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Identification of Accelerants in Fire Residues by Capillary Column Gas Chromatography

Since the early 1960s, gas chromatography has been used as a means of determining the presence of hydrocarbons in fire residues. Early investigators relied on packed columns and thermal conductivity detectors. Their results proved that the hydrocarbons could be detected in fire residue [1]. Later work [2] explored the recovery of many different accelerants from various types of fire residues. The method of Ettling's experiments [2] is questionable, and the equipment lacked the resolving power of capillary columns of the support-coated open-tubular type. The burning conditions and time element were not related to typical arson field investigation conditions. In the conclusions of the 1968 study [2], residues were analyzed by comparing a residue chromatogram to a chromatogram of a blank. The blank was a fire residue from materials not ignited by any accelerant. The chromatographic peaks that appeared on the sample chromatogram but not in the blank were attributed to the accelerant. Accelerants were not detected in several residues that had burned for more than 2 min. This conclusion is not fully supported by the present results. We find that residues from fir are more difficult to identify than those from pine. The heat intensity of burning fir volatilizes more accelerant than is characteristic of burning pine, for example. The present study was designed to expand on previous work, to build a file of representative chromatographs, to explore techniques in hydrocarbon determination, and to develop a rapid means of identifying accelerants in fire residues.

Experimental Considerations and Procedure

Three common materials of residential fires (fir, yellow pine, and nylon carpet with pad) and five easily obtainable accelerants (diesel #2, paint thinner, charcoal lighter fluid, and two grades of gasoline) were used for the sample fires. A nonaccelerated reference blank of each construction material was also burned. The woody materials, fir and pine, were cut into 152- by 25- by 25-mm (6- by 1- by 1-in.) pieces [2] and stacked 13 pieces to each fire. This number of sticks conveniently fits into a new 0.004-m^3 (1-gal) friction-top metal can. The area of each wood fire was approximately 2095 cm^2 (325 $in.^2$). Both public and private fire investigators stated that the professional arsonist typically uses 0.9 to 1.9 litres (1 to 2 qt) of accelerant to each 9 m^2 (100 ft^2) of suface. In the test fires, the equivalent of 1.9 litres to 9 m^2 (2 qt to 100 ft^2) was used. The loading of accelerant used on each square of nylon carpet was the same as for the woods. The carpet area was 1858 cm^2 (288 $in.^2$). The burnings were done outdoors on a concrete surface.

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[2] Original experimental data were measured in English customary units.

In a typical arson case the accelerant is thrown over an area, and some of it seeps into cracks, or in the case of the carpet, it is absorbed into the pad. Raw accelerant is trapped in most carpeting and remains after the fire. In constructing the test fires, we stacked the wood sticks so that a vertical tier was formed. The nylon carpet was placed over its pad on a plywood surface. The accelerant was poured on top of the wood tier or carpet and allowed to stand for 5 min before ignition. Fifteen minutes was selected as a reasonable burn time to allow for the fire to be set, detected, responded to, and extinguished. After burning for 15 min, the fires were extinguished with water, and the entire residues were placed in the 0.004-m^3 (1-gal) metal cans. Because we assumed that arson investigations can be accomplished within 24 h after suspected arson, the cans were left open for 24 h before being sealed to simulate exposure to the air. The samples were then taken to the laboratory where they were half-filled with water and steam-distilled with a light oil receiver trap [3].

Table 1 indicates the distillation time and the volume of residues obtained. These data indicate that most of the residues were obtained within 3.5 h of distillation. However, high molecular weight components required as much as 48 h. Extractions of 72 h should not be considered unreasonable.

Identification of Residues

A Perkin-Elmer Model 3920 gas chromatograph allowing programmed temperature control and having a flame ionization detector was used for the analysis. It was fitted with 30 m (100 ft) of OV-101 support-coated open-tubular column and the output was coupled to a Perkin-Elmer Model 1 electronic integrator with strip-chart recorder. The specific operating conditions employed were injector, 20 to 1 split at 250°C; column, 30 m (100 ft) support-coated open-tubular liquid phase, OV-101; flame ionization detec-

TABLE 1—*Volume of fire residue recovered from debris. Cross index to chromatograms in Figs. 1 through 5 is given in parentheses.*

	Distillation Volume, μl^a		
Fire Residue	3.5 h	48 h	Total
Yellow pine			
No accelerant	...	100	100
Exxon premium	50 (B2)	250	300
Exxon regular	75 (C2)	125	200
Diesel #2	300 (D2)	350	650
Shell charcoal fluid	750 (E2)	1000	1750
Paint thinner	200 (F2)	400	600
Carpet			
No accelerant	...	300 (A3)	300
Exxon premium	...	1000 (B3)	1000
Exxon regular	...	1200 (C3)	1200
Diesel #2	...	4000 (D3)	4000
Shell charcoal fluid	...	1400 (E3)	1400
Paint thinner	...	5000 (F3)	5000
Fir			
No accelerant		250 (A4)	250
Exxon premium	EE (B4)	EE (B5)	trace
Exxon regular	EE (C4)	EE (C5)	trace
Diesel #2	100 (D4)	100 (D5)	200
Shell charcoal fluid	EE (E4)	EE (E5)	trace
Paint thinner	EE (F4)	EE (F5)	trace

^{a}EE = ethyl ether extraction.

tor, 250°C; carrier flow, 9 ml/min helium at 69 kPa (10 psig); and temperature program, 50 to 210°C at 8°C/min with an 8-min hold at 210°C. These conditions gave 42 000 theoretical plates for n-C$_{16}$ with some loss in resolution for components before n-C$_{10}$ [4]. The total cycle time for a chromatogram was 35 min. Rapid high resolution analyses were achieved for high molecular weight components by some reduction in resolution for low molecular weight components. This chromatographic system offers high resolution in the portions of the chromatograms that follow n-C$_{10}$. Samples of 0.02 μl were injected into a 20 to 1 splitter at the head of the column so that the actual sample size was 1.0 nl. Capillary columns require sample sizes this small to prevent overloading of the column, which decreases resolution.

Time and Volume Study

The amount and character of the accelerant recovered with the amount of accelerant and the soak time prior to ignition were examined. Regular gasoline (50, 50, 100, and 400 ml) was used as the accelerant on four individual yellow pine fires with surface area of 2095 cm^2 (325 in.^{2}). One 50-ml sample was not allowed any time to soak into the wood, being ignited immediately, while the others were allowed to stand for 5 min before ignition. A blank was run for comparison. The samples that had been allowed to stand before ignition yielded the least hydrocarbon residue. No correlation with total volume of accelerant used was observed (Table 2). Based on these results and the assumed amount of time required for the arsonist to leave the scene, all fires for accelerant identification were given a 5-min soak time to simulate actual circumstances. All of the fires with accelerant showed a chromatogram analysis pattern which was characteristic of the accelerant and which could be matched to the raw accelerant.

Matching Accelerant to Recovered Residues

To establish the correlation of a residue and a known accelerant, Kovat's indexes [4] are used to match peaks between two chromatograms. By definition, the n-paraffins are used as reference and assigned values of 100z, where z is the carbon number of the paraffin. For a temperature-programmed chromatogram, the peaks between two adjacent n-paraffins, z and $z + 1$, can be indexed by the following equation:

$$100z + \frac{t_R' - t_z'}{t_{(z + 1)}' - t_z'} \times 100 = KI$$

The adjusted retention time of the sample t_R' and the adjusted retention time of the standard peak t_z' were computed from the integrator times by subtracting the retention time of the dead volume obtained from an injection of methane. This dead volume time remained constant for this study because the same column and operating conditions were used throughout. A graph of t' versus 100z could be used to establish the Kovat's

TABLE 2—*Soak time and volume recovered for regular gasoline on yellow pine test fires.*

Volume Used, ml	Soak Time, min	Volume Recovered, μl
50	0	100
50	5	250
100	5	150
400	5	225

index [4] value. A set of *n*-paraffins was injected on the column, and the chromatogram was run (Fig. 1, *A1*). The peaks between C_{10} and C_{12} of the residue and the suspect accelerant were indexed as given above. The matching peaks had the same Kovat's indexes within ±2 for a typical comparison of peaks, as shown on chromatogram C1, C2, and C5 for a gasoline. The Kovat's indexes were calculated on the basis of adjusted retention times as taken from the integrator (Table 3).

The indexes for the same peak were within the limit of ±2. Comparisons of several peaks and of the ratio of areas of adjacent peaks firmly identified the source with the residue. Some investigators [5] use higher boiling point ethylene glycol to increase distillation temperature to speed the recovery process. This technique was not used in this work to avoid the slightest chance of contamination and to minimize cost. Because of the intense fire with the fir sample, the lower boiling point components were not found.

The calculations were aided by visual comparison of the chromatograms outlined in Table 3. In general, visual comparisons were sufficient for the identification of the type of accelerant recovered.

Figures 1 through 5 contain the sample chromatograms of the listed accelerants and fire residues. A pattern for diesel fuel, Samples D1 to D5, is established in the five chromatograms by a characteristic array of peaks. The peaks arise from the nature of diesel, which is not processed through a catalytic cracker during refining and thereby exhibits the normal C_{10}–C_{18} peaks similar to the standard.

Gasolines from north central Texas are identifiable from a set of five small peaks near *KI* 1150.

The charcoal lighter fluid is easily identified by the peaks at *KI* 1000 and 1100 present in the samples E1 to E5.

Paint thinner, having prominent peaks at *KI* 1000, 1100, and 1200 and minor components at *KI* 1025, 1060, and 1065, is quite different from the other accelerants. Various brands of paint thinners and charcoal lighters may differ somewhat from the samples reported and may be difficult to identify from charred fir extractions. Fir samples may pro-

TABLE 3— *Kovat's indexes [4] for recovered residue from pine* (C2), *carpet and pad* (C3), *and fir* (C5) *as compared to original gasoline* (C1) *in the 1100 to 1600 region.*

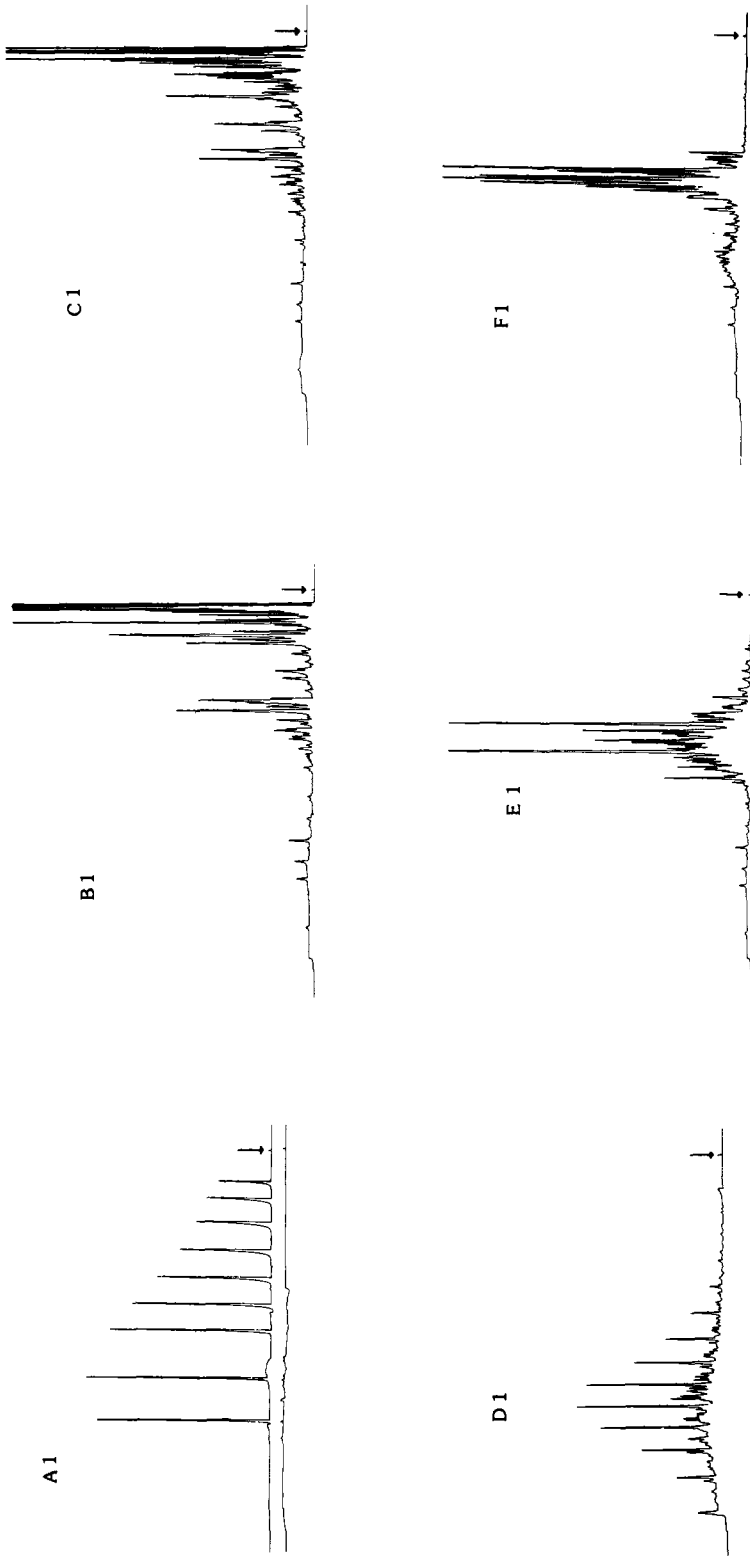| C1	C2	C3	C5
1100	1101	1102	...
1119	1119	1119	...
1121	1121	1121	...
...	1128	...	...
1136	1133	1131	...
1138	...	1136	...
1152	1152	1152	...
1162	1162	1162	...
1167	1169	1167	...
1174	1174	1174	...
1181	1181	1181	...
1188	1186	1188	1186
1200	1198	1200	1198
1206	...	...	1204
...	1211	1211	...
1315	1318	1318	1316
1331	1331	1333	1330
...	...	...	1370
1510	1511	1511	1511
1541	...	...	1541
1606	1607	1604	1607

FIG. 1—*Temperature-programmed gas chromatograms for various accelerants; A1 = Kovat's index standards [4], n-C$_8$ through n-C$_{16}$, and a column bleed/background check (no injection); B1 = Exxon premium gasoline; C1 = Exxon regular gasoline; D1 = diesel #2 fuel; E1 = Shell charcoal lighter fluid; and F1 = paint thinner.*
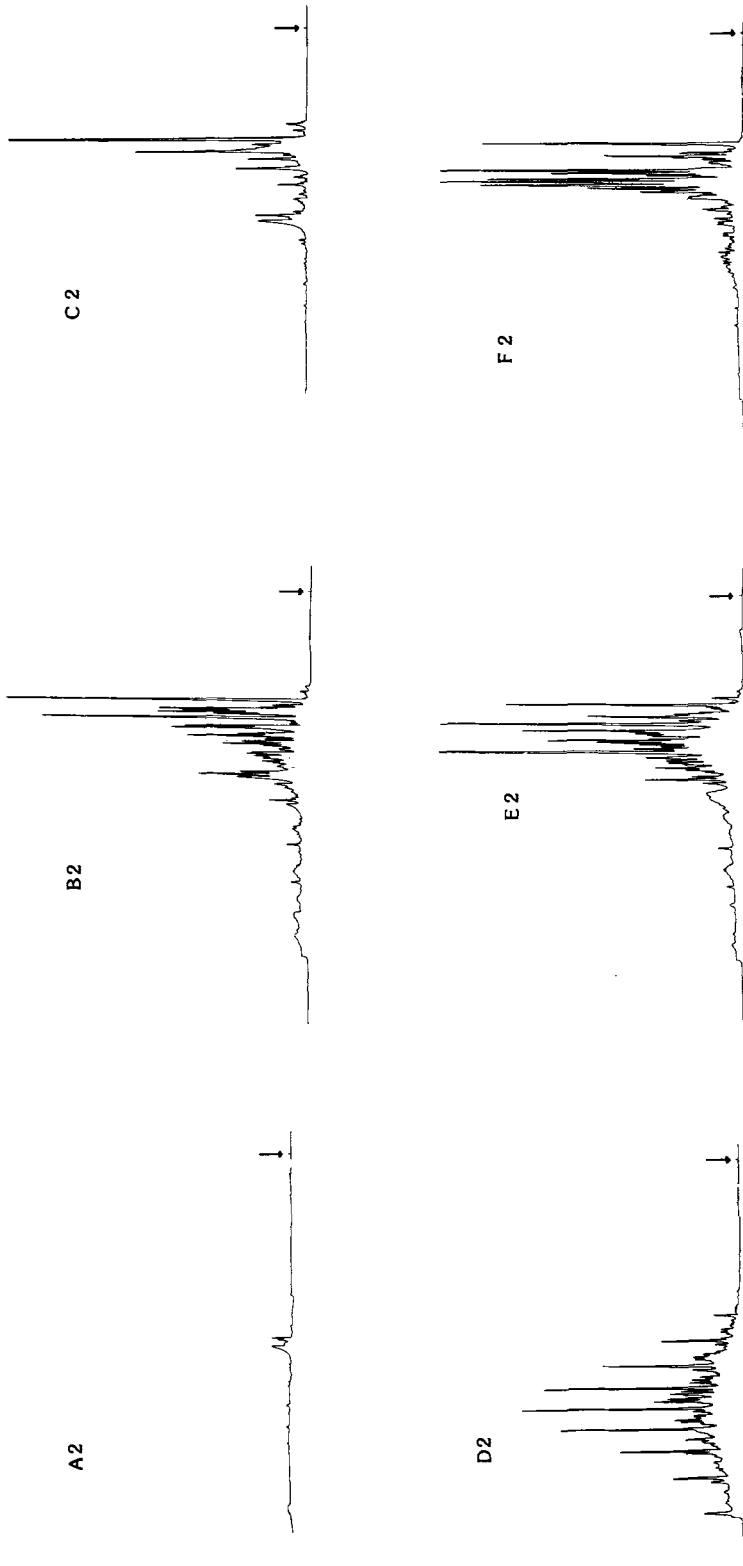
FIG. 2—*Temperature-programmed gas chromatograms for pine fire residues with various accelerants; A2 = no accelerant, 48-h distillation; B2 = accelerated with premium gasoline, 3.5-h distillation; C2 = accelerated with regular gasoline, 48-h distillation; D2 = accelerated with diesel fuel, 3.5-h distillation; E2 = accelerated with charcoal lighter fluid; and F2 = accelerated with paint thinner, 3.5-h distillation.*
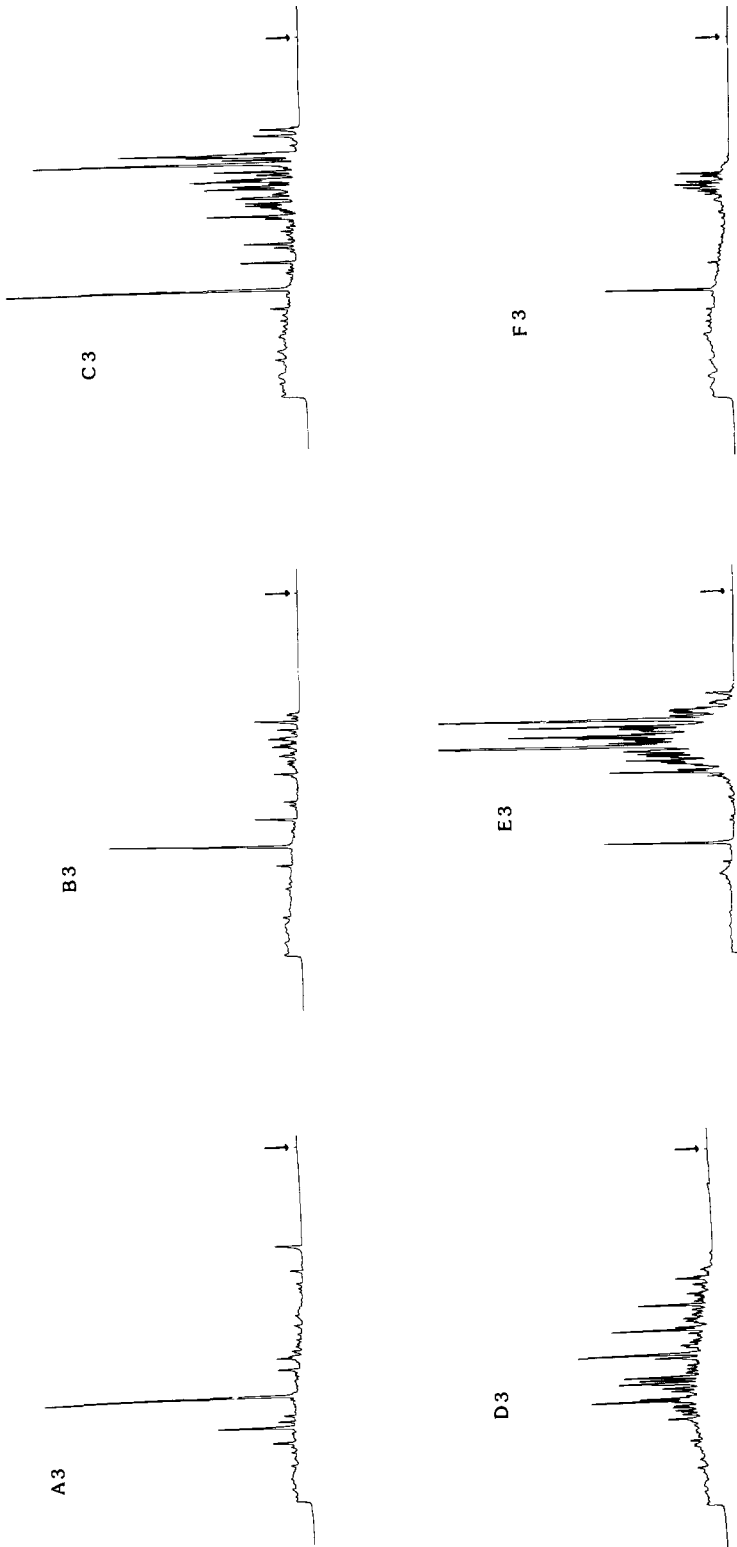
FIG. 3.—Temperature-programmed gas chromatograms for carpet with pad fire residues with various accelerants: A3 = no accelerant, 48-h distillation; B3 = accelerated with premium gasoline, 48-h distillation; C3 = accelerated with regular gasoline, 48-h distillation; D3 = accelerated with diesel fuel, 48-h distillation; E3 = accelerated with charcoal lighter fluid, 48-h distillation; and F3 = accelerated with paint thinner, 48-h distillation.
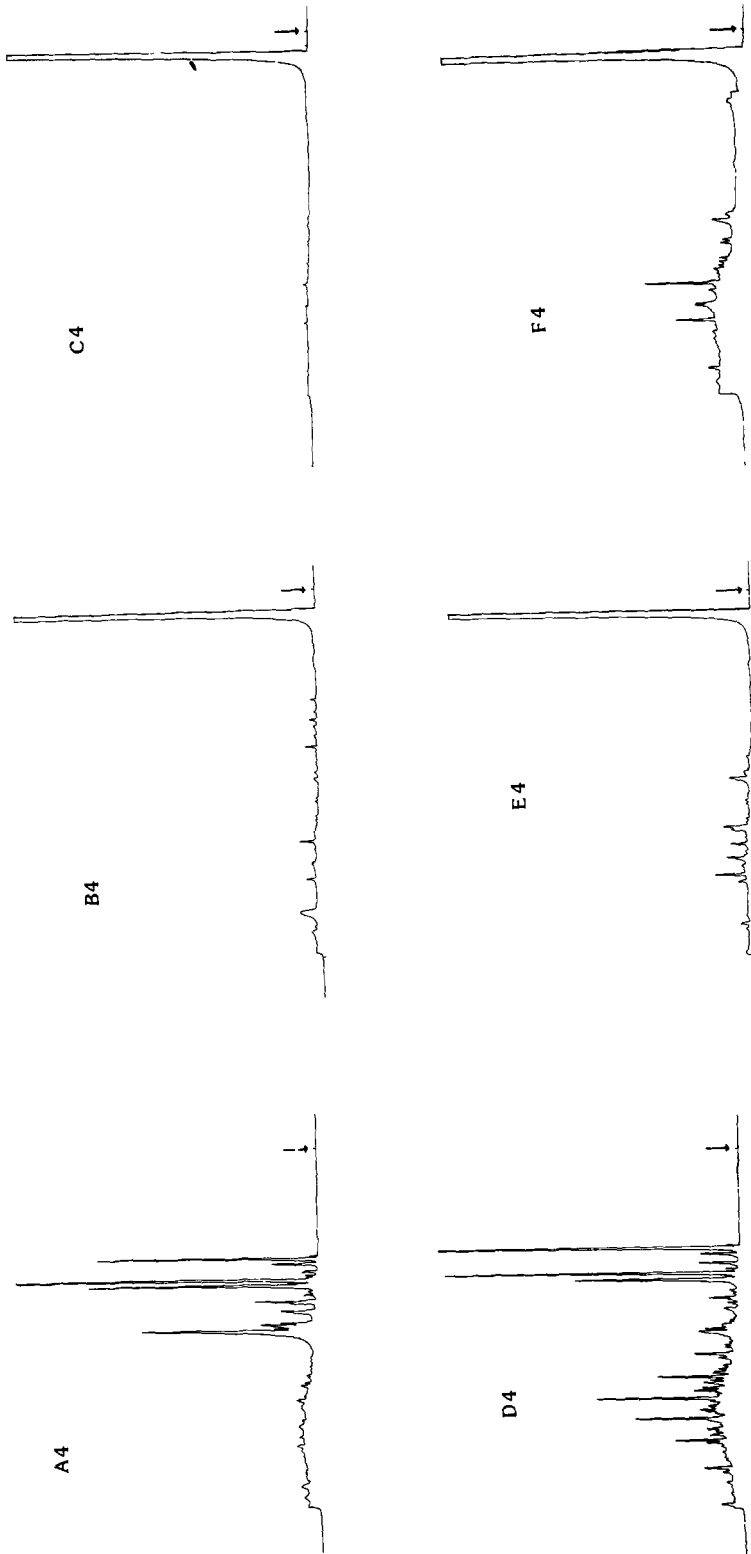
FIG. 4—Temperature-programmed gas chromatograms for fir fire residues with various accelerants; A4 = no accelerant, 48-h distillation; B4 = accelerated with premium gasoline, 3.5-h distillation; C4 = accelerated with regular gasoline, 3.5-h distillation; D4 = accelerated with diesel fuel, 3.5-h distillation; E4 = accelerated with charcoal lighter fluid, 3.5-h distillation; and F4 = accelerated with paint thinner, 3.5-h distillation.
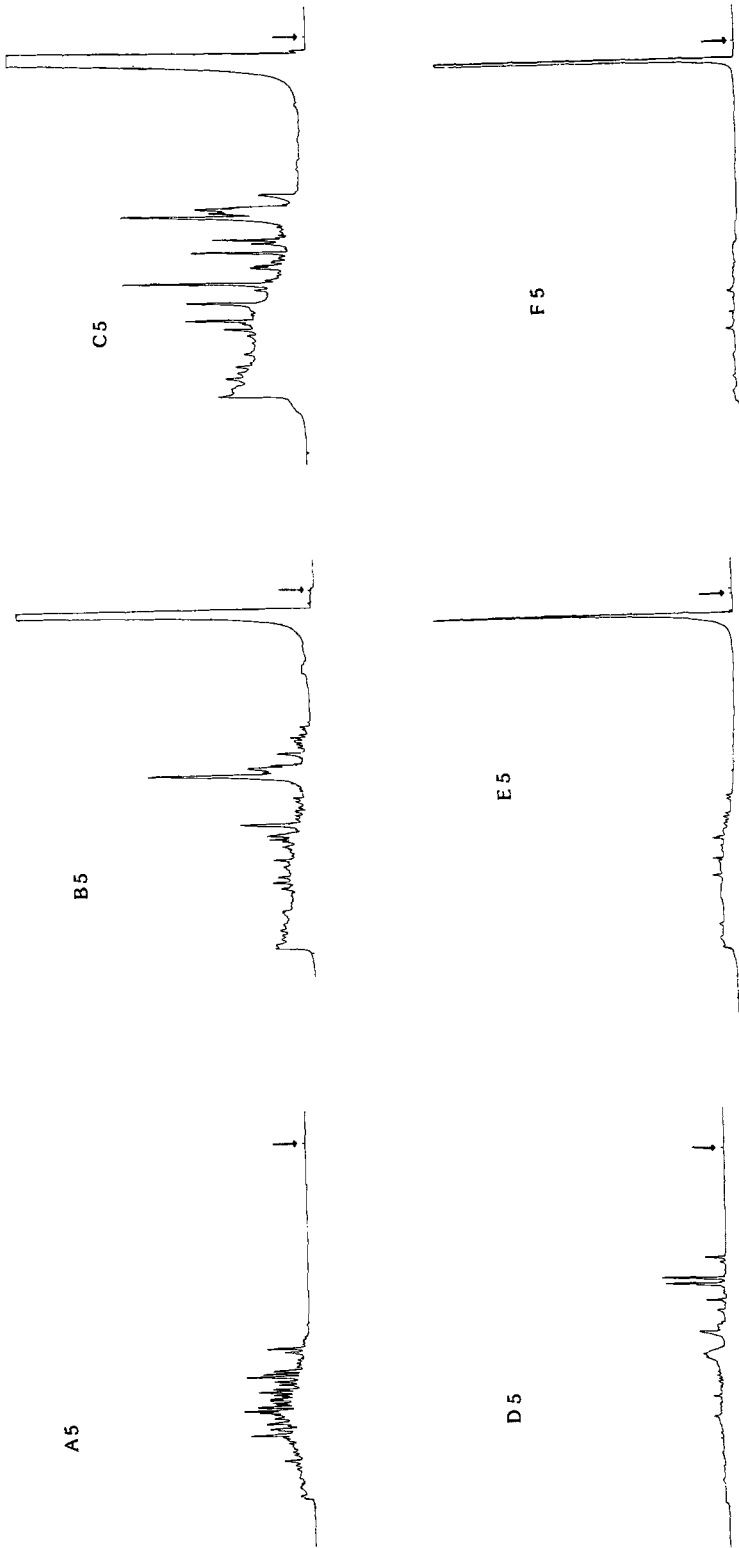
FIG. 5—*Temperature-programmed gas chromatograms for fir fire residues with various accelerants; A5 = concentrated (250:1) premium gasoline; B5 = accelerated with premium gasoline, 3.5- to 48-h distillation; C5 = accelerated with regular gasoline, 3.5- to 48-h distillation; D5 = accelerated with diesel fuel, 3.5- to 48-h distillation; E5 = accelerated with charcoal lighter fluid, 3.5- to 48-h distillation; and F5 = accelerated with paint thinner, 3.5- to 48-h distillation.*

duce such small hydrocarbon residues that minimal ether extraction may be required. The ether extract requires a 1-μl injection.

From the pine and carpet fire residues the different accelerants are visually identifiable.

Evaporation of a sample of premium gasoline to concentrate (250:1) the higher molecular weight components gives an analysis that compares favorably to the residue from the fir premium-gasoline-accelerated fire.

Comparing Samples B4 and B5 with C4 and C5, we note that a better recovery of gasoline is obtained by extension of extraction times. If accelerants of low molecular weight have been used on fir, it will be difficult to establish the nature of the accelerant.

Conclusions

The method described is a rapid qualitative means of identifying accelerants in fire residues. Residues from fires are steam-distilled. The distillate collected is analyzed by gas chromatography using support-coated open-tubular columns and the components are identified by Kovat's indexes [4]. Visual analysis of the chromatograms is plausible. Quantitative ratios of neighboring peaks are recommended for identification and reference matching.

Summary

Capillary gas chromatography in conjunction with Kovat's indexes [4] has been shown to provide a rapid technique to identify recovered hydrocarbon residues from simulated arsonist-caused fires. Data from three types of fuel (fir, pine, and carpet) treated with five types of accelerants (two grades of gasoline, paint thinner, charcoal lighter fluid, and diesel fuel) have been presented.

Studies of the recovery technique (low temperature steam distillation) as a function of distillation time indicated long distillation times were required for complete recovery of high boiling point components needed for the identification of the accelerant type.

Acknowledgment

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