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Accelerant Identification in Fire Debris by Gas Chromatography/Mass Spectrometry Techniques

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ABSTRACT: Fire debris suspected of being involved in arson fires or fire bombings is extracted and analyzed for the presence of flammable and combustible liquids by gas chromatography/mass spectrometry (GC/MS). Pentane extractions of debris or neat liquids are examined by GC/MS and the resulting GC profiles and reconstructed ion chromatograms (RICs) are used to characterize and identify accelerants. This technique, using selected ions to generate profile charts during data processing, enables the differentiation and identification of a variety of petroleum products and solvents used in arson fires.

KEYWORDS: criminalistics, arson, chemical analysis, accelerants

Pattern recognition of gas chromatograms is currently the method most widely used for the identification of accelerants commonly found in fire debris. Gas chromatography (GC) is used with a fair degree of confidence, yet with the introduction of mass spectrometry (MS), a significantly higher degree of confidence is achieved [1]. Differentiation of gasolines, fuel oils, and other flammable and combustible hydrocarbons is simplified using reconstructed ion chromatograms (RICs) of specific mass ions unique to different types of accelerants. Determination of various types of gasoline, for example, leaded or unleaded, is made possible using RIC techniques. Interfering pyrolysis products, particularly those of synthetic polymers which often hinder the identification of accelerants by GC pattern alone, are minimized using RIC techniques. Presented here is a technique currently employed by this laboratory for the recovery and identification of accelerants.

Material and Methods

Sample

Debris from fires or remnants of fire bombs collected by investigators at fire scenes are submitted to the laboratory in airtight metal cans or polyester and nylon bags. The packaging is critical to preserve residues of volatile accelerants used in arson fires. Polyethylene evidence bags are unacceptable inasmuch as gasoline and other volatile accelerants rapidly permeate

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this material. Glass containers can be used when other suitable containers are not available, but careful handling and packaging are necessary.

Equipment

Extracted samples or neat liquids are examined using a Finnigan 4000 Quadrupole gas chromatograph/mass spectrometer (GC/MS) controlled by Finnigan's INCOS Mass Spectral Data System (MSDS) utilizing a Data General Nova 3 minicomputer system. The GC column used is a 30-m, 0.25-mm inside diameter fused silica capillary column coated with SE54. The raw data are stored by the MSDS, and a Printronix 300 printer is used for hard copies of chromatograms and mass spectra. Procedures created by this laboratory using MSDS programs are used to automate data processing of sample runs.

Sample Preparation

Debris samples are screened by headspace analysis before a liquid extraction is performed. Sample debris is first heated in its container on a steam bath for 15 to 30 min. A 1.0-cm³ headspace sample is injected into a GC using a Porapak Q column connected to a flame ionization detector to detect low boiling compounds that may be present but are not discernible in a pentane extract. After this initial screen, a liquid extraction is performed using pentane.

The purity of the pentane used in the extraction should always be checked by lot or batch number. A similar volume of pentane used for extraction of debris (200 mL or more) is evaporated to a volume of 1 or 2 mL and screened for impurities. This avoids misidentification of accelerants that have constituents in common with solvent impurities found in the low range of the hydrocarbon series from C-5 through C-8.

The size and nature of the debris will dictate the amount of pentane used in the extraction. Debris composed of mainly wood or nonabsorptive materials requires just enough pentane to insure continuous contact of the solvent with the debris while shaking or swirling. Extraction in the original containers is ideal for this purpose. Very absorptive material, such as foam rubber or cotton, requires a slightly larger volume of solvent. Extraction in polyester or nylon bags is ideal for soft, porous debris because the pentane can be forced through the material by repetitive squeezing.

Once the debris is adequately extracted, the pentane is filtered into a beaker. Absorptive materials in bags are squeezed to remove as much pentane as possible. The liquid extract is then visually checked for residual water by observing whether two layers exist. If so, the aqueous layer is separated by transferring the extract to a separatory funnel and draining. The pentane is then passed through filter paper into a beaker for evaporation on a steam bath under an air stream.

Color, viscosity, and odor are used to judge how far evaporation should proceed. Evaporation should cease once a caramel color or dirty yellow is approached or when the pentane vapors are no longer evident. The final volume is very dependent upon the debris composition and the type and quantity of accelerant recovered. It is not unusual to extract as much as 25 or 50 mL of heavier fuel oils from absorptive materials.

For neat liquid samples, no preparation is necessary. If the suspected liquid is water, an extraction with approximately one-fifth volume of pentane in a separatory funnel will remove residues of accelerants in the aqueous layer. Because the extraction is generally very clean, evaporation of the pentane to a volume of less than 0.5 mL is possible.

Gas Chromatography/Mass Spectrometry

Samples are injected onto the capillary column using a split ratio of approximately 50:1 and head pressure of 138 kPa (20 psi). This results in a flow of between 1 and 2 mL/min. The

initial oven temperature is 60°C, held for 3 min, then programmed to 265°C at a rate of 20°C/min. The final temperature is held until the completion of the run. The injector and transfer line temperatures are 250°C. Helium is used as the carrier gas.

Mass spectrometry is used in the electron impact (EI) mode. A scan time of 1.0 s is used over a mass range of 34 to 300 m/e , electron multiplier setting of 1200 V, emission current at 0.4 mA, and electron energy at 70 eV.

Neat samples of gasoline and other fuels require a 0.1 μL injection volume while pentane extracts require 0.5 to 1.0 μL sample volume. These injection amounts are necessary to detect small quantities of additives such as tetraalkylleads. A total of 1000 scans at 1 scan/s takes 16 min which is sufficient to cover fuels with hydrocarbons as high as C-22. Data are accumulated by the INCOS MSDS and stored for processing by computer programs designed specifically to characterize common accelerants. GC charts and tables of RICs of specific mass ions characterizing accelerant fuels are generated to detect and confirm accelerant residues in debris samples.

Pentane extracts need special consideration to prolong source life in MS. Analysts should first determine the retention time of pentane in their capillary column, which is noticeable by an increase in source pressure. The filament should remain off until the pentane elutes.

The selection of a column for arson analysis is of primary importance when designing a GC/MS system. A capillary column coated with SES4 has proved efficient for arson analysis on the Finnigan GC/MS system. Packed columns, which are often used for other analytical work, can also be used for arson examinations but require sacrificing peak resolution as a critical trade-off. Alternative coatings for capillary columns are also available and each has its own advantages and disadvantages.

Data and Discussion

Accelerants used in arson fires or fire bombs are usually complex hydrocarbon mixtures; some, such as gasoline are composed of over 400 components. These fuels generally fall in the range of the carbon series between C-5 and C-22. Many hydrocarbon mixtures have additives that enhance their usability, such as tetraethyllead in leaded gasoline. These additives in conjunction with other common components may facilitate the use of RIC patterns to identify accelerants in the presence of interfering pyrolysis products.

The mass ions listed in Table 1 are used as the basis of analysis in characterizing the different accelerants. These mass ions represent the more abundant hydrocarbon species found in gasoline (per ASTM Test for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry [D 2789]) and other petroleum fuels.

The total ion chromatograms (TICs) of four common fuels shown in Fig. 1 were constructed scanning mass ions 34 through 300 m/e . The TICs of leaded gasoline, unleaded gasoline, lighter fluid, and kerosene are similar to results obtained from GC analysis enhanced by use of a high temperature column in the GC/MS. The high temperature column allows shorter

TABLE 1—Mass ions m/e of representative hydrocarbons found in common accelerants (ASTM D 2789).

Compound	m/e
Paraffins ($\text{C}_n\text{H}_{2n+2}$)	43, 57, 71, 85, 99
Monocycloparaffins (C_nH_{2n})	41, 55, 69, 83, 97
Dicycloparaffins ($\text{C}_n\text{H}_{2n-2}$)	67, 68, 81, 82, 95, 96
Alkylbenzenes ($\text{C}_n\text{H}_{2n-6}$)	77, 78, 91, 92, 105, 106, up to 161, 162
Indans or tetralins ($\text{C}_n\text{H}_{2n-8}$)	103, 104, 117, 118, up to 159, 160
Naphthalene (C_{10}H_8)	128
Naphthalenes ($\text{C}_n\text{H}_{2n-12}$)	141, 142, 155, 156

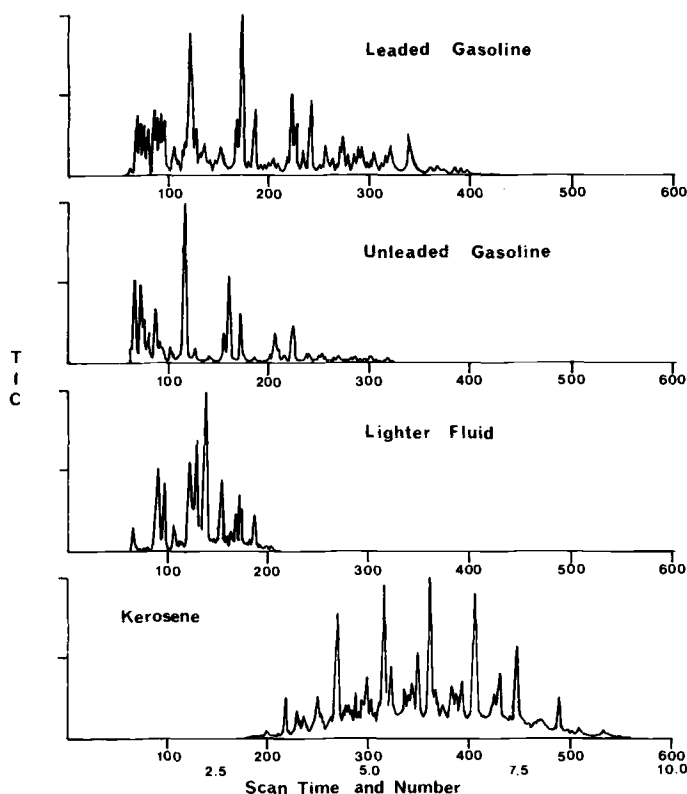


FIG. 1—The TICs of four common fuels used as accelerants are analyzed by GC/MS using a capillary column coated with SE54.

run times for the heavier fuel oils, reducing the run times to under 20 min. Major peaks are labeled by the scan number for peak-to-peak comparison when necessary.

Illustrated in Fig. 2 are RICs of specific mass ions used to screen for hydrocarbons found in common petroleum fuels. Listed in Table 2 is the relative abundance of each ion in the sample. It is apparent that the lower boiling distillates, such as gasoline, have a relatively higher abundance of the lighter hydrocarbons. In contrast, the higher boiling fractions, for example, fuel oil No. 2, contain fewer lighter hydrocarbons and a higher relative abundance of hydrocarbons from C-9 and above. This is expected considering the refining process that produces these products [2].

The straight chain hydrocarbon series is represented in Fig. 3, starting with C-10 at 142 m/e and increasing stepwise by 14 m/e up to 296 m/e or C-21. Also, from 128 through 184 m/e , are peaks representing the naphthalenes that, because of their higher boiling points, elute well after the corresponding straight chain compound. Fuel oils will have peaks representing the latter ions in the series, whereas, neat gasoline does not. Various fuel oils can also be differentiated using RICs.

The value of these RIC tables is apparent when they are utilized on samples that are highly contaminated with pyrolysis products. These compounds tend to mask the GC profile of accelerants, complicating peak-to-peak comparison of GC charts. By using the RIC tables and isolating only those ions desired to identify suspected accelerants, the interfering ions from pyrolysis products are ignored. The RIC profiles become the comparative tool instead of the less discriminating TIC.

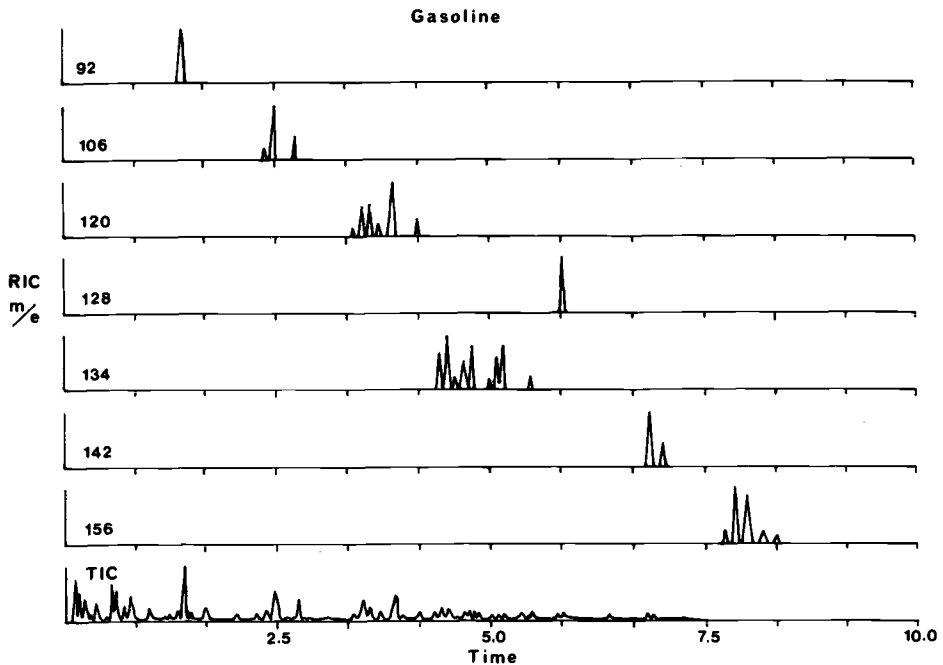


FIG. 2—An RIC table that illustrates the various hydrocarbons (from Table 1) which characterize gasoline and other volatile accelerants.

Another obvious advantage of GC/MS RIC techniques is in the identification of leaded and unleaded gasolines. The TICs of these neat liquids are slightly different, but the differences disappear when the samples are extracted from the burned debris. The RIC tables for ions 92 through 142 m/e are also similar for both gasolines. The specimens become noticeably different in the scan range between 200 and 300 m/e . This is the region where leaded alkyl compounds are detectable by distinct peaks representing the lead additives. No peaks occur in the same scan range in the unleaded gasoline. The relative retention times of these compounds are compared to toluene and methylnaphthalene in Fig. 4, and the partial mass spectrum of tetraethylplumbane (tetraethyllead) appears in Fig. 5, top.

An octane booster recently added to unleaded fuel, methyl tert-butyl ether (MTBE) [3], denotes a compound unique to unleaded gasoline. The base peak of MTBE is 73 m/e (see Fig. 5, bottom) with a retention time of about 0.5 relative to toluene. Fuels or debris suspected

TABLE 2—Relative abundance of mass ions (m/e) of GC/MS analyses of four common fuels.^a

Fuel	m/e					
	92	106	120	128	142	156
Unleaded gasoline	100	48	16	5	0.5	0.0
Leaded gasoline	97	100	50	37	8	0.2
Kerosene	11	63	71	100	71	33
Fuel oil No. 2	6	9	30	58	100	81

^aPercent of abundance calculated by dividing measured ion intensity by the intensity of the most abundant ion and multiplying the quotient by 100.

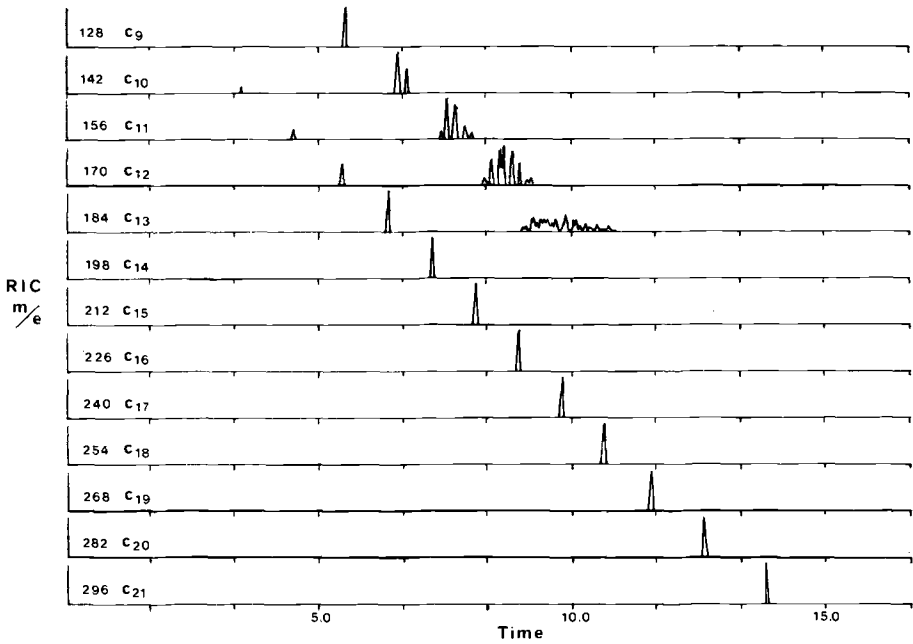


FIG. 3—This RIC table is used to characterize the straight chain hydrocarbon series typical of fuel oils.

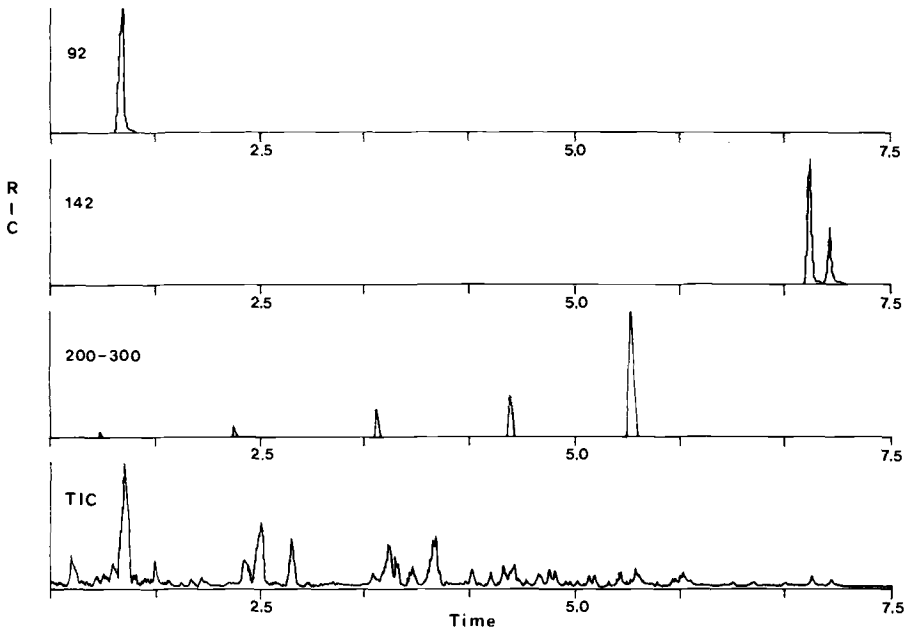


FIG. 4—Tetraalkylleads in gasoline are detected as peaks in a RIC ranging from 200 to 300 m/e with retention times beginning near toluene (92 m/e) and ending before methylnaphthalene (142 m/e).

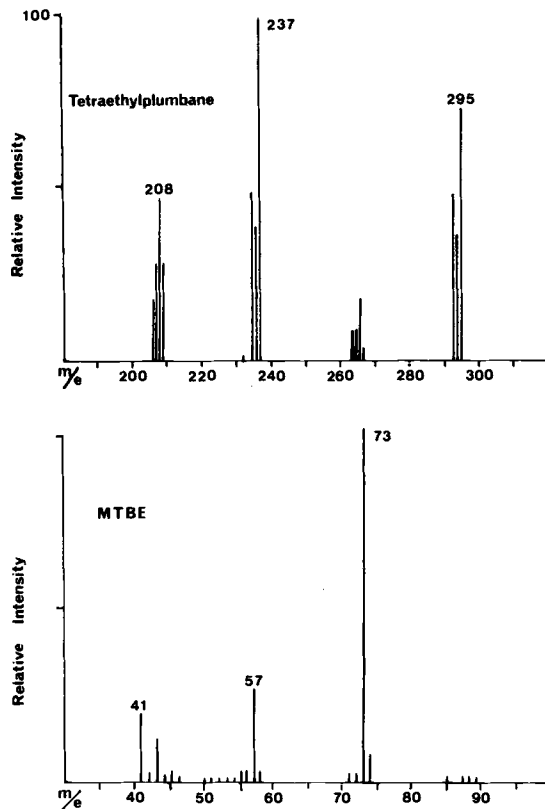


FIG. 5—(top) *The partial mass spectrum of tetraethyllead as found in leaded gasoline and (bottom) the mass spectrum of methyl tert-butyl ether, a recent additive to some unleaded gasolines.*

of containing MTBE can be screened using a heated sample and headspacing 1.0 cm^3 into a GC column designed for volatiles, for example, Carbowax 20M (see Fig. 6). A solvent wash that is carefully evaporated will contain the MTBE, but peak retention time is only 10 s after the pentane surge. In either case, the identification of MTBE is considerable proof that unleaded gasoline is present in the sample.

The analysis of fuel oils is simplified using GC/MS and a capillary column. As mentioned previously, many columns are suitable for arson GC/MS work but SE54 provides excellent results for gasoline and for heavier fuel oils. With a working temperature of 300°C and run times of less than 20 min, compounds up to C-22 will elute, which is necessary to distinguish the different fuel oils (see Fig. 7).

Automotive products, turpentine, and other common household solvents frequently used as accelerants are easily identified by GC/MS. Most household solvents have several main ingredients that can be identified and compared to the product label. Turpentine contains terpene compounds and painting solvents often use toluene, xylenes, and ketones in large percentages. Automotive products have a wide range of solvent composition; gas line anti-freeze contains methanol, xylenes account for the bulk of many carburetor cleaners, and octane boosters are composed of additives like methylcyclopentadienylmanganese tricarbonyl (MMT). A list of these compounds is found in Table 3. Some of these products are best screened by using heated headspace samples from debris and injecting them on a column designed for volatiles. The analyst must be careful not to rely solely on a headspace screen for

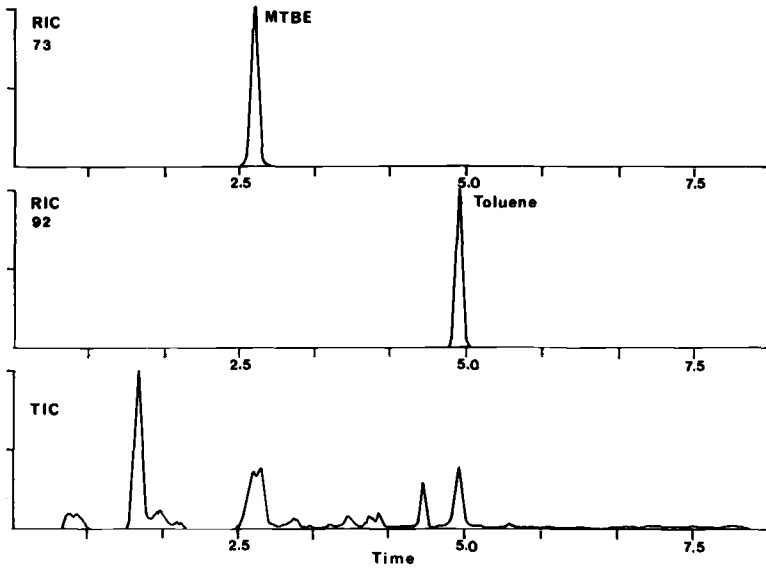


FIG. 6—A TIC of a headspace sampling of gasoline illustrates the relative retention time of MTBE to toluene when injected on a carboxack column.

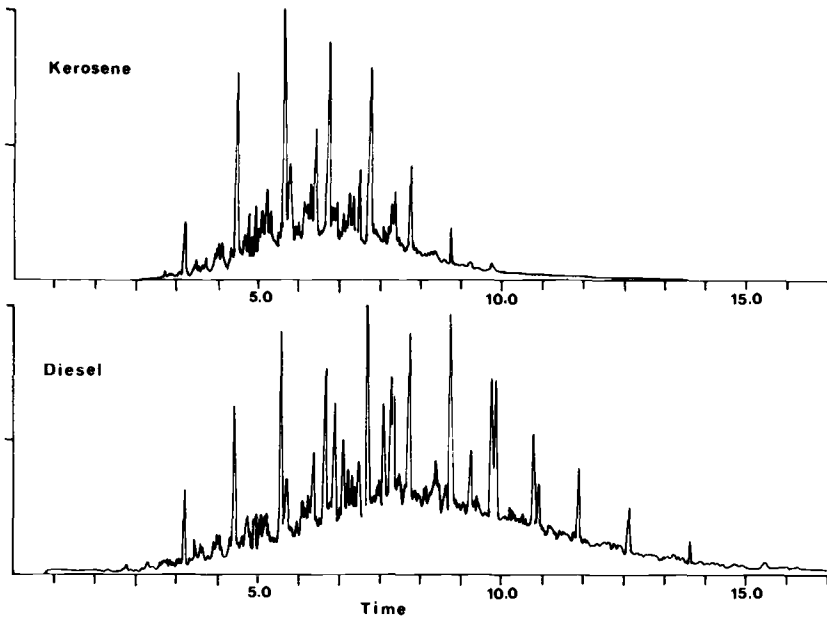


FIG. 7—A comparison of kerosene and diesel fuel TICs to illustrate the differences that occur at the latter end of the hydrocarbon series.

TABLE 3—Mass ions (m/e) of common constituents in household solvents and automotive products.

Product	Component	Significant m/e
Carburetor cleaner	xylene	105, 106
Gasline antifreeze	methanol	29, 31
Leaded gasoline	lead	200 to 300
Nail polish remover	acetone	58
Octane boosters	toluene, MMT	92, 218
Turpentine	terpenes	93
Unleaded gasoline	MTBE	73

debris samples suspected of containing many of the above products. The early eluting compounds are the first to burn or evaporate in a fire, so alternative screens are necessary to detect other less volatile components in the mixture. With such a wide range of components in the various products, the analyst can be selective in choosing those compounds most easily detectable by existing GC/MS system parameters and column arrangements.

In conclusion, common fuels and solvents used as accelerants in arson fires, such as lighter fluids, fuel oils, and gasolines, have RIC profiles characteristically unique to the composition of the fuel. Although many extracted residues cannot be specifically identified as a named product because of degradation during burning, the RIC profiles and mass spectral data will strongly suggest residues as being characteristic of a particular group of products. Establishing a reference library of accumulated data of RIC profiles and MS data will simplify the identification of common fuels used as accelerants.

Mass spectrometry notably enhances the capabilities of the analyst to detect and identify accelerants, particularly in the presence of pyrolysis and combustion products of fire. With a little practical experience in data processing, analysts can design their own RIC tables to differentiate accelerants.

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