to separate up to a thousand components in diesel samples and over three hundred in gasoline (88). A study by Frysinger and Gaines (88) applied this technique successfully to track an ignitable liquid's chemical signature in a complex fire debris sample matrix, detecting weathered ignitable liquid residues in the presence of high pyrolysate backgrounds.

Detectors—A number of detectors have been used with GC over the years, some of which are briefly discussed in Table 7.

Nevertheless, current legislation and advances in clean fuel technology have limited the use of some of these detectors, as many of the compounds in ignitable liquids that they specifically target, such as MTBE and sulfur and lead compounds, are being or have already been phased out of use, rendering these procedures obsolete (25). Hence, there is now a greater reliance on and move toward the use of mass selection devices.

GC-MS

GC-MS as a technique for use in fire debris analysis has been available for more than twenty years; however, it is only recently with the development of cheap, compact, and user-friendly models that it has become more popular for routine use (89), with around 90% of laboratories now regularly using the technique (88) and a prescribed ASTM method (6).

An MS device can display data either as mass chromatograms extracted from the total ion chromatogram (TIC) data, as specific characteristic ions via SIM, or the more in-depth target compound chromatogram (TCC) analysis. Using this latter approach, interferences and background noise can be greatly reduced, even in highly complex matrices, enabling a high degree of sensitivity to be achieved. This is particularly useful in fire debris samples and complex ignitable liquids, where overlapping GC peaks result in elevated baselines. The co-eluting peaks can be almost entirely separated by mass, as individual component species have unique molecular fragmentation patterns that can be used as a fingerprint for that class of ignitable liquid (88). In a TCC analysis, the data from the TIC are screened for specific parent/daughter fragmen-

tation ions characteristic of the ignitable liquid within a defined retention window, and their abundances are used to provide confirmation by comparison with known data for that substance (25). A composite chromatogram of no more than 30 components is produced that encompasses the key components from all target groups for a specific substance. By reducing the amount of data in this way, rapid identification is possible. A searchable database for ignitable liquid TCCs exists that has proved useful in identifying chromatograms obtained from complex debris samples (90).

Petroleum based ignitable liquids are ideal for analysis by GC-MS, as the compounds that comprise the majority of petroleum distillates—namely alkanes, cycloalkanes, and aromatic hydrocarbons—produce several species of characteristic ions for each of the major classes (25) (see Table 1).

Extraction of the ion fragments specific to the aromatics present in gasoline enables an identifying chromatographic fingerprint to be generated (91). These fragments include toluene and xylenes (m/z 91), the C_3 and C_4 alkyl-benzenes (m/z 105 and 119, respectively), plus naphthalene and the alkyl naphthalenes (m/z 128, 142, 156). Although not necessarily the most abundant, these components are generally more persistent, particularly at the elevated temperatures experienced during a fire, and are thus more likely to become concentrated and subsequently more readily detectable (92). Additionally, investigation of the higher-boiling alkyl-biphenyl components (m/z 168, 192, 196) becomes possible with samples that are highly evaporated, at which point these components become detectable (92).

For those commonly encountered ignitable liquids comprising mainly aliphatic species—diesel, kerosene, aviation fuel—identification is carried out on the basis of the fragments at m/z 57 and 71. Where the ratio of m/z 57 to m/z 71 falls between 1.5 and 1.6, the liquid is determined to be kerosene or diesel, specific classification being based on the differing carbon chain lengths. When the ratio is higher than this or falls below 1, and has a chain length of C_8 – C_9 , the sample is determined to be aviation fuel (92). The presence of alkenes in these traces with an m/z 55 would be indicative of the trace being caused by polyethylene degradation (92).

One major problem with GC-MS arises when the target compounds and background materials contain ions with the same mass. This most commonly occurs in fire debris analyses when the sample matrix consists of petroleum-based products, particularly burned carpet (88). Carpet pyrolysates can include large amounts of alkylbenzenes—such as ethyl-, propyl-, and butylbenzene—all of which are found in, and used diagnostically for petroleum-derived ignitable liquids. Their presence thus makes positive detection and identification of the target compound at best difficult if not impossible.

A study by Almirall and Furton (72) on the controlled burning of 35 commonly encountered substrates with subsequent analysis by pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) investigated this problem of common target compounds arising from other sources. They determined that while identifying alkanes and aromatics for ignitable liquid residues are often found in burn products, the chromatographic patterns produced are markedly different from the ignitable liquid residues themselves.

Interference Problems and Developments in MS Detection—Interfering compounds are a recognized problem in the analysis of ignitable liquid residues, and may be attributable to one or more sources—naturally from the background of a substrate material, its manufacture, or contamination; from pyrolysates generated during its combustion; or from substrate combustion products (72).

The presence of ignitable liquid products containing Isopar H and Norpar (straight-chain alkanes) in both burned and unburned

samples of vinyl flooring has been determined in a GC-MS study by Wells to derive from plasticizers used during the vinyl manufacture process (93). This can lead to complications for fire investigators as Isopar H and Norpar products are also commercially available in products such as charcoal starters, copier toners, and industrial cleaning solvents; thus, their presence in vinyl flooring samples is not necessarily indicative of ignitable liquid use and should be treated with caution.

Both animal and human subcutaneous fat have been demonstrated to produce significant quantities of volatiles under combustion that can be detected in subsequent smoke and fire debris. The *n*-aldehydes in the C₅–C₁₀ range were found to predominate, with *n*-alkanes, alkenes, and other aromatics also detected, which may be misconstrued as being of ignitable liquid origin (49).

Almirall and Furton (72) examined the pyrolysis products of 35 commonly encountered background materials, ranging from varieties of carpet and flooring to packaging materials and compact disks, and determined that many of the identifying compounds used to determine the presence of ignitable liquid residues, such as 2-methylnaphthalene, are frequently detected.

Complications with GC can arise through co-elution of matrix and pyrolysis volatiles, and from microbial degradation of samples. Existing methods to counter these cannot be used on a microscale, and are not always successful. Furthermore, the optimized data-interpretation schemes for GC-MS i.e., mass chromatograms and TCC, which are necessitated by the limited mass resolving power of the technique, are not completely ideal. Mass chromatograms can be somewhat convoluted, with TCC not only requiring prior determination of the optimal target ions but also that these persist in the sample at detectable levels (94), a particular problem for fire debris where samples have been exposed to harsh environmental conditions. A procedure developed by Rodgers et al. (94) attempted to address these issues by using a technique known as Fourier transform ion cyclotron (FT-ICR) mass spectrometry. This procedure poses an attractive alternative for the analysis of complex mixtures due to its ultrahigh mass resolving power, high accuracy (<1 p.p.m.), and rapid analysis capability (<10 min), enabling it to provide baseline resolution of multiple different elemental composition species that may vary only nominally in mass, without prior chromatographic separation. Hence, it is capable of providing the molecular formulas for all peaks present in the spectrum. While in previous methods the complexity of the sample mixture was the stumbling block, with FT-ICR it is the uniqueness of the highly complex yet resolved patterns that provides the fingerprint that enables specific identification. The forensic viability of this technique was successfully demonstrated through the discrimination and identification of weathered and unweathered ignitable liquids in fire debris samples (94).

Tests on the weathered/unweathered samples revealed two distinct weathering patterns (94). While the compositional diversities of gasoline, kerosene, mineral spirits, paint thinner, and lighter fluid become similar or reduced with increasing weathering, in diesel and turpatine the mass spectral complexity in fact increases with weathering over 50%.

Through the analysis of two different brands of mineral spirit by this technique, it was determined possible to differentiate and identify two ignitable liquids within the same commercial petroleum class, as the two samples studied had markedly different *m/z* distributions relative to each other (94).

Fire debris samples constituted one complex and one simple ignitable liquid, namely turpatine and lighter fluid, respectively. Through both visual comparison of spectra and peak matching of

the mass scale-expanded segments of the fingerprints generated to a library of the weathered standards (in this case an 85% weathered sample for each), positive identification was possible from the fire debris extracts. In the case of turpatine, identification was still possible despite the presence of an additional 249 peaks from matrix and pyrolysis components, with as many as five peaks of the same nominal mass (94).

Rella et al. (92) used thermal cold trap desorption with gas chromatography-mass spectrometry (TCT-GC-MS) to counter matrix interference effects common to fire debris samples and enrich the traces of target analyte compounds in weathered gasolines, successfully detecting amounts of a 50% weathered standard on an inert sand matrix down to 3 nL. Injected samples of weathered gasoline underwent on-line thermal desorption with cryofocusing, before identification by GC-MS. Thermal treatment was found to reduce matrix interference effects while enriching the desorbed compounds, giving a high degree of sensitivity. The technique is also advantageous in that it requires very little sample manipulation, eliminating the need to use solvents, saving time, money, and disposal problems associated with extraction procedures. Furthermore, due to the high efficiency of cold trap enrichment, detection was possible on trace sample sizes (100–150 mg), enabling further analyses to be performed.

Gas Chromatography with Tandem Mass Spectrometry (GC-MS/MS)

In GC-MS/MS, the selectivity of the basic process is improved via the implementation of sequential mass spectrometry through a second coupled mass spectrometer, enabling the fragmentation pathways of target ions to be tracked (88). Interferents present in the sample may produce ions of the same mass as the original parent target ion; however, subsequent fragmentation patterns are likely to be different (95). The MS/MS process exploits this phenomenon by targeting the characteristic ion and subjecting it to collision-induced dissociation (CID), and then monitoring the parent–daughter ion transitions, rejecting those that do not follow the expected pathway. In this way, the effects of matrix interferences can be greatly minimized, while at the same time improving the signal-to-noise ratio of target ions (96).

MS/MS has proven more sensitive than MS in the analysis of alkylbenzenes and naphthalenes, important diagnostic components of ignitable liquids, particularly gasolines; however, with alkanes, extensive fragmentation results in a marked loss of sensitivity (25). In addition, such is the sensitivity of the technique to particular classes of compound—over and above those detectable by MS, it is capable of identifying residues from domestically occurring speciality solvents where only the aromatic to alkane ratios differentiate them from evaporated petrol—it should always be used alongside conventional GC-MS and is best utilized as a secondary confirmatory analysis (95).

Nevertheless, the ultra-specificity of this technique has proven effective in dramatically reducing interferences from GC-MS profiles attributable to pyrolysis products, while it is also beneficial in simplifying complex patterns (88). Moreover, it has proven highly efficient in trace analytical work for dealing with weak signals, as demonstrated by Sutherland in a case study where ultra-trace levels of highly weathered petrol were confirmed using the technique (97).

Other Methods

Besides GC, a number of other techniques exist that can provide useful information on a submitted sample, although it should be

noted that in all cases, these are recommended as complementary secondary analyses to a routine GC method.

Where liquid samples are submitted in appreciable volumes or if distillation has been performed to isolate the neat volatile, traditional measurements of physical properties like refractive index and flash point can provide some useful information on a substance, although in terms of actually characterizing ignitable liquids they are generally of little use (46). Infrared (IR) spectroscopy can provide some information on the chemical structure of liquid samples obtained by the distillation of fire debris, although typically the procedure requires around 20 μ L of sample.

Work by Dhole and Ghosal (98) led to the development of procedures for analyzing debris-derived residues of petrol, diesel, and kerosene by thin-layer chromatography (TLC) and high-performance thin-layer chromatography (HPTLC).

Several successful studies have been performed into the application of the ultraviolet/visible fluorescence technique to the analysis of petroleum distillates. Advances in this field, when used in conjunction with modern high-performance liquid chromatography (HPLC) technology, have provided detailed characterizations of ignitable liquids, as demonstrated in the work by Alexander et al. (99)

Vapor-phase ultraviolet spectroscopy, already a well-established procedure for the analysis of volatile compounds (100), has been applied to the determination of aromatic ignitable liquids, and has the potential to provide additional information to that obtainable by GC methods, particularly in cases where one sample component in high excess masks another. This technique has a number of advantages, being simple, cheap, and rapid, while also providing an acceptable degree of sensitivity and discrimination for use in casework. It cannot, however, be used to detect polycyclic aromatic hydrocarbons or alkanes, ruling out its use where diesel or paraffin are suspected due to their predominantly alkane compositions (101).

Summary

Arson investigation techniques have come a long way since the 1950s, with once benchmark procedures such as vacuum and steam distillation, and GC-FID detection, now considered somewhat archaic, superseded by greatly improved modern methods like headspace enrichment, SPME, and mass spectrometric detection. These techniques have increased the sensitivity and discriminatory power achievable in the analysis of fire debris samples by several orders of magnitude. Similarly, on-scene detection may greatly benefit by the advent and implementation of portable GC and MS devices, the ability of the latter to provide results within 30 sec without recourse to laboratory testing, a clear advantage to scene investigators in situations where time is a factor.

The growing popularity of multi-dimensional GC techniques—particularly comprehensive two-dimensional GC—has the potential to revolutionize fire debris analysis, enabling extremely complex samples with high pyrolysates backgrounds to be deconvoluted and hence permit discrimination and identification—something not possible using traditional methods or even GC-MS.

The authors also see scope in the future use of smoke residues in arson investigation. Following on from Pinorini's work studying PAHs, with further research and development, a procedure may become viable for discriminating and identifying the presence of an accelerant in a soot sample.

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