Jack Nowicki,[1] *M.S.*

An Accelerant Classification Scheme Based on Analysis by Gas Chromatography/Mass Spectrometry (GC-MS)

ABSTRACT: Gas chromatography/mass spectrometry (GC-MS) using ion chromatography profiling allows the arson examiner to gather information about the chemical nature of the hydrocarbons present in a fire debris sample. Fragment ions have been identified that provide specific analyses for alkanes, cycloparaffins, aromatics, naphthalenes, and dihydroindenes. An accelerant classification scheme currently used only classifies accelerants by their boiling point ranges into light, medium, and heavy petroleum distillates and gasoline. Many flammable liquids do not properly fall into one of these categories. An expanded accelerant classification scheme that takes into account the chemical nature of the accelerant, in addition to its boiling point range, is described here.

One of the most challenging problems a forensic chemist faces is to analyze the debris collected from the scene of a suspected arson fire for residue of a flammable liquid. A fire debris sample is processed in three steps. First, the chemist must isolate from the debris any volatile hydrocarbons that may be the remains of a liquid accelerant. Next, the chemist analyzes the extract by gas chromatography (GC). Finally, the chemist interprets the gas chromatogram and determines whether the sample contained a flammable liquid. Each step of the analysis is crucial; if the analyst mishandles any step, an improper conclusion, either a false negative or false positive finding, can result. This point was demonstrated in a recent collaborative test consisting of 4 samples in which, out of the 73 laboratories that responded, 65 laboratories misidentified at least 1 of the samples [1].

The techniques used to extract and analyze fire debris samples for accelerant residues are the subject of many articles. Review articles by Midkiff [2] and by Brettell and Saferstein [3–5] chronicle how arson analysis in the laboratory has evolved. The technique most widely used for extracting hydrocarbons from fire debris is dynamic headspace sampling (also known as purge-and-trap or absorption-elution). This technique detects the entire boiling point range of hydrocarbons found in flammable liquids with a sensitivity that is unmatched by other techniques, although it does not recover alcohols or other oxygenated compounds as effectively. In those cases, the technique of static headspace sampling can be utilized, or the chemist can wash the debris with a small amount of a solvent, such as pentane or carbon disulfide. The technique of solvent extraction is

particularly suitable for small nonporous materials such as glass fragments or concrete chips.

The forensic chemist's essential tool for analyzing the complex hydrocarbon mixtures that comprise most flammable liquids is gas chromatography. As the development of the dynamic headspace technique has added sensitivity, chromatographic resolution has been improved with the introduction of capillary GC columns. Over 80% of the laboratories that responded to the collaborative test indicated that they utilized capillary columns rather than packed columns.

Traditionally, gas chromatographs used for the analysis of fire debris samples have been equipped with the low-cost, nonspecific flame ionization detector (FID). The chemist compares the FID chromatogram of the fire debris extract with the chromatographic patterns of known flammable liquid standards. If the chemist finds a standard that matches the unknown pattern, he can conclude that a particular type of flammable liquid was present. However, this comparison is not always simple. The chromatogram of the extract may not reflect the presence of an accelerant, but could be caused by the burnt debris itself. This is often the case when the debris is a synthetic material, such as carpeting, foam padding, or floor tile. These types of materials will break down when subjected to the extreme heat of a fire and will create pyrolysis products that will appear as peaks in the chromatogram. Some of these pyrolysis products may even be the same chemicals that are commonly found in flammable liquids. The peaks that originate from the burnt debris can obscure peaks from an added accelerant, making it difficult to compare the pattern directly with the standards and to identify the accelerant used. Patterns produced by pyrolysis products sometimes can be differentiated from those of flammable liquids when capillary columns are used, but inconclusive results will still be common.

The ideal GC detector will be specific to the hydrocarbons found in flammable liquids, yet will ignore the pyrolysis products from the debris. The detector that best accomplishes this is the mass spectrometer.

Gas Chromatography/Mass Spectrometry (GC-MS) In Arson Analysis

One way the chemist can use GC-MS for fire debris analysis is to identify every component in the sample. Modern GC-MS systems have data stations with built-in libraries of reference mass spectra. However, the mass spectra of two hydrocarbons that are very close in chemical structure may be almost identical and the data station may not be able to distinguish between different isomeric forms of a hydrocarbon. The chemist needs further information, such as the peak's retention index, before making an unequivocal identification. Therefore, identifying every component can be a time-consuming process which still does not make it easier for the chemist to compare the chromatogram with known standards.

TABLE 1—*Characteristic fragment ions for the hydrocarbon chemical classes.*

Chemical Class	Fragment Ions
Alkanes	57,71,85,99
Cycloparaffins	55,69,83,97
Aromatics	91,105,119,133
Naphthalenes	128,142,156
Dihydroindenes	117,131,145,159
Terpenes	93,136

The chemist can utilize GC-MS more effectively by using the technique of ion chromatography profiling. In this technique the chemist first identifies the molecular weight of those ion fragments that are most characteristic of the hydrocarbons found in accelerants. The GC-MS data station then replots a chromatogram that displays only those peaks which contain the ion fragments of interest. Peaks are eliminated if they do not contain those characteristic ion fragments. This technique was first applied to fire debris analysis by Smith [6], who termed it "mass chromatography." The ion fragments which are characteristic of the various classes of hydrocarbons found in accelerants have been discussed by several authors [6–8] and are summarized in Table 1.

Identification and Classification of Flammable Liquids

After obtaining a chromatogram, the chemist must interpret the data and identify the nature of the flammable liquid. This is the area that has received the least attention in the literature. Most papers that have discussed the analysis of fire debris by gas chromatography have relied on direct visual comparison of the unknown sample with chromatograms of known standards to identify an accelerant. Two papers have discussed identifying accelerants through computer-assisted treatment of GC and GC-MS data [9,10].

An accelerant classification scheme is currently used within the forensic science community which divides flammable liquids into five general classes, based primarily on their boiling point ranges [11,12]. This classification system was developed prior to the introduction of the GC-MS techniques and is concerned primarily with where the peaks lie and not with what type of chemicals they indicate. This type of classification scheme is obsolete in light of the additional information that can be obtained by GC-MS analysis. An accelerant can be classified more precisely by its chemical nature rather than by its boiling point alone.

The boiling point range of chemicals appearing in the sample extract can be affected by several factors, such as the presence of additional peaks due to pyrolysis products of the fire debris, along with loss of the lower boiling point fractions as a result of weathering of the accelerant during the fire. These changes create the potential for the chemist to misclassify the accelerant or, worse, to identify an accelerant when none is present. The arson examiner needs an accelerant classification scheme that takes into account the chemical composition of a flammable liquid. This type of scheme has been discussed by Bertsch et al. [13] and by Holzer and Bertsch [14].

This paper will describe an updated system for the classification of accelerants based on GC-MS analysis, focusing on selected fragment ions which are characteristic of the types of hydrocarbons found in common flammable liquids.

Experimental Procedure

A Hewlett-Packard 5890 gas chromatograph and 5870 mass selective detector (MSD) were used. The data were collected by a ChemStation equipped with Revision 3.2 software.

The gas chromatographic conditions were as follows:

    Column: 40-m by 0.18-mm DB-1, 0.4-mm film thickness
    Injector temperature: 250°C
    Transfer line temperature: 280°C
    Oven temperature: 50°C initially for 5 min
                        Ramp 5°/min to 250°C
                        Hold at 250°C for 15 min
    Carrier gas: helium at 20 psi (138 kPa)
    Split ratio: 35:1

Liquid samples were run. They were prepared by diluting 5 µL of sample with 10 drops of carbon disulfide. Ion chromatograms for each of the chemical classes of interest were generated through the use of a ChemStation macro program written by this author. The retention indices of the hydrocarbons were calculated using ChemStation Revision 3.1 software.

Discussion

An accelerant classification scheme based on the boiling point range and chemical composition of the flammable liquid is presented in Table 2. Each class is discussed in further detail below.

TABLE 2—*Accelerant classification guidelines.*

Class	Hydrocarbon Range[a]	Chemical Criterion
Light petroleum distillates	C5 to C11	alkanes: characteristic pattern cycloparaffins: characteristic pattern aromatics: benzene to C9 aromatics naphthalenes: none
Light petroleum-based product	C5 to C11	alkanes: may be present cycloparaffins: may be present aromatics: may be present naphthalenes: none other: alcohols, acetates, or ketones may be present
Gasoline	C5 to C14	alkanes: present but variable cycloparaffins: not significant aromatics: characteristic pattern naphthalenes: characteristic pattern dihydroindenes: characteristic pattern
Medium petroleum distillates	C8 to C12	alkanes: characteristic n-alkanes cycloparaffins: characteristic pattern aromatics: not significant naphthalenes: not significant
Isoparaffin products	C7 to C14	alkanes: characteristic isoparaffins cycloparaffins: none aromatics: none naphthalenes: none
Heavy petroleum distillates I	C8 to C18	alkanes: characteristic n-alkanes cycloparaffins: not significant aromatics: may be present naphthalenes: may be present
Heavy petroleum distillates II	C9 to C23	alkanes: characteristic n-alkanes cycloparaffins: none aromatics: may be present naphthalenes: may be present

[a]These ranges represent the extreme limits for the class. Many products will exhibit narrower ranges than those listed.

Light Petroleum Distillates

The previous definition of a light petroleum distillate (Class 1 accelerant) as containing "at least 4 major peaks in the C4 to C6 range and no major peaks above C8 or toluene" is not appropriate for several reasons:

1. In any sample for which solvent extraction or absorbent-elution with carbon disulfide is performed, most of the C4 to C6 region will be obscured by the solvent. With the Hewlett-Packard GC-MSD, the detector cannot be turned on until the solvent has passed through the column.
2. The upper limit of *n*-octane or toluene is arbitrary and not realistic.
3. The term "petroleum distillate" implies a narrow boiling point range cut of crude oil from the refinery. It is not proper to use this term for products that contain chemicals not derived from a petroleum source [15], or where the distillate fraction has been chemically modified by refinery operations such as alkylation, reformation, or catalytic cracking.

An example of a light petroleum distillate fraction, called "straight run gasoline" at the Mobil Oil refinery, is presented in Fig. 1. The retention indices of its major peaks are labeled on the chromatogram and can be identified by referring to the retention indices of the hydrocarbons listed in Table 3. A light petroleum distillate fraction exhibits the following compositional features: the alkanes before *n*-octane are present and can extend as far as *n*-undecane. Cycloparaffins from C6 to C9 will be present. Aromatics from benzene through the C9 aromatics can be found.

Examples of three commercial products that can be classified as light petroleum distillates are given in Figs. 2, 3, and 4. Note that there is a great deal of consistency in each of their alkane, cycloparaffin, and aromatic ion chromatograms and that they can be related to the light fraction refinery sample.

Light Petroleum-Based Products

This class encompasses commercial products whose components fall into the same boiling point range as the light petroleum distillates but whose chemical composition differs significantly from that class of accelerant. Examples of this class include a product in which the aromatic component has been significantly increased in relation to the alkane and cycloparaffin components (Fig. 5), or products to which compounds such as alcohols, acetates, or ketones have been added to the distillate fraction (Figs. 6 and 7). Many lacquer thinners and commercial solvents will fall into this class.

Gasoline

Examples of gasoline are presented in Figs. 8 and 9. Aromatics are the most abundant hydrocarbon class in gasoline and provide the best criterion for its identification. The region of the C9 to C11 aromatics is particularly useful as it is consistent within different samples of gasoline and is detectable in even highly weathered gasoline samples. Napthalene and the methyl and dimethyl naphthalenes form a pattern that is characteristic and essential for the identification of heavily weathered gasoline samples. The dihydroindene series, while not a major component of gasoline, does give a consistent pattern, which is especially noticeable in weathered gasoline (Fig. 10).

Alkanes and cycloparaffins are not useful in the identification of gasoline. The cycloparaffin content of gasoline is negligible. Alkanes are present but can vary greatly in proportion from sample to sample. It is important to recognize, however, that the *n*-
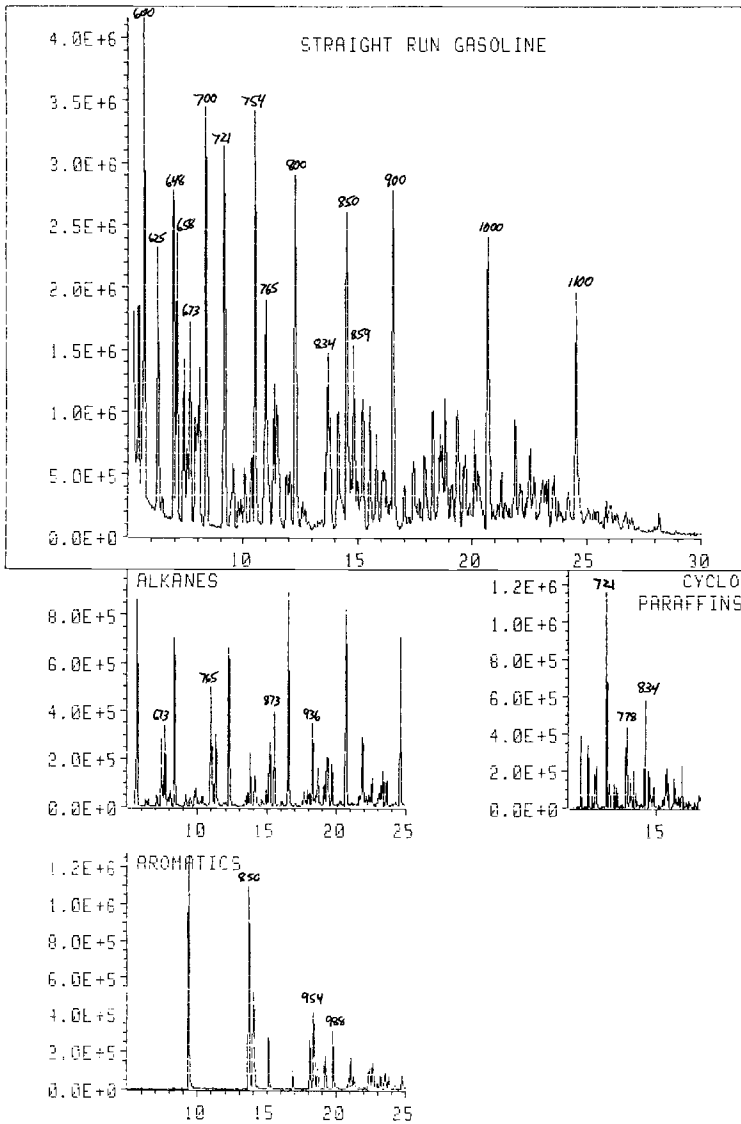
FIG. 1—*Chromatogram and ion chromatography profiles of straight run gasoline (Mobil).*

alkanes are normally found in gasoline and that their presence does not necessarily signify that a medium or heavy petroleum distillate has been mixed with the gasoline.

Medium Petroleum Distillates

The medium distillate refinery cut of petroleum consists primarily of alkanes and cycloparaffins. If aromatics are present, their concentration will be small in relation to that of the aliphatic compounds. A medium petroleum distillate is characterized by a "bell-shaped" chromatogram with prominent *n*-nonane, *n*-decane, *n*-undecane, and sometimes *n*-dodecane peaks (Fig. 11). Paint thinners and mineral spirits are the primary examples of this class.

TABLE 3—*Kovats retention indices for hydrocarbons found in accelerants.*

Compound	Retention Index	Compound	Retention Index
Alkanes			
3-Methylpentane	578	n-Octane	800
n-Hexane	600	2,3,5-Trimethylhexane	817
2,2-Dimethylpentane	621	2,2-Dimethylheptane	820
2,4-Dimethylpentane	626	2,2,3-Trimethylhexane	824
3,3-Dimethylpentane	653	2,4-Dimethylheptane	830
2-Methylhexane	664	2,6-Dimethylheptane	837
2,3-Dimethylpentane	667	3,3-Dimethylheptane	840
3-Methylhexane	673	2,3-Dimethylheptane	858
3-Ethylpentane	685	4-Ethylheptane	862
n-Heptane	700	2-Methyloctane	866
2,5-Dimethylhexane	730	3-Methyloctane	873
2,4-Dimethylhexane	733	n-nonane	900
3,3-Dimethylhexane	740	4,4-Dimethyloctane	927
2,3-Dimethylhexane	759	2,6-Dimethyloctane	936
2-Methylheptane	765	4-Methylnonane	963
4-Methylheptane	766	5-Methylnonane	966
3,4-Dimethylhexane	769	n-Decane	1000
3-Methylheptane	773	n-Undecane	1100
3-Ethylhexane	774		
Cycloparaffins			
Methylcyclopentane	625	1,2-Ethylmethylcyclopentane	791
Cyclohexane	658	1t2-Dimethylcyclohexane	798
1,1-Dimethylcyclopentane	671	1t3-Dimethylcyclohexane	805
1c3-Dimethylcyclopentane	682	1c2-Dimethylcyclohexane	829
1t3-Dimethylcyclopentane	684	n-Propylcyclopentane	832
1t2-Dimethylcyclopentane	688	Ethylcyclohexane	834
Methylcyclohexane	721	1,1,3-Trimethylcyclohexane	839
1,1,3-Trimethylcyclopentane	723	1,1,4-Trimethylcyclohexane	842
Ethylcyclopentane	732	1,3,5-Trimethylcyclohexane	854
1,2,4-Trimethylcyclopentane	740	1,2,4-Trimethylcyclohexane	878
1,2,3-Trimethylcyclopentane	747	1,2-Methylpropylcyclopentane	887
1c3-Dimethylcyclohexane	778	1,3-Ethylmethylcyclohexane	891
1t4-Dimethylcyclohexane	779	1,2-Ethylmethylcyclohexane	909
1,1-Dimethylcyclohexane	786	i-Propylcyclohexane	921
1,3-Ethylmethylcyclopentane	790	n-Propylcyclohexane	932
Aromatics			
Benzene	648	1-Methyl-3-n-propylbenzene	1044
Toluene	754	1,4-Diethylbenzene	1049
Ethylbenzene	850	n-Butylbenzene	1049
p-Xylene, m-xylene	859	5-Ethyl-1,3-dimethylbenzene	1051
o-Xylene	882	1,2-Diethylbenzene	1054
i-Propylbenzene	915	1-Methyl-2-n-propylbenzene	1060
n-Propylbenzene	945	2-Ethyl-1,4-dimethylbenzene	1070
1,3-Ethylmethylbenzene	954	4-Ethyl-1,3-dimethylbenzene	1072
1,4-Ethylmethylbenzene	956	4-Ethyl-1,2-dimethylbenzene	1079
1,3,5-Trimethylbenzene	962	2-Ethyl-1,3-dimethylbenzene	1085
1,2-Ethylmethylbenzene	971	3-Ehtyl-1,2-dimethylbenzene	1098
1,2,4-Trimethylbenzene	988	1,2,4,5-Tetramethylbenzene	1111
sec-Butylbenzene	1003	1,2,3,5-Tetramethylbenzene	1116
1,2,3-Trimethylbenzene	1015	1,2,3,4-Tetramethylbenzene	1148
1,3-Diethylbenzene	1041		

TABLE 3—*Continued.*

Compound	Retention Index	Compound	Retention Index
Naphthalenes			
Naphthalene	1179	1,4-Dimethylnaphthalene	1420
2-Methylnaphthalene	1293	2,3-Dimethylnaphthalene	1424
1-Methylnaphthalene	1309	1,2-Dimethylnaphthalene	1441
2-Ethylnaphthalene	1392	1,8-Dimethylnaphthalene	1457
2,6-Dimethylnaphthalene	1395	2,3,6-Trimethylnaphthalene	1529
1,7-Dimethylnaphthalene	1406	2,3,5-Trimethylnaphthalene	1536
Dihydroindenes			
Dihydroindene	1027	Methyl dihydroindene	1146
Methyl dihydroindene	1134		
Other Compounds			
Methyl ethyl ketone	560	Cellosolve acetate	878
Ethyl acetate	586	*n*-Amyl acetate	900
i-Butanol	610	alpha-Pinene	937
n-Butanol	642	Chlorotoluene	942
2-Hexanone	766	beta-Pinene	980
Butyl acetate	795		

Isoparaffin Products

In the past few years, several products have appeared on the market that consist solely of isoparaffins (branched alkanes). These Isopars are catalytically synthesized, and therefore, it is improper to refer to them as petroleum distillates. They contain essentially no aromatics, cycloparaffins, or *n*-alkanes. They are being used increasingly in such products as charcoal starter fluids and odorless paint thinners because of their improved stability and lack of odor. Examples are found in Figs. 12 and 13.

Heavy Petroleum Distillates

Like medium petroleum distillates, heavy petroleum distillates are readily characterized by their *n*-alkane pattern. Where medium petroleum distillates exhibit a fairly symmetrical and narrow "bell shape," heavy petroleum distillates contain a much broader boiling point range of compounds.

The previous classification scheme divided heavy petroleum distillates into two subclasses, based primarily on how far the *n*-alkane series extended. It is possible to make such a distinction between heavy petroleum distillates, although it is also possible that there will be products that will overlap classes.

One class of heavy petroleum distillate is similar to the medium petroleum distillates in that *n*-nonane, *n*-decane, and *n*-undecane are prominent peaks. The difference is that the pattern will continue past *n*-dodecane, sometimes as far as C17 or C18. This class may also contain a significant aromatic component whose pattern will be very similar to that of gasoline (Fig. 14). Kerosene and some brands of charcoal starter fluids fall into this class.
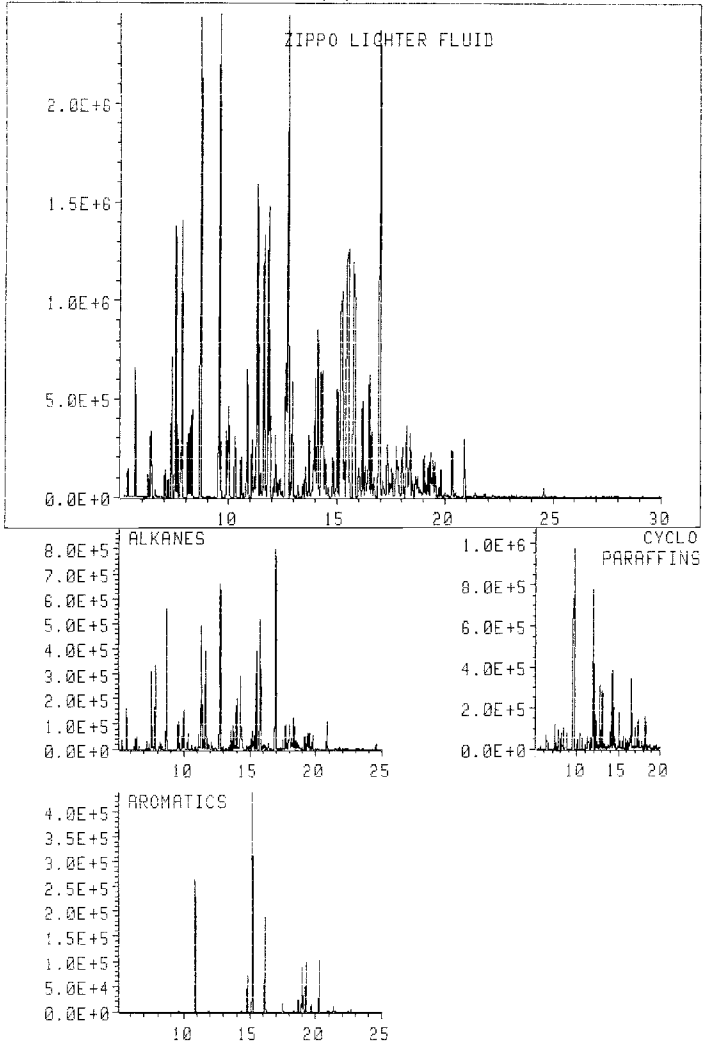
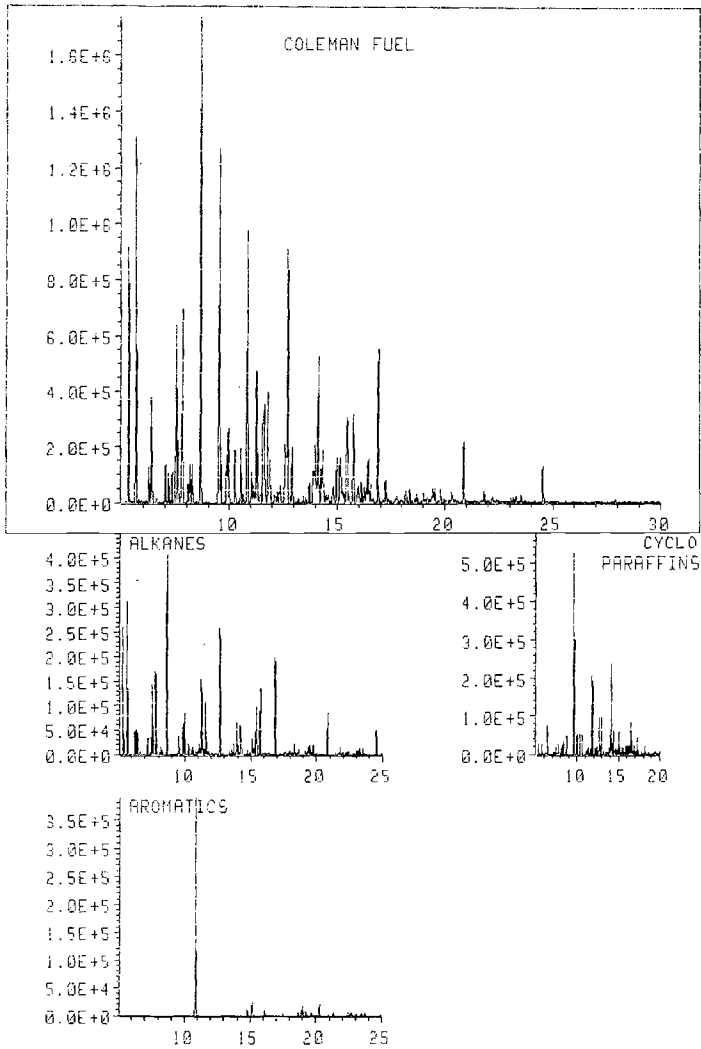FIG. 2—*Chromatogram and ion chromatography profiles of Zippo lighter fluid.*

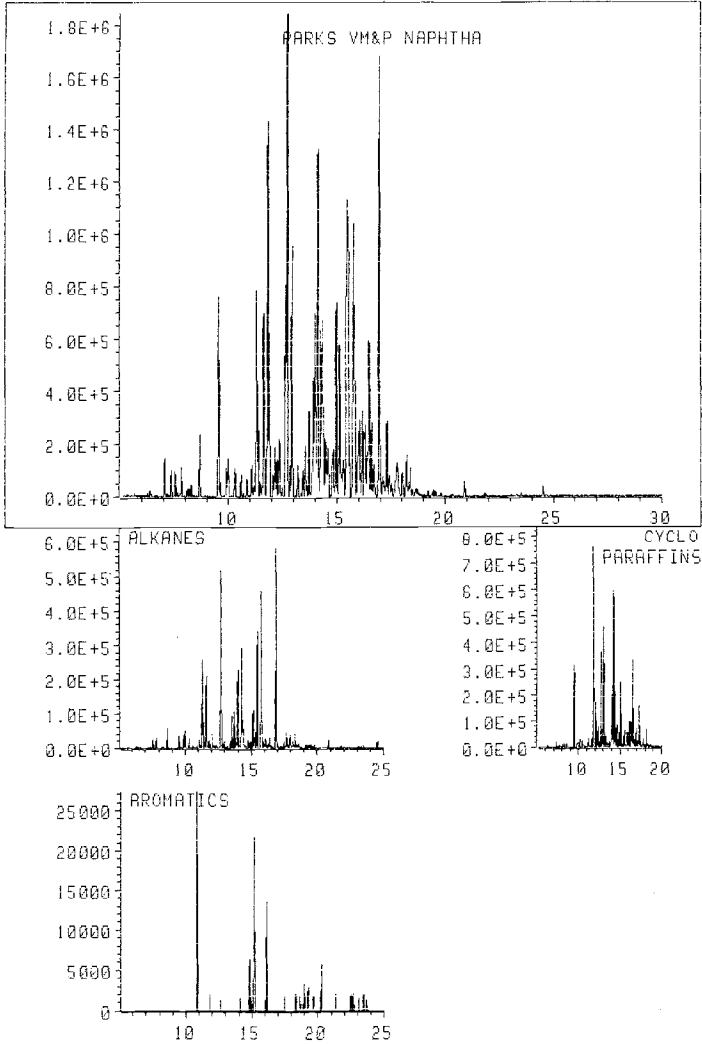FIG. 3—*Chromatogram and ion chromatography profiles of Coleman fuel.*

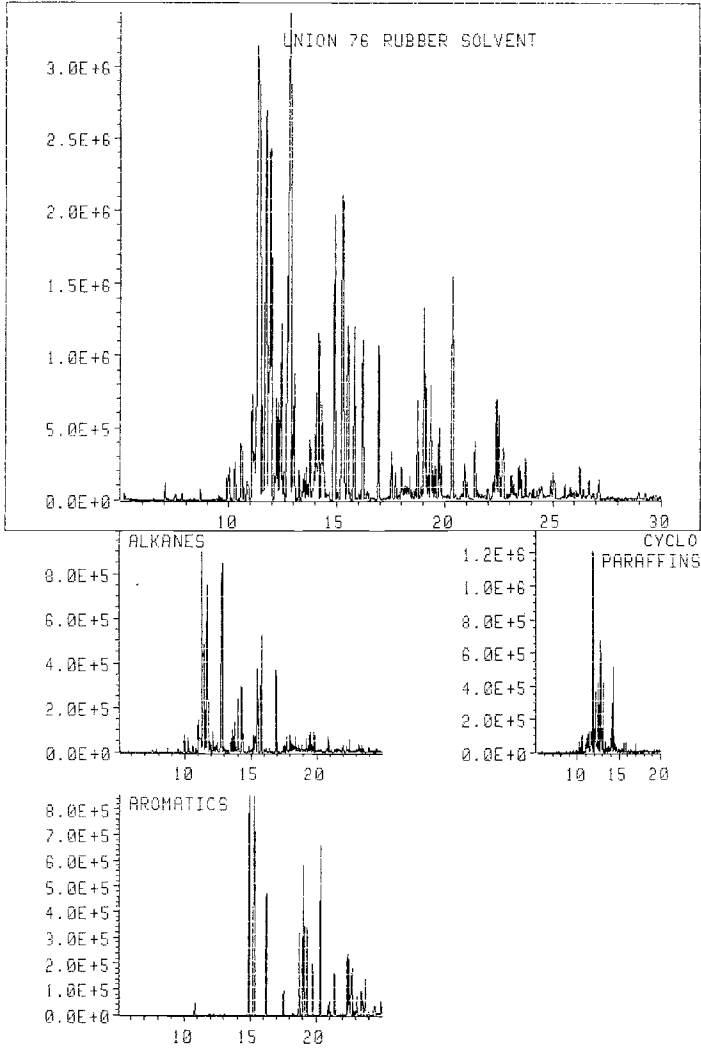FIG. 4—*Chromatogram and ion chromatography profiles of Parks VM & P naphtha.*

FIG. 5—*Chromatogram and ion chromatography profiles of Union 76 rubber solvent.*
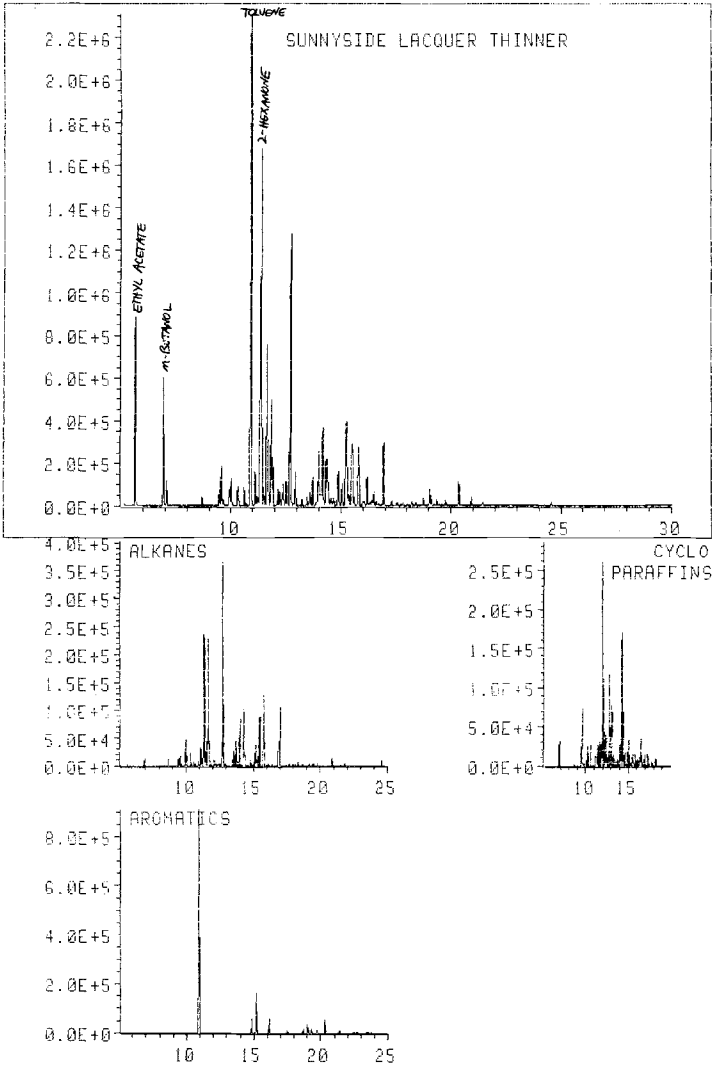
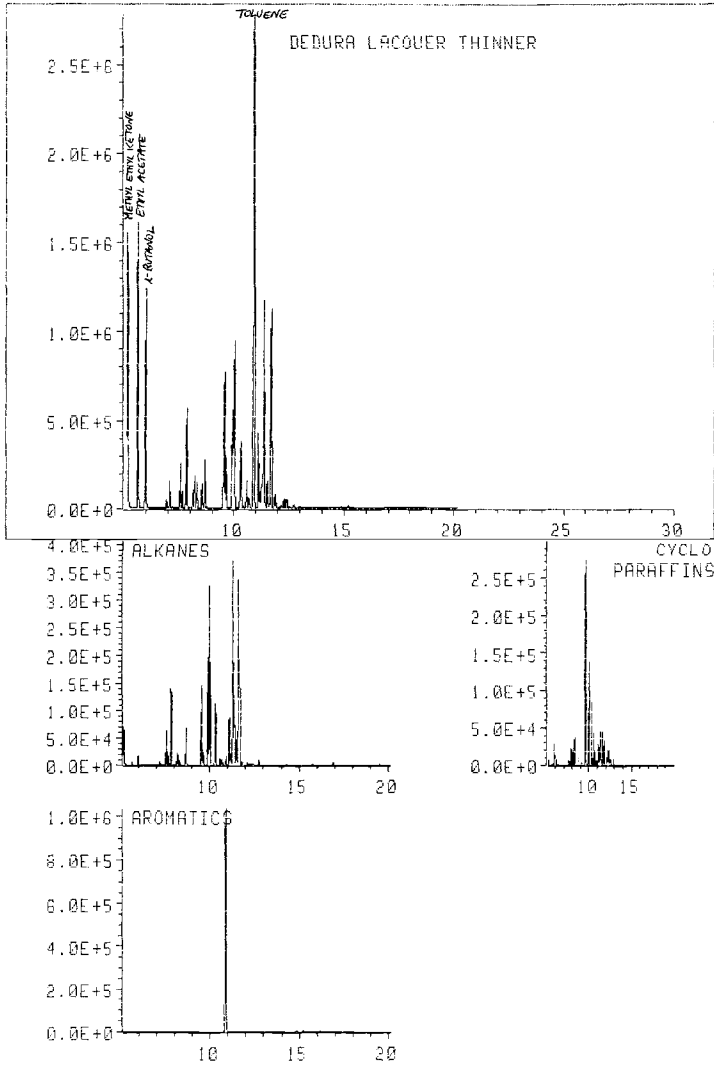FIG. 6—*Chromatogram and ion chromatography profiles of Sunnyside lacquer thinner.*

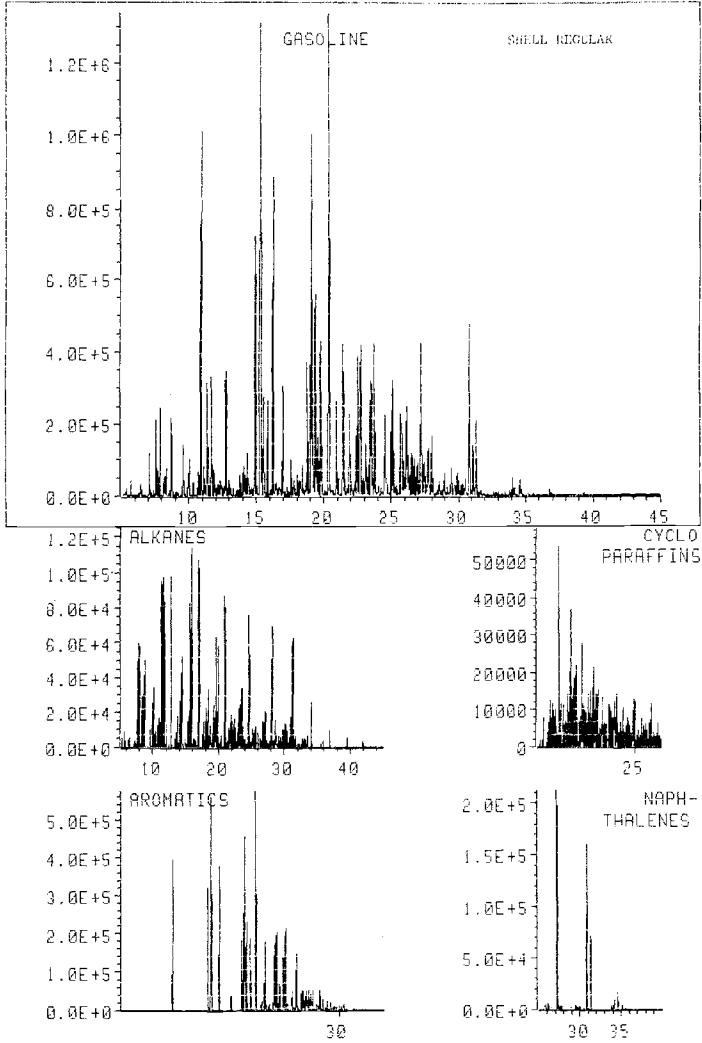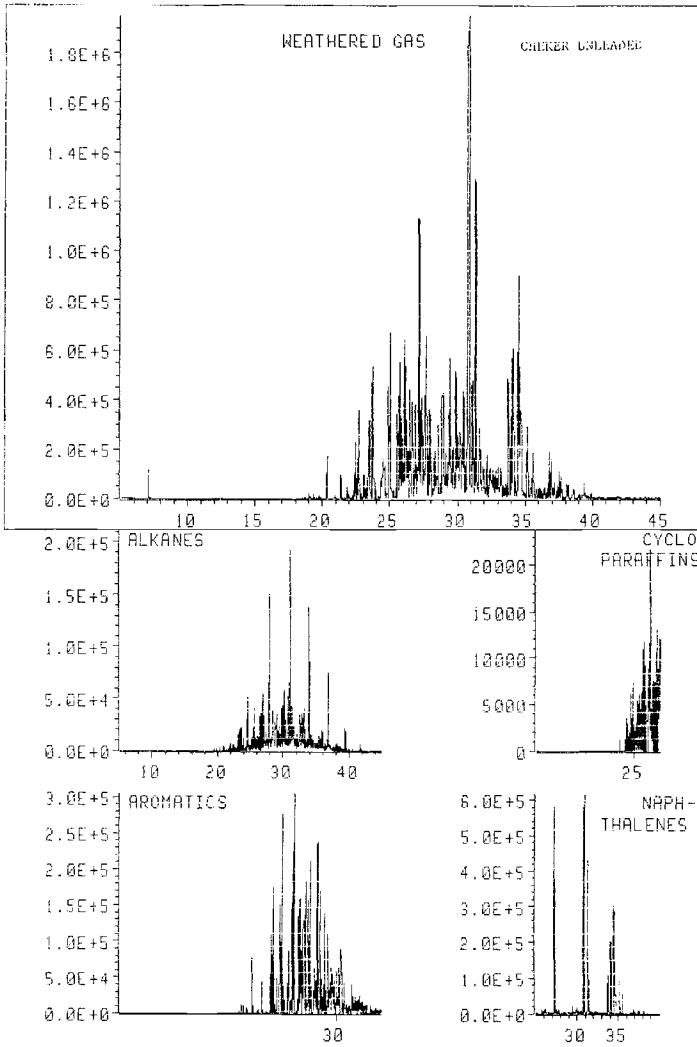FIG. 7—*Chromatogram and ion chromatography profiles of Dedura lacquer thinner.*

FIG. 8—*Chromatogram and ion chromatography profiles of gasoline.*

FIG. 9—*Chromatogram and ion chromatography profiles of weathered gasoline.*
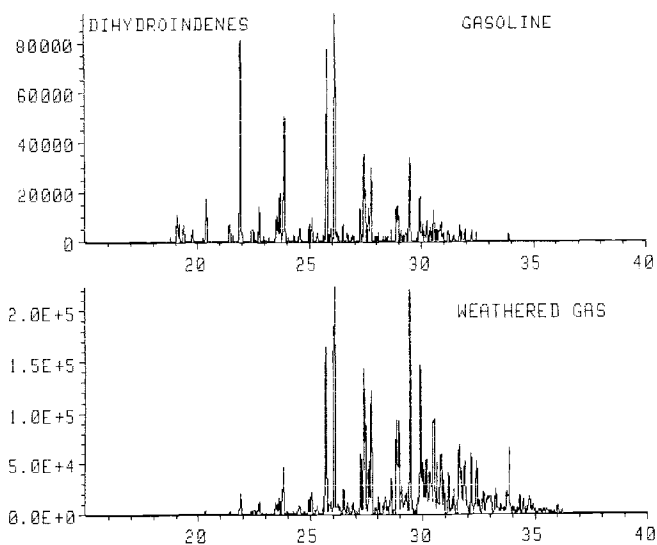
FIG. 10—*Dihydroindene ion chromatography profile of gasoline and weathered gasoline.*

The second class of heavy petroleum distillates is characterized by a higher boiling point range. While *n*-nonane, *n*-decane, and *n*-undecane may still be present, they are minor components when compared with the *n*-alkanes between C12 and C17. The *n*-alkane pattern of this class can extend as far as C23. Aromatics may still be present, but in this class the methylnaphthalenes and dimethylnapthalenes become prominent (Fig. 15). Examples of this class are diesel fuel and fuel oil No. 2.

Other Accelerants

As with any classification scheme, there are always going to be samples that do not easily fit into any of the categories. Some, like turpentine, form their own class. With others the analyst can use GC-MS to describe them as accurately as possible. Any classification scheme is just a tool, guidelines for consistent reporting of results, and not an inviolable set of rules.
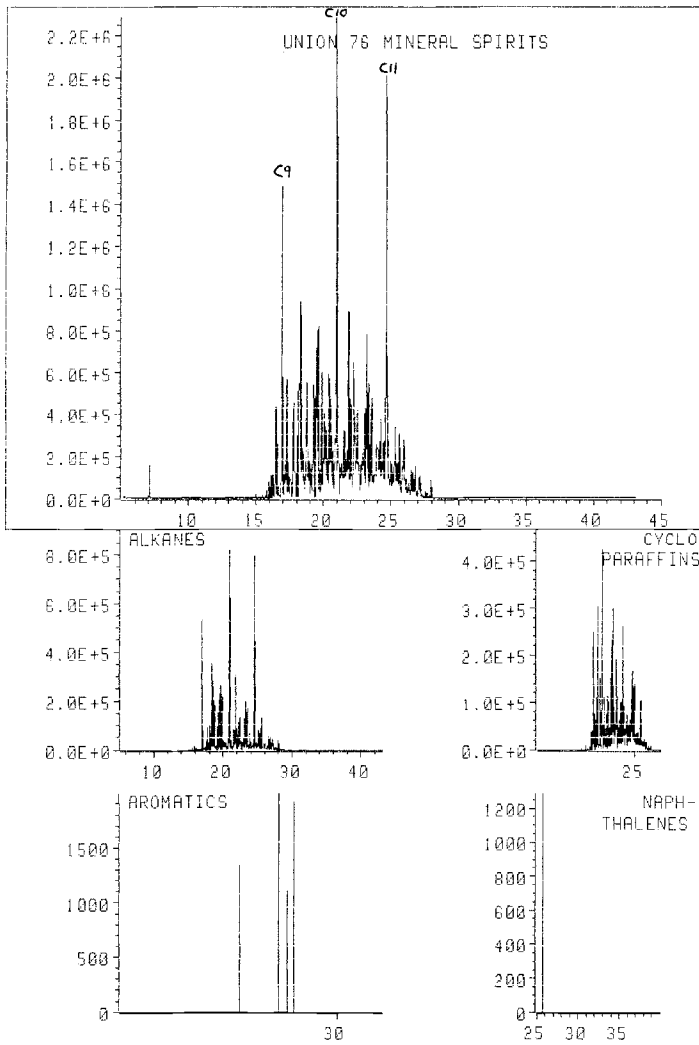
Acknowledgments

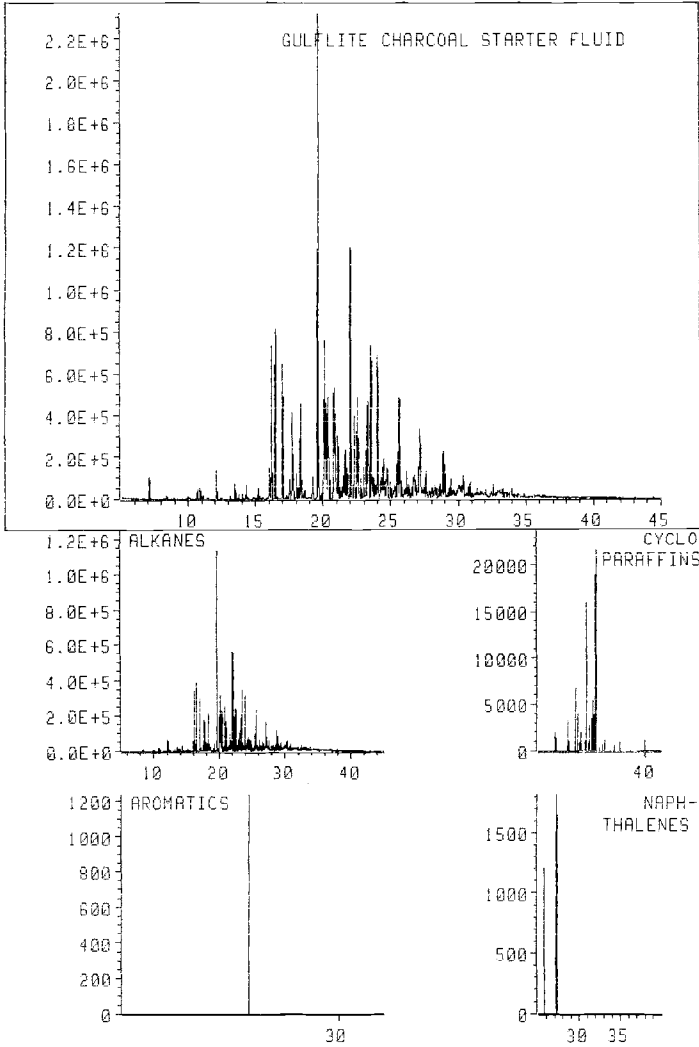FIG. 11—*Chromatogram and ion chromatography profiles of Union 76 mineral spirits.*

FIG. 12—*Chromatogram and ion chromatography profiles of Gulfite charcoal starter.*
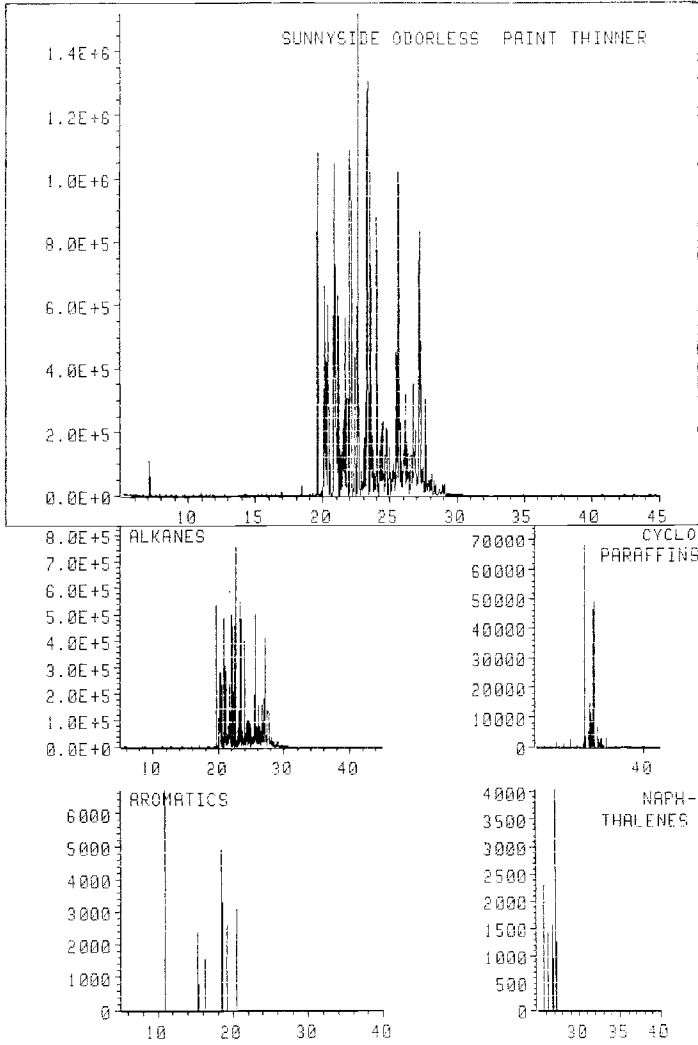
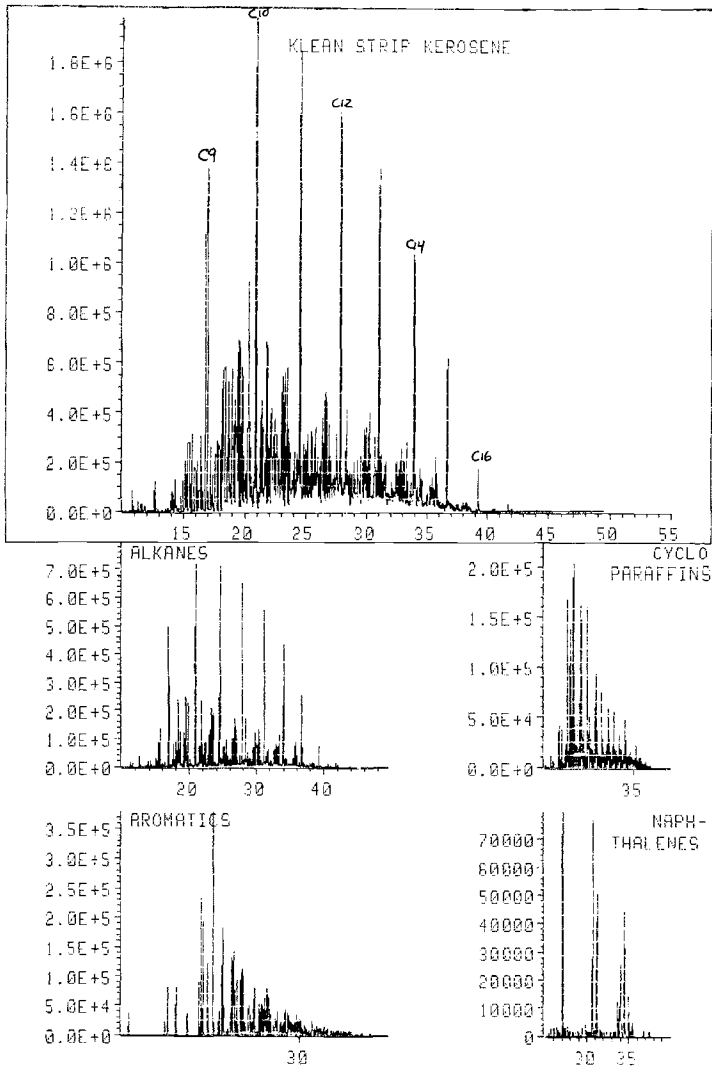FIG. 13—*Chromatogram and ion chromatography profiles of odorless paint thinner.*

FIG. 14—*Chromatogram and ion chromatography profiles of Klean-Strip kerosene.*
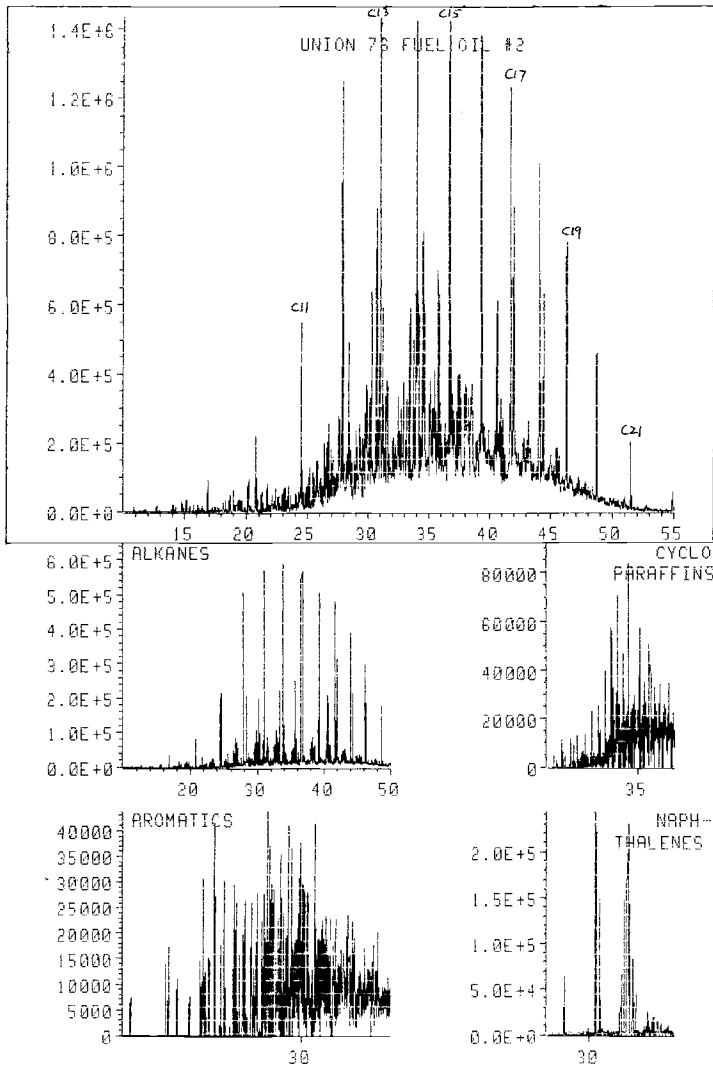
FIG. 15—*Chromatogram and ion chromatography profiles of Union 76 fuel oil No. 2.*

References

[1] "Flammable Liquids Analysis," Crime Laboratory Proficiency Testing Program Report No. 88-9, Collaborative Testing Services, Inc., Herndon, VA, 1988.

[2] Midkiff, C. R., "Arson and Explosive Investigation," *Forensic Science Handbook*, Richard Saferstein, Ed., Prentice-Hall, Englewood Cliffs, NJ, 1982.

[3] Brettell, T. A. and Saferstein, R., "Forensic Science," *Analytical Chemistry*, Vol. 57, No. 5, 1985, pp. 175R–187R.

[4] Brettell, T. A. and Saferstein, R., "Forensic Science," *Analytical Chemistry*, Vol. 59, No. 12, 1987, pp. 162R–174R.

[5] Brettell, T. A. and Saferstein, R., "Forensic Science," *Analytical Chemistry*, Vol. 61, No. 12, 1989, pp. 95R–109R.

[6] Smith, R. M., "Mass Chromatographic Analysis of Arson Accelerants," *Journal of Forensic Sciences*, Vol. 28, No. 2, April 1983, pp. 318–329.

[7] Kelly, R. L. and Martz, R. M., "Accelerant Identification in Fire Debris by Gas Chromatography/Mass Spectrometry Techniques," *Journal of Forensic Sciences*, Vol. 29, No. 3, July 1984, pp. 714–722.

[8] Smith, R. M., "Arson Analysis by Mass Spectrometry" *Forensic Mass Spectrometry*, J. Yinon, Ed., CRC Press, Boca Raton, FL, 1987.

[9] Tontarski, R. E. and Strobel, R. A., "Automated Sampling and Computer Assisted Identification of Hydrocarbon Accelerants," *Journal of Forensic Sciences*, Vol. 27, No. 3, July 1982, pp. 710–715.

[10] Wineman, P., "A 'Target Compound Ratio' Approach to the Detection of Petroleum Fuels and Solvents in Highly Contaminated Extracts of Fire Debris," paper presented at the Symposium on Recent Advances in Arson Analysis Detection, Las Vegas, NV, 1985.

[11] "Accelerant Classification System," *Arson Analysis Newsletter*, Vol. 6, No. 3, 1982, pp. 57–58.

[12] "Guidelines for Laboratories Performing Chemical and Instrumental Analysis of Fire Debris Samples," *Fire and Arson Investigator*, Vol. 38, 1988, pp. 45–46.

[13] Bertsch, W., Sellers, C. S., Holzer, G., and Babin, K., "Analysis of Suspect Arson Samples by GC and GC-MS," *LC-GC*, Vol. 6, No. 11, 1988, pp. 1000–1014.

[14] Holzer, G. and Bertsch, W., "Recent Advances Toward the Detection of Accelerants in Arson Cases," *American Laboratory*, Vol. 20, No. 18, December 1988, pp. 15–19.

[15] Midkiff, C. R., "Is It a Petroleum Product? How Do You Know?" *Journal of Forensic Sciences*, Vol. 31, No. 1, Jan. 1986, pp. 231–234.

Address request for reprints or additional information to
Jack Nowicki, M.S.
Forensic Scientist
Illinois State Police
Suburban Chicago Forensic Science Laboratory
1401 S. Maybrook Drive
Maywood, IL 60153