

Differentiation of Asphalt and Smoke Condensates from Liquid Petroleum Distillates Using GC/MS*

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ABSTRACT: A method of comparing selected ion profiles of fire debris extracts for the purpose of differentiating background residues produced by burning asphalt from liquid petroleum distillates is discussed. Passive headspace concentration (ASTM E 1412) has the capacity to fractionate asphalt condensates, resulting in the production of chromatographic patterns remarkably similar to fuel oils. By examining the alkenes produced when asphalt burns, the smoke condensates can be differentiated from kerosene or diesel fuel.

KEYWORDS: forensic science, criminalistics, asphalt, fire debris, gas chromatographic analysis, mass spectrometry

Asphalt is a key component of many structures, particularly roofs. The differentiation of asphalt and its pyrolysis products from intentionally added ignitable liquid residues (accelerants) is thus a critical task of the fire debris analyst.

Adsorption/elution methods of headspace concentration of fire debris samples have been in routine use for more than a decade. Passive headspace concentration, as described in ASTM E 1412 (1), is one of the most commonly used methods of separation of ignitable liquid residues for a number of reasons. The method is straightforward, requiring very little sample preparation time, it requires only an oven for equipment, and it is nearly nondestructive (2). In the range of hydrocarbons below C₂₀, where most ignitable liquids are found, no significant fractionation occurs during the separation process. Figures 1A and 1B show a comparison of 50% weathered kerosene and that same liquid processed through our passive headspace concentration procedure. No differences are evident. Even if the residue is a Class 5 product, separation artifacts do not present serious problems in interpretation, as shown in Figs. 1C and 1D, which is a similar comparison of 50% evaporated diesel fuel.

One of the disadvantages of passive headspace concentration is the ability of the procedure to cause fractionation of heavy hydro-

carbon mixtures, resulting in the production of chromatographic patterns which may be difficult to differentiate from ignitable liquid residues. This is particularly true of polyethylene condensates and of asphalt. Problems of asphalt contamination have been known since adsorption/elution techniques were first introduced for fire debris analysis. In 1982, Lentini and Waters (3) observed the production of chromatographic patterns resembling kerosene and diesel fuel with the use of dynamic headspace concentration and GC/FID, using both packed and capillary columns. The recommendation at that time was to remove asphalt from fire debris samples, and to interpret patterns with caution when the presence of asphalt was suspected.

Polyethylene decomposition products have also been known to produce patterns which meet ASTM E 1387 (4) criteria for ignitable liquid residues, but the production of “double peaks” rather than a pattern dominated by single tall n-alkane peaks, has been known as a diagnostic feature of polyethylene decomposition products since capillary columns came into widespread use. Keto (5) recently discussed methods of differentiating aliphatic patterns produced by polyolefin pyrolyzates, and correctly pointed out that such pyrolyzates contain little or no branched alkanes. The presence of branched alkanes in a pattern containing polyolefin pyrolyzates was interpreted as an indication that a mixture of polyolefin pyrolyzates and a petroleum distillate may exist. While this may be true, a remarkable coincidence of background and ignitable liquid residue concentrations would need to exist in order for the branched alkanes, the olefins produced by pyrolysis, and normal alkanes to be present and readable on the same chart.

The pyrolyzates of asphalt do contain branched alkanes which are remarkably similar to the branched alkanes present in kerosene and diesel fuel. This study was undertaken to determine a means of differentiating asphalt pyrolyzates, which are common in many structure fires, particularly in large commercial fires, from ignitable liquid residues.

Materials and Methods

Sample Preparation

Cured asphalt, which had been exposed to the Georgia sun for nearly ten years, was obtained from the roof deck of our laboratory. Comparison with asphalt from other sources revealed this to be typical roofing asphalt. Polyethylene samples examined included a milk jug and a plastic bag. Kerosene and diesel fuel were obtained from a local service station.

Approximately 5 g of the cured asphalt and polyethylene were placed in 30 mL ceramic crucibles and ignited with a Bunsen flame. After the material had melted and ignited, the flame was extin-

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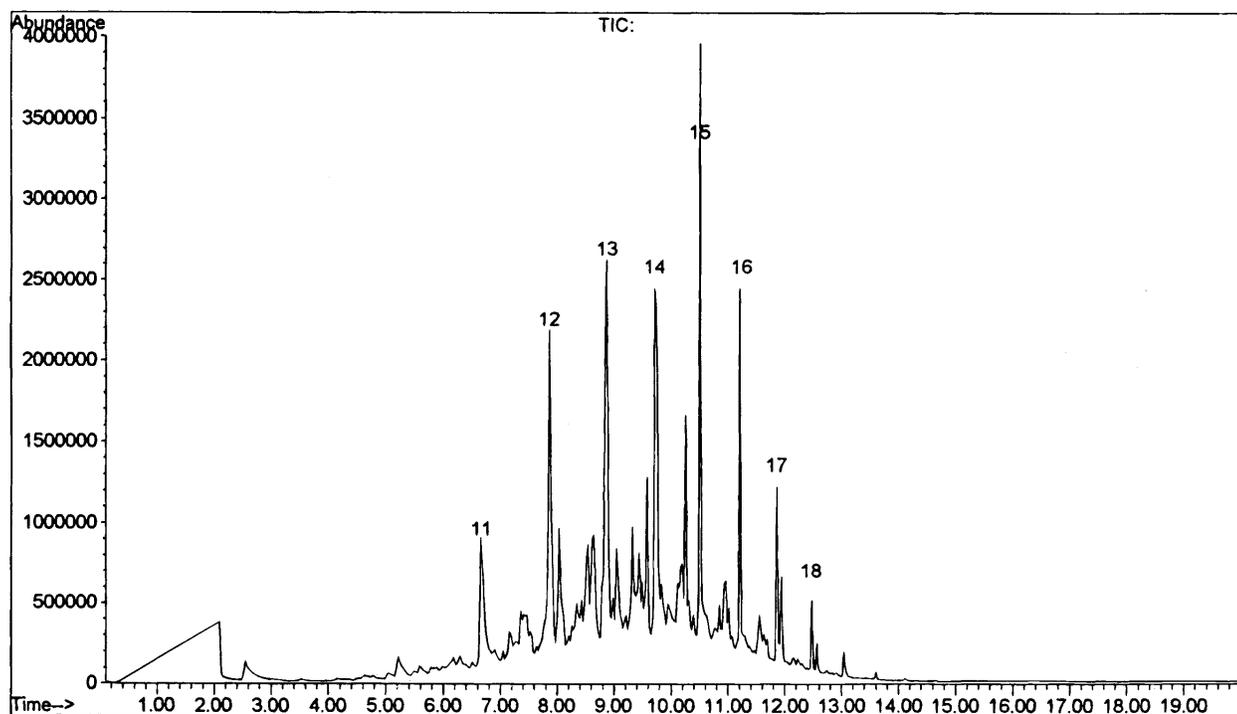


FIG. 1A—50% Weathered kerosene, 1% in diethyl ether (0–20 min).

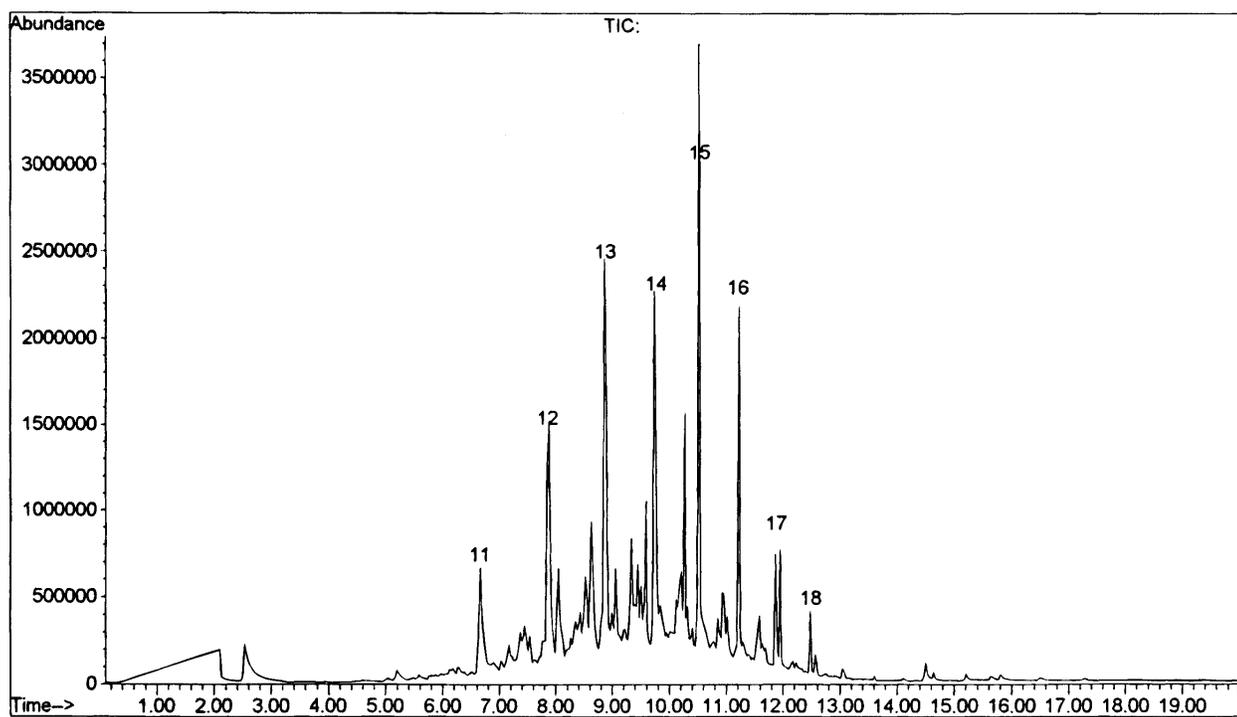


FIG. 1B—10 μL of 50% weathered kerosene, subjected to passive headspace concentration (0–20 min). No fractionation is evident.

guished by placing a watch glass over the crucible. The crucibles and watch glasses were placed in separate one-quart paint cans and separated according to ASTM E 1412.

One-eighth of a Pro-Tek strip was suspended in each can, and the temperature was raised to 80°C for a period of sixteen hours.

The strips were then removed and placed in autosampler vials to which 0.5 mL of diethyl ether spiked with 100 PPM tetrachloroethylene was added.

Kerosene and diesel fuel standards were prepared by placing 10 μL of 50% weathered liquid into a one-quart paint can and extract-

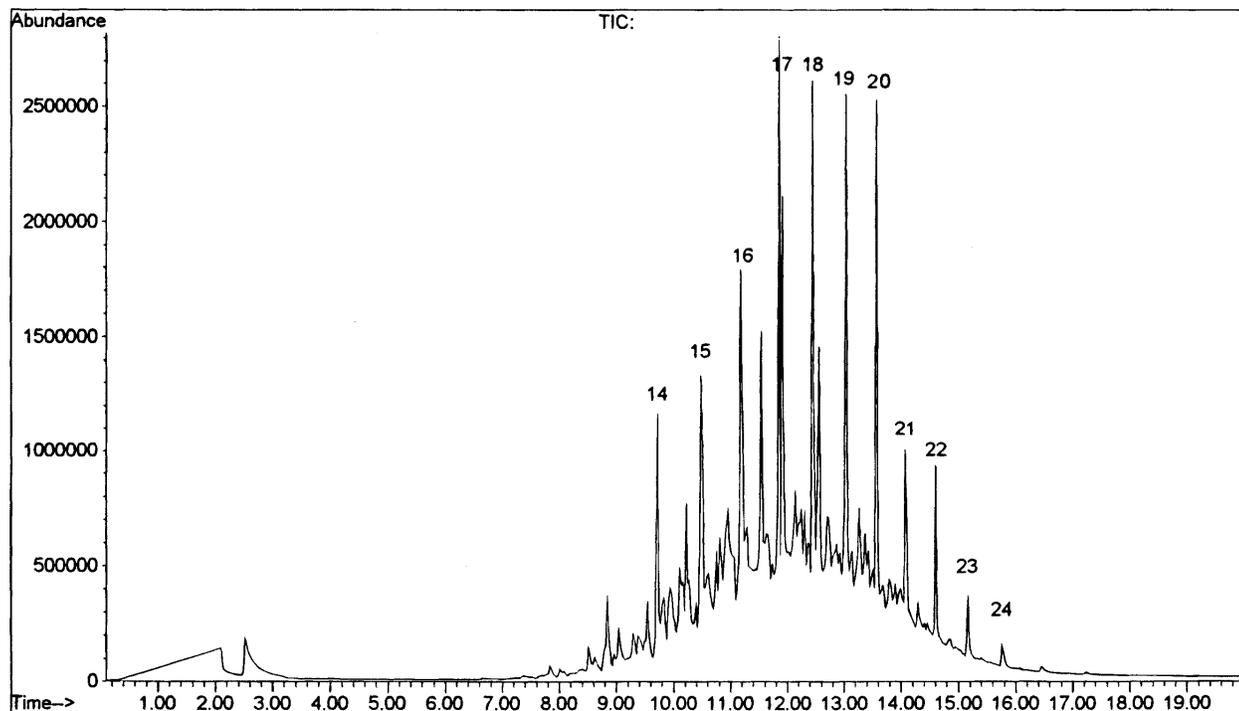


FIG. 1C—50% weathered diesel fuel, 1% in diethyl ether (0–20 min).

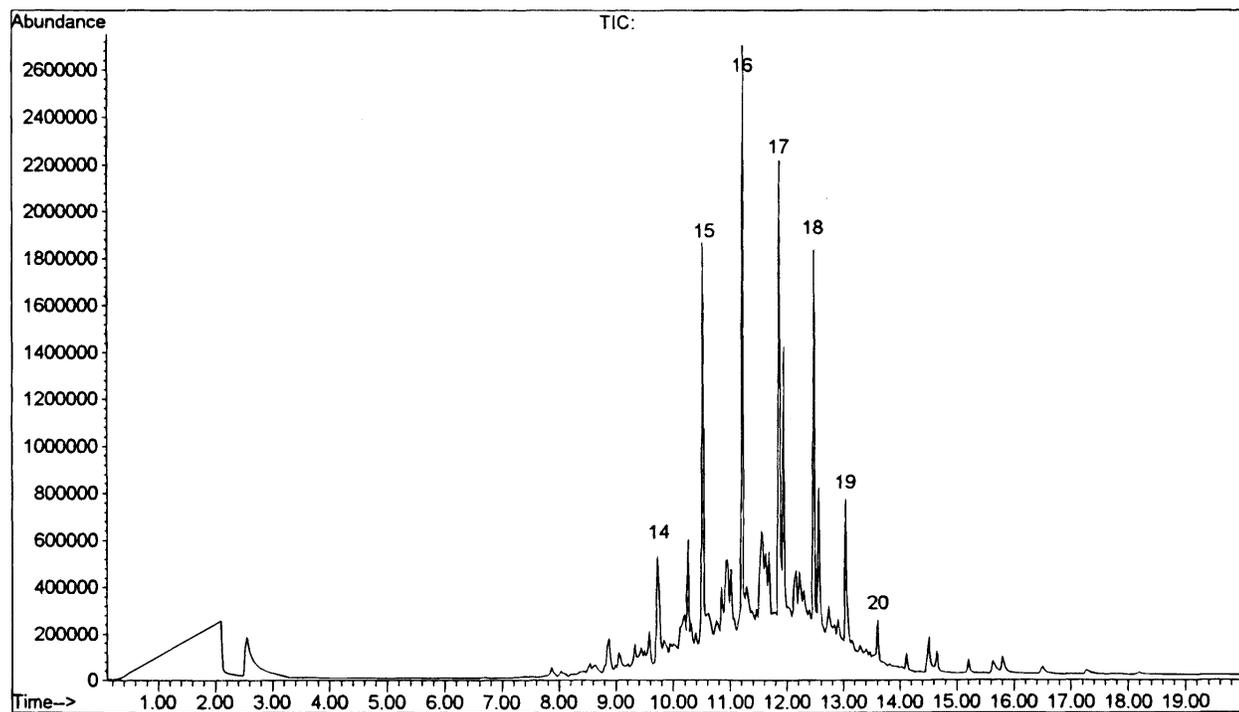


FIG. 1D—10 µL of 50% weathered diesel fuel, subjected to passive headspace concentration (0–20 min). Note the cut-off of compounds above C₂₀.

ing as described above. For comparison purposes, 1% solutions of these weathered liquids in diethyl ether were analyzed directly.

In order to differentiate the effects of burning from the effects of the separation process, a portion of the smoke condensates from the watch glasses was analyzed directly after dissolving in ether.

GC/MS Operating Parameters

In order to be able to see the higher boiling components of asphalt, our usual ignitable liquid residue program was adjusted upward. Operating parameters are shown in Table 1.

A selected ion monitoring (SIM) program was used to acquire

TABLE 1—GC/MS operating parameters.

Instrument	: Hewlett-Packard Model 5890 Series II Gas Chromatograph Hewlett-Packard Model 5971A Mass Selective Detector Hewlett-Packard Model 7673 Automatic Liquid Sampler (Hewlett-Packard, Avondale, PA)
Column	: HP 1 Nonpolar Capillary, 25 meters by 0.2 mm ID, 0.5 micron film thickness.
Carrier	: Helium at 100 kPa.
Injection	: 1 microliter, splitless.
Temperature Program	
Initial Temperature:	100°C
Initial Hold:	4 min.
Ramp Rate:	20°C/min.
Final Temperature:	300°C
Final Hold:	16 min.
Total Run Time:	30 min.
Mass Spectrometer	
Solvent Off Time:	0.3–2.0 min.
Ions Scanned:	31, 45, 55, 57, 71, 78, 83, 91, 105, 117, 119, 128, 131, 142, 156, 168
Dwell Time per Ion:	50 msec.
Ionization:	Electron Impact

the data, since this method of acquisition results in cleaner ion chromatograms than acquisition in the scan mode (6). Comparison of the “total ion chromatograms” produced by this SIM method with chromatograms obtained using a full (33–300 AMU) scan revealed no detectable differences.

The use of a capillary column was required in order to resolve the n-alkanes from the terminal alkenes produced by the decomposition of asphalt and polyethylene. In an early study of polyolefin pyrolyzates, Voorhees et al., using a packed column, were unable to achieve adequate resolution, and reported finding only the alkenes (7). Later, using a capillary column, Sugimura and Tsuge were able to resolve the diene-alkene-alkane components of each of the peaks in the packed column chromatogram (8). Irwin proposed the use of these triplets as a resolution check for capillary columns (9). A close examination of the branched alkane pattern between n-alkane peaks also demands the use of a capillary column.

Results and Discussion

When exposed to fire temperatures, many of the compounds produced by asphalt are similar to those produced by burning polyethylene. This is not an unexpected result, as there is no reason to believe that the pyrolysis products of a C₆₀ straight-chain hydrocarbon should be significantly different from the pyrolysis products of a C₆₀ ethylene polymer. Solid hydrocarbons were suggested by Voorhees, et al., as alternatives to polyethylene for use as an internal pyrolysis standard.

When subsequently subjected to a passive headspace concentration, the asphalt smoke condensate becomes fractionated to give an appearance similar to kerosene or diesel fuel. The profiles shown in Fig. 2 are from an ether extract of known asphalt, not subjected to burning or headspace concentration. Comparison of the selected ion profiles for Ion 55 and Ion 57 shows no significant quantities of alkenes in the sample. This determination is made by comparing

the peaks in the selected ion profiles. The Ion 55 profile is essentially the same as the Ion 57 profile, except that the abundance of Ion 55 is lower. An abundance of alkenes is characterized by the presence of doublets in the ion profiles, particularly in Ion 55. Note that in the unburned asphalt chromatograms, there are no significant n-alkane peaks present below C₂₂.

Once the asphalt has been burned, however, low molecular weight alkanes and alkenes can be seen in the total ion chromatogram of a passive headspace extract (Fig. 3). There is a near peak-for-peak correspondence between the total ion chromatogram for this fractionated asphalt and that of 50% weathered kerosene (Fig. 4), including the branched alkane patterns. There are only subtle differences between these two patterns, which are not readily visible in the total ion chromatogram.

Comparison of the selected ion profiles for Ion 55 with Ion 57, however, reveals a distinct difference between the two profiles. The burned asphalt exhibits a peak in front of the normal alkane, which on the Ion 55 profile is significantly taller than the normal alkane peak. In contrast, there is virtually no change in the pattern between Ion 57 and Ion 55 for kerosene. This is the major diagnostic feature which allows the differentiation of fuel oils from asphalt. The comparison of the two ions from asphalt and kerosene is shown in Fig. 5.

This effect is even more pronounced when asphalt smoke condensate is examined. Figure 6 shows the condensate dissolved in ether, compared to that same condensate separated by passive headspace concentration. A significant fractionation has occurred, and again, the condensate looks remarkably like kerosene. The quantity of kerosene-like hydrocarbons in the condensate was significantly higher than that found in the burned asphalt itself. As with the burned asphalt, the branched alkane pattern was very similar to that of kerosene. The olefins produced by pyrolysis, however, are somewhat more pronounced in the condensate extract than in the burned asphalt extract, as shown in the time expanded total ion chromatogram (Fig. 7). A comparison of the selected ion profile for Ion 55 and Ion 57 again shows the predominance of the olefins in the Ion 55 pattern (Fig. 8).

While looking at the whole pattern is necessary, we found it useful to examine closely the C₁₆ through C₁₈ region, where the diagnostic features described above could be more easily visualized. Neither kerosene nor diesel fuel was observed to exhibit any change in pattern when Ions 55 and 57 were compared (Fig. 9), only the abundance changed. In the asphalt smoke condensate, shown in Fig. 10, the presence of a single alkene peak in front of each normal alkane peak was easier to observe in both the Ion 57 and Ion 55 profiles when compared with diesel fuel. Another diagnostic feature of the asphalt smoke was the relatively low quantity of pristane and phytane observed in the pattern.

A “negative” diagnostic feature is exhibited when the sample is checked for the presence of alkyl cyclohexanes. These compounds, ranging from pentyl to decyl cyclohexane, can be seen when Ion 83 is profiled. Kerosene and diesel fuel profiles exhibit alkyl cyclohexane peaks that are as tall or taller than the n-alkane peaks. In asphalt, on the other hand, the Ion 83 profile is dominated by the alkene peaks. The alkyl cyclohexane peaks are much smaller. A comparison of the Ion 83 profiles of asphalt smoke condensate and diesel fuel is shown in Fig. 11.

The major diagnostic feature, however, is the significant relative increase in the height of the olefin peak compared to the alkane peak when Ion 55 is examined. This increase demonstrates that the peak does, in fact, represent an olefin and not a branched alkane.

The behavior of asphalt when exposed to burning and subse-

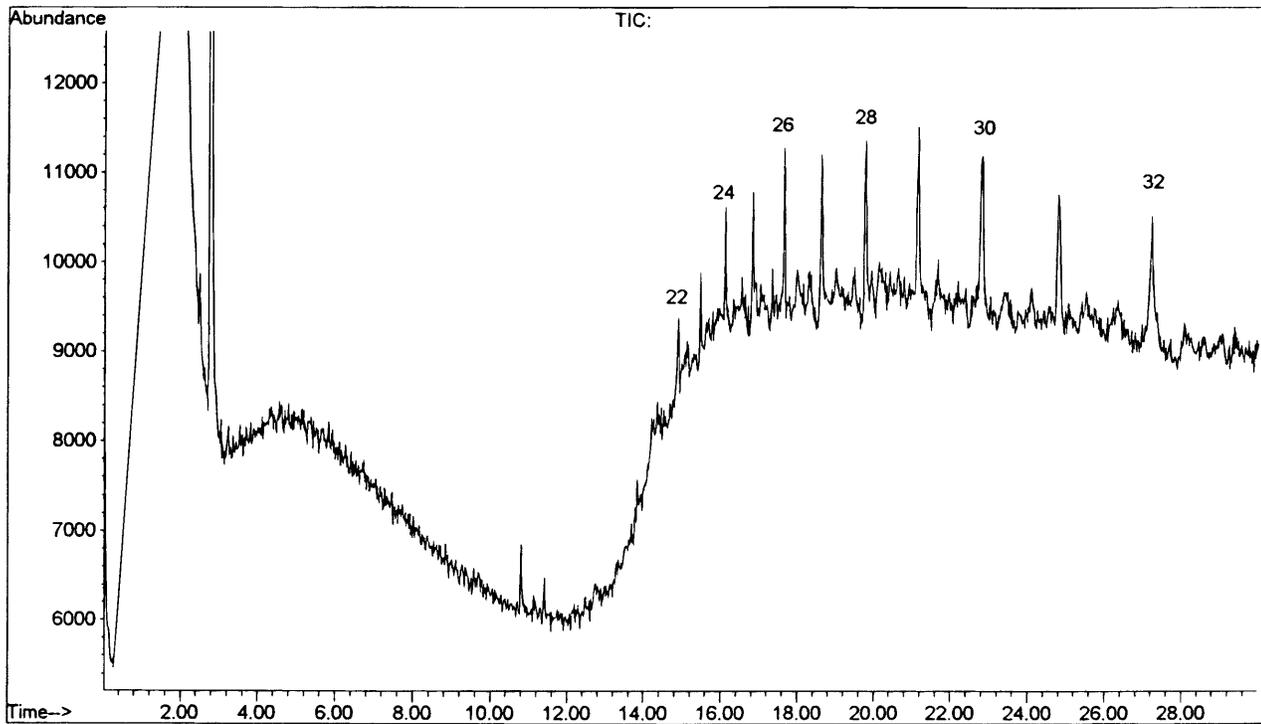


FIG. 2A—Cured, unburned asphalt, dissolved in ether.

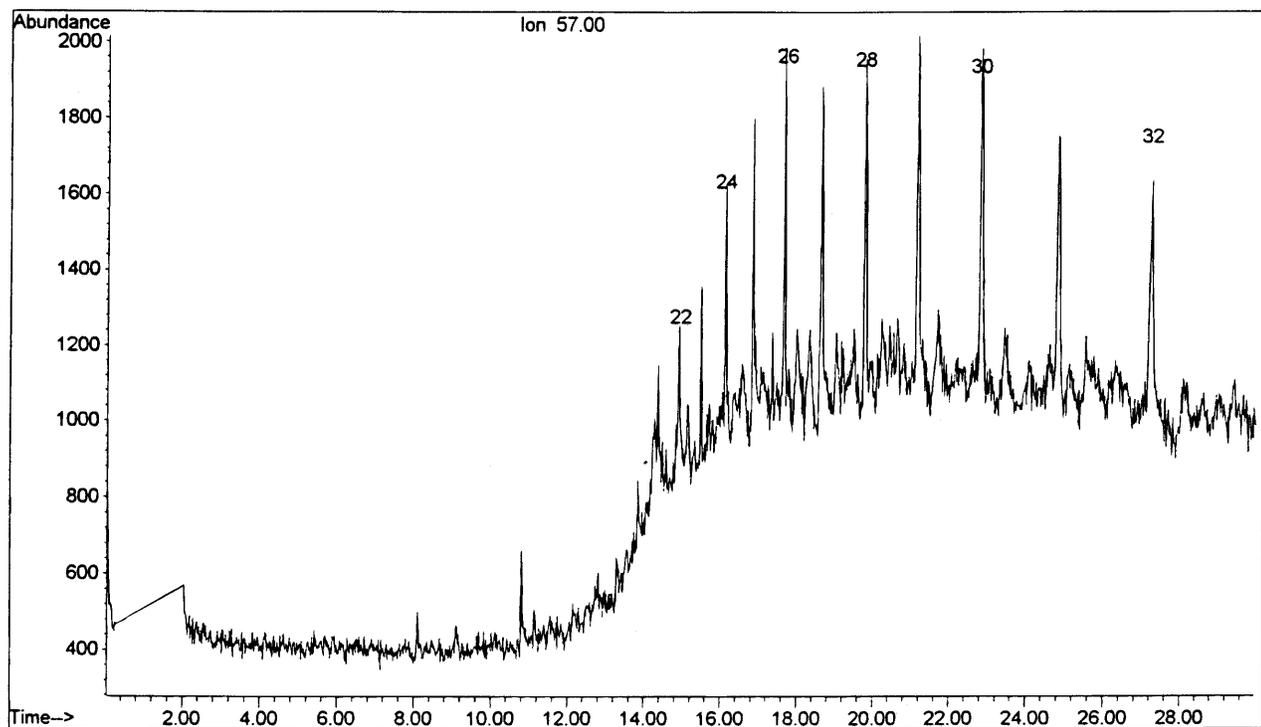


FIG. 2B—Ion 57 profile of cured unburned asphalt.

quent headspace concentration was compared with the behavior of polyethylene. Both high and low density polyethylene were examined, but no differences were detected between the two types of plastic. (Polypropylene pyrolyzates were easily distinguished from polyethylene and did not produce patterns resembling ignita-

ble liquid residues.) Figure 12 is a comparison of the LDPE smoke condensate dissolved in ether, versus that same condensate subjected to a passive headspace concentration. The fractionation previously observed with diesel fuel and asphalt smoke condensate occurs, but the multiple nature of the peaks is readily evident, and

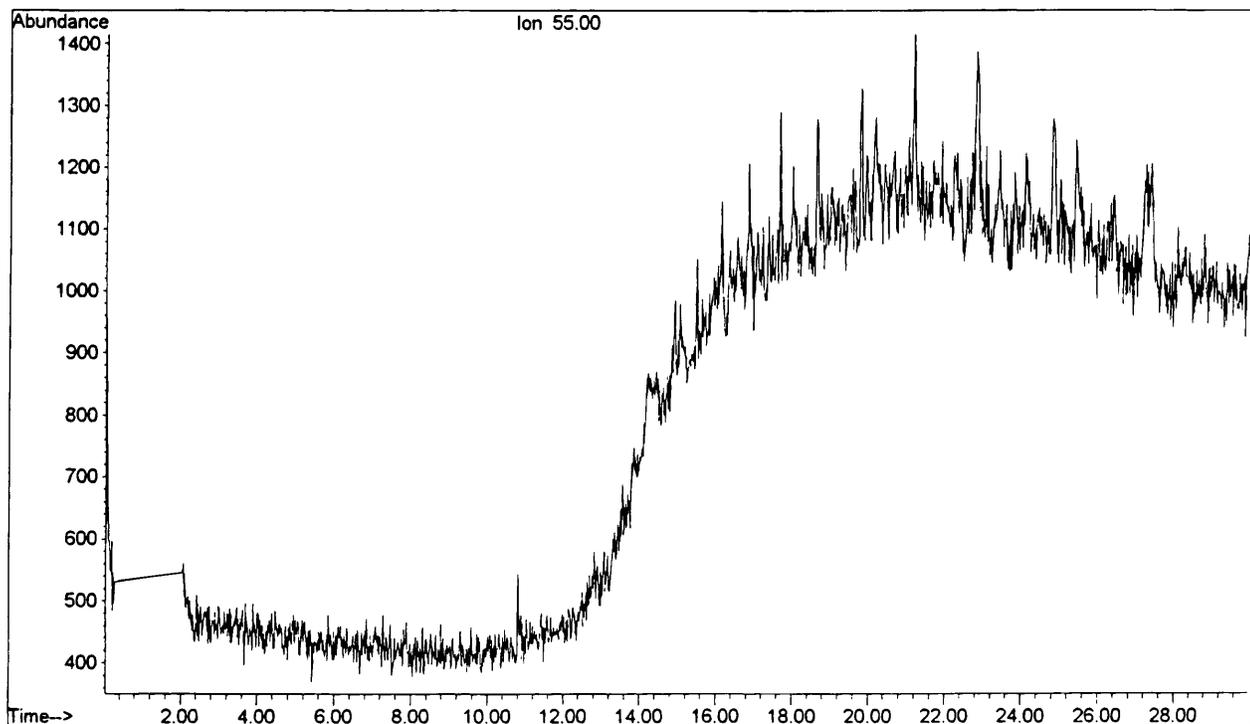


FIG. 2C—Ion 55 profile of cured unburned asphalt.

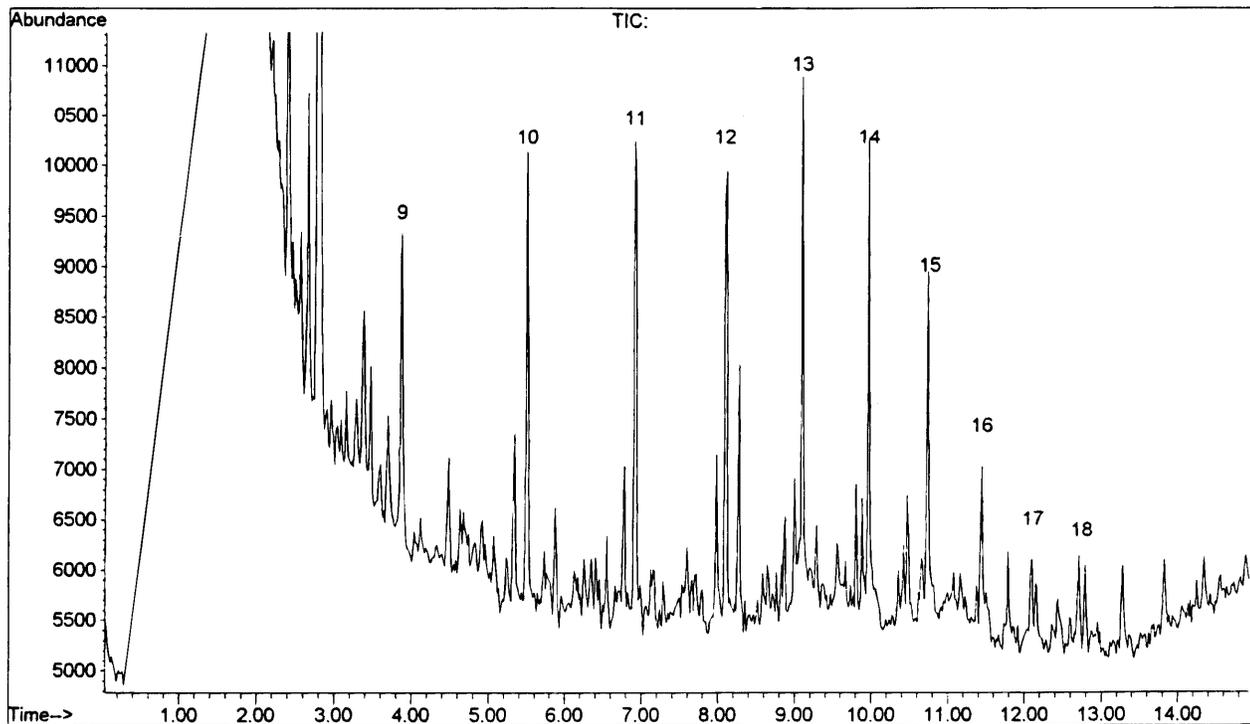


FIG. 3—Burned asphalt, subjected to passive headspace concentration (0–15 min).

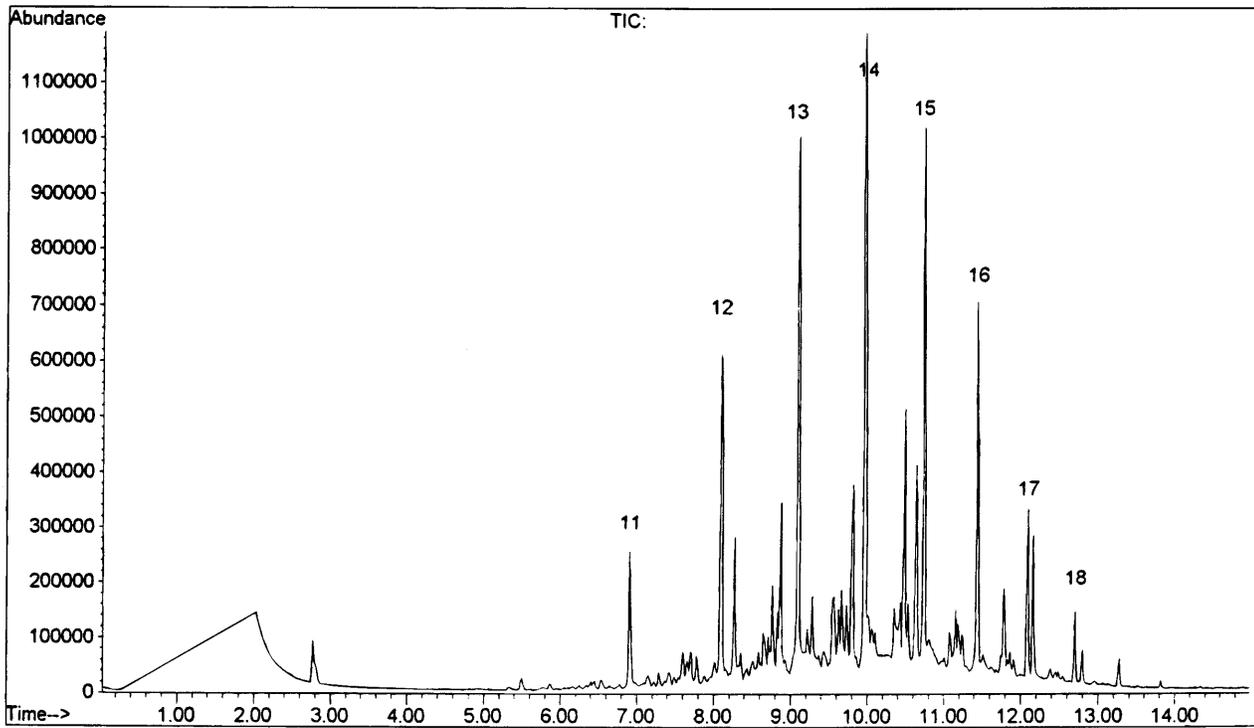


FIG. 4—50% weathered kerosene, subjected to passive headspace concentration (0–15 min).

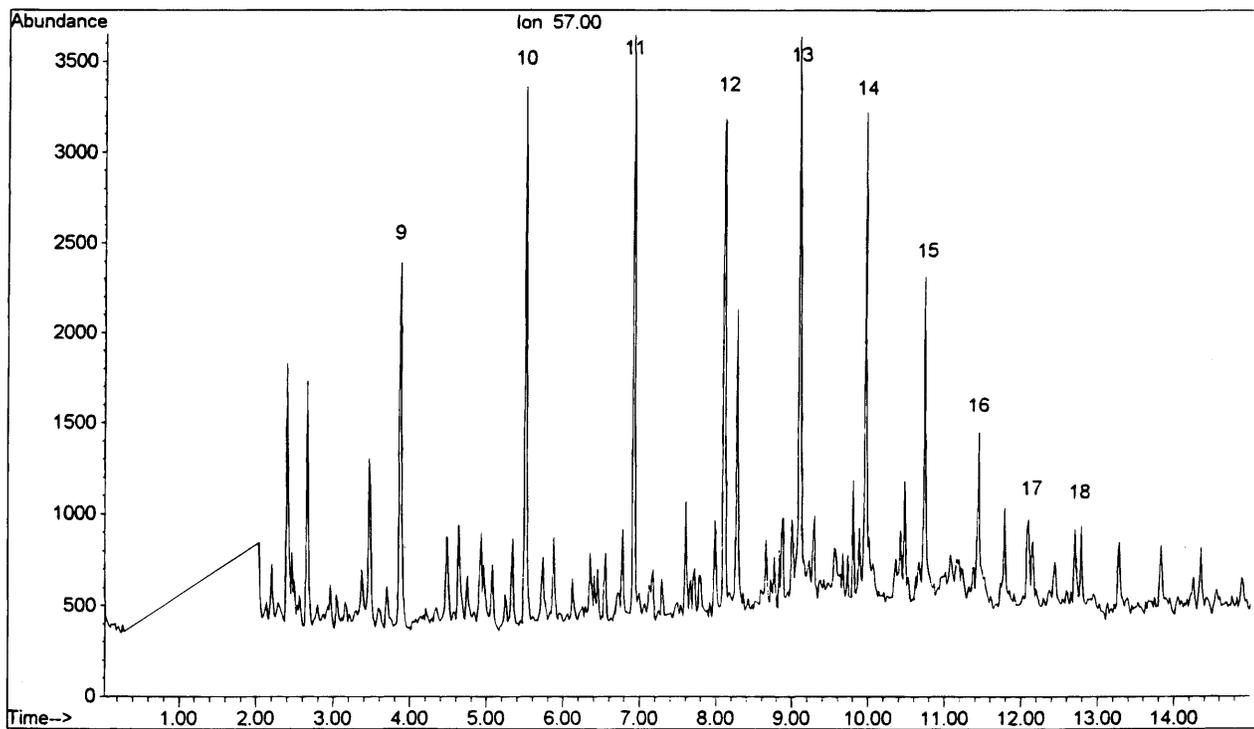


FIG. 5A—Ion 57 profile of cured asphalt, burned and subjected to passive headspace concentration (0–15 min).

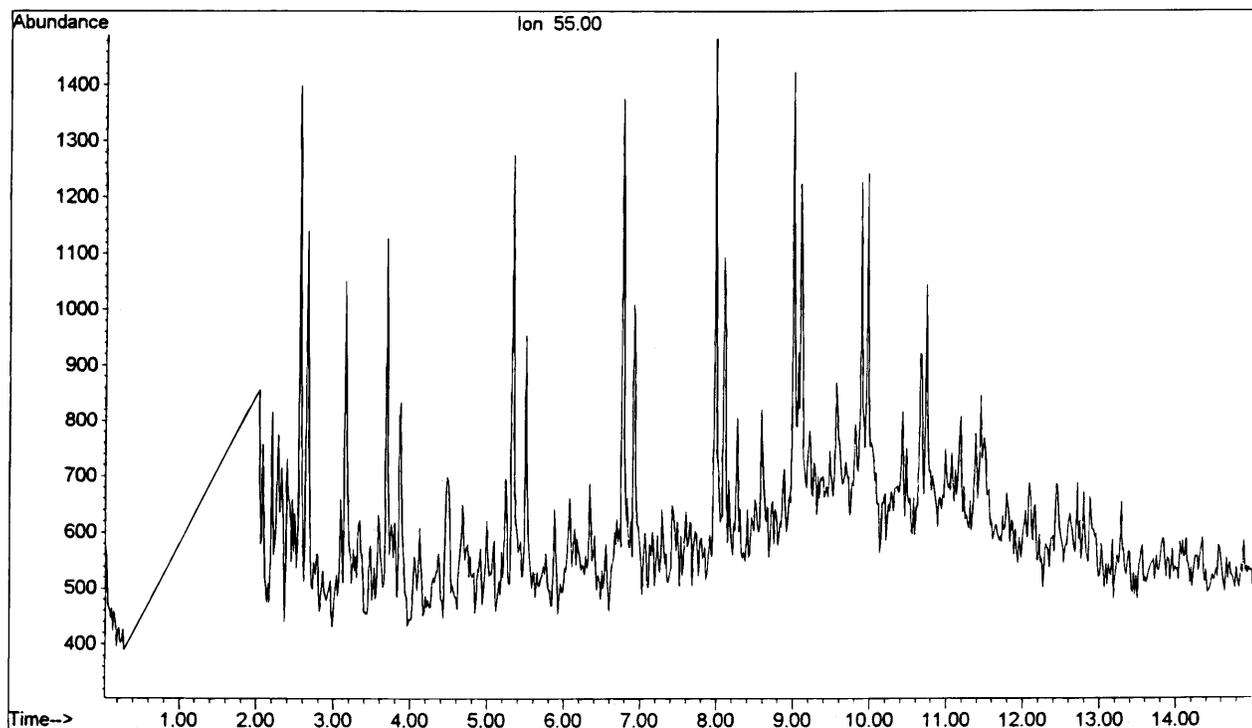


FIG. 5B—Ion 55 profile of cured asphalt, burned and subjected to passive headspace concentration (0–15 min). The first peak in each doublet is the alkene.

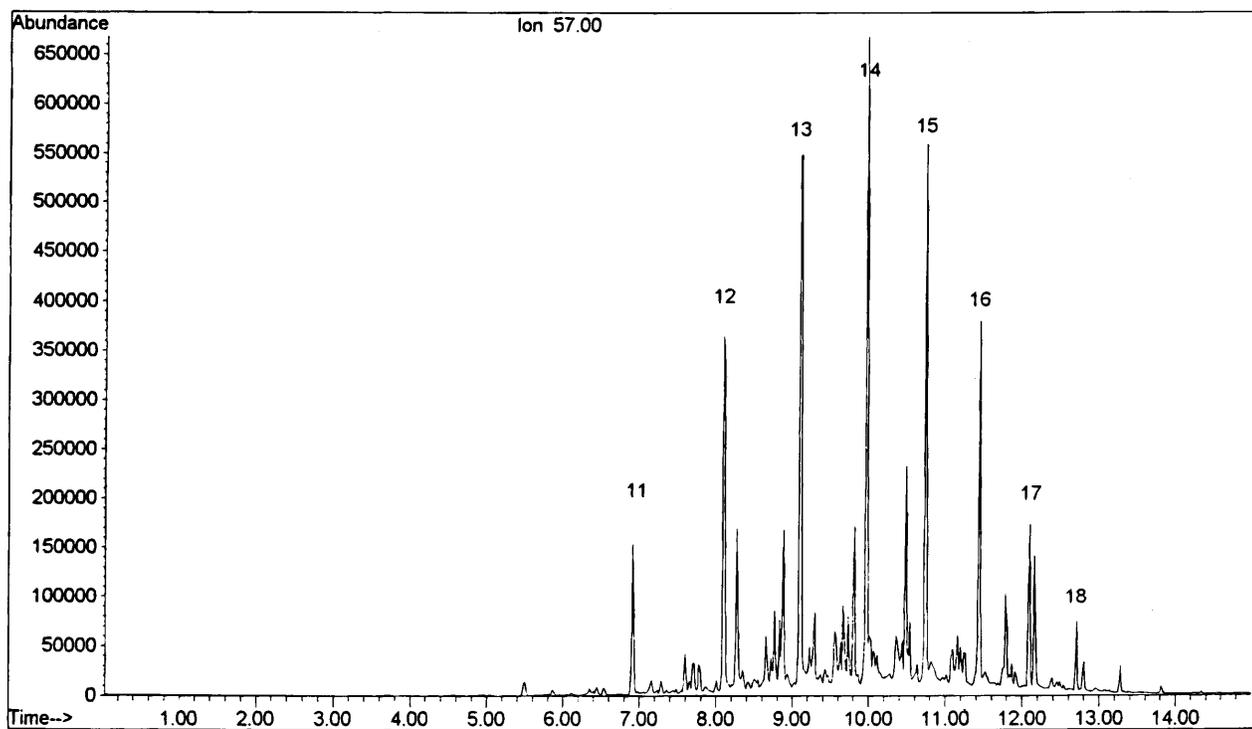


FIG. 5C—Ion 57 profile of 50% weathered kerosene, subjected to passive headspace concentration (0–15 min).

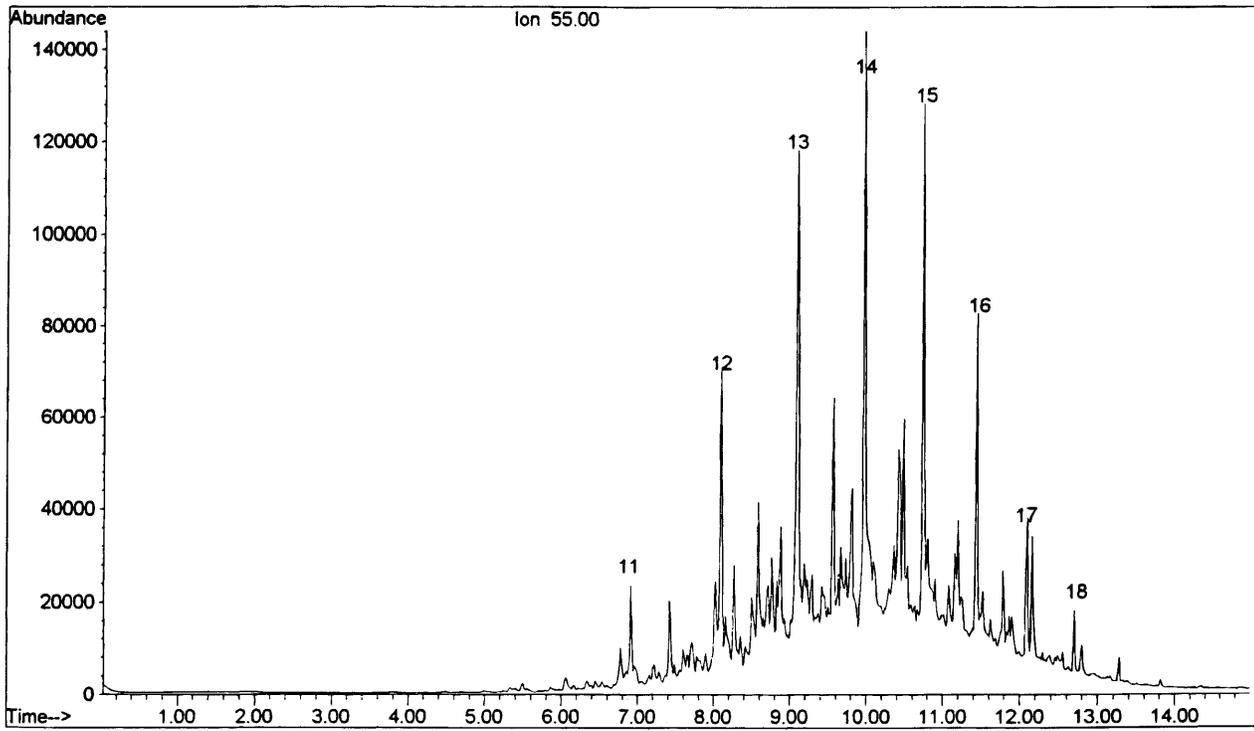


FIG. 5D—Ion 55 profile of 50% weathered kerosene, subjected to passive headspace concentration (10–15 min). Note that no doublets appear, as they do in the asphalt profile.

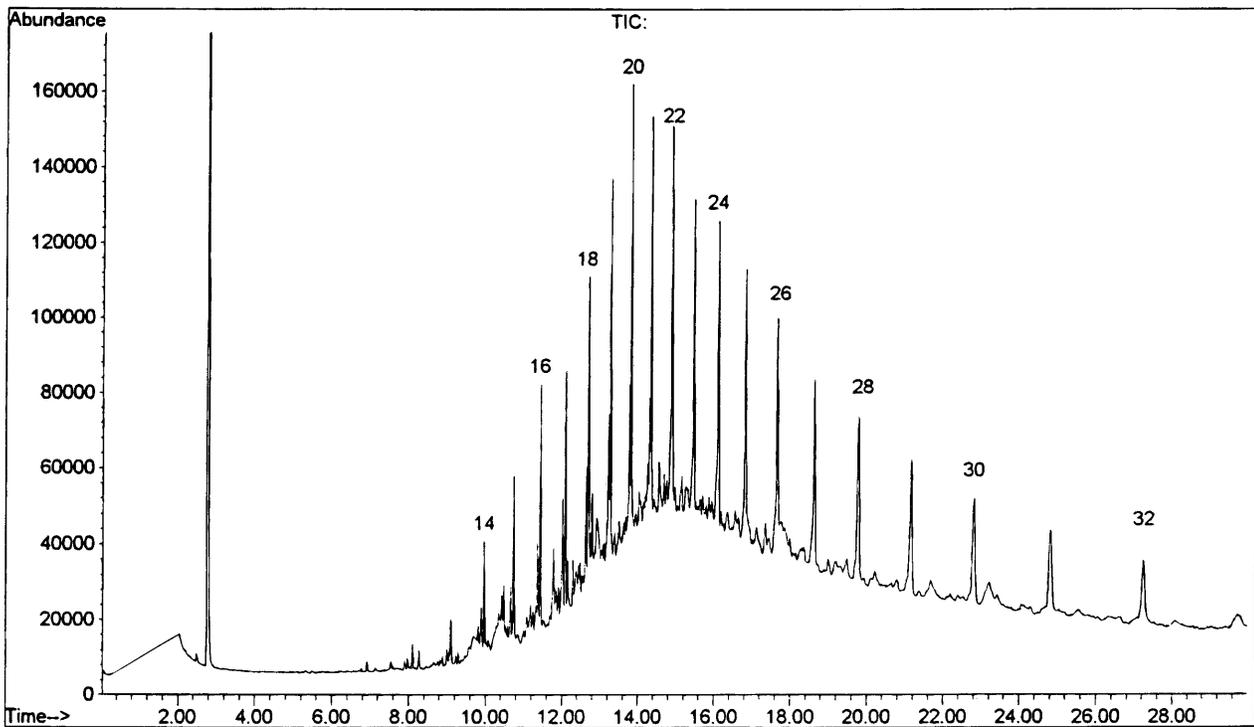


FIG. 6A—Asphalt smoke condensate, analyzed directly.

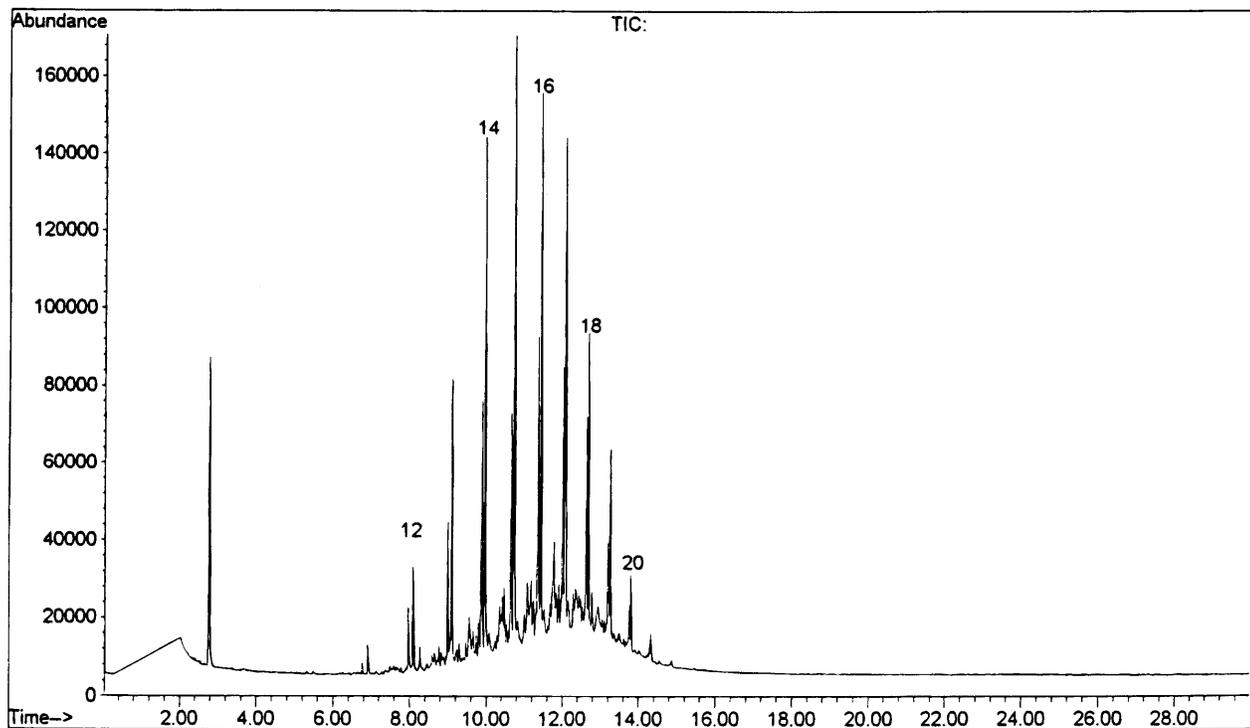


FIG. 6B—Asphalt smoke condensate, subjected to passive headspace concentration. Significant fractionation has occurred in the separation step.

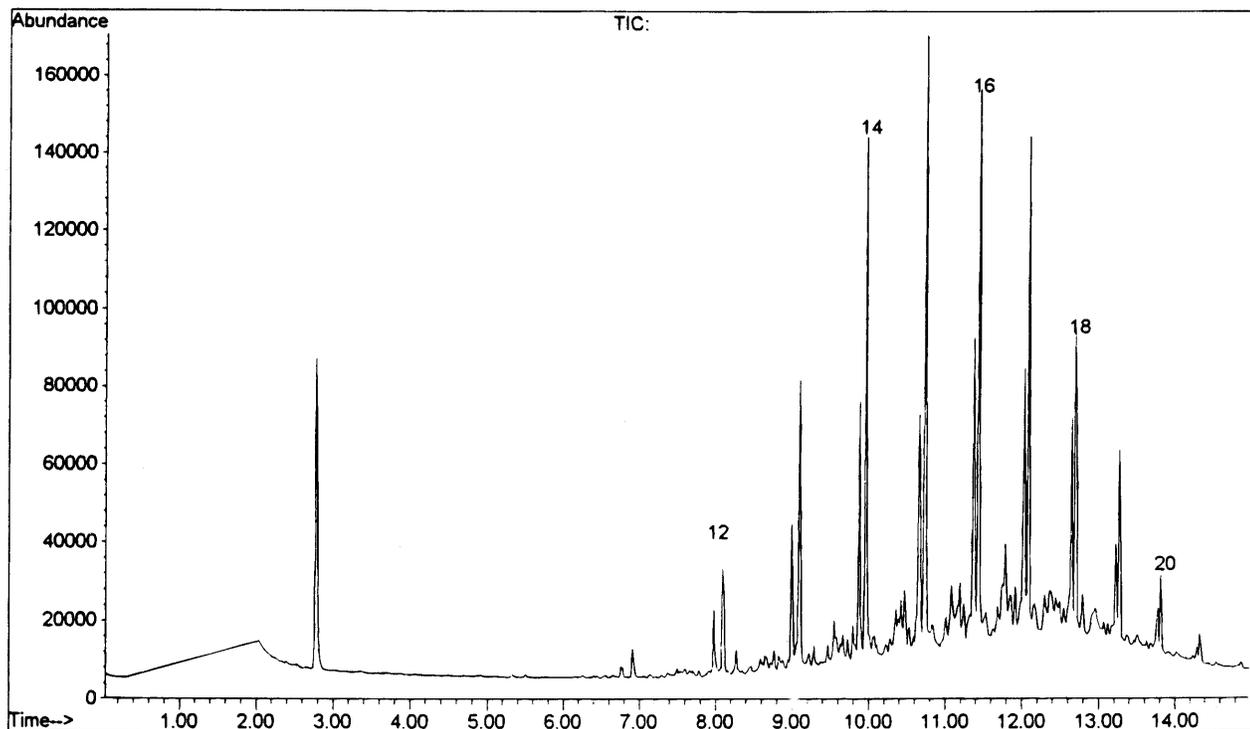


FIG. 7—Time expanded view of Fig. 6B. Asphalt smoke condensate, subjected to passive headspace concentration (0–15 min).

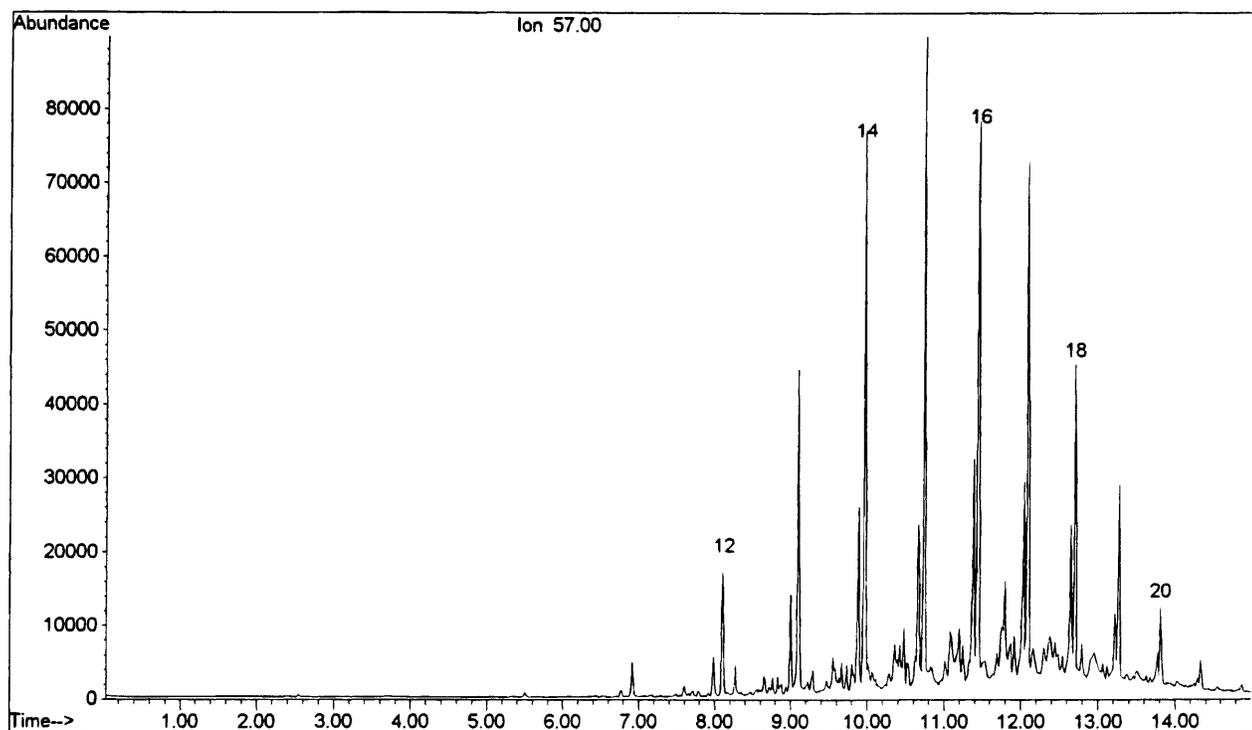


FIG. 8A—Ion 57 profile of asphalt smoke condensate, subjected to passive headspace concentration (0–15 min). Alkane peaks are 2–3 times taller than the alkene peaks which precede them.

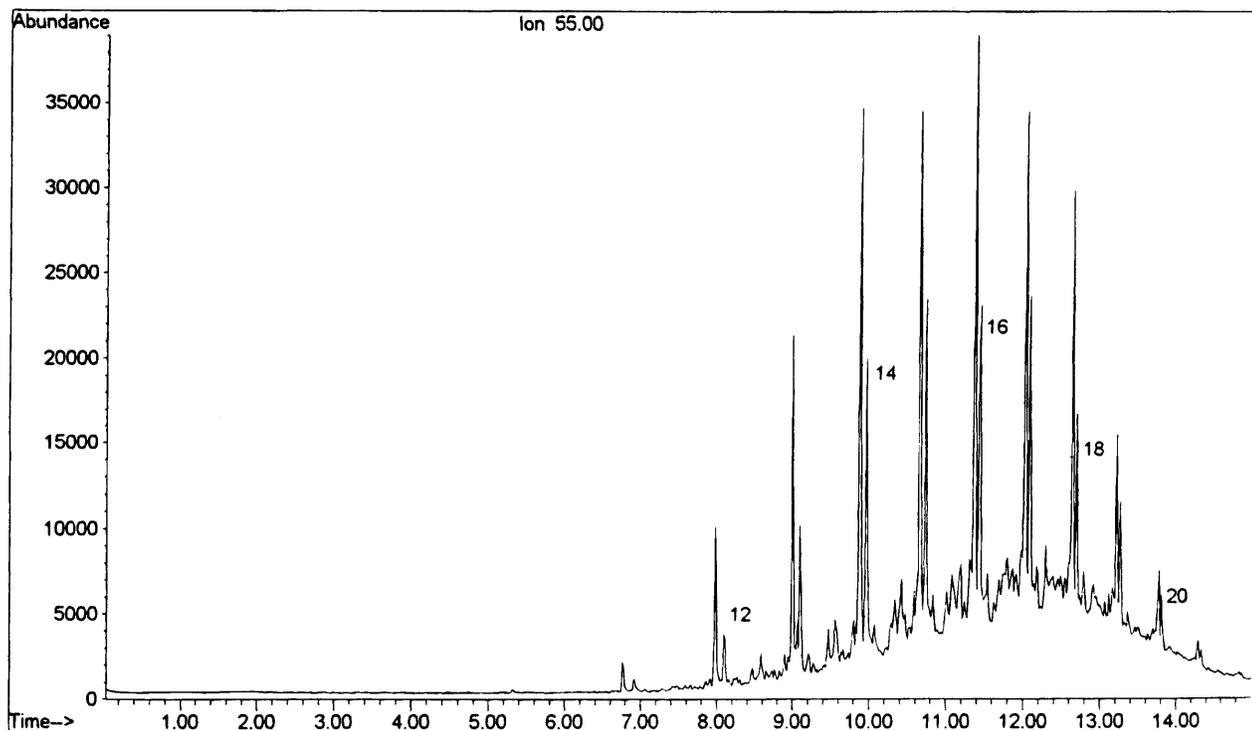


FIG. 8B—Ion 55 profile of asphalt smoke condensate, subjected to passive headspace concentration (0–15 min). Note the change in the ratios of the alkane and alkene peaks. Alkene peaks are now 50–100% taller than the alkane peaks which follow them.

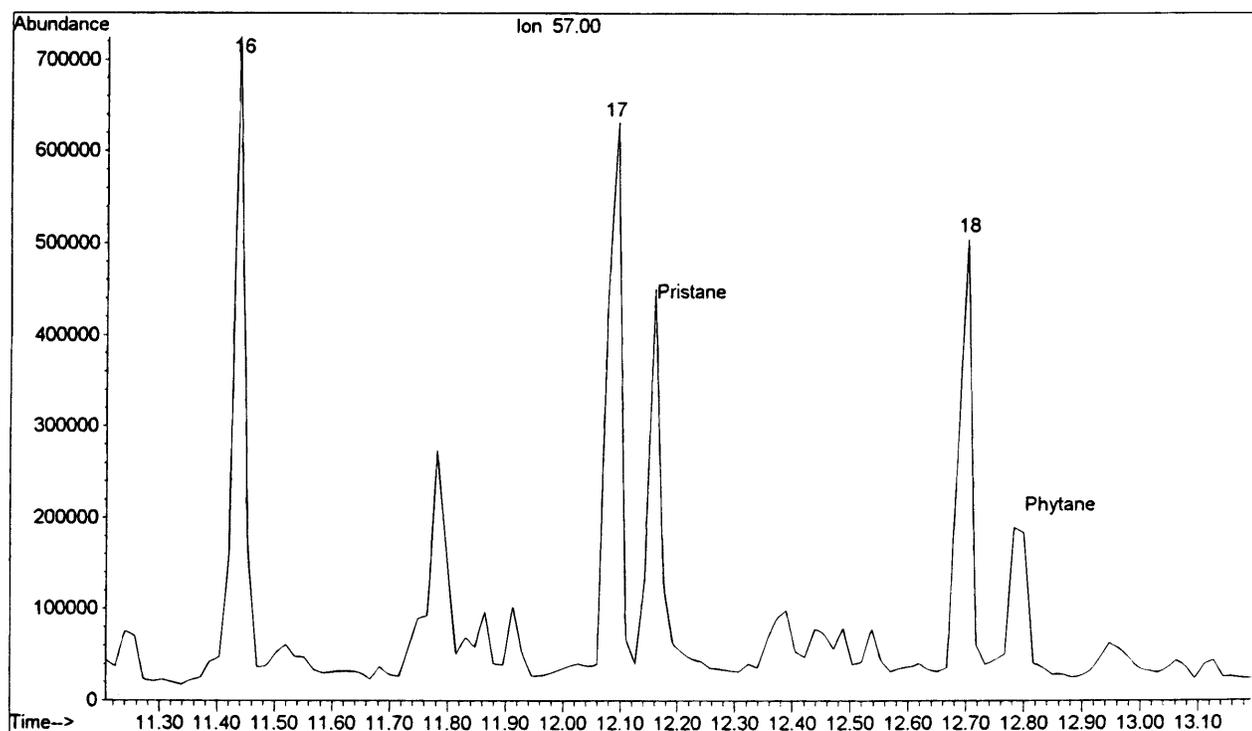


FIG. 9A—Ion 57 profile of 50% weathered diesel fuel in the C₁₆ to C₁₈ region (11–13 min).

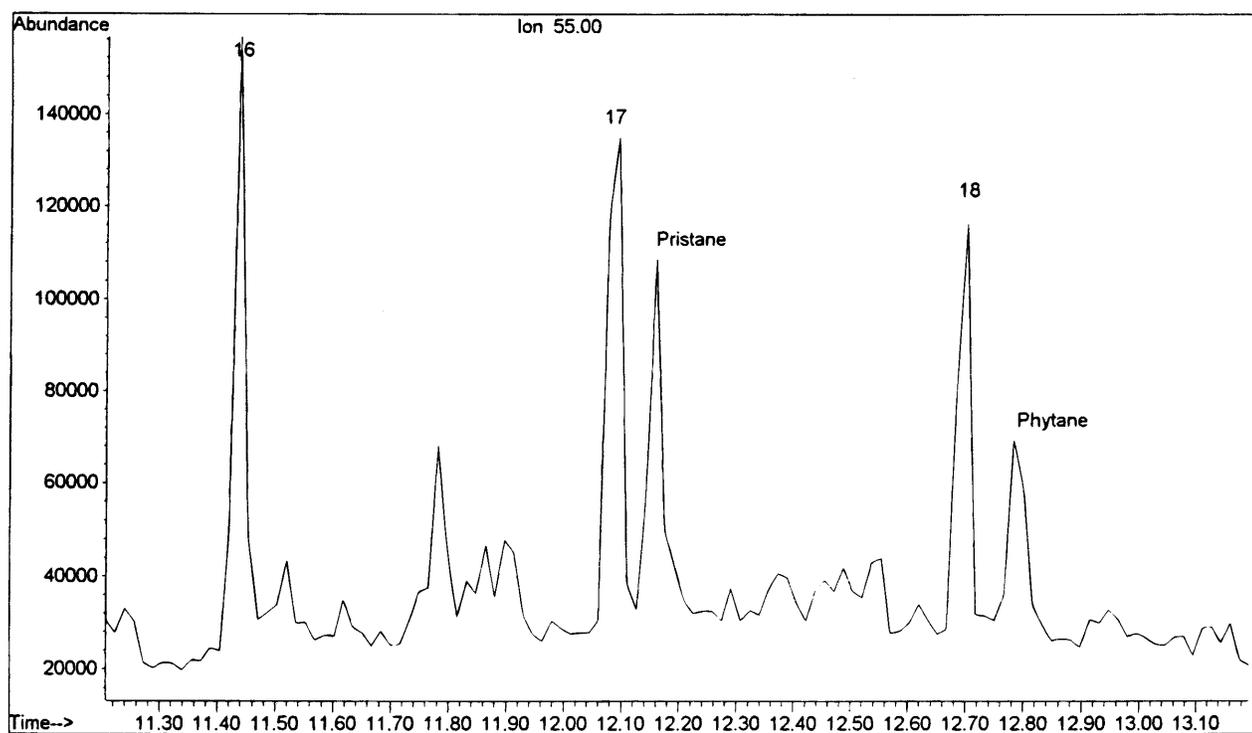


FIG. 9B—Ion 55 profile of 50% weathered diesel fuel in the C₁₆ to C₁₈ region (11–13 min). This pattern is identical to the one shown in Fig. 9A with about 20% of the abundance.

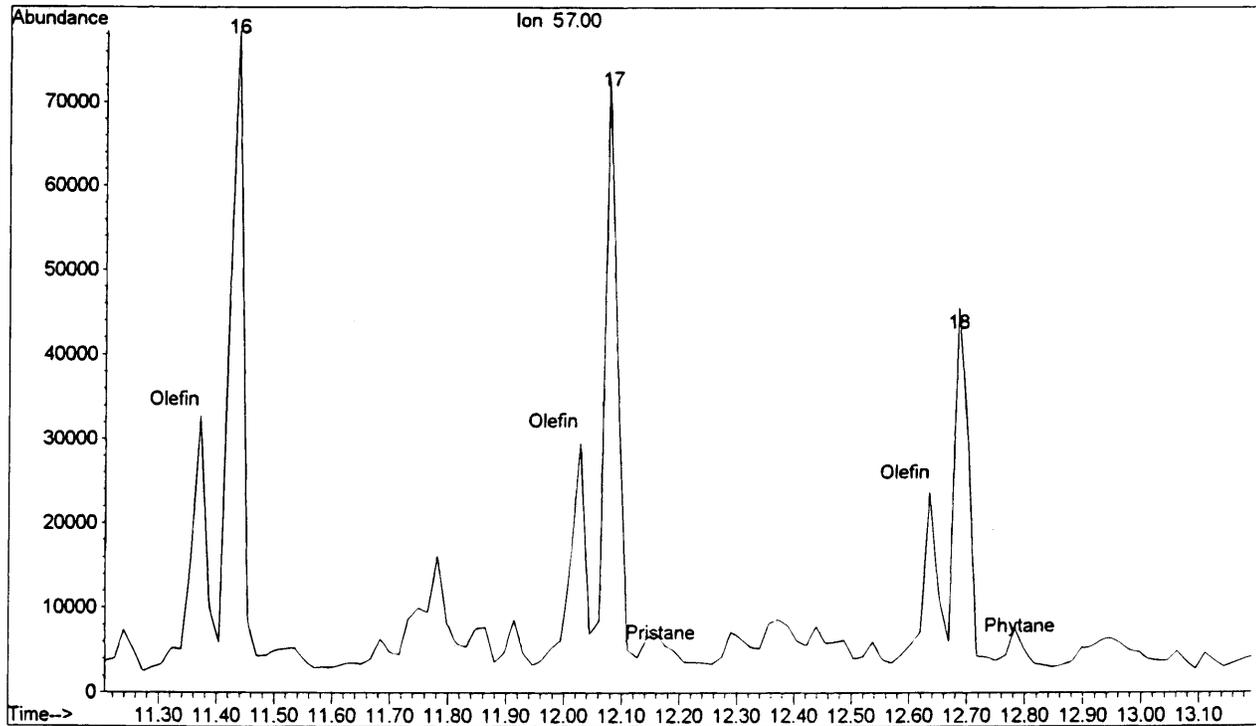


FIG. 10A—Ion 57 profile of asphalt smoke condensate in the C₁₆ to C₁₈ region (11–13 min).

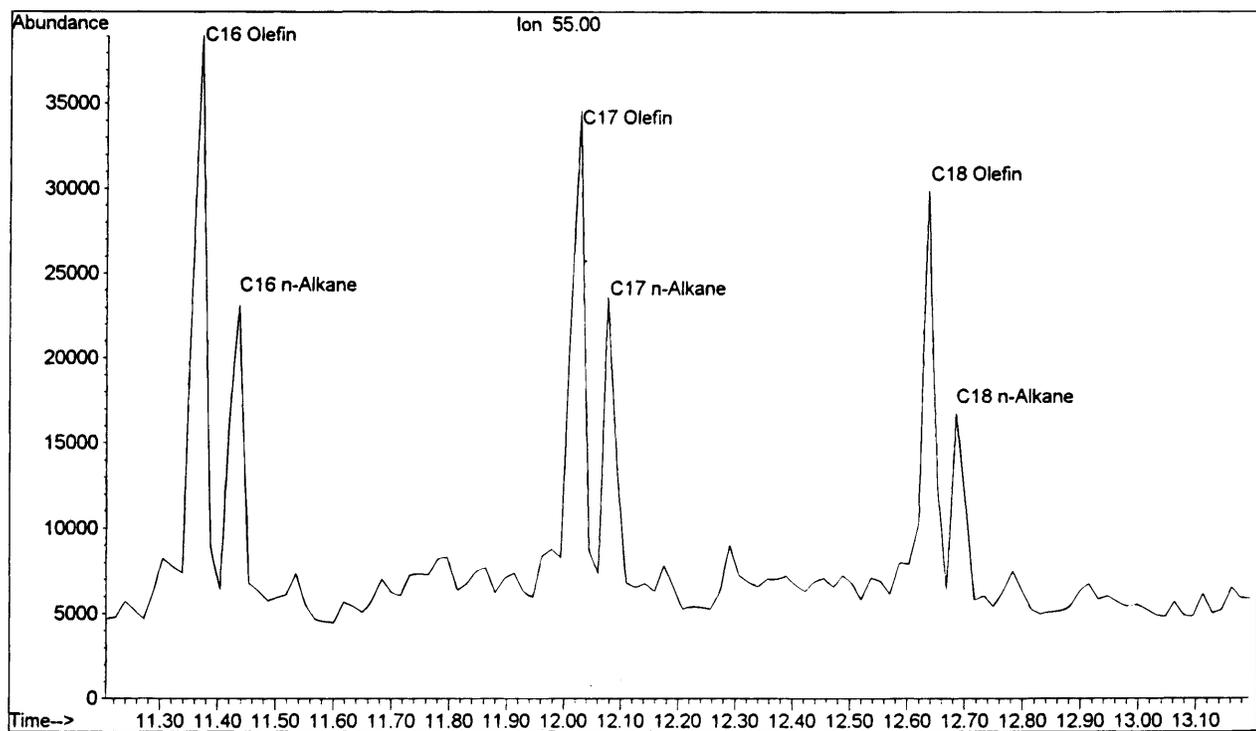


FIG. 10B—Ion 55 profile of asphalt smoke condensate in the C₁₆ to C₁₈ region (11–13 min). Note the dominance of the olefin peaks.

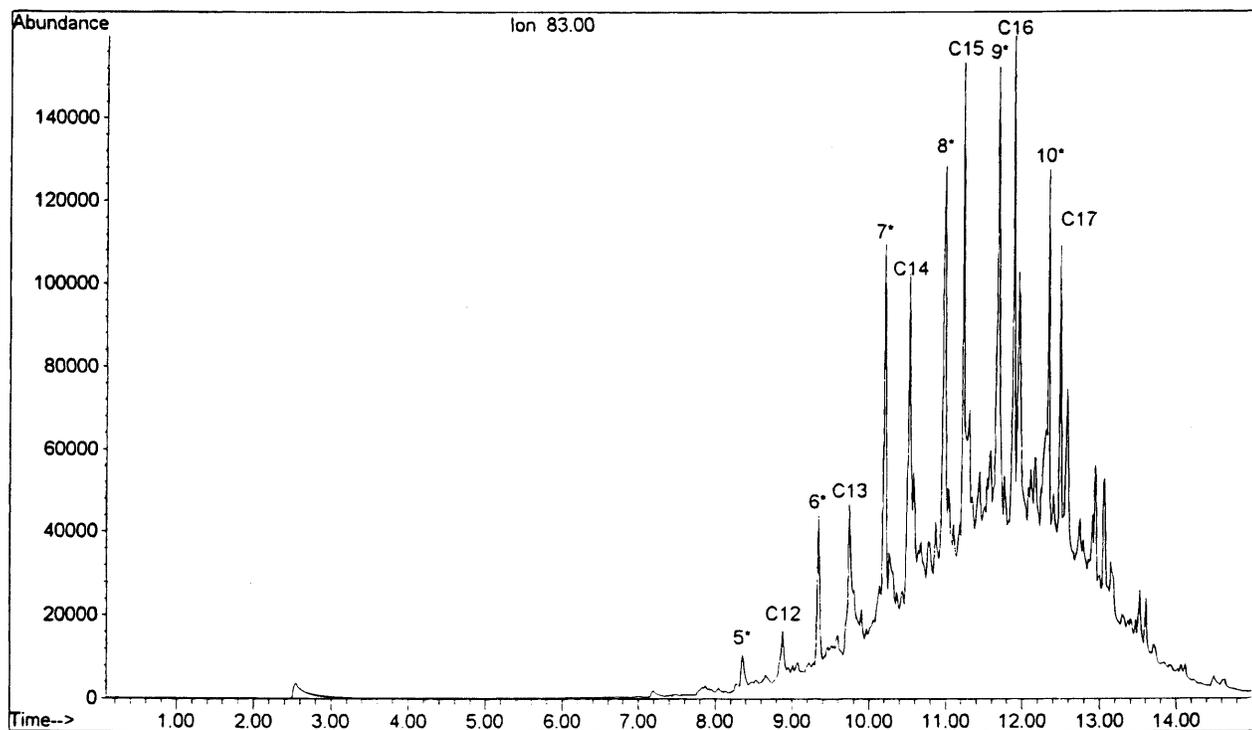


FIG. 11A—Ion 83 profile of diesel fuel (0–15 min). Numbers followed by an asterisk indicate alkyl cyclohexane peaks.

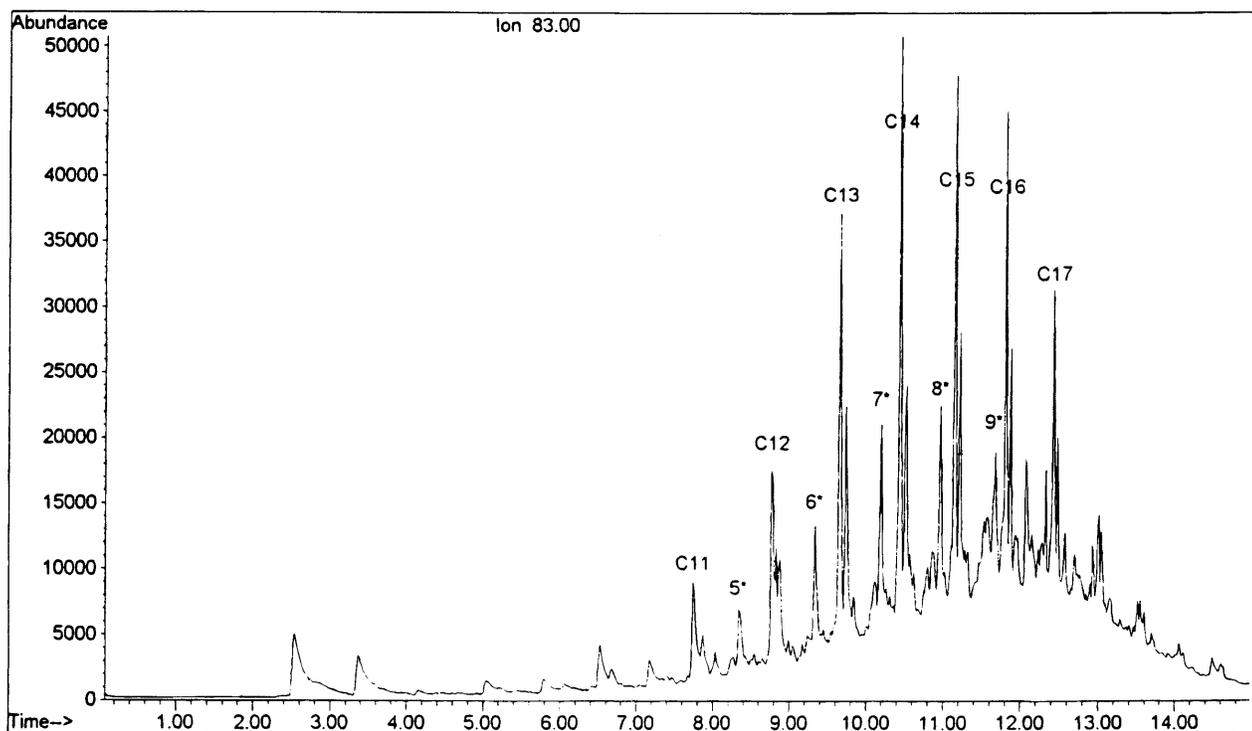


FIG. 11B—Ion 83 profile of asphalt smoke condensate (0–15 min). Numbers followed by an asterisk indicate alkyl cyclohexane peaks. Carbon numbers indicate olefins.

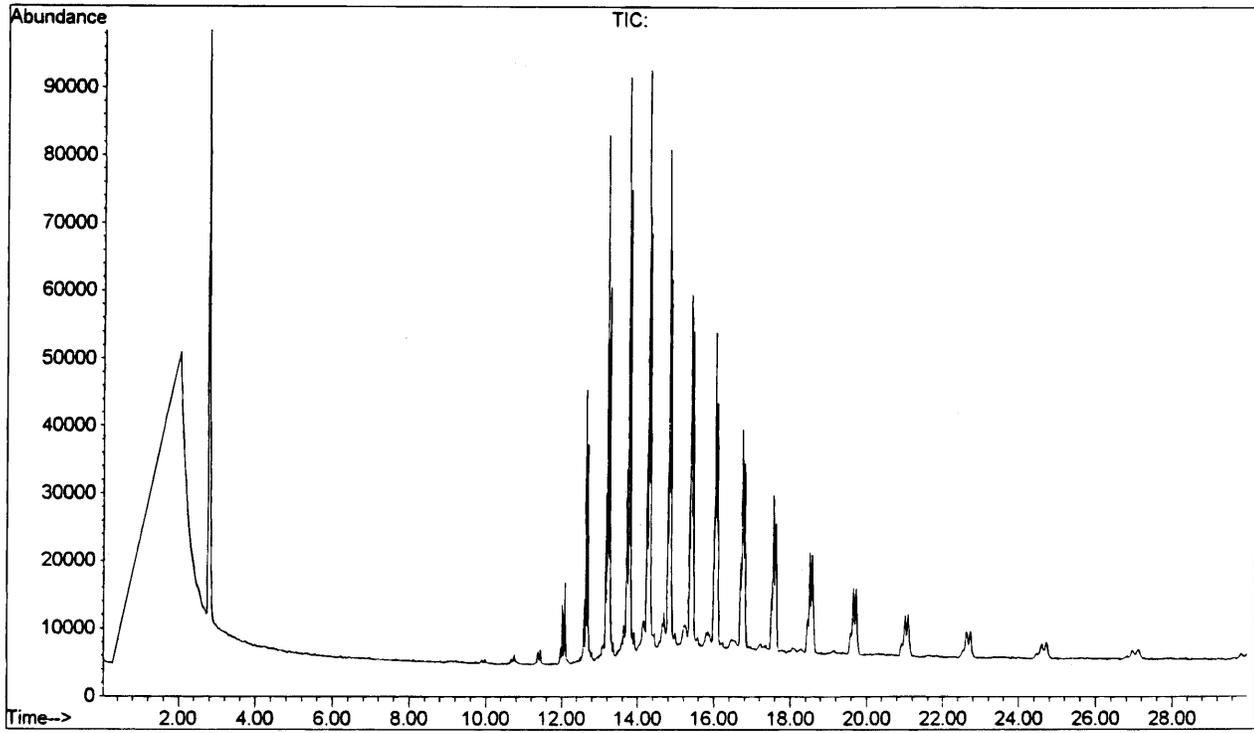


FIG. 12A—Polyethylene smoke condensate, analyzed directly.

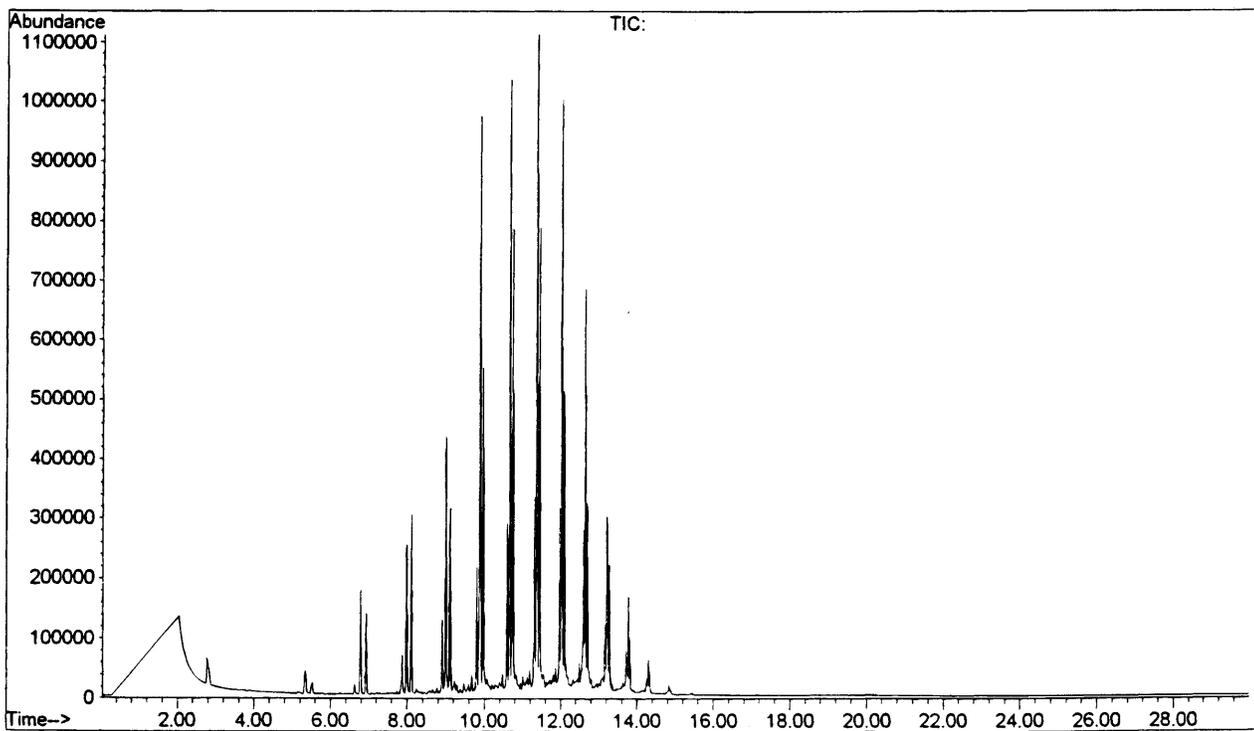


FIG. 12B—Polyethylene smoke condensate, subjected to passive headspace concentration.

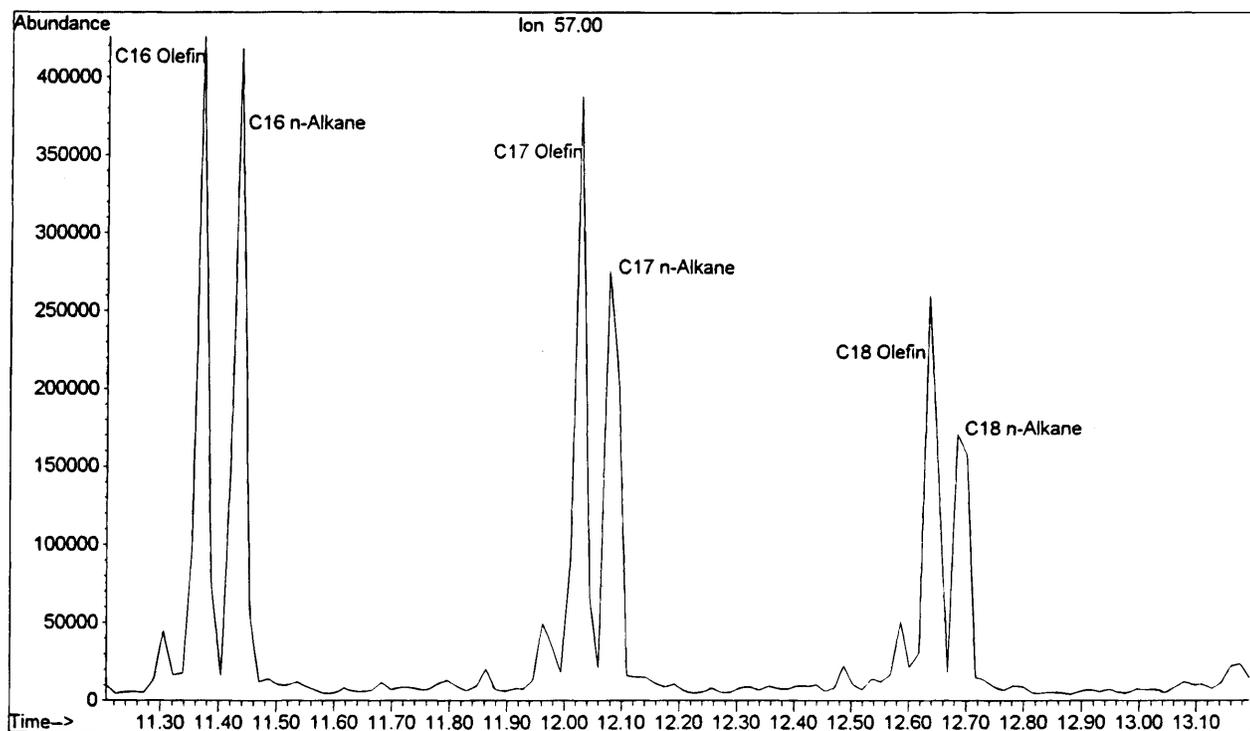


FIG. 13A—Ion 57 profile of polyethylene smoke condensate in the C_{16} to C_{18} region (11–13 min).

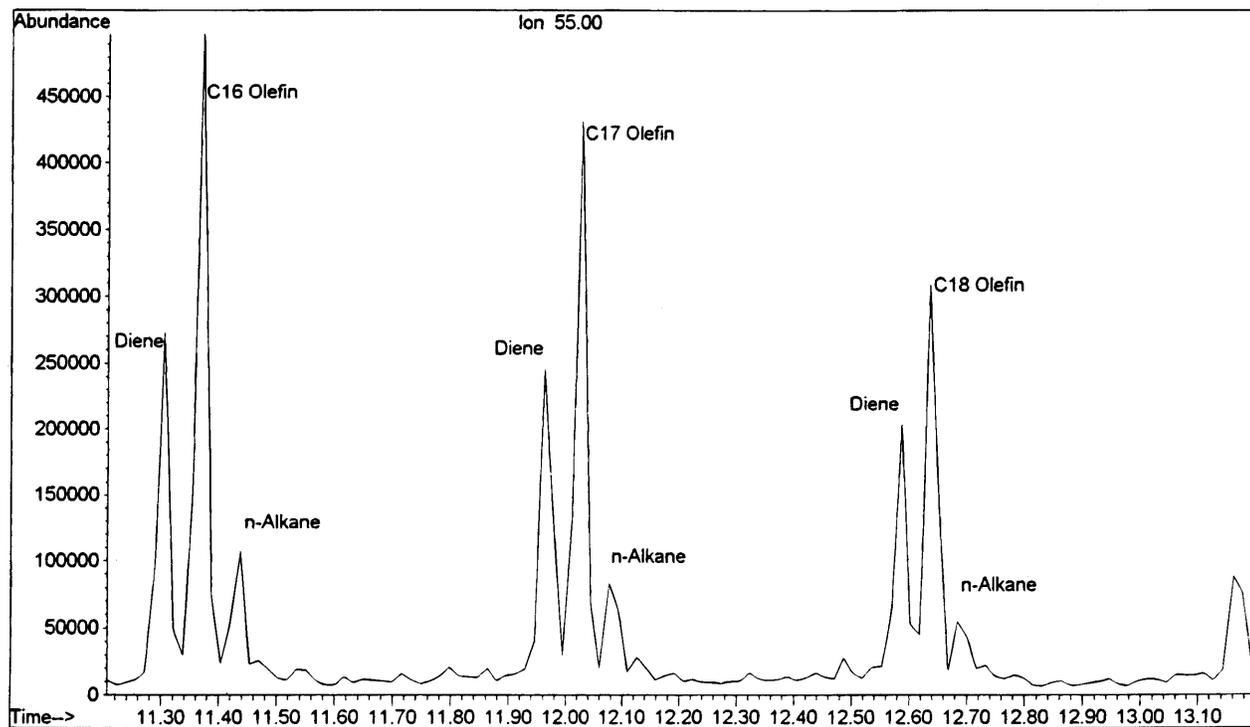


FIG. 13B—Ion 55 profile of polyethylene smoke condensate in the C_{16} to C_{18} region (11–13 min).

the olefin peak dominates even in the Ion 57 pattern. When Ions 57 and 55 are compared (Fig. 13), the same diminution of the normal alkane peak can be observed. No significant quantities of pristane, phytane, or cycloalkanes are observed in the polyethylene smoke condensate.

Conclusion

The presence of asphalt in a sample of fire debris has previously been described as a factor which could complicate or invalidate the determination of the presence of an ignitable liquid residue.

The fact that asphalt smoke condensate, which may be found a significant distance from a fire's origin, can be mistaken for kerosene or diesel fuel makes a close examination for the presence of olefins a requirement when headspace concentration techniques are used and the presence of fuel oil is suspected. While burned asphalt residues may be observed visually and removed from a sample of fire debris, the presence of asphalt smoke condensate is not so easily detected. These condensates are likely to be present in samples from any fire which involves the roof structure, particularly large commercial fires.

The analytical method described here will allow a distinction to be drawn between building material pyrolysis products and ignitable liquids which may have been used as an accelerant.

Acknowledgments

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