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GC/MS Data from Fire Debris Samples: Interpretation and Applications

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ABSTRACT: Mass chromatography is currently being adapted by many forensic laboratories as the preferred approach for interpreting GC/MS data from fire debris samples. This paper first describes software approaches for minimizing interferences and for facilitating the identification of petroleum liquids when using this approach. Next, guidelines are developed for recognizing chromatographic distortion that often occurs when petroleum liquids are recovered using the popular solid adsorption/elution method. It is seen that for a given petroleum liquid, paraffinic:aromatic ratios can vary eight fold depending on the recovery conditions and sample concentration. Finally, the application of these software tools and guidelines to case samples is illustrated, and an approach for categorizing an exemplar collection on the basis of qualitative features and peak height ratios is demonstrated.

KEYWORDS: forensic science, fire debris, solid adsorption/elution, recovery procedures, ignitable liquids, arson, gas chromatography, mass spectrometry

Although the usefulness of GC/MS for fire debris analysis has long been recognized, its widespread adaptation by the forensic community has not been swift. This is partly due to the complexity and costs associated with GC/MS, but also with the difficulty of displaying and interpreting the resulting data. Although alternatives have been proposed, it appears that most laboratories are currently adapting the mass chromatographic approach to GC/MS data interpretation. This approach is based on the realization that the numerous compounds in a petroleum liquid can be grouped into only a few classes, such as paraffins, light aromatics, heavy aromatics, and naphthenes (alkylcyclics), and that each of these classes can be characterized by a limited number of ions in the mass spectra. The basic principles of mass chromatography (MC) were laid out as early as 1983 by Smith (1), who realized that the identification of individual hydrocarbons in recovered petroleum liquids was difficult and not especially helpful, but that the overall chromatographic pattern of each group was highly characteristic. To prepare mass chromatograms for the paraffin group, for instance, Smith extracted separate chromatograms for the m/z ions 57, 71, 85, and 99, which he then added together over the time frame of interest. Similar mass chromatograms were prepared for six other groups such as naphthenes and alkylbenzenes. Identification was then made by comparing the mass chromatograms of questioned

samples and exemplars, a process often involving more than 100 peaks (2,3). More recently this approach has been popularized by the analysts at Pinellas County (4).

Compared to alternative approaches, the overwhelming advantage of mass chromatography is that it preserves the complex patterns of the initial liquid, which in the opinion of this author is essential for unambiguous identification. Another advantage is that mass chromatography does not require calibration for individual compounds or even the specific identification of the peaks employed. This is important since petroleum liquids contain hundreds of compounds, and calibration for more than a small fraction of these is not practical.

On the other hand, the primary limitation of mass chromatography is its susceptibility to interferences, which occur because ions are summed over the entire chromatogram whether or not target compounds are present. Another difficulty is the lack of convenient software for generating and interpreting GC/MS data. One goal of the work described below was thus to develop convenient software tools for minimizing interferences while still preserving the advantageous features of mass chromatography.

Quite aside from instrumental issues, another factor complicating data interpretation is that the static adsorption method, currently the most common protocol for recovering petroleum liquids in fire debris, yields a distorted version of what is actually present. This effect was illustrated by Newman and others (5), who exposed carbon strips for a range of times to known concentrations of a petroleum mix. These analysts observed that shorter exposures favored the recovery of the lighter compounds falling in the C_7 to C_{10} region of the chromatogram, while longer exposures and higher concentrations favored the later eluting compounds falling in the C_{14} to C_{20} region. Under some conditions, portions of the chromatogram were essentially lost.

This effect is consistent with the standard adsorption models in which the available molecules compete for a limited number of adsorption sites. According to this model, the smallest compounds, having the highest vapor pressure, arrive at the carbon strip first and are adsorbed in most abundance. At higher concentrations or longer times, the heavier compounds gradually arrive and displace the lighter components. Although not mentioned by Newman (5), aromatic compounds tend to bind tightly to activated carbon, and at the start of our study there was a concern, subsequently borne out, that aromatics might displace paraffinic compounds on the carbon strip. This is important since some classification schemes rely on the relative amounts of paraffins and aromatics to identify certain classes of petroleum liquids (4,6). More to the point of this paper, while this model explains the observed phenomena, it does not help the analyst who must judge the fidelity of the recovered sample without prior knowledge of the sample concentration. For instance,

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does an unusually high aromatic content in a recovered sample imply the presence of an aromatic solvent, or only that the carbon strip is overloaded? Accordingly, one goal of this paper is to describe tools we have found helpful for recognizing a distorted chromatogram when dealing with an unknown sample.

Another factor complicating the life of the arson analyst is the increasing diversity of petroleum liquids available on the retail market. Perhaps 15 years ago, most liquids encountered by the arson analyst could be classified as gasoline or a petroleum distillate. Such materials were limited by the number of available crude oil sources and could be characterized by expected ratios of n-alkanes, branched alkanes, aromatics, and naphthenes. However, current technology allows refiners to produce each of these classes in nearly pure form or seemingly any admixture bearing no obvious relationship to the initial crude oil. As a case in point, a chromatogram dominated by aromatic compounds was once a sure signature of gasoline. Currently, though, the arson analyst must be able to distinguish between gasolines and aromatic solvents, which can yield quite similar aromatic patterns with identical proportions of aromatic and paraffinic compounds. These developments mean that the analyst must now maintain a larger exemplar collection, along with tools for distinguishing these various classes of ignitable liquids.

The following discussion first addresses various software procedures (i.e., macros) for displaying the mass chromatograms, for minimizing interferences, and for distinguishing various classes of petroleum liquids. Taken together, we refer to this family of macros as the "Pyrographics" program. Next, we discuss indicators for assessing whether the material recovered by the carbon strip accurately reflects the actual sample. Finally, we present the results of applying these software tools to our rather extensive library of exemplars, and illustrate how some of the more difficult cases received by our laboratory have been resolved by application of these tools.

Experimental

GC/FID analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a split/splitless injector operated in the split mode. Split ratios were approximately 80:1. Chromatographic conditions were as follows: column type—J&W Scientific DB-1, 15 m × 0.25 mm × 0.25 μm film thickness; carrier gas—He; flow rate—nominally 1.0 mL/min; injector pressure—9.5 psig @ 40°C, programmed to maintain a constant flow; initial temperature—40°C for 2.0 min, followed by a temperature ramp of 25°C/min to 300°C, then 300°C for 2 min.

GC/MS analyses were performed on a Hewlett Packard 5890/5970 system under ChemStation model G1034C control. Chromatographic conditions were essentially the same as for the GC/FID, except that the initial injector pressure was 1.0 psig. All data were collected in the full-scan mode.

Activated Carbon Strips (type ACS-50) were purchased from Albrayco Laboratories (Cromwell, CT). Strips were baked at 300°C for 4–16 h to remove background contaminants and were then cut into individual 9 × 9 mm coupons, referred to here as ACS coupons.

Volatile components in solid samples, contained in metal friction lid containers unless otherwise noted, were recovered using the static adsorption/elution (SAE) method. In particular, an ACS coupon was impaled on a bent paperclip, the paperclip was held to the lid of the container by a magnet placed externally on the lid, and the metal friction lid container (MFLC) was placed in a 65°C oven

for periods ranging from 1–16 h. Upon removal from the oven, the coupon was retrieved and eluted with approximately 150 μL of carbon disulfide (J. T. Baker, Ultra Resi-Analyzed).

Petroleum liquid exemplars were obtained from local outlets such as service stations, or in the case of some ASTM miscellaneous-class solvents, from the original manufacturer or refiner. A gasoline:kerosene:diesel mixture, referred to herein as a SAM mix, was prepared by adding equal volumes of these liquids.

Selected materials of construction were pyrolyzed by placing a few square inches in an uncoated, 1-quart MFLC and playing a torch over the surface of the material until limited ignition occurred. The lid was then placed lightly in place, and heating was continued until thick smoke was observed exiting the can.

Software Considerations

In developing the software described below, we have attempted to account for certain observations and problems encountered during our initial attempts at employing GC/MS: (a) Interferences can originate from pyrolysis of the substrate (e.g., terpenes from wood) or from spectral interferences between the various groupings in the ignitable liquid (e.g., alkanes contributing to the alkene mass chromatogram). (b) Exemplars and case samples may be analyzed many months apart, and the pattern recognition process must be insensitive to gradual changes in retention time and instrumental response that inevitably occur. (c) The complete set of patterns for an individual sample should be summarized on a single page, since a more lengthy format is not practical when dealing with extensive exemplar collections. (d) Forensic scientist employing pattern recognition on a regular basis soon come to recognize certain peaks as characteristic of an ignitable liquid, even if the examiner is unsure of their exact identities. Software for pattern recognition should preserve such peaks and continue their use. (e) Memorizing appropriate macro commands is difficult and frustrating. Accordingly, all the functions should be executed using pull-down menus and dialogue boxes in a Windows format. Because not all the desired features could be optimized in a single macro, separate macros were written with each emphasizing certain functions. The most important of these are described below.

The first module, referred to as *Summed Groups*, prepares mass chromatograms for paraffins ("alkanes"), aromatics, and naphthenes ("cycloalkanes," or simply "cyclics") and displays these along with a total ion chromatograph (TIC) on a single page (Fig. 1). See also Table 1 for a listing of the peaks referenced throughout this paper. The mass chromatograms generated by *Summed Groups* is similar those of previous workers but with some modifications. First, we display the later part of the aromatic profile on an expanded y-axis (fourth panel in Fig. 1) to compensate for the depleted level of heavier aromatics in reformulated gasolines. Second, to minimize interferences we have based the aromatic mass chromatogram strictly on the molecular ions listed in the figure. (Ions 106, 120, 134, 118, 132, 128, 142, and 156 correspond to C₂-alkylbenzenes, C₃-alkylbenzenes, C₄-alkylbenzenes, indane, methylindane, naphthalene, methylnaphthalene, and dimethylnaphthalene, respectively.) This choice is based on the observation that aromatics are essentially the only class in petroleum fuels yielding a strong molecular ion, and that major fragment ions are seldom even-numbered, at least for compounds found in petroleum liquids. Another consideration is that the m/z ions 91 and 105 used by some investigators are prone to interference from terpenes, a common class of pyrolysis products. The third difference from previous workers is that the spectral interference from the alkane group in

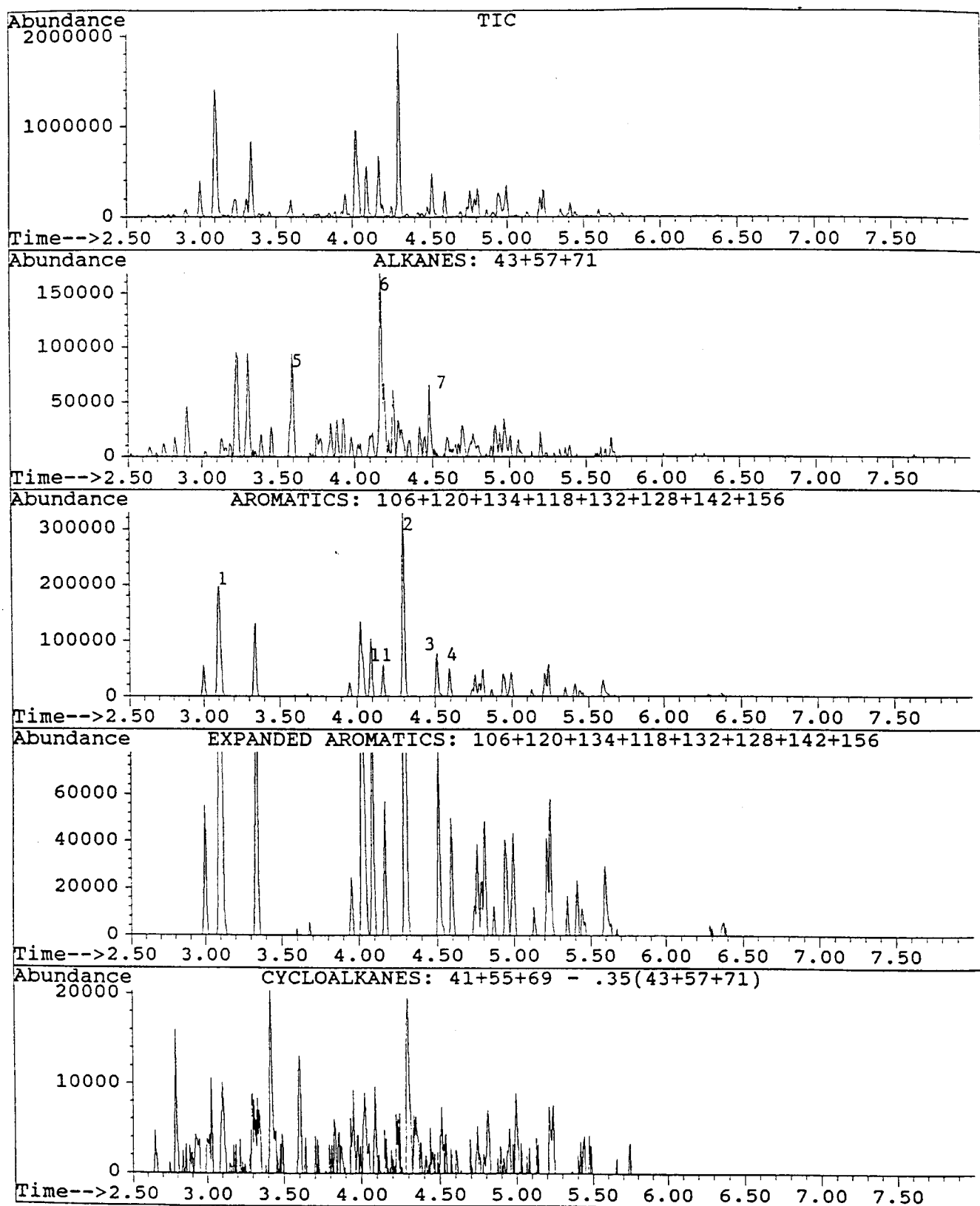


FIG. 1—Mass chromatograms of evaporated, reformulated gasoline prepared by Summed Groups. Peak identities are listed in Table 1, and the individual ions summed are listed in the figure.

TABLE 1—Peaks and peak groupings for characterizing petroleum liquids.

Peak No.	Designation in Text	Description
1	X	coeluting m & p xylenes
2	P	pseudocumene (1,2,4-trimethylbenzene)
3	P+1	trimethylbenzene following P
11	P-1	C ₃ -alkylbenzene immediately preceding P
4	I	indane
5	C ₉	nonane
6	HC#6	unidentified branched saturated hydrocarbon coeluting with P - 1. Sometimes a doublet. Often the dominant alkane in evaporated gasoline.
7	C ₁₀	decane
8	t-alkanes	highest peak in the alkane mass chromatogram in the 3.7–8.0 min window (retention index = 9.1 to 16.1)
9	t-arom	highest peak in the aromatic mass chromatogram in the 3.7–8.0 min window (i.e., beginning immediately after xylenes)
10	t-cyclics	highest peak in the cyclic mass chromatogram in the 3.7–8.0 min window
12	DMN	dimethylnaphthalenes

the cyclic mass chromatogram is compensated for. This is accomplished by multiplying the alkane mass chromatogram by 0.35 and subtracting the result from the sum of ions 41 + 55 + 69 to arrive at a cyclic mass chromatogram exhibiting minimal alkane contribution. (The factor 0.35 is an approximation determined from the analysis of isoparaffinic solvents believed to be free of cyclics.) The format shown in Fig. 1 has proven to be convenient for summarizing the mass chromatographic patterns for most exemplars and suffices for most sample identifications. In addition, it has proven to be quite rugged in that it is not affected by drift in retention times. (We have not needed to adjust the time windows for this module in over a year.)

The value in using the molecular ions to construct the aromatic mass chromatograms is illustrated in Fig. 2, showing aromatic mass chromatograms for a gasoline (panels C and E) along with those for an artificial sample consisting of charred coniferous wood intentionally spiked with the same gasoline (panels B and D). For comparative purposes, panel A contains the total ion chromatogram (TIC) for the wood/gasoline sample. Panels B and C were calculated using the odd fragment ions 91 + 105 + 119, permitted by ASTM and used by some authors. Panels B and C differ significantly, especially in the important region between 3.7 to 4.6 min corresponding to C₃ alkylbenzenes and indane, and it seems unlikely that the presence of gasoline could be recognized in Panel B. In contrast, panels D and E, containing the corresponding mass chromatograms constructed with the even molecular ions, are nearly identical, and the aromatic pattern typical of gasoline (and other petroleum liquids) is readily recognized.

Of course, even with the judicious selection of ions the analyst must still be aware of some interferences, such as those of methylstyrene/indane ($m/z = 118$) and dimethylstyrene/methylindane ($m/z = 132$), but these pairs are well separated in retention time, and the methyl styrenes, if present, are normally preceded by a large styrene peak. Another interference that occurs in dearomatized solvents is that the weak molecular ions for the C₉, C₁₀, and C₁₁ normal alkanes contribute to the naphthalene series in the aromatic mass chromatogram, but this is accompanied by large alkane peaks occurring at the same time. It should also be kept in mind that alkenes, sometimes arising from pyrolyzed substrates, will appear

in the cycloalkane mass chromatogram. The most serious interference situation, though, tends to occur in the latter part of the aromatic panel for complex samples. Recall that mass chromatograms are prepared by first generating extracted ion chromatograms (EICs) covering the entire period (2.5 to 8 min in Fig. 1), followed by the addition of the EICs to arrive at the mass chromatogram. Thus, the lighter ions such as 106, 120, and 134 continue to contribute to the latter part of the aromatic mass chromatogram well after their corresponding compounds have eluted, at which point they are subject to interferences due to minor fragment ions from heavier compounds. In practice, the usefulness of the aromatic mass chromatogram tends to be limited by such interferences.

The *Merged Aroms* module developed in our laboratory addresses this difficulty by limiting each EIC to the window during which a given isomeric family is known to elute. Each of the individual EICs is then “merged,” which in the lexicon of the ChemStation macro language means that all the EICs are displayed in the same window but with a different color for each ion. For instance, the 106 ion (ethylbenzene and xylenes) is extracted from 2.5 to 3.5 min, the 120 ion (C₄-alkylbenzenes) is extracted from 3.5 to 4.5 min, etc., and then all ions are merged into a single screen. The effects of this approach are seen in Fig. 3, showing the TIC, the aromatic mass chromatogram, and the merged aromatic profile for a diesel fuel. The TIC in this figure shows no sign of an aromatic profile, the mass chromatogram exhibits only the first part of the aromatic profile, while the merged aromatics chromatogram displays a complete, interference-free aromatic profile. Similar results have been achieved with case samples. As can be seen, the merged aromatic approach markedly improves the rejection of unwanted interferences.

In keeping with our general approach, the labeled peaks in Fig. 3 and elsewhere do not imply that we have unambiguously identified the indicated compounds. The peak identities shown are generally based on the presence of the molecular ion at the retention index expected from the literature (7), and not on comparison to known standards. Nevertheless, these patterns appear consistently in petroleum distillates and can reasonably be expected to be the indicated compounds.

Another pyrographics module, referred to as *Ratios*, calculates the ratios of peak heights in specified time windows and, as an option, enters these ratios into a spread sheet. The peaks used for this purpose, primarily those listed in Table 1, were chosen as promising candidates for discerning various types of petroleum liquids, as discussed more fully below. The major application of the *ratios* module has been to categorize items in the exemplar collection and subsequently to help recognize some of the less common petroleum liquids in case samples.

The aforementioned macros, among others, can be executed either manually from the ChemStation menu or automatically as part of a method. In addition, all parameters such as retention time windows are entered through ChemStation dialogue windows.

Pattern Distortions During Recovery

To assess the effect of the SAE method on the fidelity of the resulting chromatographic patterns, a series of 1-qt metal friction lid containers were spiked with a volume of SAM mix (1, 3, 10, 25, or 100 μL), and one can from each spiking level was sampled at each of four sampling times (1, 2, 4, or 16 h) according to the SAE procedure. In addition, four exposure conditions were repeated one time each for a total of 24 exposures. Coupons were then eluted with 150 μL of CS₂, analyzed by GC/FID and GC/MS, and total

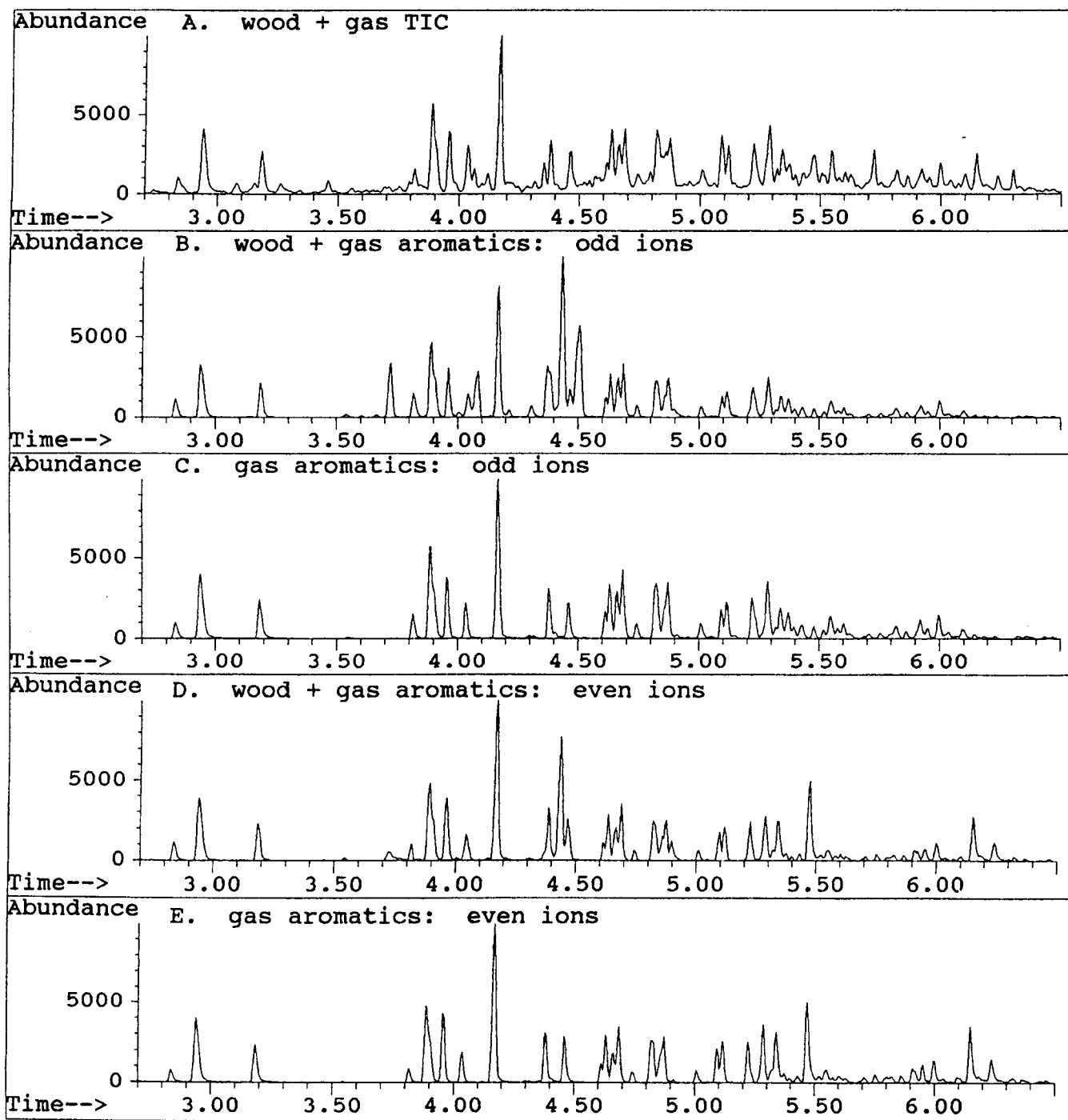


FIG. 2—Minimizing interferences in mass chromatograms by the proper selection of the individual ions. A. TIC for a mixture of charred wood + gasoline. B. Aromatic mass chromatogram for sample A, prepared from the odd ions 91, 105, and 119. C. Aromatic mass chromatogram of the evaporated gasoline used in A, calculated with the same odd ions. D. Aromatic mass chromatogram of A prepared from the even molecular ions 106, 120, 134, 118, 132, 128, 142, and 156. E. As for C, but calculated using the even ions. A, B, and D were calculated from the same GC/MS data file, as were C and E.

areas under the chromatogram (GC/FID) or TIC (GC/MS) were then measured using the ChemStation manual integration mode. In addition, the peak heights of closely spaced alkane and aromatic compounds were measured as one indication of distortion resulting from the SAE recovery method.

The total ion chromatographs (TICs) arising from the two-hour exposures in this series, along with the SAM mixture prepared by simple dilution, are seen in Fig. 4. Here all chromatograms are

scaled to a peak height of 10,000 counts for ease of display. The total areas and peak heights of the unscaled chromatograms, though, were seen to encompass the range encountered in case samples, suggesting that these chromatograms represent typical working conditions.

According to adsorption models, one would expect the total area under the chromatogram to approach a constant saturation value with increasing concentration regardless of the exposure time, at

least when using a universal detector such as the FID. This was indeed the case, as is illustrated in Fig. 5 for GC/FID chromatograms. While the saturation value for the carbon strips used in this study is not precisely defined, it can be seen that the curves tend to approach a constant value corresponding to roughly 10,000 k area counts when using the GC/FID. For unknown samples, then, one would expect distorted chromatograms as this limit is approached. (When selecting a saturation value, it is helpful to bear in mind that its main utility is to provide a benchmark for predicting saturation effects, not in characterizing the carbon strip in some absolute sense.)

For the GC/MS data for the same series, a curve similar to Fig. 5 is obtained but with a saturation value of approximately 3.3×10^9 . For routine case samples, though, we prefer to measure total areas first with the GC/FID because of the wider dynamic range, uniform response, and better stability of this instrument.

Of course, normal fire debris samples do not contain SAM mixtures and are often saturated with water, and it is natural to ask whether similar saturation limits can be expected for a range of realistic samples. This issue was addressed by comparing the saturation values of diesel and gasoline separately, with and without wa-

ter, to that of the SAM mix. Briefly, ACS coupons were exposed for 16 h at 65°C to 100 μ L of the petroleum liquid placed on a paper towel in a one-quart metal friction lid container. For half the samples, the paper towel was saturated with water before exposure. All samples were recovered as usual and analyzed by GC/FID. The resulting total areas were reasonably consistent, considering the sample variation encountered. The presence of moisture had no observable effect on the total chromatographic area, and the total area of the diesel and SAM mix were equivalent. The total area of the gasoline was approximately 65% of that of the diesel, a difference easily accounted for by the tendency of the split injector to discriminate against lighter components. These values suggest that saturation values are likely within a factor of two for arson samples within the range of materials tested.

Some authors (4) have proposed using peak height ratios to distinguish among various petroleum liquids, an approach which presumes that such ratios are preserved by the recovery procedure. Using the data from the series of 24 SAM exposures described above, this presumption was tested by plotting the peak height ratios for some of the peaks in Table 1 as a function of total area of the TIC. Figure 6 shows the peak height ratios for branched hydrocarbon #6

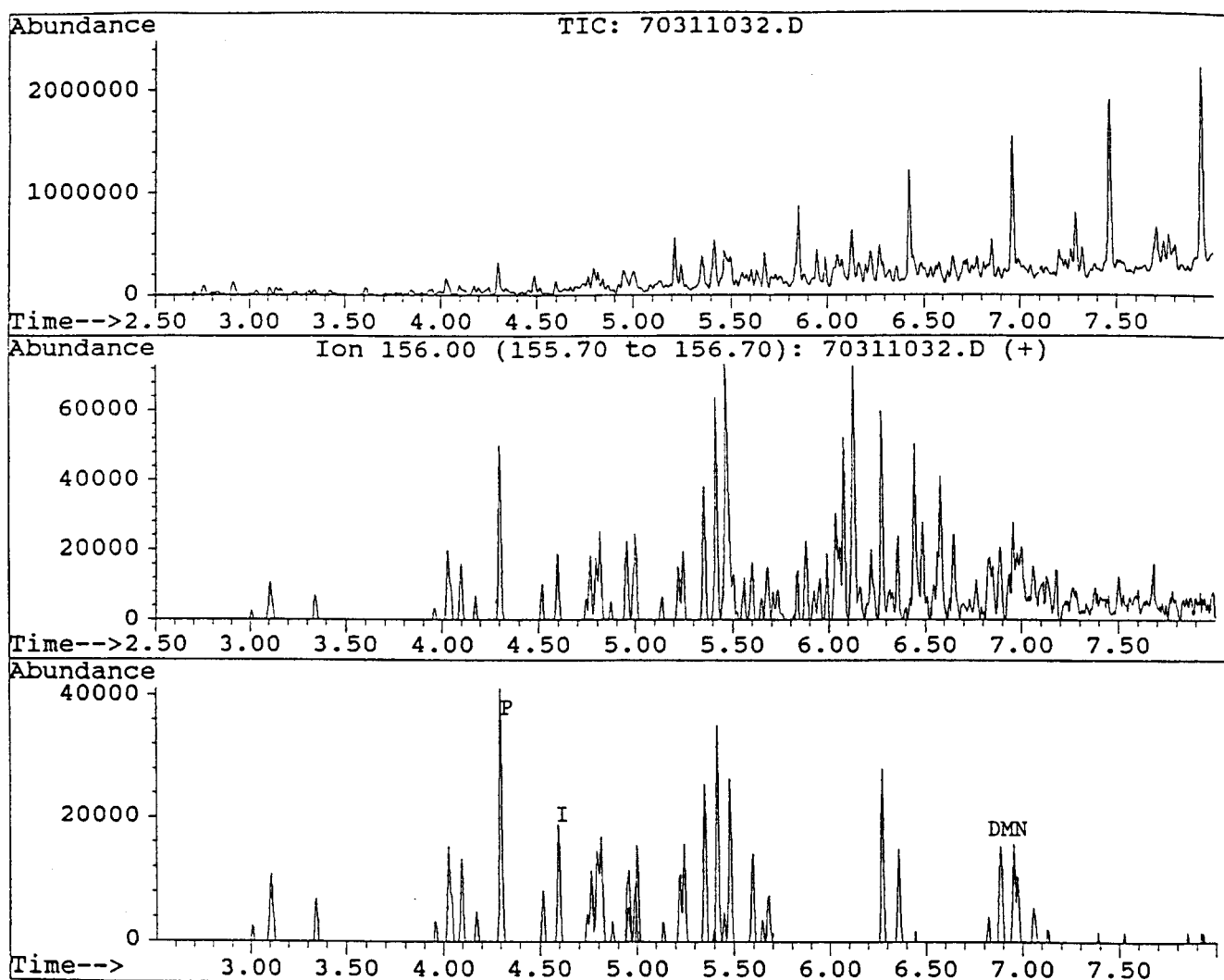


FIG. 3—Isolation of the aromatic group in diesel fuel using the merged arom routine. Top panel: TIC; middle panel: aromatic mass chromatogram; bottom panel: merged aromatic profile.

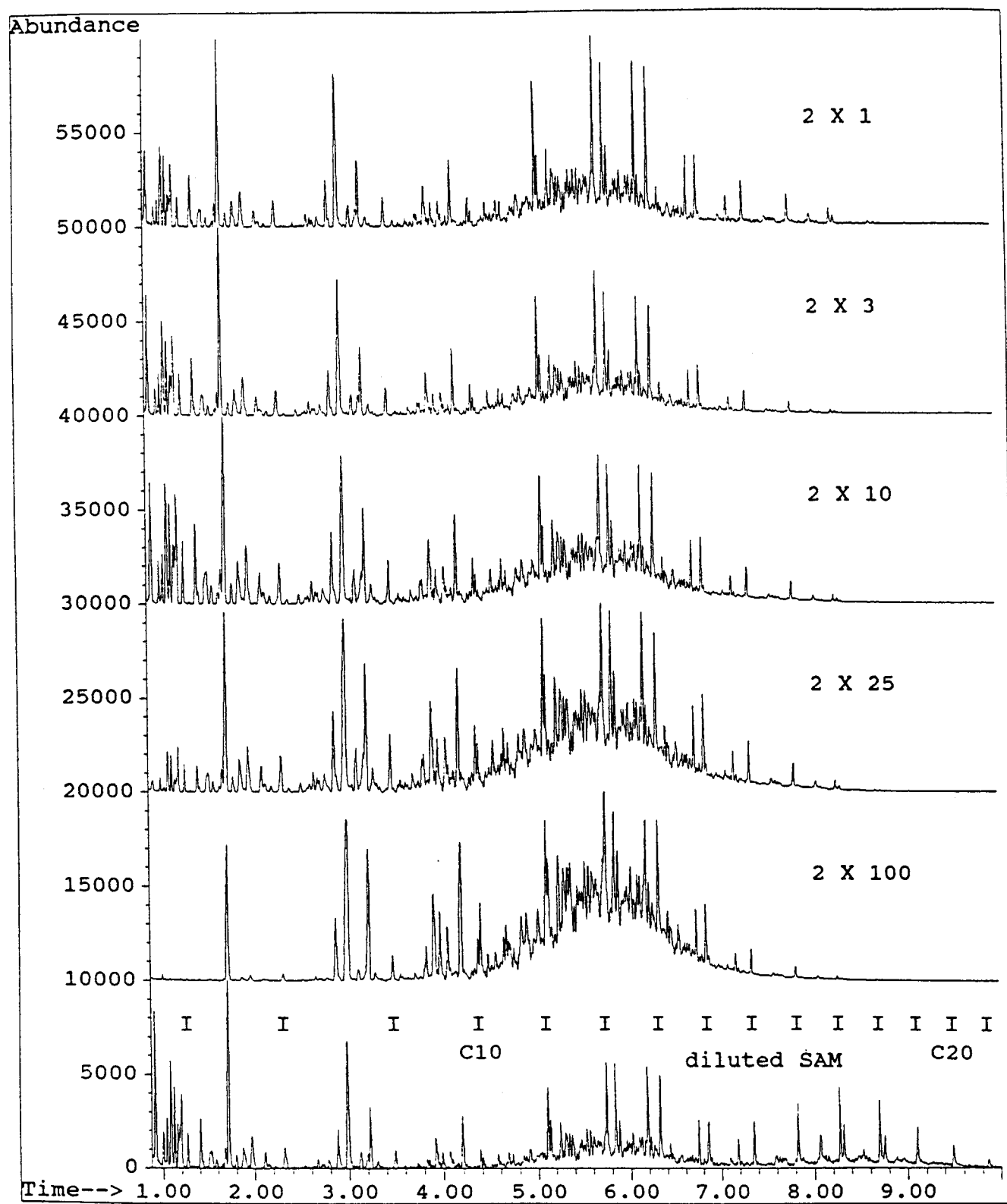


FIG. 4—Total ion chromatograms for a SAM mix collected by the solid adsorption/elution procedure with a two-hour exposure. The "I" markers shown in the bottom chromatogram indicate elution times for n-alkanes. Labels in the chromatograms indicate adsorption time and SAM amount (i.e., "2 X 10" means a 2 h exposure and 10 μ L of SAM).

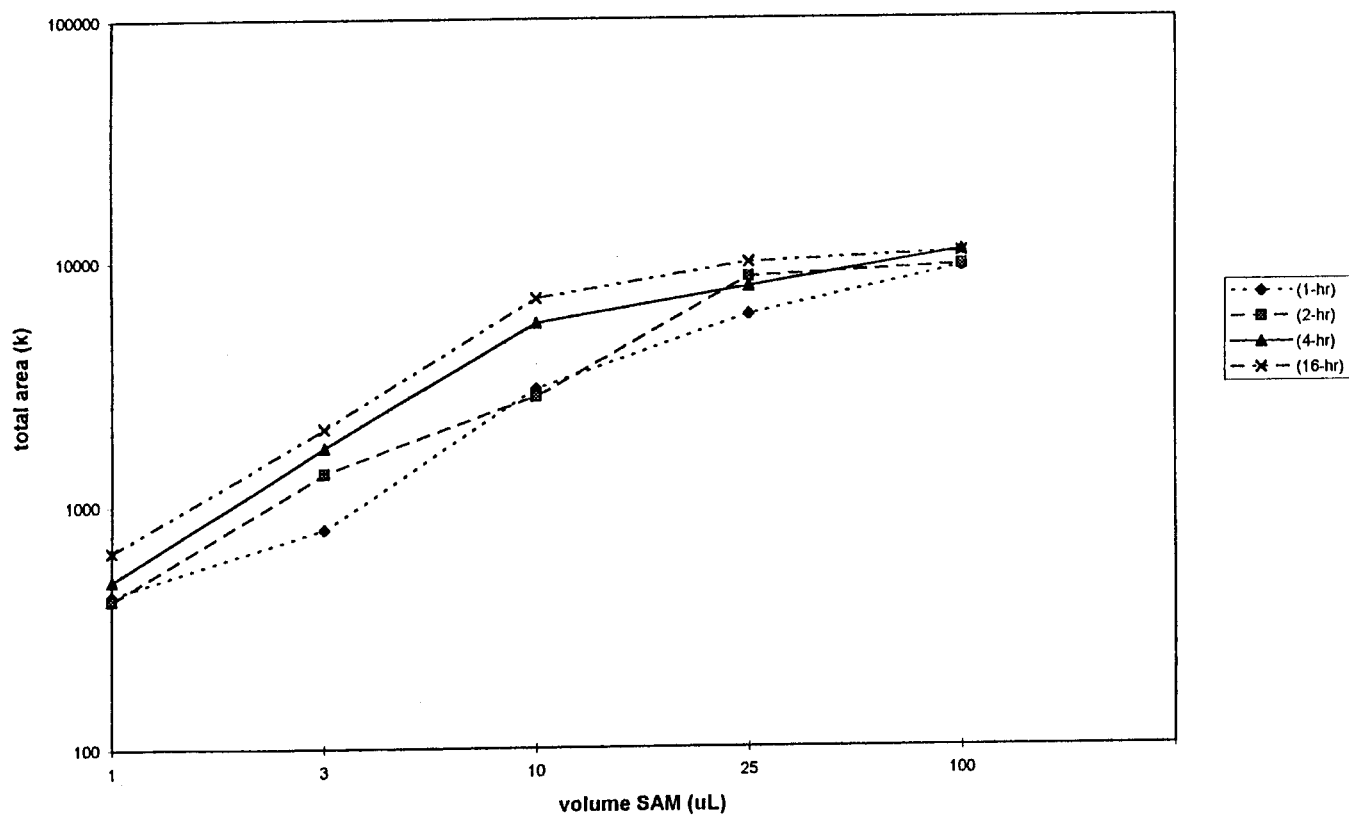


FIG. 5—Effect of SAM concentration on the total area of the GC/FID chromatogram. The indicated times are the exposure periods of the activated carbon strip.

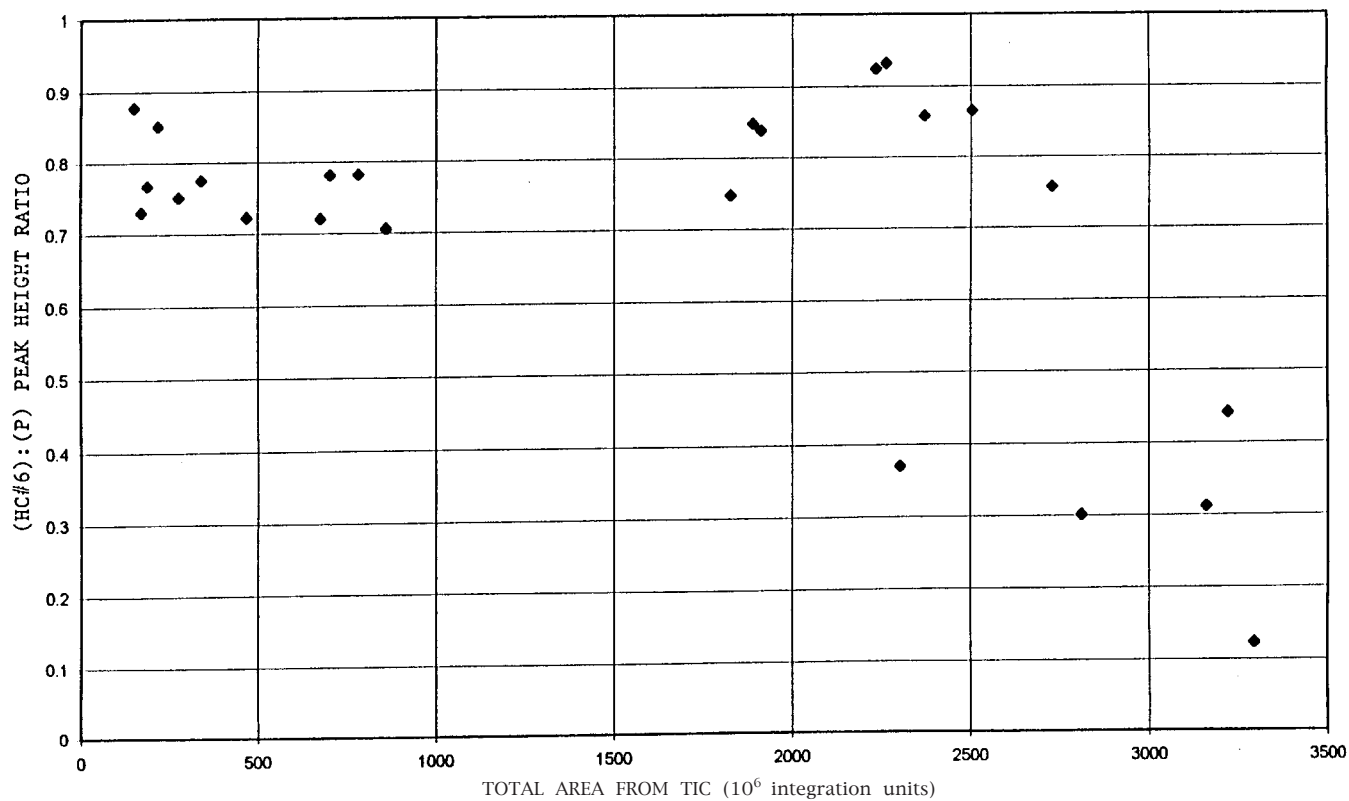


FIG. 6—Dependence of the (HC#6):(pseudocumene) peak height ratio on the total chromatographic area for data obtained by GC/MS. Peak heights for HC#6 and pseudocumene were measured on the alkane and aromatic mass chromatograms, and the total area was measured on the total ion chromatogram.

and pseudocumene, (HC#6):(P), taken from the mass chromatograms, and Fig. 7 shows similar data for the nonane/xylene pair. These peaks were chosen since they are commonly present in ignitable liquids recovered from fire debris. As can be seen in the Fig. 6, the peak height ratio is stable up to approximately 65% of saturation and then decreases approximately eight fold as the saturation limit of 3.3×10^9 counts is approached. A more complex behavior is seen in Fig. 7, where the peak height ratio first increases approximately two-fold, and then decreases to approximately one-half of the initial value. This behavior is reproducible in that it was observed in a second series of SAM mixtures exposed under similar conditions. This pattern occurs because aromatic compounds easily saturate the MS detector, an effect observed as slightly broadened and shortened peaks. Thus, the initial rise seen in Fig. 7 is due to the onset of instrumental saturation in the MS, while the subsequent dip is due to saturation of the carbon strip. When the same ratio is calculated using GC/FID data only (Fig. 8), the resulting plot shows a stable ratio until the carbon strip is within 80% of saturation, followed by a nominal seven-fold decrease, a reasonable result in view of the greater linear dynamic range of the FID. It

should also be mentioned that some peak height ratios, such as those of adjacent aromatics of comparable peak height, are little affected by saturation of the carbon strip. The significance of these ratios will be discussed more fully in the next section, but in the meantime it is clear that saturation effects can measurably alter peak height ratios.

To confirm these observations, most of the measurements represented by Figs. 5–8 were repeated by exposing a second series of cans. The shapes of the resulting curves were the same, but one cautionary note applies. In particular, for the GC/MS used for these experiments, tuning the MS can change the sensitivity (i.e., peak area per unit mass) by several fold, and the total chromatographic area at saturation changes correspondingly. We have thus found it necessary to monitor MS sensitivity by analyzing a standard SAM mix of constant concentration after each tune. (This is reportedly not a problem with newer instruments, for which the sensitivity is less affected by the tune.) In comparison, changes in sensitivity has not been a concern for the FID, which is nevertheless monitored by routinely analyzing standard samples. Regarding the ratios shown in Figs. 6 and 7, it should be noted that two

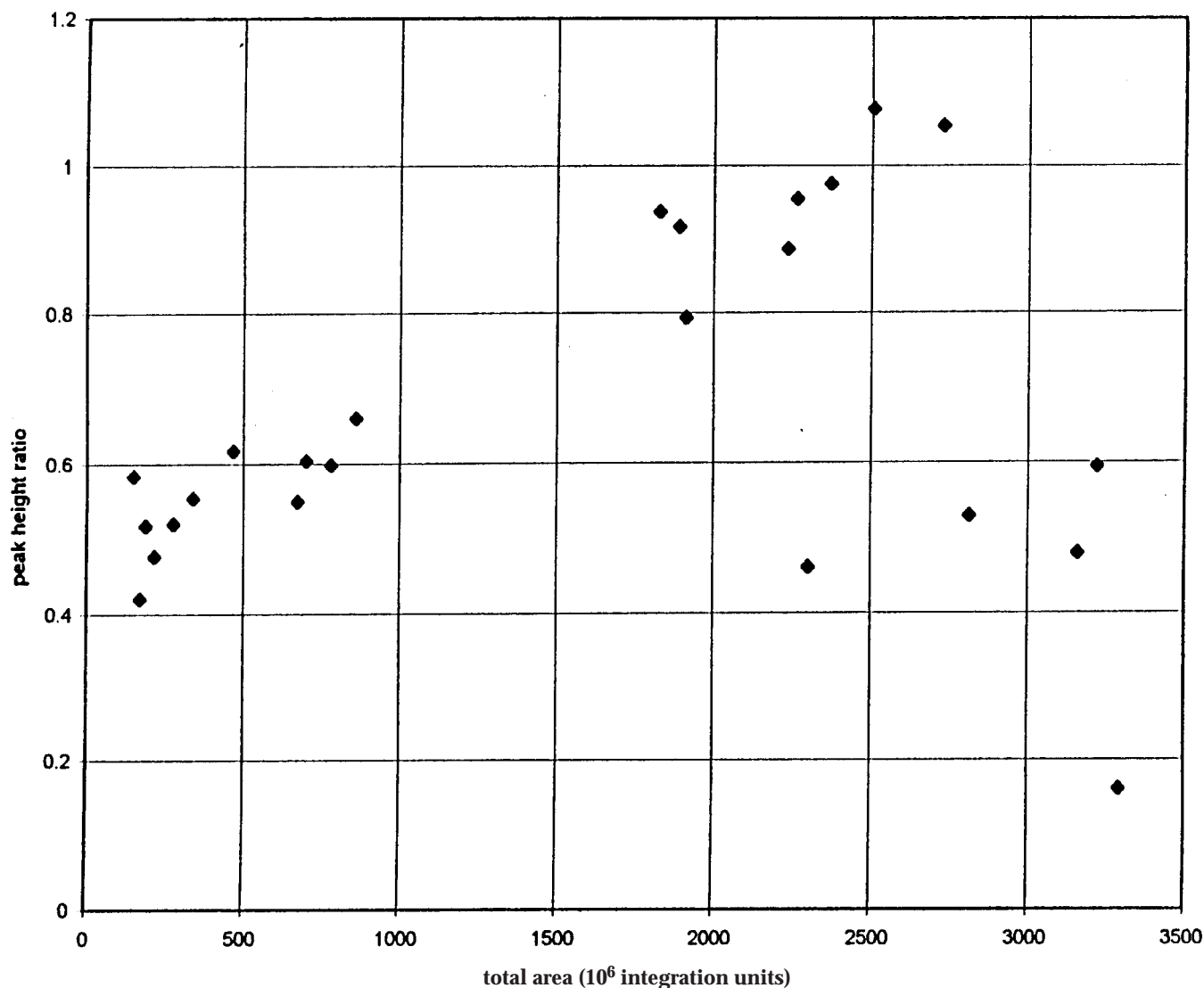


FIG. 7—Dependence of the (nonane):(xylene) peak height ratio on the total chromatographic area for data obtained by GC/MS. Peak heights for nonane and xylene were measured on the alkane and aromatic mass chromatograms, and the total area was measured on the TIC.

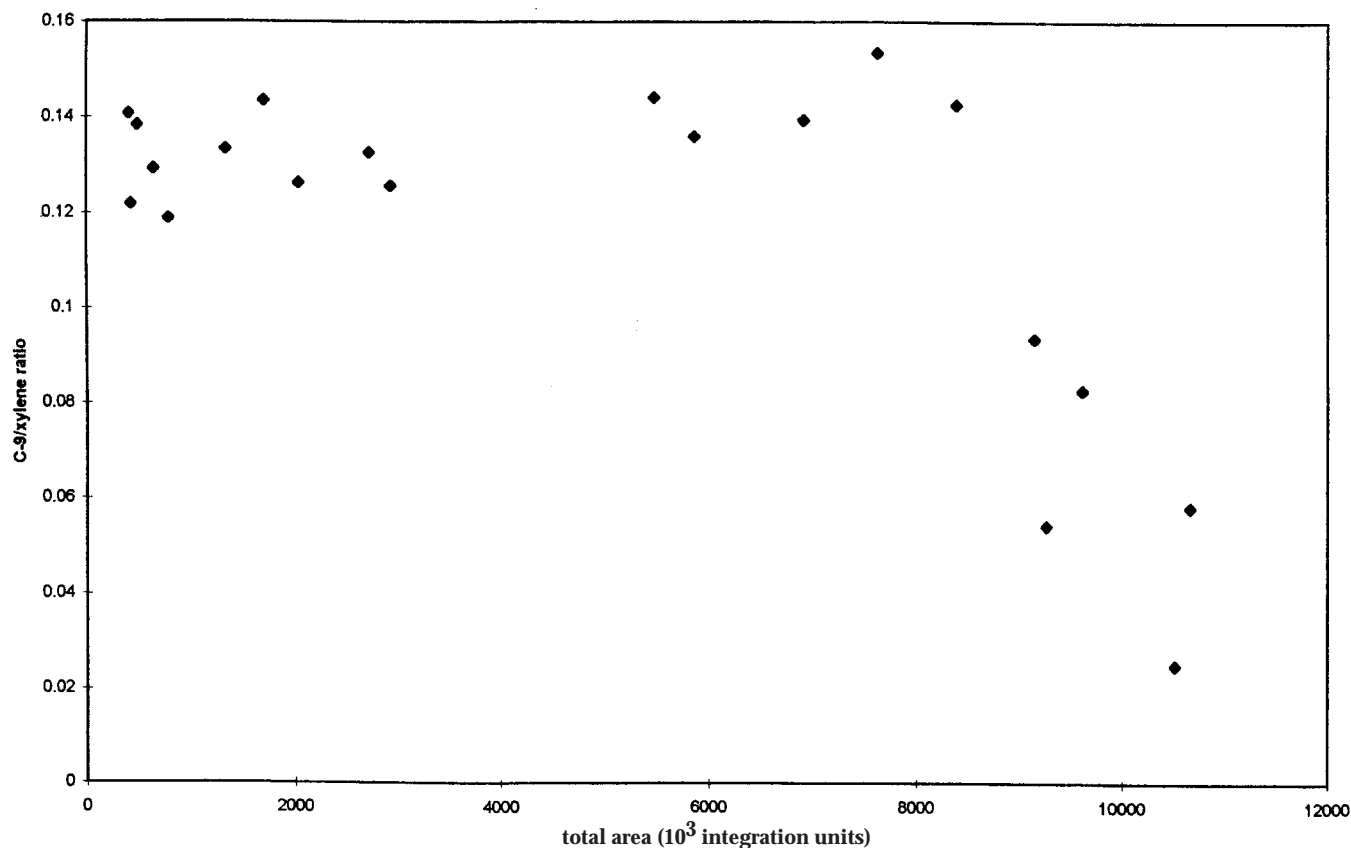


FIG. 8—Dependence of the (nonane):(xylene) peak height ratio on the total area of the chromatogram, obtained from a GC/FID.

coupons exposed to the same concentration for the same time typically yielded ratios within 10% of each other, a small variation compared to the saturation effects shown.

Taken together, these observations lead to general guidelines for dealing with distortion in samples recovered using carbon strips: (1) From the SAE exposures taken at different times and concentrations (Fig. 4 and similar plots for 1, 4, and 16-h exposures), it can be seen that some distortion occurs at any loading, although normally not enough to prevent proper identification. (2) Around 60% of saturation, the peaks around toluene are slightly attenuated but clearly visible; at 80% of saturation, the toluene region is markedly suppressed with respect to the C₁₀–C₁₂ region, (e.g., Fig. 4, 100 μ L exposure). (3) Regardless of the loading on the carbon strip, for 1-h exposures (not shown), peaks at or above C₁₄ are significantly attenuated or lost. This could conceivably lead to mistaking a kerosene for a medium petroleum distillate. For a 2-h exposure, peaks above C₁₄ are attenuated but still visible up to C₁₆. The important C₁₇ doublet is present but could be easily overlooked. For a 4-h exposure (not shown), the C₁₇ doublet is present, but C₁₈ and larger peaks could be overlooked. For a 16-h exposure (also not shown), the C₁₇ and C₁₈ peaks are clearly visible but later peaks can be overlooked or missing. Given these observations, it is questionable whether the SAE method as used in this study can reliably distinguish between a diesel and kerosene class liquid, even with a 16 h exposure. (4) For the GC/MS, the highest peaks in the TIC tend to become attenuated at higher loadings due to the limited dynamic range of the MS detector. (Compare, for instance, the 5–7 min region of the chromatograms in Fig. 4.) This phenomenon tends to mask the presence of the n-alkane series, a characteristic

of petroleum distillates, in heavily loaded samples. Mass chromatograms should be reviewed for unusually high or broadened peaks, since these indicate instrumental saturation and biased peak ratios. (5) The total area under the chromatogram approaches a constant saturation value that is roughly (within a factor of two) independent of the exposure time or type of petroleum liquid present (6). The (Alkane):(aromatic) peak height ratios can be stable up to 90% of saturation. However, considering the uncertainties in extrapolating saturation values determined with artificial mixtures to actual case samples, it is recommended that ratios be viewed skeptically whenever the total area is within 25% of the expected saturation value. (6) Inspection of the GC/FID chromatograms (not shown) indicates that significant attenuation of the region around the carbon disulfide peak, the location of light oxygenated solvents, occurs near 20% of saturation. This phenomenon makes more difficult the detection of an alcohol in the presence of a heavier distillate (7). Although not addressed in this study, in practice another common indicator of chromatographic distortion occurs when two carbon strips are exposed to the same sample for different time periods (e.g., one strip for two hours and the second strip for 16 h). A large change in pattern indicates that at least one recovered sample is distorted, while similar patterns for both strips suggests that recovery is suitable.

In spite of these cautionary notes, it should not be inferred that valid interpretations cannot be made with distorted data. The intent here is not to require further work to obtain a distortion-free chromatogram, but rather to alert the analyst to potential differences between recovered samples and liquid exemplars. While these guidelines derive from our experience with carbon strips, it is likely that

similar principles apply to samples recovered by solid phase microextraction (SPME) or other adsorptive methods.

To apply these guidelines the laboratory must first establish a saturation value for their analytical system by recovering and analyzing a few samples of known concentration. Once this has been accomplished, quality control procedures should be adequate to show that the total area under the chromatogram, the relative peak heights, and the peak positions are stable over time, or that changes can be accounted for. Whatever mixture is used for quality control procedures should include all the peaks used to calculate peak height ratios (e.g., Table 1), whether or not the identity of these peaks is explicitly known. Finally, it should be recognized that split-mode GC injectors often discriminate against the lighter components in a mixture, and that this effect tends to decrease the total peak area for those mixtures, such as gasoline, weighted towards lighter components. This effect should be monitored by analyzing a mixture containing constant amounts of light and heavy components. In our own laboratory, we have found a n-alkane series and SAM mix to be adequate for monitoring instrument performance.

Applications: Exemplar Characterization

The first application of Pyrographics was to characterize the liquids in our exemplar collection in terms of both qualitative features (Table 2A) and peak height ratios (Table 2B). The goal here was to assist the examiner in rapidly recognizing possible ignitable liquids in case samples. In these tables, the first column identifies the petroleum liquid in terms of the standard ASTM classifications (8)

followed by the number of exemplars in our laboratory falling in that class. Those peak ratios enclosed in parenthesis represent extreme examples and typically include outliers among our collection, while those ratios not enclosed should be interpreted to mean that most samples fall within the indicated range. In the case of gasoline, enclosed ratios represent all 61 samples in our collection, while the unenclosed figures represent the 21 samples collected most recently (in the Fall of 1996).

The characteristics listed in these tables do not include the standard ASTM classification criteria, although these still apply. It might be mentioned in passing, though, that not all exemplars represented in this table fall neatly into a single ASTM class. For instance, is a medium petroleum distillate lacking aromatics still a distillate, considering that it has undergone post-distillation treatment to remove objectionable odors? Further, the unmodified distillates in our collection do not always fall strictly into one of the ASTM distillate categories. Even isoparaffinic and naphthenic solvents may not fall neatly into separate classes, since isoparaffins sold under the Isopar trade name can contain up to 60% cyclics, while naphthenic solvents can contain as little as 35% cyclics (manufacturer's literature). This situation is not a problem, though, since the intent of Table 2 is not to uniquely categorize a sample, but rather to assist the analyst in locating an exemplar, which should then be compared to the unknown sample on a peak-by-peak basis. While others have employed peak height ratios to classify and identify petroleum liquids, we emphasize relying on such ratios primarily to assist the examiner in locating an exemplar as part of the overall pattern recognition process (1,4).

TABLE 2A—Distinguishing characteristics of ignitable liquids (qualitative features).

ASTM Class‡	Aromatics*	General Characteristics of Chromatograms†		
		Merged Aromatic Profile	Alkane Mass Chromatogram	TIC
automotive gasolines, n = 57	Y	Xylenes to Me ₂ Naphthalenes. Patterns consistent among gasolines.	(branched alkanes) ~/>> (n-alkanes). Major branched alkane peak under the P - 1 peak is common.	Dominated by aromatics for toluene and above.
aromatic solvents, n = 13	Y	Usually narrower range than gasoline.	(a) alkanes missing, or (b) alkanes present and (branched alkanes) << (n-alkanes).	dominated by aromatics.
MPD, n = 16	Y	Similar to gasoline, but P+1 peak sometimes enhanced.	(branched alkanes) ~/<< (n-alkanes)	dominated by paraffins + cyclics.
MPD, n = 16	N	N/A	(branched alkanes) ~/<< (n-alkanes)	dominated by paraffins + cyclics.
kerosene, n = 10	Y	Similar to gasoline, but P+1 peak sometimes enhanced. Me ₂ -Naphthalene complex present.	(branched alkanes) ~/<< (n-alkanes)	dominated by paraffins + cyclics.
kerosene, n = 10	N	N/A	branched alkanes ~/<< n-alkanes	dominated by paraffins + cyclics.
diesels, n = 9	Y	Similar to gasoline, but weighted to heavy ends. P+1 peak sometimes enhanced. Pronounced Me ₂ Naphthalene complex.	(branched alkanes) ~/<< (n-alkanes)	dominated by paraffins + cyclics.
isoparaffins, n = 16	N	N/A	n-alkanes missing.	Relatively simple compared to most petroleum liquids. Dominated by paraffins.
Naphthenic/paraffinic solvents, n = 9	N	N/A	(branched alkanes) ~/>> (n-alkanes)	V. complex. Dominated by paraffins + cyclics.

* Denotes whether aromatics are present. "Y" = yes and "N" = no.

† Inequality symbols refer to relative peak heights. i.e., "(branched alkanes) ~/>> (n-alkanes)" means that the peak heights of the branched alkanes are comparable to, to much greater than, those of the n-alkanes.

N/A: not applicable

‡ "n" denotes the number of exemplars considered for this class.

TABLE 2B—Distinguishing characteristics of ignitable liquids (quantitative features).

ASTM Class†	Aromatics Present†	Peak Height Ratios*							
		(C ₉)/(X)	HC #6/P	C ₁₀ /P	P + 1/P	I/P	HC #6/C ₁₀	t-alkanes/t-arom	t-cyclics/t-alkanes
automotive gasolines, n = 57	Y	0.16–0.64 (.13–1.9)	0.40–2.0 (.25–2.5)	.40–2.0 (.25–2.5)	.22–.33 (.22–.47)	.10–.24 (.10–.40)	.87–14 (.57–14)	.51–2.5 (.39–2.8)	.048–.36
aromatic solvents, n = 13	Y	<.01–>35, or N/A	<.02–.17	<.01–1.0	.10–3.1	.01–1.0	.19–.22§ or N/A	<.08–1.0 or N/A	.12–.15, or N/A
MPD, n = 16	Y	>20 (>8)	2–18	8–20 (5–40)	.28–1.1	.038–.25	.28–.50	5–40	.16–.56
MPD, n = 16	N	N/A	N/A	>200 (>70)	N/A	N/A	.25–1.6 (.02–1.6)	>65	.20–.40
kerosene, n = 10	Y	10–40 (6–40)	1.1–3.6	8–12	.40–1.0	.087–.23	.13–.31	8–15 (3.8–15)	.066–.23
kerosene, n = 10	N	N/A	N/A	>80 (>8)	N/A	N/A	.14–.35 (.14–.68)	>100	.15–.37
diesels, n = 9	Y	3–18	.60–4.3	7.8–18 (1.8–18)	.20–.72	.2–.4	.18–.36	10–24 (7–40)	.10–.20
isoparaffins, n = 16	N	N/A	N/A	N/A	N/A	N/A	N/A	>250	.031–.10
Naphthenic/Paraffinic solvents, n = 9	N	N/A	N/A	N/A	N/A	N/A	.5–5	>250 (>50)	.11–.41

* See Table 1 for peak definitions. Inequality symbols refer to relative peak heights. i.e., “(branched alkanes) ~/>> (n-alkanes)” means that the peak heights of the branched alkanes are comparable to, to much greater than, those of the n-alkanes.

N/A: not applicable (i.e., peaks absent).

† Denotes whether aromatics are present. “Y” = yes and “N” = no.

‡ “n” denotes the number of exemplars considered for this class.

§ Narrow range likely due to limited number of suppliers.

One of the more striking qualitative features observed in the merged aromatic chromatogram was the consistent occurrence of the characteristic dimethylnaphthalene (DMN) cluster for all diesel fuels (see Fig. 3). The single caveat to this statement is one exemplar in our collection (not included in Table 2) described as a wood oil. This product satisfied the ASTM criteria for a diesel fuel but was free of aromatics, evidently to avoid objectionable odors in its intended application. The DMN complex was also seen in all kerosenes except those which have been dearomatized, although it tends to be weaker in kerosenes than diesel fuels. An exception to this statement is a single kerosene in our collection depleted in naphthalene and methylnaphthalenes but still containing lighter aromatics. The occurrence of this complex in an unknown sample is thus one indication of a fuel oil.

Aside from the DMN complex, the merged aromatic profiles for different petroleum classes tend to be quite similar. The merged aromatic profile for gasoline is weighted towards lighter ends (i.e., xylenes) while diesel is weighted towards the naphthalene isomers, but as is well known, weighting is altered by evaporation during a fire. Compared to gasoline, the distillates often but not consistently exhibit an enhanced P + 1 peak, but in this context a single peak from a fire debris sample is hardly conclusive given the presence of extraneous pyrolysis products. These observations strongly suggest that an aromatic profile in itself is not sufficient evidence for classifying a petroleum liquid.

Another qualitative observation regards the merged aromatic profile for gasolines collected in 1996 compared to those collected two or more years earlier. By 1996 California had implemented the reformulated gasoline program, and this resulted in significantly lower levels of aromatics in the C₁₀–C₁₃ regions of the chro-

matogram. Nevertheless, the isomeric patterns were essentially unchanged and were still useful for identification.

The initial motivation for calculating peak height ratios was simply to distinguish between evaporated gasoline and aromatic solvents, the problem being that both materials exhibit a similar aromatic profile and low (t-alkanes):(t-arom) ratio. This subject has recently caused some consternation among arson analysts, at least when working with highly evaporated samples containing abundant pyrolysates. Recently Lothridge and coworkers (4) recommended that aromatic solvents could be distinguished by their lack of aliphatics, but examination of our exemplar collection showed this to be true only in some instances. Indeed, company literature reports that aromatic solvents may contain up to 30% paraffins, a claim consistent with our observations. The aromatic solvents in our collection basically fall into two classes: (a) those essentially free of paraffins, and (b) those containing a distillate fraction in addition to a dominant aromatic fraction. The latter can be distinguished from gasoline on the basis of the dominant n-alkanes in the alkane mass chromatogram; in comparison, in the gasoline mass chromatograms the branched alkanes are dominant or comparable in height to the n-alkanes. These observations are consistent with the ratios presented in Table 2B in that the (t-alkane):(t-aromatic) ratios for gasolines and aromatic solvents overlap, while the (HC#6):(C₁₀) and (HC#6):(P) ratios are distinctive. Regardless of which type of aromatic solvent is suspected, however, reference to the alkane mass chromatogram is needed for unambiguous identification.

Referring to Table 2B, it can be seen that the individual ratios for different petroleum liquids are frequently close or overlap. Thus, distinguishing different groups solely on the basis of a single ratio is a questionable approach, especially for fire debris samples com-

plicated by substrate pyrolysis products and recovery considerations. Given this situation, we have found the most useful approach is to consider all the criteria in the table in parallel to help identify a likely set of exemplars, rather than relying on a single characteristic. If this approach proves ineffective, revisit the table and consider the next most likely set of candidates. Flow chart approaches relying sequentially on individual characteristics should generally be avoided. In spite of these warnings, it is also clear that many ratios differ markedly and are useful for distinguishing various

petroleum classes. For instance, even given a badly distorted chromatogram, it is unlikely that an MPD would be mistaken for an evaporated gasoline.

Application to Questioned Samples

The samples discussed below are intended to illustrate the utility of GC/MS for resolving some of the more challenging cases received in our laboratory.

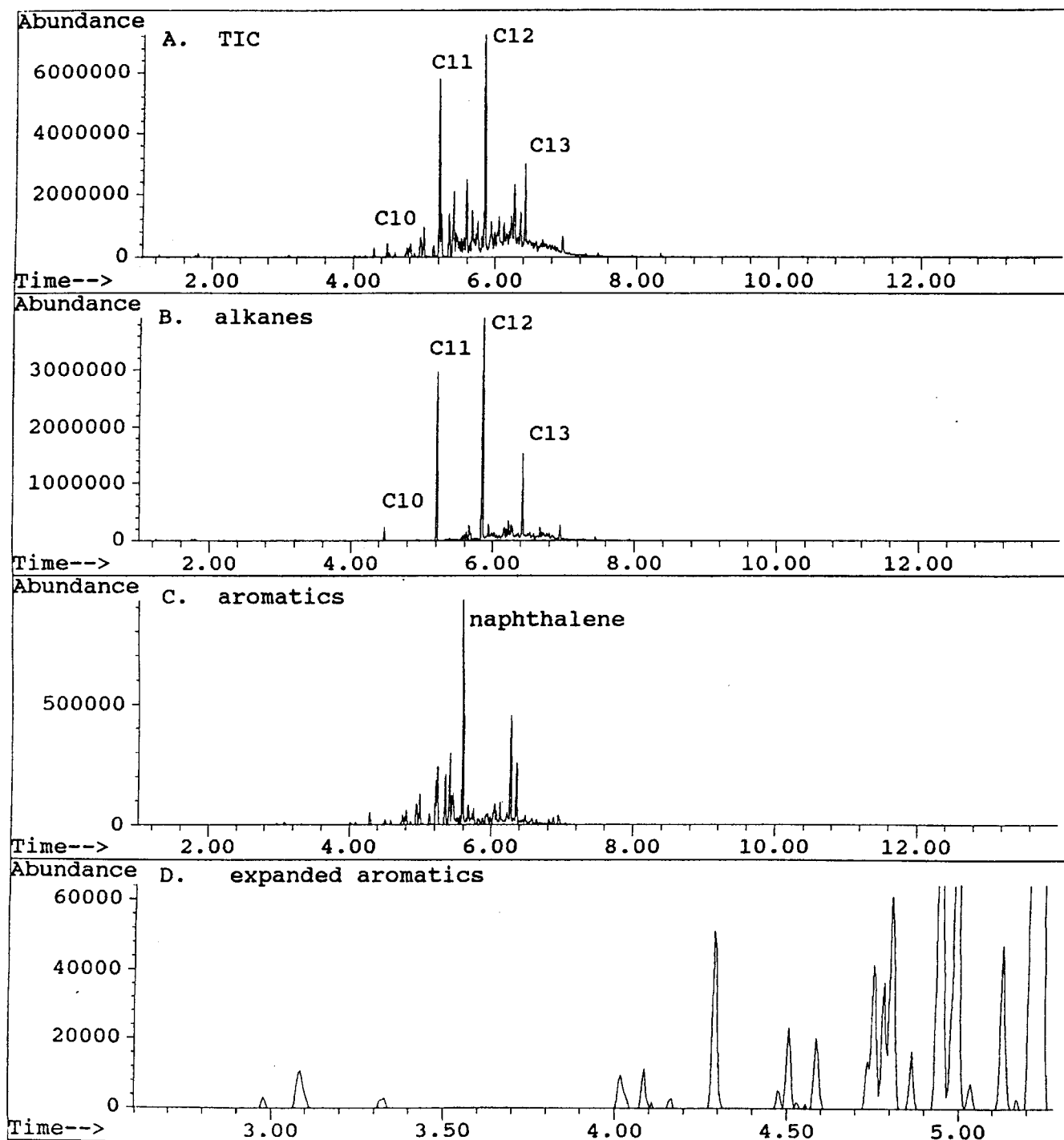


FIG. 9—TIC and mass chromatograms for Case I. This item does not contain a medium petroleum distillate but is consistent with evaporated gasoline and NCR forms.

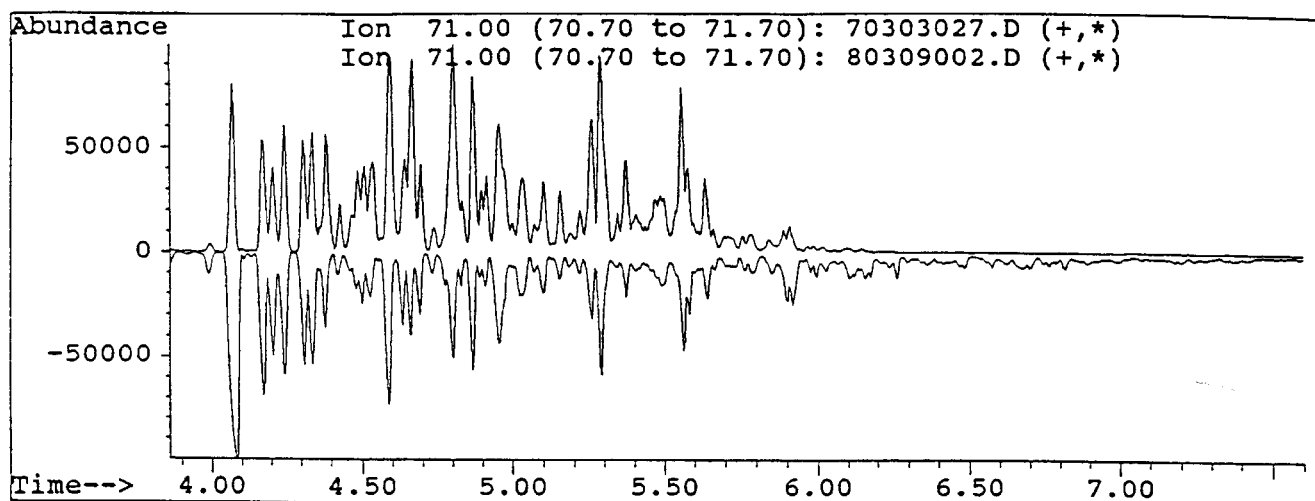


FIG. 10—Comparison of a case sample (positive chromatogram) and an isoparaffin charcoal starter (negative chromatogram).

Case I—This item was first analyzed primarily by GC/FID before our GC/MS software tools were developed, although a single SAE extract was analyzed and archived for later consideration. When the Pyrographic tools were available perhaps one year later, this case was revisited to test the utility of the new software.

This case item consisted of a 5-gallon paint bucket holding lightly charred papers. Because the lid had not been completely sealed, it was expected that the contents would be highly evaporated, although a strong petroleum odor was still present. Recovery by the SAE method and initial analysis by GC/FID yielded a bell-shaped chromatogram with major n-alkane peaks for C₁₁, C₁₂, and C₁₃, suggesting the presence of an evaporated medium petroleum distillate. However, an exhaustive search of the GC/FID chromatograms in our exemplar collection failed to find a match for the minor peaks in this sample, although some MPDs did contain n-alkanes through C₁₃. Further examination of the contents of the can revealed the presence of carbonless (“NCR”) business forms buried under other debris. These are known to contain n-alkane solvents, a fact confirmed by analysis of business forms from our stock room. When the n-alkanes were removed from consideration and the minor remaining peaks expanded to full scale, a typical gasoline pattern was recognized although an aromatic solvent could not be excluded in this instance.

Subsequent reduction of the archived GC/MS data using the Pyrographics programs resulted in the chromatograms shown in Fig. 9. As for the GC/FID data, the total ion chromatogram (TIC) resulted in prominent normal alkanes and a Gaussian shape, suggestive of an evaporated medium petroleum distillate. Reference to the alkane mass chromatogram, however, immediately ruled out the possibility since it was nearly devoid of branched alkanes. Equally important, the fine structure (minor peaks) in the TIC resembled the aromatic chromatogram (panel C) but showed no similarity to the minor alkane peaks—a feature also inconsistent with distillates. In addition, the (C₉:xylene) ratio was approximately 0.8, typical of a gasoline or an aromatic solvent. Closer examination of the aromatic mass chromatogram showed the presence of all major aromatic compounds from xylene to dimethylnaphthalenes in ratios consistent with highly evaporated gasoline. This is seen in part in the expanded aromatic mass chromatogram (panel D), but much more clearly in the merged aromatic profiles. (Unfortunately, the merged aromatic profiles could not be included in this paper due to

the need for color and the wide dynamic range encompassed.) In brief, the mass spectral approach led to the same conclusion as above, but in a much more direct and rapid manner. Of course, either approach requires the examiner to recognize the NCR forms as the source of normal alkanes. One lesson learned from this case was that a few n-alkanes along with a bell-shaped curve do not in themselves justify a finding of an MPD, ASTM guidelines notwithstanding (8).

Case II—When this sample of nondescript burned debris was recovered by the SAE method and analyzed by GC/MS, the alkane and cyclic mass chromatograms were both complex, roughly bell shaped, and nearly identical to each other. No n-alkanes were present, and the aromatic profile was essentially absent. These characteristics suggested a naphthenic/paraffinic solvent but excluded other petroleum liquids. However, because the (cyclic):(alkane) ratio for this sample was significantly higher than that of any exemplar in our collection, a naphthenic/paraffinic solvent was readily ruled out, and negative results were reported.

Case III—When this debris sample was recovered by the SAE method and analyzed by GC/MS, the resulting TIC and alkane mass chromatogram were essentially identical, with both exhibiting a series of peaks in the C₉ to C₁₂ region. These chromatograms were less complex than those of naphthenic solvents, and no n-alkane series was present. Cyclic compounds were nearly absent, and a (cyclic):(alkane) ratio of 0.05 was calculated. These results directed the analysts to search among the isoparaffin exemplars, where a match was rapidly found for this case item (Fig. 10). While this case could have been solved equally well by GC/FID alone, the additional information available from the mass chromatograms assisted the analyst in recognizing a pattern and facilitated a rapid interpretation of the data.

Case IV—Since asphalt shingles and tar paper are common construction materials deriving from the distillation of petroleum, it is important to demonstrate that these materials can be distinguished from common petroleum liquids that might be used as an accelerant. Accordingly, asphalt shingles and tar paper underlayment were obtained from a house being prepared for destruction as part of a fire department training exercise. Portions of these materials were

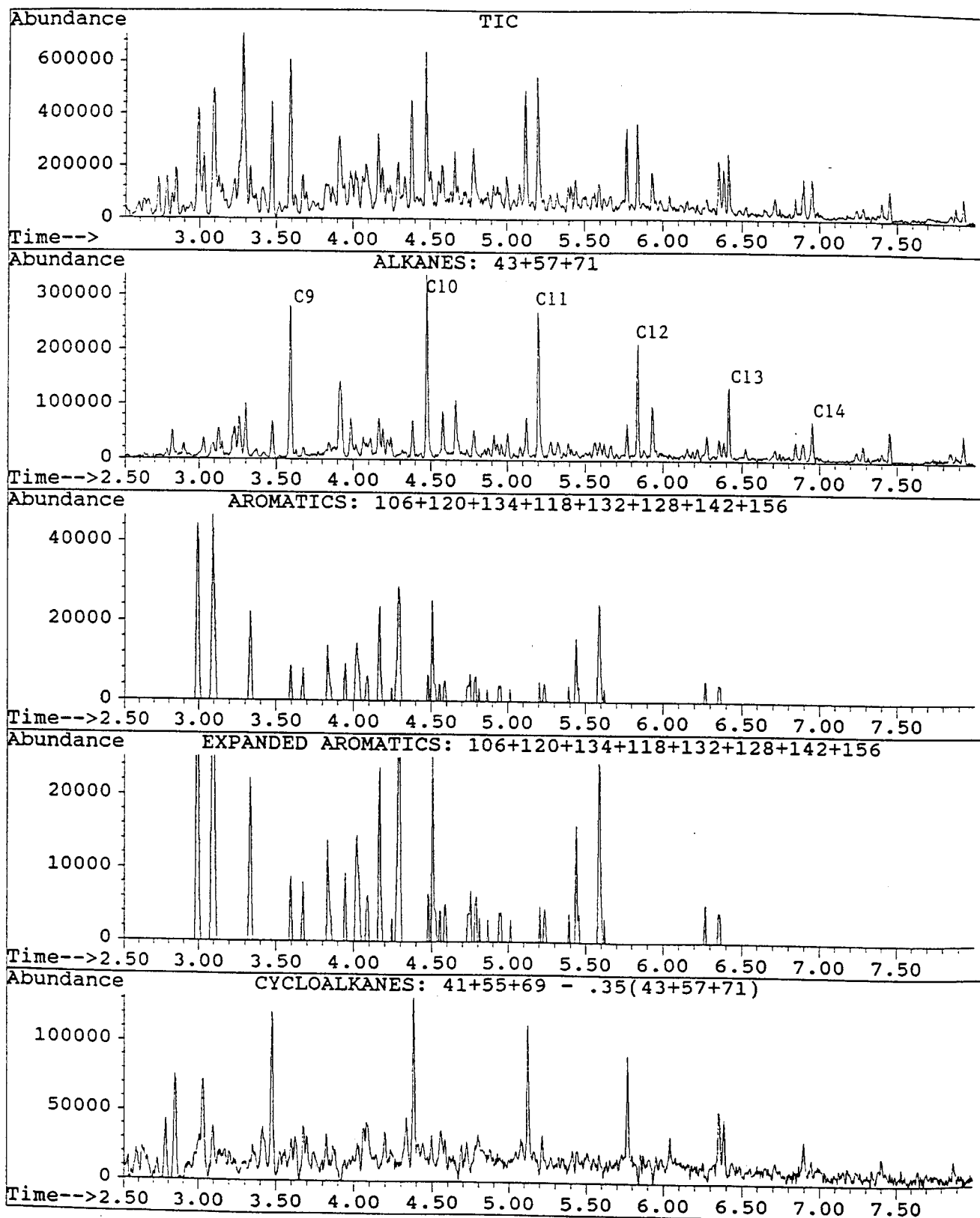


FIG. 11—Mass chromatograms of pyrolyzed asphalt shingles and tar paper.

pyrolyzed as describe above, and two pyrolyzed and one unpyrolyzed sample were recovered by the SAE method and analyzed by GC/MS. The unpyrolyzed sample yielded no significant peaks, and one of the pyrolyzed samples yielded a complex chromatogram with no recognizable pattern. However, the second pyrolyzed sample resulted in an alkane mass chromatogram exhibiting a bell-shaped n-alkane series from C₈ to C₁₇, typical of kerosene (Fig. 11). The C₁₇ and C₁₈ peaks were too weak to ascertain whether the phytane and pristane peaks were present, and a (t-cyclic):(t-alkane) ratio of 0.4 was somewhat high but not unreasonable for a distillate fuel. What distinguished this sample from a distillate, though, was a series of alkenes appearing in the cyclic mass chromatogram and a series of corresponding doublets in the TIC. Equally important, the minor peaks in the alkane mass chromatogram did not match any exemplar in our collection. Thus, by considering the totality of the data, the analyst should not mistake pyrolyzed asphalt or tar for a petroleum fuel. Similar results have recently been reported by Lentini, who also noted the value of the m/z 83 ion for distinguishing distillates from pyrolyzed asphalt (9).

A similar experiment was performed with a pyrolyzed polyolefin garbage bag, a material chemically similar to asphalt. However, the resulting patterns were quite distinct from a petroleum liquid. In particular, the TIC was dominated by a series of multiplex peaks, and the cyclic mass chromatogram exhibited a pronounced alkene series (again, similar to results reported by Lentini). Further, the (cyclic):(alkane) ratio in this instance was 1.7, far larger than that of any exemplar in our collection.

Case V—This case item yielded an alkane mass chromatogram with a series of n-alkane peaks from C₉ to C₁₈ following a roughly bell-shaped curve, suggestive of a fuel oil. This series of n-alkanes was also visible as a minor component in the TIC, which was apparently dominated by pyrolysates. However, no supporting evidence for a fuel oil could be found: First, the “fine structure” (the small peaks between the n-alkanes) did not match any exemplar in our collection. And second, the merged aromatic profile was distorted or absent. Without such supporting evidence, it was felt that the observed pattern might derive from pyrolyzed polyolefin or asphalt, and negative results were reported.

Case VI—This item consisted of unused flooring that was intentionally pyrolyzed in our laboratory and recovered by the SAE method. The identity of this material, which was taken from what appeared to be a salesperson’s set of flooring samples, was uncertain but appeared to be a vinyl linoleum with a foam backing. Although no petroleum liquid was added, many of the aromatics found in petroleum were observed in this pyrolyzed material (Fig. 12). Especially noteworthy is that isotopic pattern of the so-called “castle group” (C₃-alkyl benzenes near 4.0 min) mimics that found in petroleum liquids. It might also be noted that the dimethylnaphthalene group is similar to that seen in diesels (Fig. 3), but careful inspection shows this group to be visibly distorted. Nevertheless, this pattern is readily distinguished from a petroleum liquid because the patterns of the other isomeric groups are seriously distorted or are entirely missing. Further, the alkane and TIC mass

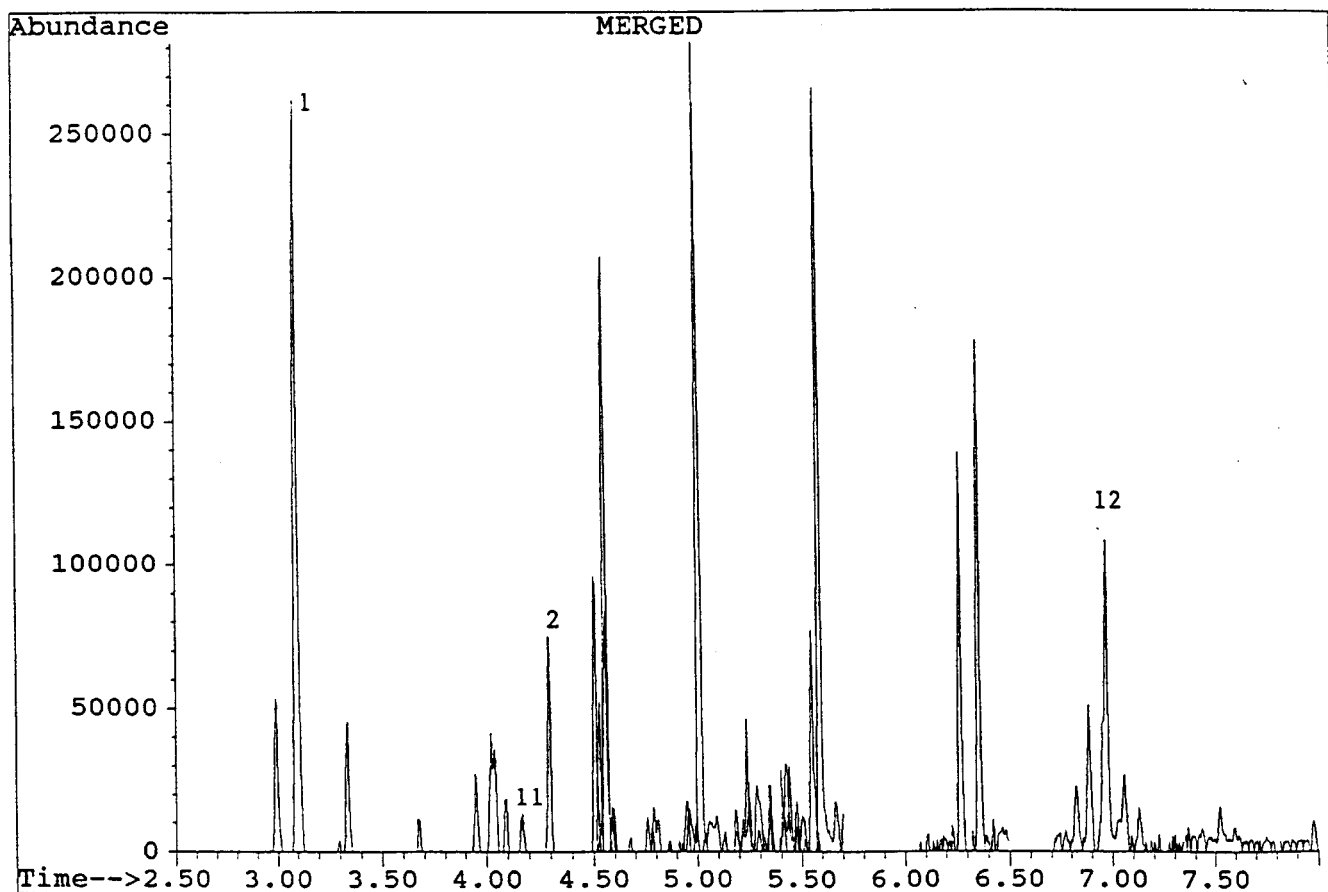


FIG. 12—Merged aromatic profile from the pyrolysis of cushioned “linoleum” floor covering.

chromatograms do not resemble those of a petroleum liquid. This example is included to illustrate the importance of displaying all the aromatic isomer groups on the same scale when analyzing fire debris samples.

Case VII—This case item consisted of a slightly charred carpet from a suspected arson site. When recovered by the SAE protocol and analyzed by GC/MS, the TIC was typical of gasoline but the (alkane):(aromatic) ratios were atypically low, suggesting that an aromatic solvent should be considered as a possible source. However, because the total chromatographic area for this sample was approximately 60% of saturation, some distortion might be expected. More importantly, though, the alkane mass chromatogram was consistent with a gasoline exemplar but inconsistent with the aromatic exemplars in our collection. For this reason it was concluded that gasoline was present in this sample. This example illustrates the importance of relying on the overall chromatographic pattern, as opposed to a few isolated ratios.

Case VIII—This case item consisted of a dark liquid, apparently water, possibly contaminated with a petroleum liquid. Sample recovery was by solvent extraction, followed by volume reduction and initial analysis by GC/FID. The C₂- and C₃-alkylbenzene regions of the chromatogram were typical of gasoline, but later regions of the chromatogram, which are essential for identification, were partly masked by apparent pyrolysates. Subsequent analysis by GC/MS resulted in clear aromatic and alkane mass chromatograms consistent with a gasoline exemplar, thereby enabling the detection of gasoline in this sample.

Summary

Much of the literature regarding the GC/MS analysis of fire debris tends to focus on the ability of this method to better discern petroleum liquids in the presence of complex pyrolysis mixtures, that is to say, on the lower false negative rates achievable with GC/MS compared to GC/FID alone. In routine casework this promise is indeed often realized, especially in those borderline situations where the petroleum liquid is partially but not entirely

masked by pyrolysis products (e.g., Case VIII, above). From a practical point of view, though, an equally important advantage is that GC/MS analysis greatly expedites the data interpretation phase of casework. Rather than puzzling over a GC/FID chromatogram or exhaustively searching exemplar collections, the examiner can simply run a questionable sample by GC/MS, and the extra information then available often suffices to allow the examiner to rapidly arrive at a firm conclusion.

Acknowledgments

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