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Gas Chromatography-Mass Spectrometry of Simulated Arson Residue Using Gasoline as an Accelerant

Because gasoline is the most common accelerant used in arson [1], the forensic scientist would like to be able to determine whether or not fire residues contain traces of gasoline. This is a difficult analytical problem since (1) gasoline is a complex mixture of hydrocarbons and special purpose additives and its composition varies unpredictably by brand and refinery runs, and (2) the changes in gasoline composition during the vagaries of a fire are not easy to predict.

Several articles have dealt with the analysis and comparison of arson residues by gas chromatography (GC) [2-13]. This technique is unsurpassed in its ability to both separate and quantitate volatile fractions in complex mixtures and has been applied to the characterization of a number of fire accelerants, including kerosene, gasoline, fuel oil, and turpentine.

Much effort has been directed toward the comparison of different gasolines by GC with the goal of individualizing them by brand name. Unfortunately, current refining and marketing practices in the petroleum industry together with changes in gasoline composition during storage make this goal practically impossible [14]. This hindrance together with the evaporative and chemical changes suffered by gasoline during a fire motivated the present work, in which we have identified specific compounds common to a number of simulated arson residues generated under laboratory conditions.

Although gasoline is a complex mixture, there are certain unique compounds that can be recovered from these simulated residues that we believe to be specific to gasoline [15]. These studies must be extended to cover a wider range of simulated conditions to confirm our findings.

Simulated Residues

During the course of a gasoline-fueled fire, the composition of the original gasoline may be changed by both selective volatilization and combustion. In the first case, the heat of the fire tends to deplete the gasoline of its more volatile components and leave the gasoline enriched in the higher boiling point materials that were originally present in small amounts only. Comparison of the original and residue GC traces would then show the latter to be depleted in low-boiling point materials, such as xylenes and tri- and tetramethylbenzenes, and more concentrated in the naphthalenes, anthracenes, and the higher polycyclic aromatic hydrocarbons (PAH). The extent to which these compositional

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changes occur depends strongly on the specifics of the fire temperature and ventilation, among other factors. Additionally, volatilization of gasoline under these conditions is not generally considered within "good distillation practice." For example, there is no fractionation column, and the temperature of the distilling pot is not carefully controlled. Thus, on the basis of selective volatilization alone, the residue might be almost identical to the virgin gasoline, or a viscous tarry mass, or something in between. In the present work, this phenomenon was simulated by examining residues obtained at different stages in the distillation of a gasoline sample with the use of a purposely inefficient fractionation column. To determine whether or not heating alone had a significant effect on its composition, a gasoline sample was evaporated to constant weight at room temperature.

In the case of combustion, in addition to water and carbon dioxide, high-molecular-weight PAH, not present in the original gasoline, are produced during burning [16]. Recently it was pointed out that even a "clean" methane-air flame gives rise to substantial amounts of these higher PAH [17]. Therefore, the presence of PAH such as pyrenes and chrysenes might be indicative of gasoline residue much the same as the presence of lower aromatics such as xylenes and trimethylbenzenes is associated with virgin gasoline.

Experimental Methods

Apparatus

Samples were analyzed on a Finnigan 3200 gas chromatograph-mass spectrometer with the 6000 data system under the following operating conditions:

Gas chromatograph

Column: 5 ft (1.5 m) by 2 mm inside diameter glass "U," 3% OV-1, 100-120 Gas Chrom Q

Carrier gas: methane at 20 ml/min

Injector: 250°C

Column temperature: 45 to 250°C at 10°C/min; hold at 250°C (coincident with Scan 300)

Sample size: 0.1 μ l

Time base: 100 scans = 6.86 min

Mass spectrometer

Scan range: 65 to 566 atomic mass units (AMU)

Integration time (ms/AMU): 65 to 165:1; 166 to 566:8

Source pressure: 1 torr (133 Pa) methane

Ionizing voltage: 100 eV

Preamplifier range: variable; 10^{-6} to 10^{-8} A/V

Electron multiplier (continuous dynode): -1400 V

Preparation of Gasoline Residues (Mobil Hi-Test)

Distillation—A 1.0-litre sample of gasoline was distilled from a round-bottom flask equipped with a heating mantle, short downward adapter, and water condenser. Distillation was started at 30°C. When the distillation temperature reached 190°C, the pot residue (29 ml) was transferred to a Microware® still, and the distillation continued until about 10 ml of pot residue remained. The virgin gasoline and the 29 and 10-ml pot residues were analyzed by gas chromatography-mass spectrometry (GC-MS).

Evaporation—A sample of 6.81 g of gasoline was evaporated in a 100-ml beaker in a hood for 3 days to yield 14.2 mg (0.207%) of a viscous red oil.

Burned Sample—About 10 ml of gasoline was ignited and kept burning in a 100-ml

beaker by using a propane torch. The final products were a thin red film that covered the beaker bottom and black soot on the beaker sides. A small amount of benzene was added, and the beaker was covered with a watch glass and placed on a hot plate to permit extraction of the soot by the boiling benzene. Most of the benzene was evaporated prior to GC analysis.

Procedure

Virgin gasoline and the distillation residue samples were injected neat into the GC, and the MS preamplifier was adjusted to its less sensitive ranges to avoid saturation by the early GC peaks. Standard hydrocarbon samples were dissolved in xylene and analyzed as described above. During some runs, the sensitivities were changed by factors of ten by switching the preamplifier gain control over the range from 10^{-6} A/V to 10^{-8} A/V.

The total GC effluent was routed into the ion source of the MS, where the methane carrier gas was used as the chemical ionization (CI) reagent gas. The PAH all had prominent protonated molecular ($M + 1$)⁺ CI peaks with little or no observable fragmentation. Initial classification of the gasoline components into specific classes of PAH was made on the basis of the molecular weight of the nonmethylated parent PAH, that is, naphthalene: $C_{10}H_8 = (128 + H^+) = m/e$ 129. Methyl substitution increases the molecular weight 14 AMU for each methyl group; thus, the homologous methylnaphthalene series has CI molecular ions at 129, 143, 157, 171, and so on. Similarly, other molecular ions for some parent PAH are shown in Fig. 1: phenanthrene; anthracene, 179; pyrene, 203; fluoranthene, 203; chrysene; benz [α] anthracene, 229; and perylene, 253.

Results

The reconstructed gas chromatograms (RGC) of a series of distilled and evaporated gasoline samples are shown in Figs. 2 through 5. The major classes of compounds versus their scan number, that is, GC retention volume, are given in Table 1; specific compounds whose identities have been confirmed by both their mass spectral parent ion and GC retention volumes are given in Table 2 and appear as numbered peaks in the figures.

A cursory look at Figs. 2 through 5 shows that the major components shift from the xylenes (Scans 15 to 20) in the virgin sample (Fig. 2) to tetramethylnaphthalenes (Scans 150 to 165) in Fig. 5.

Several components at high retention volumes (Scans 265, 292, and 329) in the virgin sample (Fig. 2) are not present in any of the subsequent runs; presumably, they are decomposed at temperatures below 190°C, the cutoff point of the first fraction. In addition, as the gasoline volume is reduced either through evaporation or distillation, higher PAH appear in greater relative abundance. The RGC of virgin gasoline does not reveal the presence of the known numbered compounds (Table 2) above 2,3-dimethylnaphthalene.

Toward the end of this concentration process, relatively small changes in the residue concentration result in quite dramatic changes in the appearance of the RGC. The sample in Fig. 3 is virgin gasoline concentrated 35 times (1000 ml reduced to 29 ml); yet, it still consists mainly of compounds boiling lower than trimethylnaphthalene. Figures 2 and 3 have several good points of comparison, particularly the trimethylbenzenes, that justify assignment of the sample as being derived from gasoline. After an additional 2.9 times concentration (Fig. 4), the residue RGC begins to show rather large qualitative differences from the virgin sample. There are no trimethylbenzenes, and the RGC is dominated by the alkyl naphthalenes. Fluoranthene, or an isomer, becomes observable at Scan 270. Finally, at 480 times concentration by room temperature evaporation (Fig.

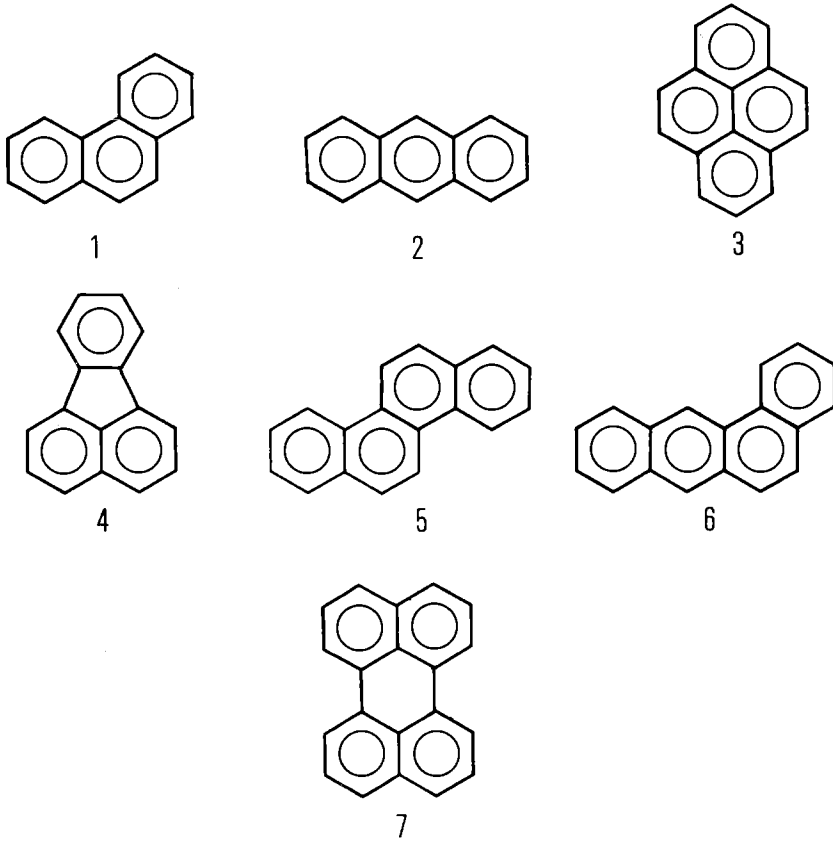


FIG. 1—Representative polycyclic aromatic hydrocarbons; (1) phenanthrene; (2) anthracene; (3) pyrene; (4) fluoranthene; (5) chrysene; (6) benz [α] anthracene; and (7) perylene.

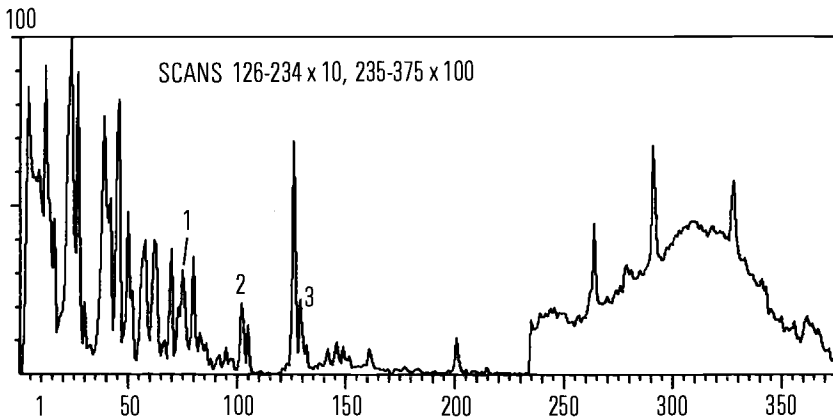


FIG. 2—Reconstructed gas chromatogram of virgin gasoline.

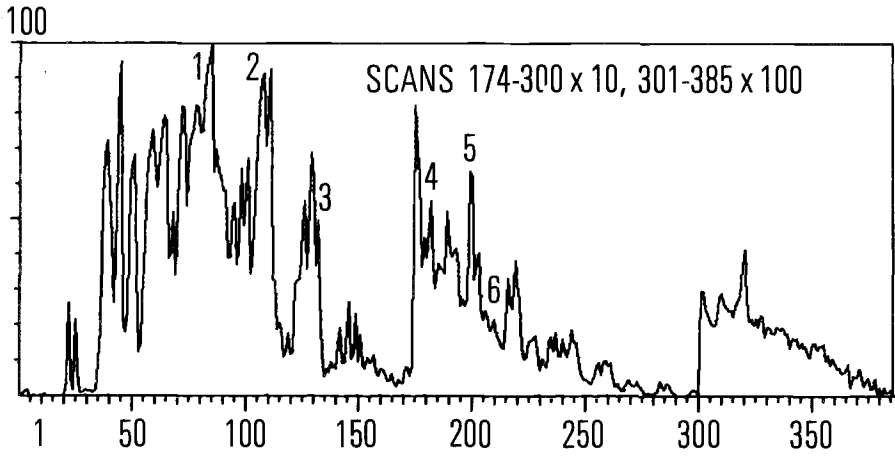


FIG. 3—Reconstructed gas chromatogram of the first pot residue fraction, boiling point less than 190°C, concentrated 35 times.

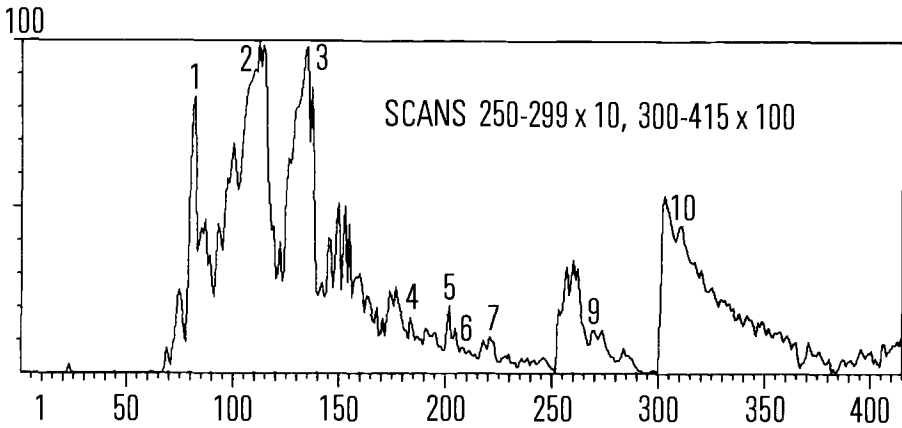


FIG. 4—Reconstructed gas chromatogram of the second pot residue fraction, boiling point approximately 250°C, concentrated 100 times.

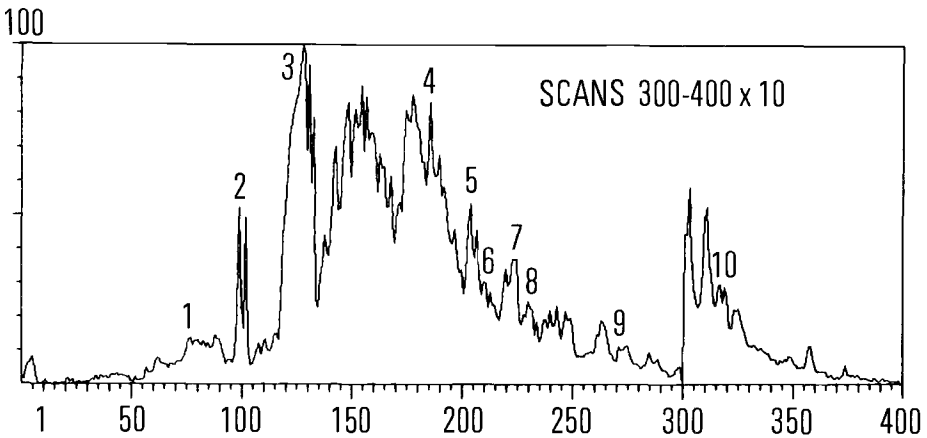


FIG. 5—Reconstructed gas chromatogram of evaporated gasoline, concentrated 480 times.

TABLE 1—Percentage of relative abundances^a of compounds in gasoline distillate fractions.

Compound	Scan	FIG. 3				
		Fig. 2 Virgin	Concentrated 35 Times	Fig. 4 Pot Residue	Fig. 5 Evaporated	Fig. 6 Burned
Toluene	14	90	0	0	0	0
Xylenes	15-30	100	95	<1	0	0
Trimethylbenzenes	35-55	70	80	0	0	0
Tetramethylbenzenes	55-70	35	90	5	0	0
Naphthalene	80	35	100	85	1	1
Methylnaphthalene	100-107	20	90	100	50	75
Dimethylnaphthalene	125-135	7	75	98	100	100
Trimethylnaphthalene	140-155	1	25	50	80	50
Tetramethylnaphthalene	150-165	0.5	0	0	70	5
Anthracene	175	0	1	5	20	30
Methylanthracene	200-210	0	3	8	25	30
Dimethylanthracene	205-225	0	2	5	10	25
<i>m/e</i> 313	265	0.2	0	0	0	0
Diocetyl phthalate (?)	292	0.3	0	0	0	0
Diocetyl phthalate (?)	329	0.2	0	0	0	0

^a Rough estimates from the general appearance of the RGC curves.

TABLE 2—Specific compounds confirmed by retention volume and mass spectral data.

No.	Compound
1	naphthalene
2	2-methylnaphthalene
3	2,3-dimethylnaphthalene
4	phenanthrene/anthracene
5	2-methylanthracene
6	9-methylanthracene
7	fluoranthene
8	pyrene
9	chrysene/benzo [α] anthracene
10	perylene

5), still greater relative amounts of the higher PAH are shown. Except for the sharp dimethylnaphthalene peaks centered around Scan 100, Fig. 5 is markedly dissimilar from Figs. 2 and 3.

Thus, by simple distillative or evaporative processes, the appearance of the GC traces changes to the point where only several compounds present in the original gasoline are present in the concentrates.

In an actual arson case the residue extracts would contain, in addition to the gasoline concentrates, materials derived from the combustion and pyrolysis of wood, plastics, and other debris. The problem of interferences can be alleviated by the use of limited mass scans (LMS) of a particular mass ion. In this technique, the intensity of a certain mass ion, for example $m/e = 143$ for methylnaphthalene, is plotted versus the scan number. Other compounds that co-elute but have different molecular weights are not shown in the LMS curves. Thus, the MS acts as a selective detector for the compounds of interest. The naphthalene peak and the two dimethylnaphthalene peaks are quite distinctive and appear in all of the samples at reproducible retention volumes. Although the LMS technique is not intended to rectify poor GC technique, efficient resolution of a complex real-life sample can be quite time-consuming, particularly for arson residue extracts of variable composition.

To approximate more closely "real" arson residue, a sample of gasoline was burned,

and the dark red, oily residue was analyzed by GC-MS (Fig. 6). The curve has a relatively flat distribution and the trimethylnaphthalenes are the major components (Table 1). There are many PAH at longer retention times. Several LMS derived from Fig. 6 are

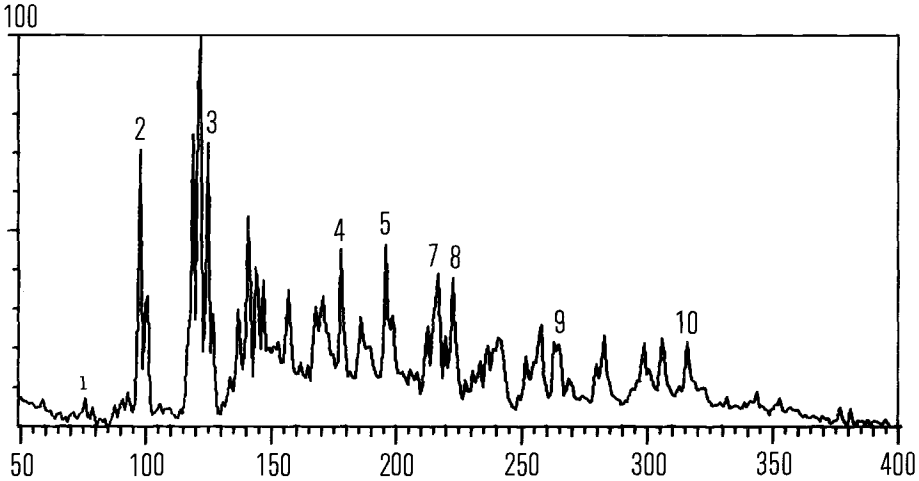


FIG. 6.—Reconstructed gas chromatogram of burned gasoline.

shown in Fig. 7 for different homologous series of methyl PAH: naphthalenes, anthracenes/phenanthrenes, $C_{16}H_{10}$, $C_{18}H_{12}$, and $C_{20}H_{12}$. No structural assignments for the last three ring systems have been made. Among other possibilities, $C_{16}H_{10}$ could be pyrene or fluoranthene; $C_{18}H_{12}$ could be chrysene, naphthacene, or benzanthracene; and $C_{20}H_{12}$ could be benzopyrene, perylene, or cholanthrene. It is noteworthy that the complex mixture in Fig. 6 has been separated into five different homologous series of methyl PAH. Except for the peaks of Scan 216 of the anthracene and $C_{16}H_{10}$ series, none of the other components overlap, and there are approximately 30 separate PAH components.

Discussion

The use of GC techniques to determine whether or not gasoline was used as an accelerant in arson cases depends strongly on the ability to match characteristic gasoline components with residue extracts found at the scene of a fire. In particular, the modification of gasoline composition under such diverse conditions as evaporation, combustion, and pyrolysis must be shown to provide some characteristic mixtures of compounds that can be compared with standard samples. The distilled, evaporated, and combusted samples must all contain the same key components because it is unreasonable to assume that the gasoline residue in an arson residue extract is different from pure gasoline strictly because of, for example, evaporative processes, and that combustion did not play a role in its history.

The presence of PAH in the concentrates but not in the virgin gasoline can be explained by either a dilution or chemical effect. The PAH are present at low concentrations in the virgin gasoline; hence, they are too dilute to be easily observed in the RGC. Alternatively, distillation at elevated temperatures in the presence of air might promote the formation of PAH. The reactivity of these samples was affirmed by the observation that, after several days in the laboratory under the influence of air (and perhaps the fluorescent lights), distillate fractions that were originally colorless turned increasingly

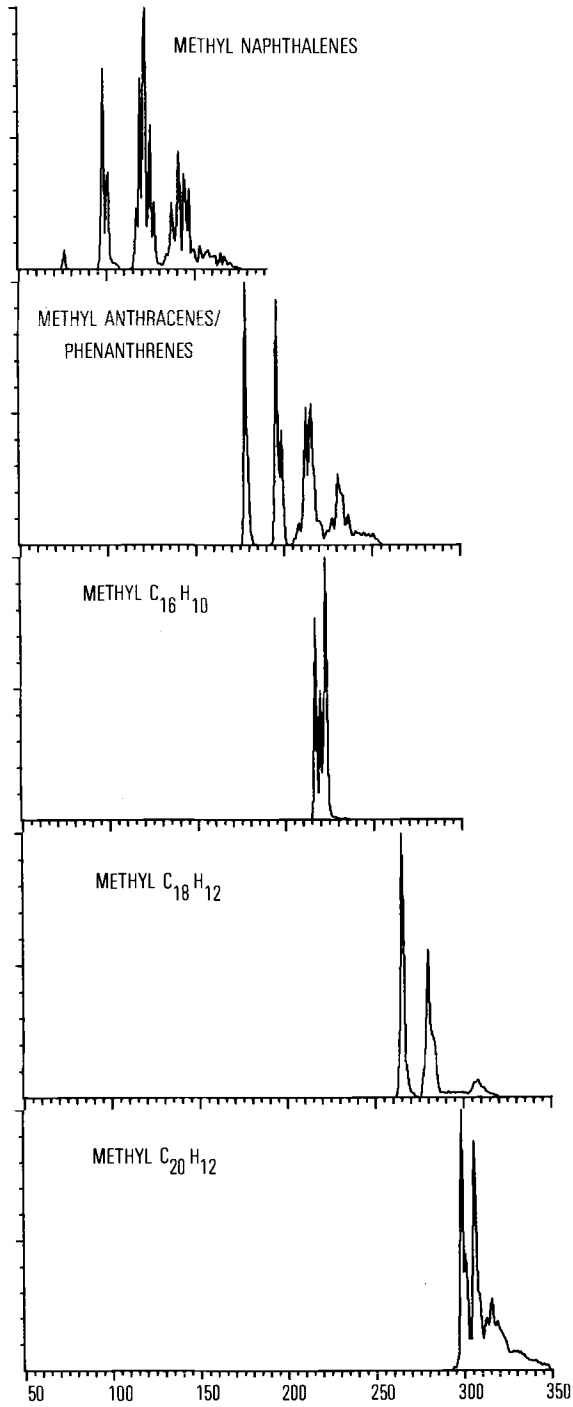


FIG. 7—Limited mass scans of burned gasoline.

yellow to brown. Although anaerobic distillations could confirm whether or not the PAH are formed during exposure to oxygen and heat, the point to be stressed is that more concentrated simulated arson residues contain PAH, whatever their source. In other words, anaerobic conditions would not be expected to prevail after a fire.

The data generated in the present study indicate that naphthalene, methylnaphthalenes, and perhaps the lower methylanthracenes might be signal compounds in determining whether or not gasoline was used as an accelerant in a fire. In particular, the mono- and di-methylnaphthalenes appear particularly attractive for this purpose as they are easily discernible in the virgin (Fig. 2), evaporated (Fig. 5), and burned (Fig. 6) samples.

The very fact that gasoline is a complex, unique material should provide many points of comparison between real and laboratory standard residue. If it can be shown that under a wide variety of test conditions the same distinctive compounds are always present, then analytical techniques that are simpler and less expensive than GC-MS could be used to assay for these specific components. Methods for the analysis of PAH, including thin-layer chromatography and luminescence spectroscopy, have been reviewed by Hutzinger [18].

Conclusions and Summary

A number of gasoline residue samples generated under a wide variety of conditions show the presence of specific PAH. Computerized gas chromatography-mass spectrometry with methane chemical ionization has been used to characterize samples of simulated arson residue derived from gasoline by distillation, evaporation, and combustion. The more concentrated samples show the presence of higher PAH not seen in the original gasoline or the early distillation residues. If these materials can be distinguished from compounds derived from wood, plastics, and other fire debris, routine analytical techniques can be developed, based on the presence of these characteristic PAH, to determine whether or not gasoline was used as an accelerant in a suspected arson case.

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