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Fluorescence of Petroleum Products IV. Three-Dimensional Fluorescence Plots and Capillary Gas Chromatography of Midrange Petroleum Products

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ABSTRACT: Midrange petroleum products such as charcoal lighters and paint thinners represent a potential source of evidence in arson fires which have been little studied. The objective of this study is to characterize a series of 22 such products using capillary gas chromatography (GC) and three-dimensional (3-D) fluorescence spectroscopy.

It was found that 3-D fluorescence is well able to differentiate among products whose characteristics, including GC, are quite similar. It can also determine if two samples could be the same brand or not. When samples are evaporated or combusted, it is still possible to obtain 3-D fluorescence spectra and GCs. The GCs are even more nondescript, whereas evaporated 3-D spectra are reproducible and characteristic although they do not correlate well with those of neat samples. 3-D fluorescence spectra of combusted samples do not reproduce well because of the inability to properly control the conditions of combustion.

KEYWORDS: criminalistics, petroleum products, arson, chromatographic analysis, midrange hydrocarbons, charcoal lighters, paint thinners, midrange petroleum products

A number of different types of materials are used as accelerants in arson fires. The most common are petroleum distillates such as gasoline- and kerosene-based materials (kerosene, fuel oils, and so forth). The detection and analysis of these common accelerants have been the subject of numerous books and articles over the past 30 years or so. A class of hydrocarbons which have not been given much attention are the so-called midrange petroleum products. These consist mainly of charcoal lighters, paint thinners, and certain synthetic turpentine products. Because many of these products are commonly found around the home, they have the potential to be used as accelerants in arson fires or to be involved in a fire in which some other material may have been the accelerant or in an accidental fire. It is therefore somewhat surprising that these materials have not been the subject of much research into classification and methods of detection and analysis. Indeed, an examination of the literature turns up little in the way of research specific to this class of products, and the only method reported for the analysis of these materials is gas chromatography (GC), either packed column or capillary.

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The technique of three-dimensional (3-D) fluorescence has been used previously in the analysis of several types of petroleum distillates including motor oils [*1*], gasolines and lubricants [*2*], and, petrolatum products [*3*].

The present study reports the use of 3-D fluorescence in conjunction with capillary gas chromatography to characterize representative mid-range petroleum distillates.

The objectives of this study were as follows:

(1) to determine if midrange petroleum products could be classified in groups according to their fluorescence and gas chromatographic characteristics and to see to what extent the two groups correlate,

(2) to determine if the 3-D fluorescence spectrum and the gas chromatogram of a given midrange petroleum product is unique with respect to the other members of its class,

(3) to determine if the 3-D fluorescence spectrum and the GC of an unknown sample of a midrange petroleum product can be matched to the particular brand from which it came,

(4) to determine if samples which have been partially (50%) or totally evaporated can be matched to a particular brand, and

(5) to determine the effects of combustion upon the 3-D fluorescence spectra and GCs of selected midrange petroleum distillates.

Materials and Instrumentation

Twenty-two midrange petroleum products were selected for the study. They were obtained either from commercial sources or from the Bureau of Alcohol, Tobacco and Firearms National Laboratory, Rockville, Maryland. The samples are as follows [a code for each sample assigned for this project appears in ( ) after the brand name]:

Sunnyside (PT01)
Tru-test (PT02)
Parks (PT03)
Sunnyside odorless (PT04)
UGL Raizoff (PT05)
NASCA (PT06)

Charcoal Lighters

Gulf Lite (CL01)
Poly-start (CL02)
Northland (CL03)
Wizard (CL04)
Farmlite (CL05)
Boron (CL06)
Sparks (CL07)
Chefs Choice (CL08)
Gulf Lite (another batch, CL09)

Mineral Spirits and Miscellaneous Others

Varsol (MS01)
Parks 100% (MS02)
Hechinger (MS03)
Sears Tirpolene (TT01)
Sears Lacquer Thinner (LT01)
Parks Shellac Thinner (ST01)
GUM Turpentine (GT01)

The fluorimeter was a Perkin-Elmer MPF-66 Spectrofluorimeter equipped with Perkin-Elmer Model 7300 Data Station and PR-310 Printer/Plotter. The instrumental conditions for the analyses, determined empirically were as follows:

EX scanning range	205 to 273 nm
EX scanning range	275 to 400
EX and EM slits	5 nm
EX wavelength increment	2 nm
Scan speed	120 nm/min
Number of scans	35

The gas chromatograph was a Varian Model 3300 equipped with a Model 601 Data Station and Hewlett-Packard Think Jet printer. The capillary column was a J&W DB-1, 30-*M*, 0.25-micron coating. The chromatographic conditions for all samples were as follows:

Initial column temperature	50°C
Initial hold time	4 min
Final column temperature	200
Program rate	10°/min
Final hold time	6 min
Injecter and detector temperatures	250
Injection size	0.5-2 μL

Procedures, Results, and Discussion

The first step in the procedure was to obtain suitable 3-D fluorescence plots for all of the samples. Solutions of 1000, 100, and 10 ppm in spectrograde cyclohexane (Burdick & Jackson) were prepared for each sample. These were all prescanned to obtain the optimum concentration conditions. This was accomplished by adjusting the concentration for the samples so that the ratio between the scatter peak and most intense fluorescence peak intensities were approximately constant. The 3-D spectra were compiled as previously reported [*1-3*].

Comparison of 3-D Spectra

When it was necessary to compare 3-D plots to determine if they were similar or not, two methods were used. The first was direct visual comparison of the printed plots. Here the number of peak regions, their wavelength maxima, and their relative intensities were examined. The plots were usually detailed enough to permit determination of whether they had a common source or not. In addition, the software provided a subtraction algorithm whereby two 3-D plots are subtracted spectrum-by-spectrum and the resulting difference plot is displayed. Even though two samples which had the same source would yield a difference plot that had non-zero fluorescence, the intensity of the peaks would be much lower than the intensities of the sample spectra. More important, a Pearson's Q was determined by the software for the peak differences between the samples. In those cases where the samples had a common source, the Q value was typically above 0.9 (1.0 representing perfect correlation). In most of the samples which did not have a common source, Q was less than 0.9. We have not yet researched this algorithm to determine if this "rule" can be relied upon in all cases, so visual comparison was used as the determining factor.

Neat Samples

From the 3-D spectra, each sample can be put into one of five groups. All of the samples were at 10 ppm except those noted in parentheses:

Group	1	2	3	4	5
	GT01	PT03	PT05	CL09(1000)	ST01
	CL03	MS02	LT01	CL01(1000)	
	TT01			CL05(100)	
	CL08			CL06	
	CL02(1000)				
	PT06(100)				
	MS01				
	PT02				
	MS03				
	CL07				
	CL04				
	PT01				

Figure 1 *a* through *e* are 3-D stacked plot spectra of a representative of each group.

Likewise, GCs were obtained of all 22 neat samples. They fell into 9 groups. Group 2 is empty intentionally so that spectra and chromatograms which fell into corresponding groups were numbered the same.

Group	1	2	3	4	5	6	7	8	9
	PT01		PT05	CL05	ST01	PT04	CL09	GT01	CL01
	PT03		LT01	CL06					
	PT06								
	MS02								
	CL04								
	PT02								
	TT01								
	MS01								
	MS03								
	CL02								

Figure 2 *a* through *h* show representative chromatograms for each of the eight groups.

When the groups are compared, it is found that many of the samples fall into the same fluorescence and GC group. These are listed below:

Group	1	3	4	5
	PT01	PT05	CL05	ST01
	PT02	LT01	CL06	
	PT06			
	TT01			
	MS01			
	MS03			
	CL02			
	CL03			
	CL04			
	CL07			
	CL08			

The above table shows that, at the concentrations chosen, 16 out of the 22 samples can be grouped the same way by both fluorescence and GC. Thus, merely by running the GC and fluorescence, one can immediately identify the samples that do not fall into the corresponding groupings (assuming that the samples came from the pool of 22 used here).

Examination of the chromatograms in Group 1 shows that they are quite similar and it is not possible to distinguish one brand from another solely by GC. Examination of the 3-D stacked and contour plots of the 22 samples indicate that about two thirds of them can be readily distinguished from each other and the other third. However, approximately one third

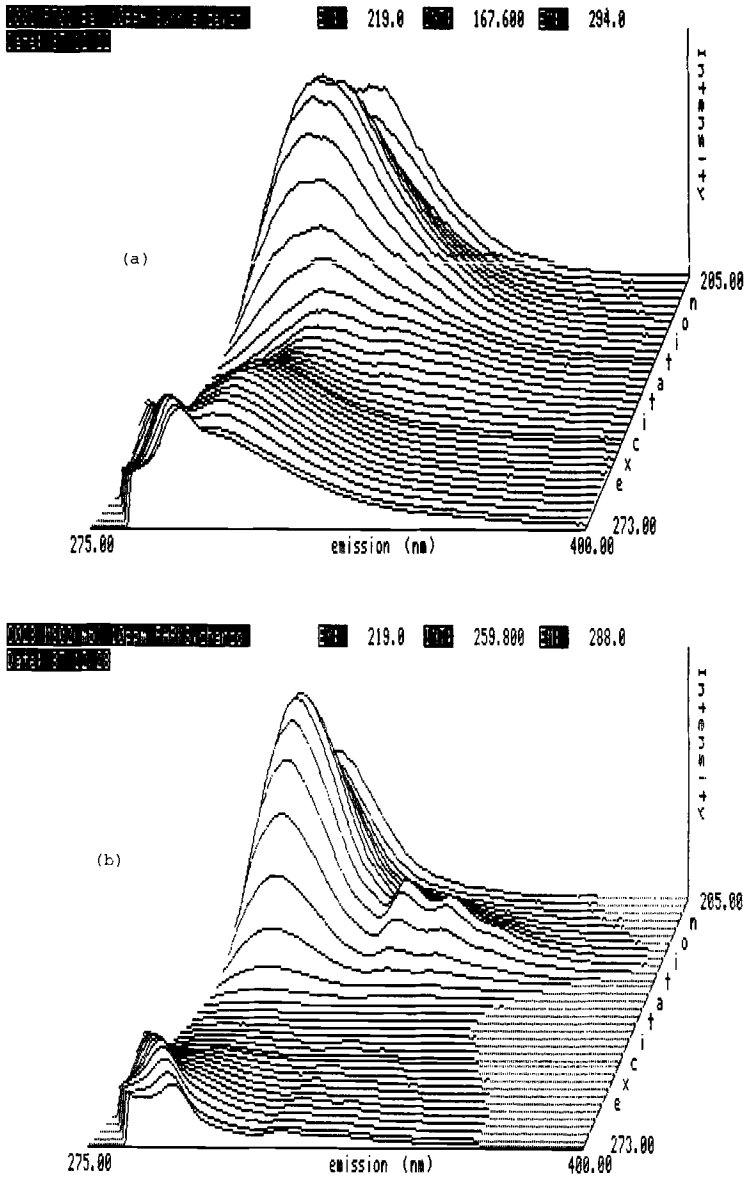


FIG. 1—*Stacked plot emission 3-D plots of representative members of each of the five groups in which the midrange products are classified:* (a) *Group 1, PT01;* (b) *Group 2, MS02;* (c) *Group 3, PT05;* (d) *Group 4, CL06; and* (e) *Group 5, ST01.*

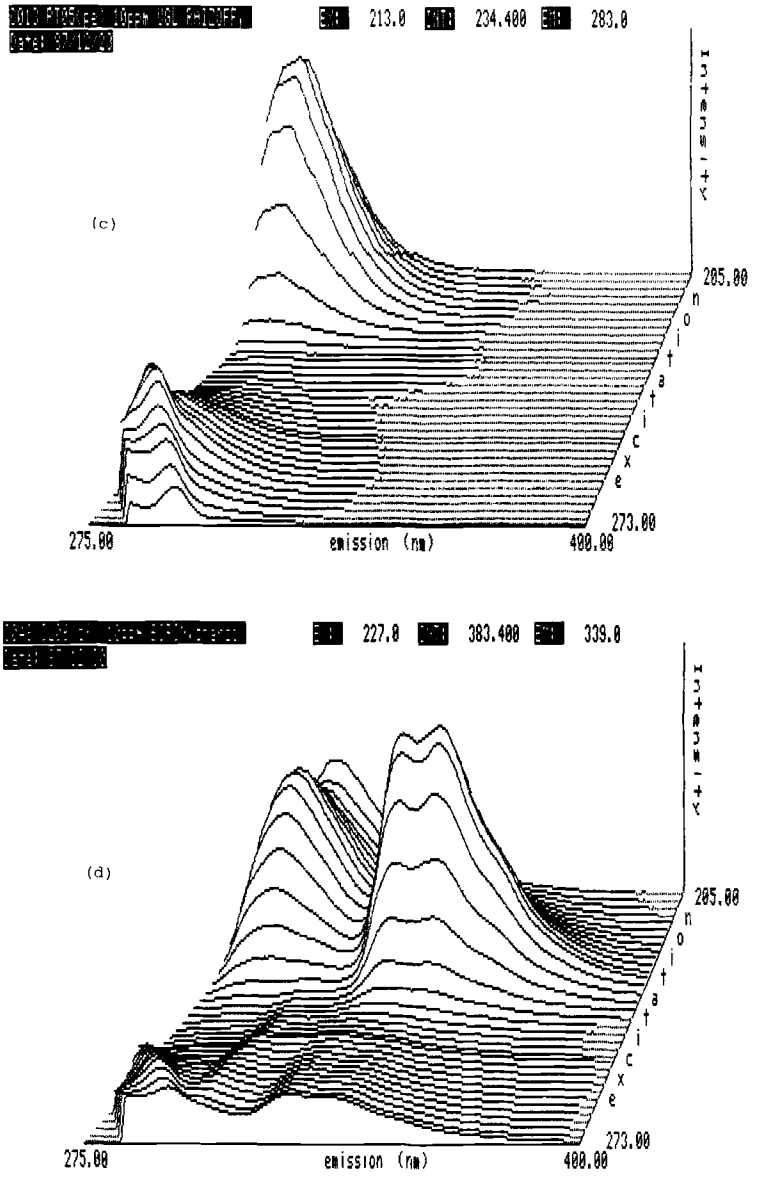


FIG. 1—*Continued.*

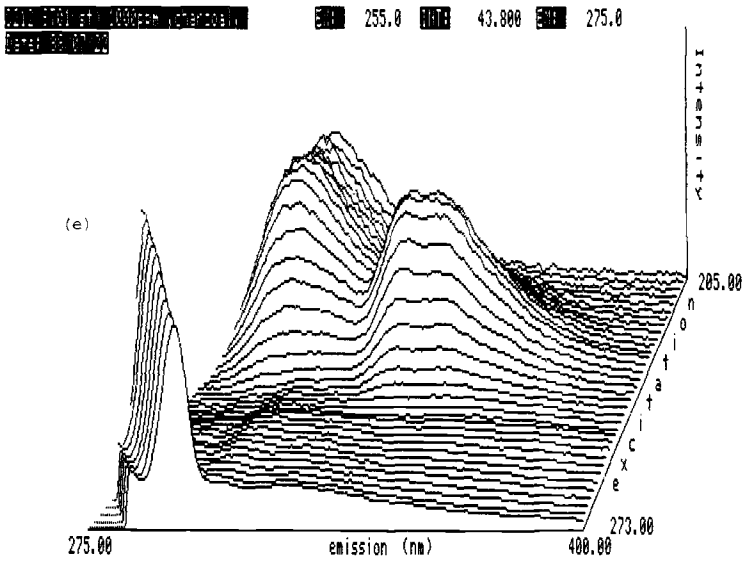


Fig. 1—*Continued.*

of the samples are too visually similar to distinguish if the fluorescence at only one concentration is obtained. Since fluorescence is highly dependent upon concentration, running samples at different concentrations may yield a set of spectra which can distinguish them from the others. For us to be able to explore this further, a concentration study was performed on 6 of the samples.

Concentration Study

This study examined the following samples:

Group	1	2(fluor)	3	4
	CL03 PT01 PT02	PT03	LT01	CL05

For each sample, 3-D fluorescence measurements were taken at concentrations of 1000, 500, 100, 50, 10, and 5 ppm. Both stacked plots and contour plots were obtained for each sample at each concentration. The results of this study showed that the spectra for a single sample at different concentrations differed markedly. See Fig. 3 *a* through *f* for the stacked spectra of a sample at different concentrations. In addition, although it would be difficult to distinguish among two samples in the same group at one concentration, obtaining spectra at more than one concentration increases discriminating power substantially.

Blind Test to Compare Two Samples

The next step in the study was to determine if GC and 3-D fluorescence can be used if two samples taken from the 22 were of the same brand or of different brands. Seven pairs of samples were studied. GCs were obtained of each member of a pair. Then 3-D fluorescence

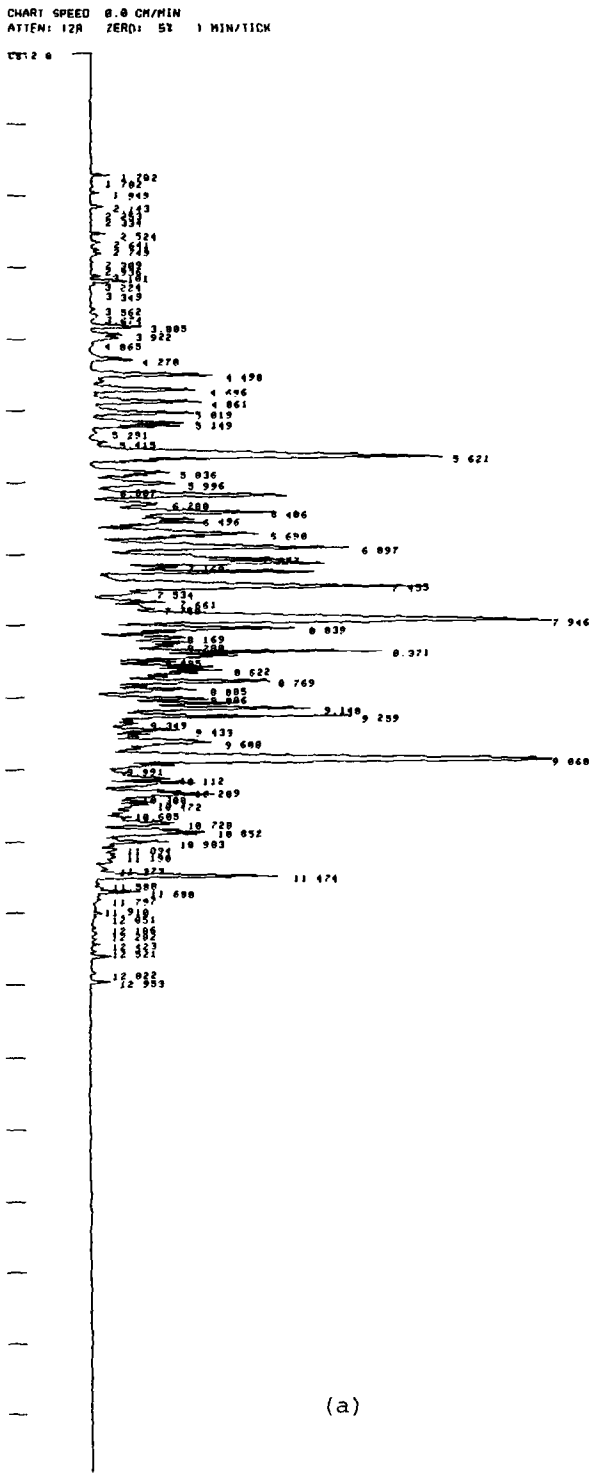
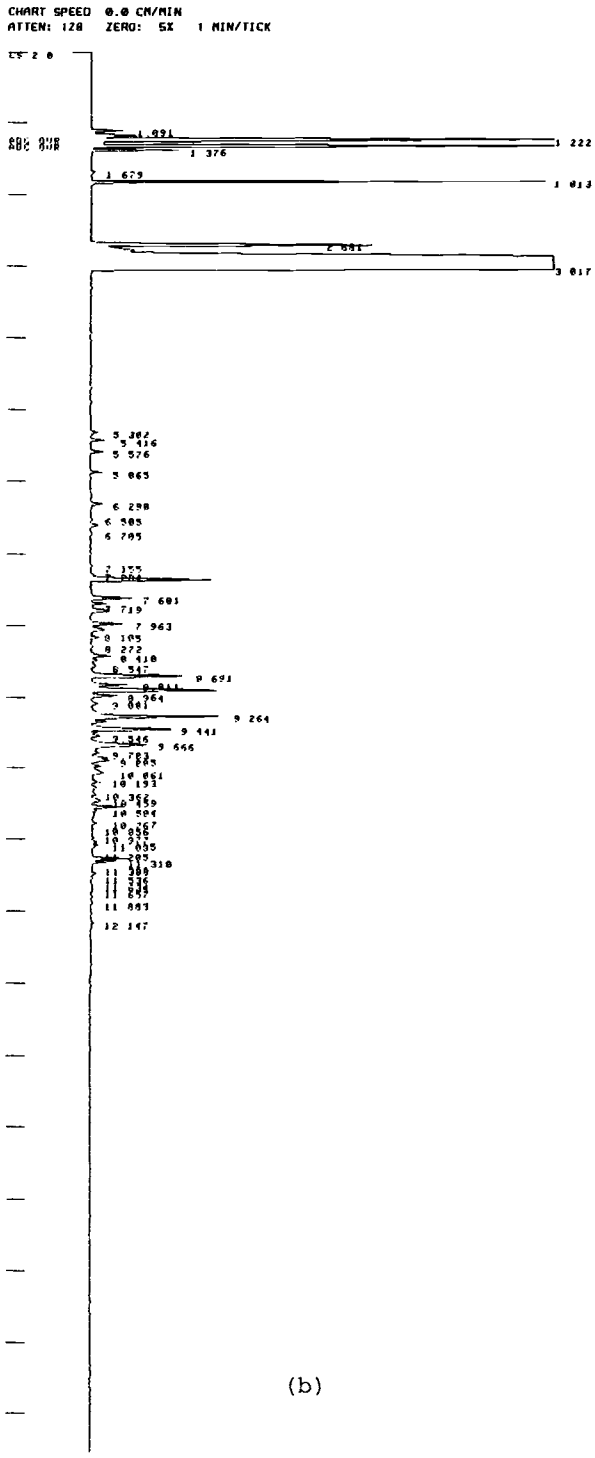


FIG. 2—*Capillary GCs of representative members of each of the eight groups in which the midrange products are classified:* (a) *Group 1, MS02;* (b) *Group 3, PT05;* (c) *Group 4, CL06;* (d) *Group 5, ST01;* (e) *Group 6, PT04;* (f) *Group 7, CL09;* (g) *Group 8, GT01; and* (h) *Group 9, CL01.*



(b)

FIG. 2—*Continued.*

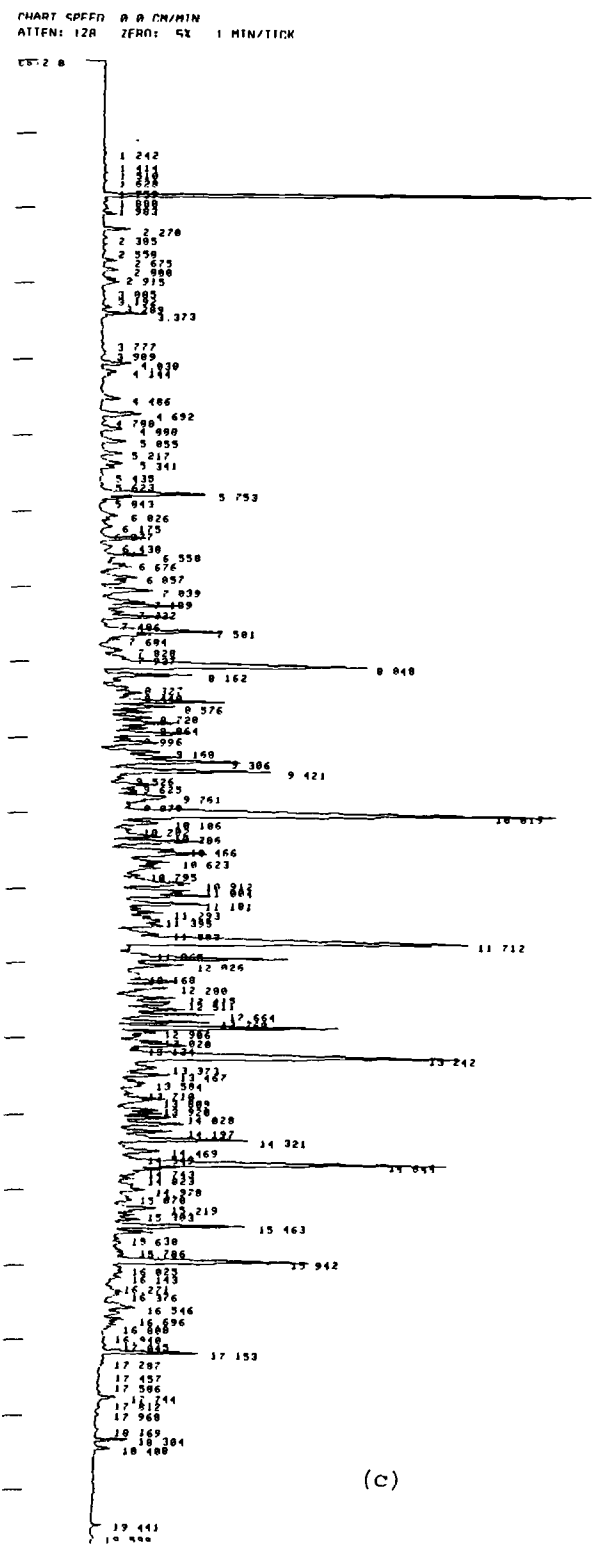
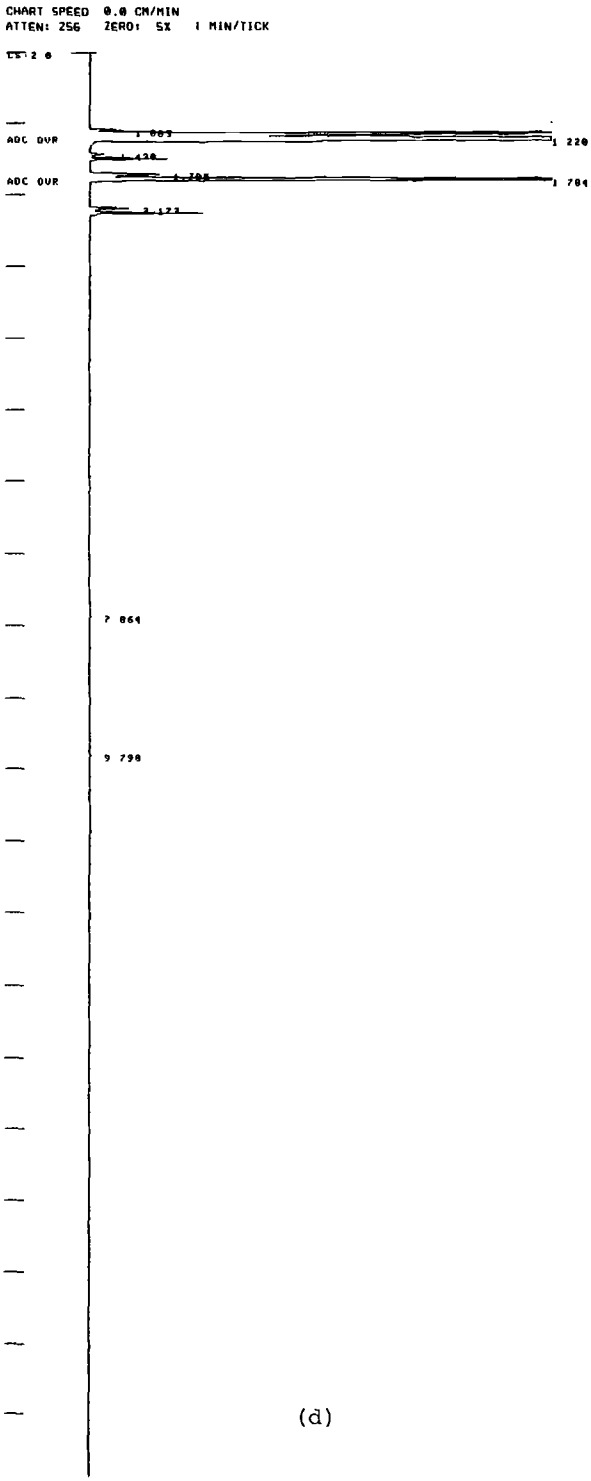


Fig. 2—*Continued.*



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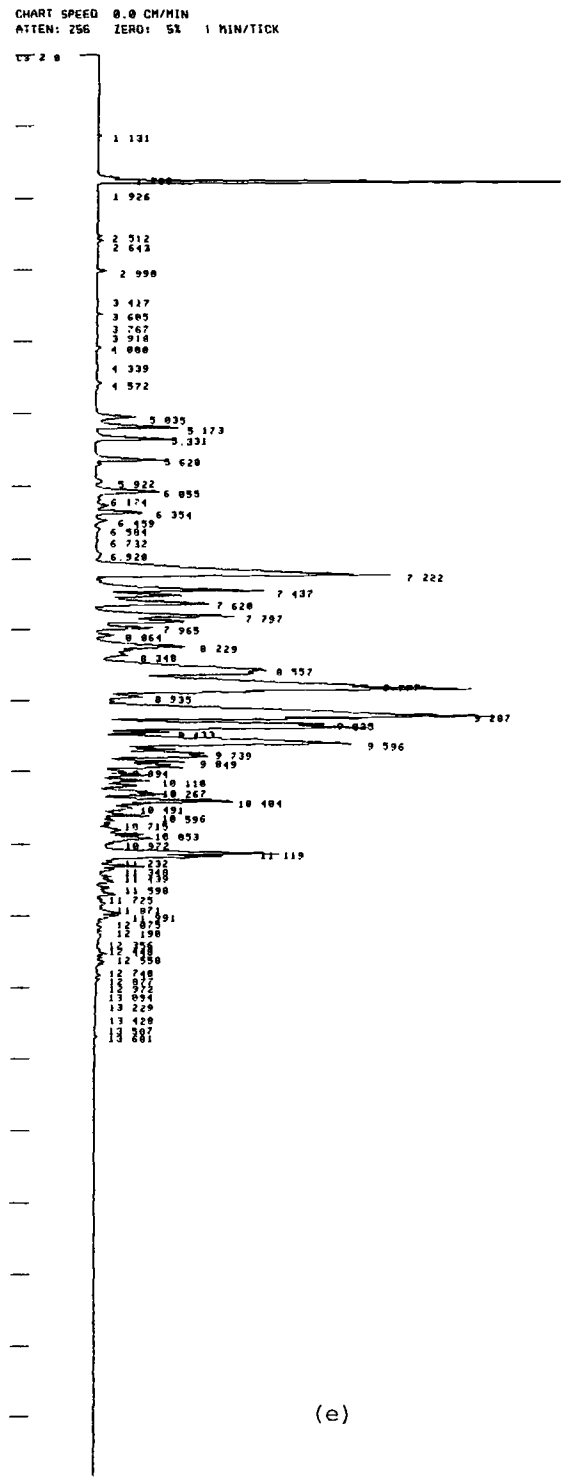

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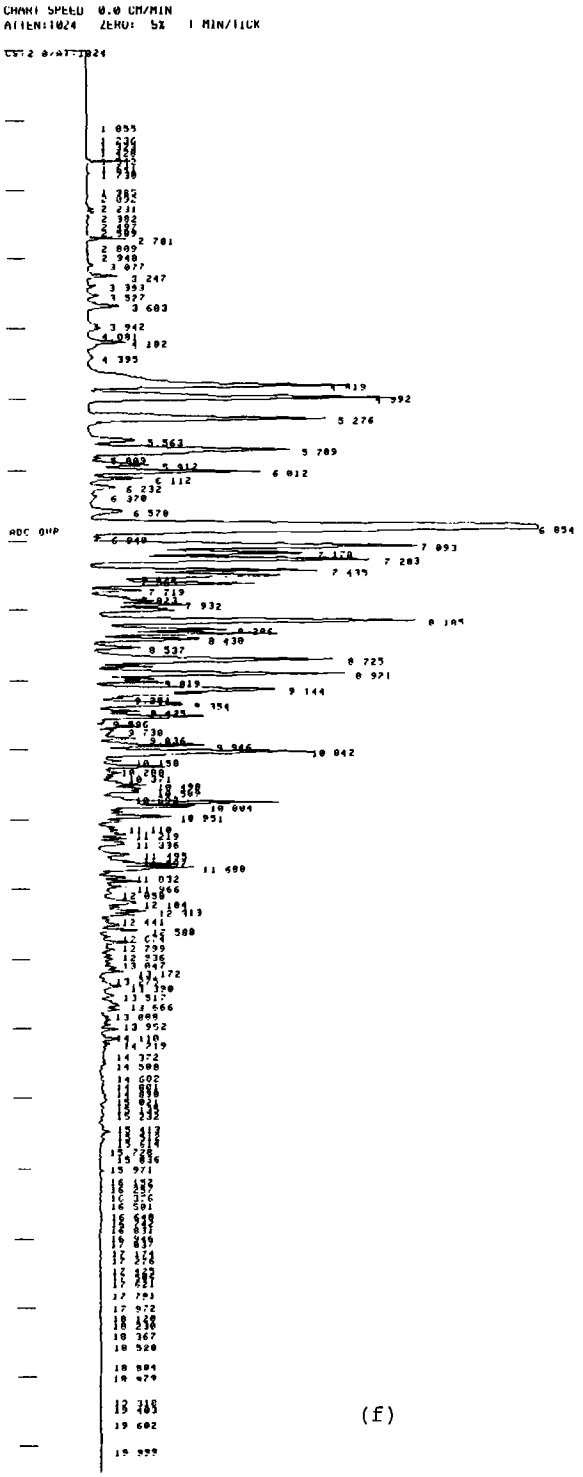

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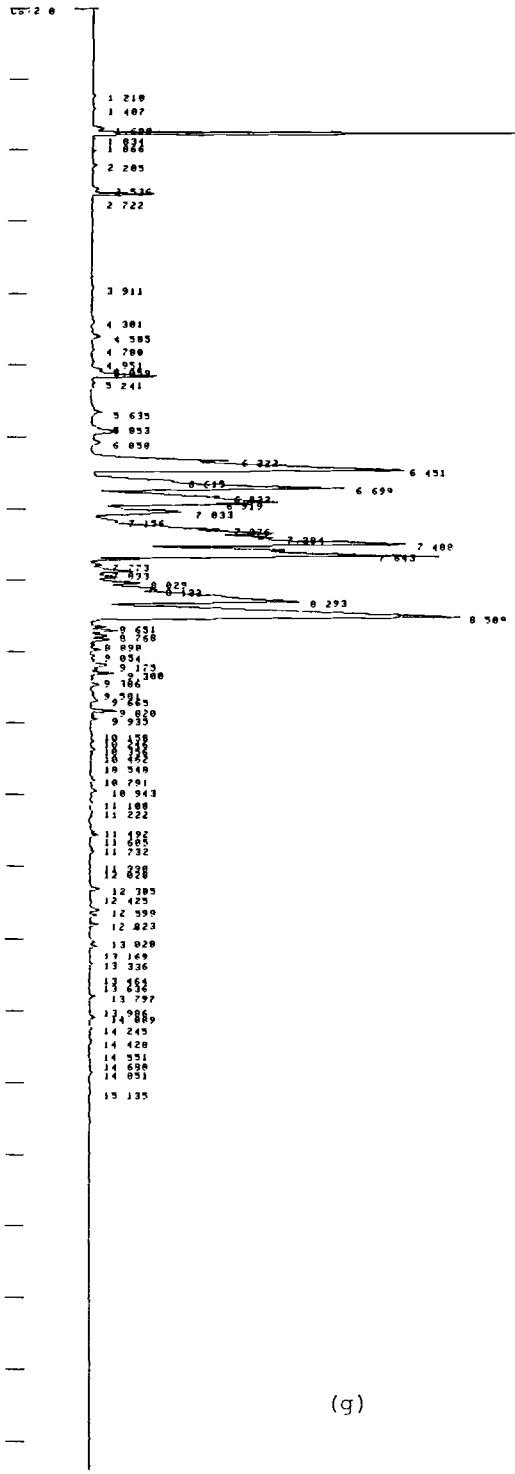

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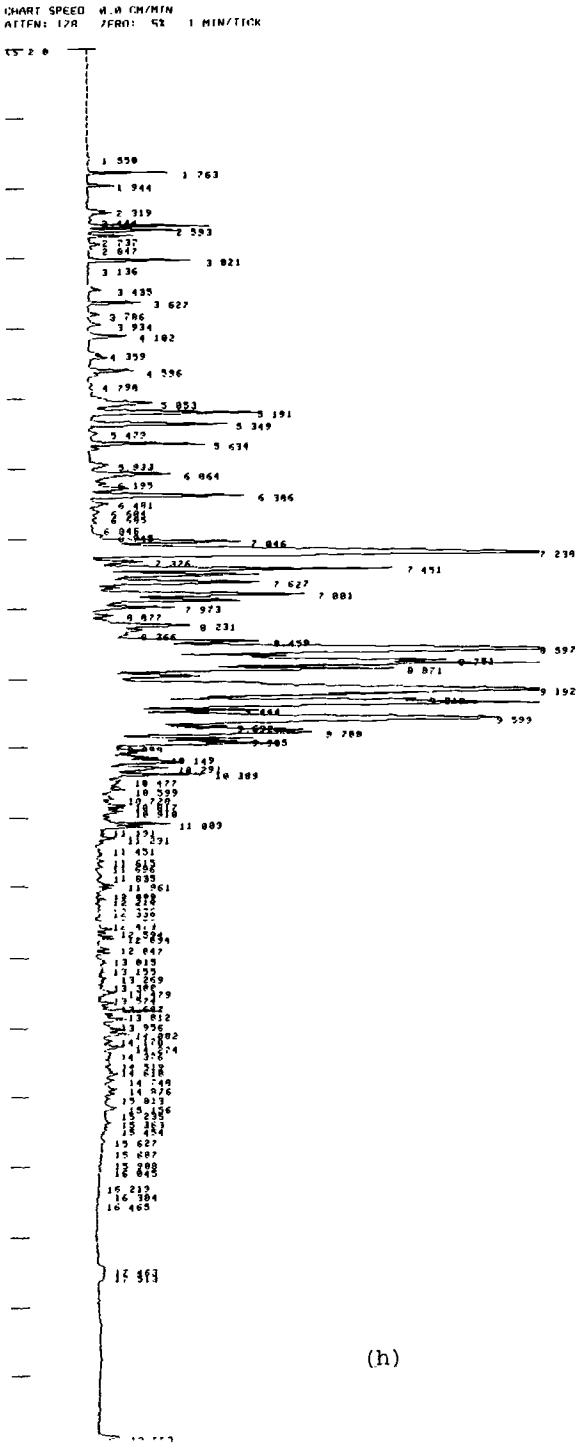


(h)

Fig. 2—*Continued.*

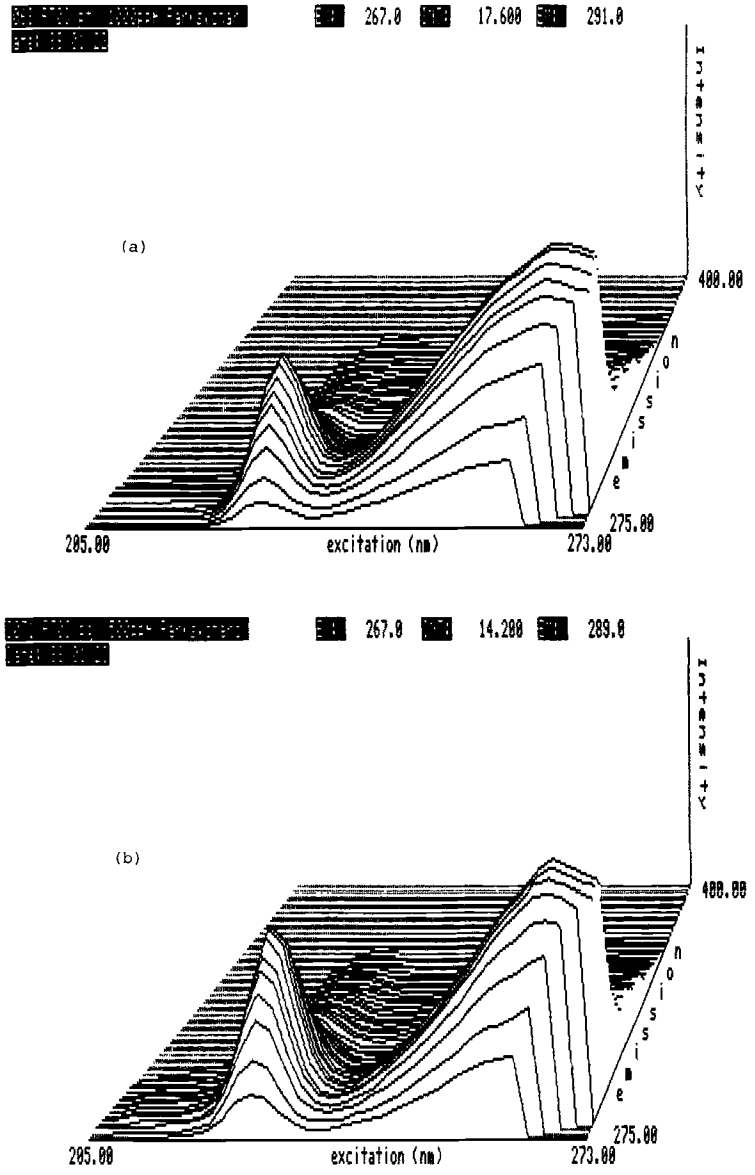
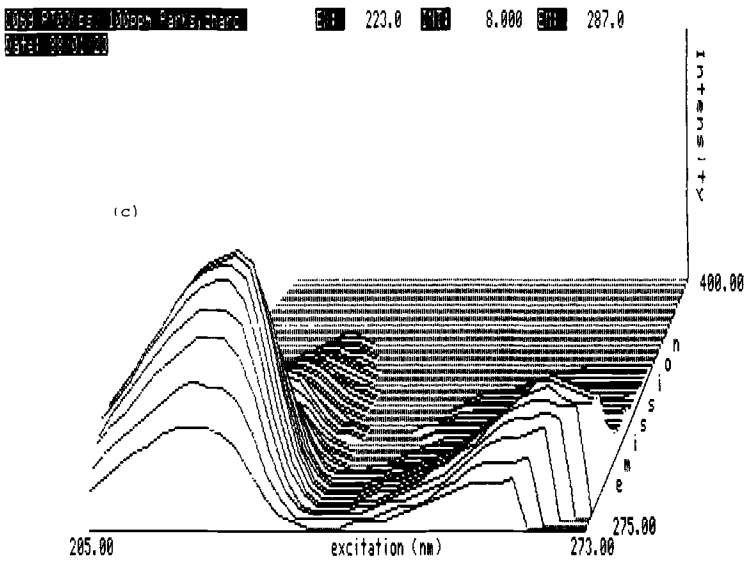


FIG. 3—*Stacked plot spectra of sample PT03 at different concentrations (ppm):* (a) *1000,* (b) *500,* (c) *100,* (d) *50,* (e) *10, and* (f) *5.*



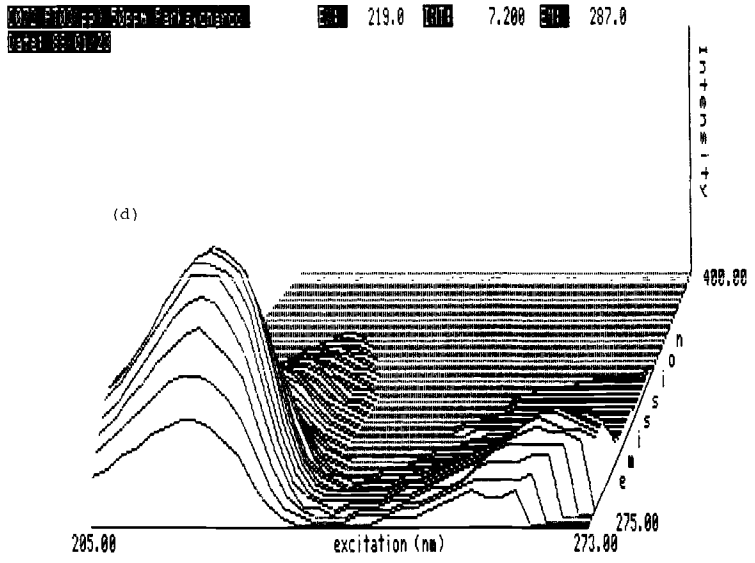


FIG. 3—*Continued.*

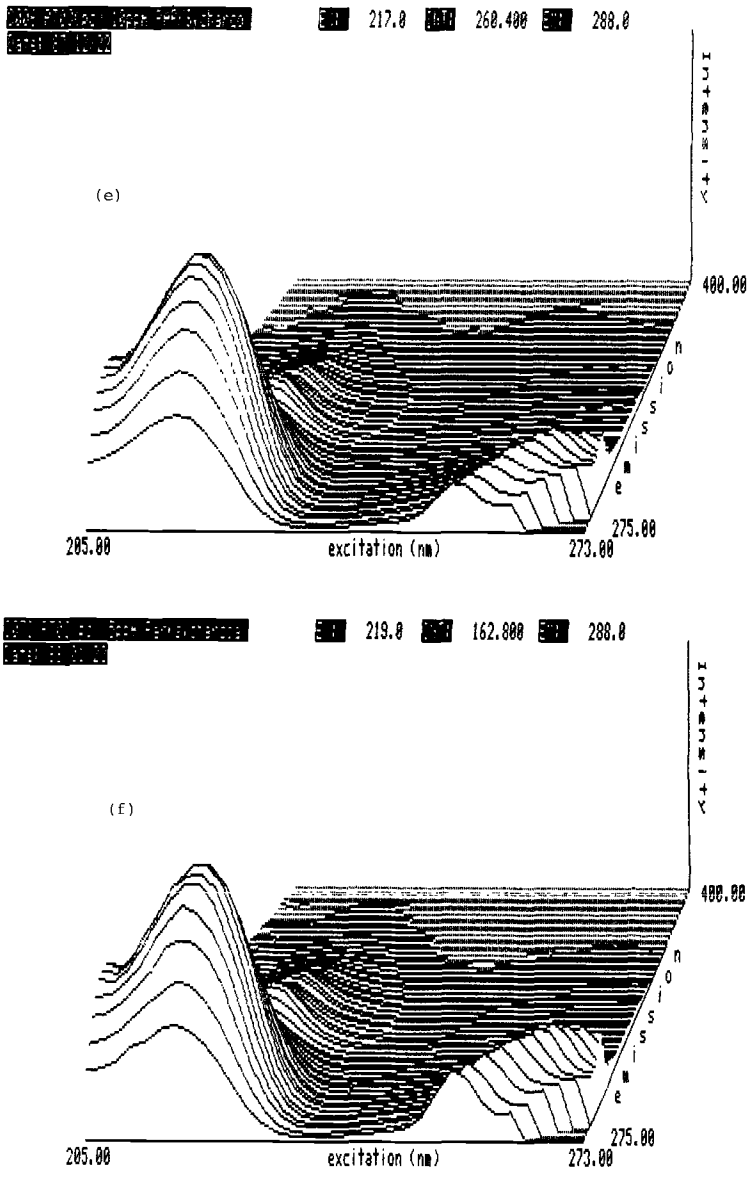


Fig. 3—*Continued.*

plots were obtained at 10 ppm. If no conclusion could be reached from these data, then additional fluorescence measurements were taken at other concentrations. The criterion used for reaching conclusions was that only if the pairs of spectra showed no significant differences at any concentration would they be declared to be of the same brand. The results of the study were as follows ("diff" means that the results showed that the two samples came from different sources; "same" means that they were the same brand):

Sample Pair	GC	Fluorescence	Conclusion
1	same	diff	diff
2	diff	diff	diff
3	same	same	same
4	diff	diff	diff
5	diff	diff	diff
6	same	same	same
7	same	diff	diff

The compositions of the pairs of samples is given below:

1.	A-PT03	B-MS02
2.	A-CL03	B-CL08
3.	A-PT02	B-PT02
4.	A-MS03	B-TT01
5.	A-CL05	B-CL06
6.	A-CL04	B-CL04
7.	A-PT01	B-PT02

The results show that GC was correct in 57.1% of the cases, whereas 3-D fluorescence was correct 100% of the time although several concentrations were run. Figure 4 *a* through *d* show the 3-D contour spectra for two pairs of samples.

Evaporated Samples

The next step in the study was to determine what effects, if any, there would be on the fluorescence and GC of the midrange petroleum products when they are partially or totally evaporated. It is expected that the GCs would, of course, be altered significantly, losing much of the volatile fractions even with partial evaporation. Changes in fluorescence are more difficult to predict. The moieties responsible for fluorescence are presumably the aromatics and polycyclic compounds which may be present in these products. They would be expected to be among the less volatile fractions and would not be much affected by partial evaporation.

Eight samples were used to examine the effects of evaporation. They include four charcoal lighters (CL01, CL02, CL03, and CL04) and four paint thinners (PT01, PT02, PT03, and PT04). Of each sample 50 mL was first evaporated to 25 mL, and then GCs and fluorescence measurements were taken in the same manner as with the neat samples. Then the 25-mL samples were evaporated until no liquid remained. For GC, the residues were dissolved in 20 μL of cyclohexane, and 2-μL samples were injected. For fluorescence, the residue was dissolved in 3.5 mL of cyclohexane which was used for measurements.

For GC, the results were as expected. With the 50% evaporated samples, all of the GCs were changed from those of the neat sample, and all changed approximately the same way. With the totally evaporated samples, it would appear that there was some nonvolatile residue left, but the GCs were quite nondescript and would not be suitable for identification purposes. This is different than the results that one gets with gasoline or wherein a nonvolatile residue is left after all of the visible liquid is evaporated. Figures 5–7 show GC of a neat sample and the same sample at 50 and 100% evaporation.

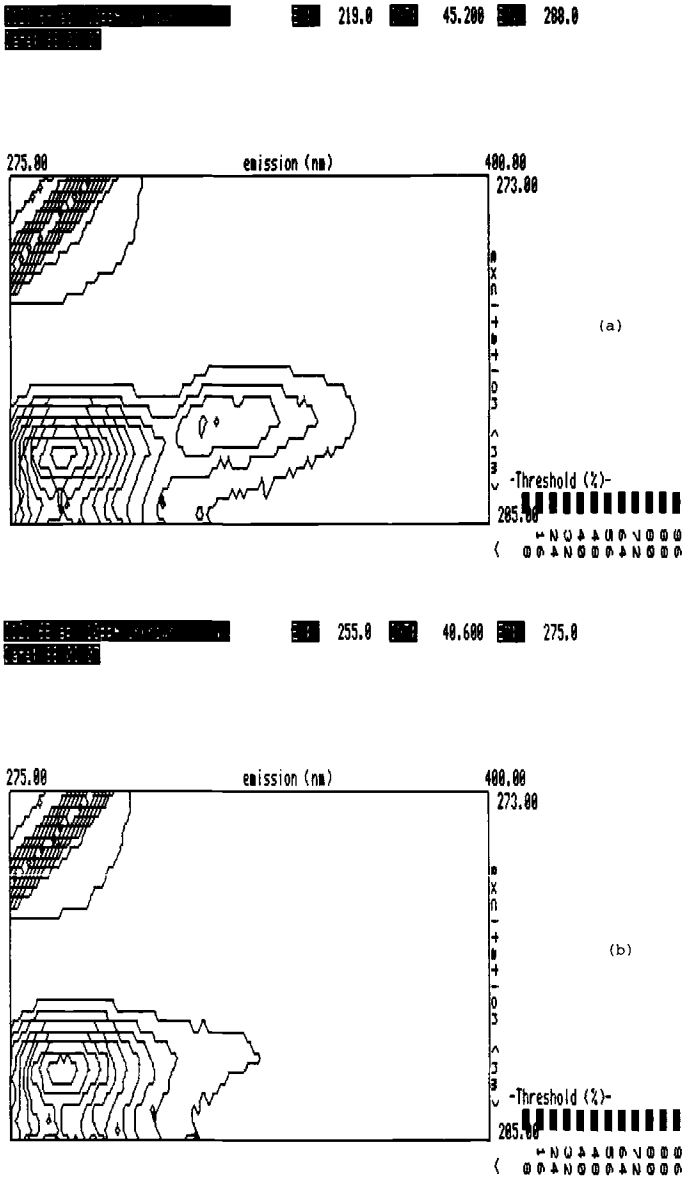


FIG. 4—*Contour plots for two pairs of samples in blind test:* (a) *Sample 6A, CL04;* (b) *Sample 6B, CL04;* (c) *Sample 7A, PT01; and* (d) *Sample 7B, PT02.*

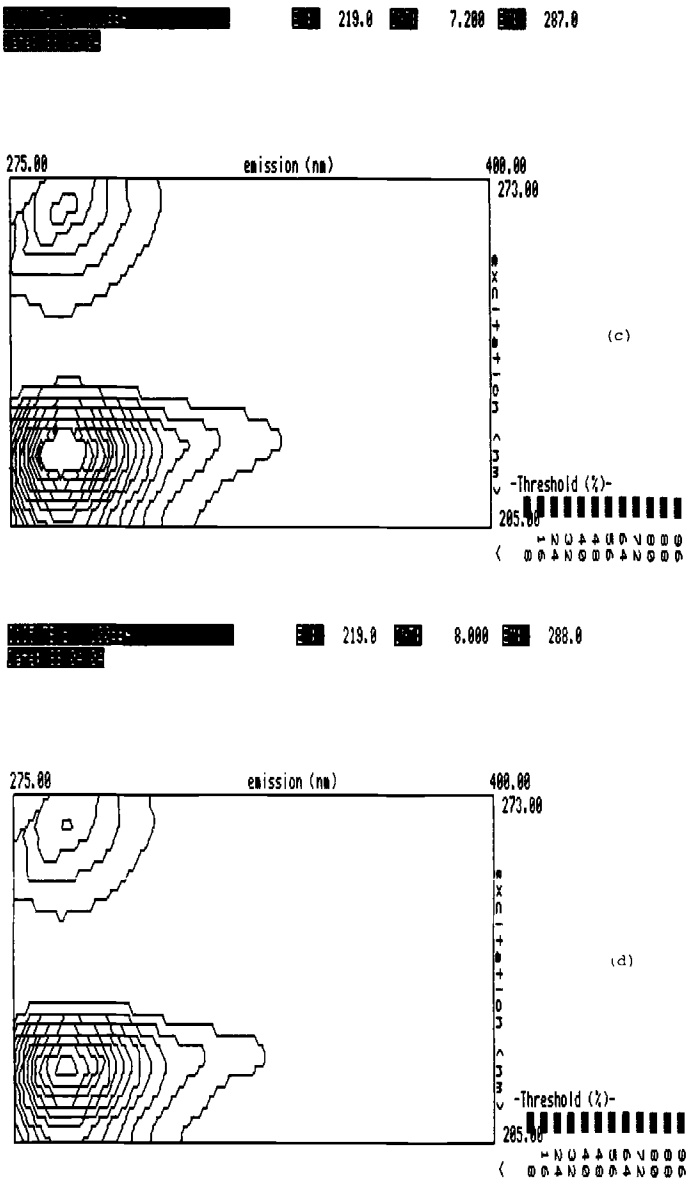


FIG. 4—*Continued.*

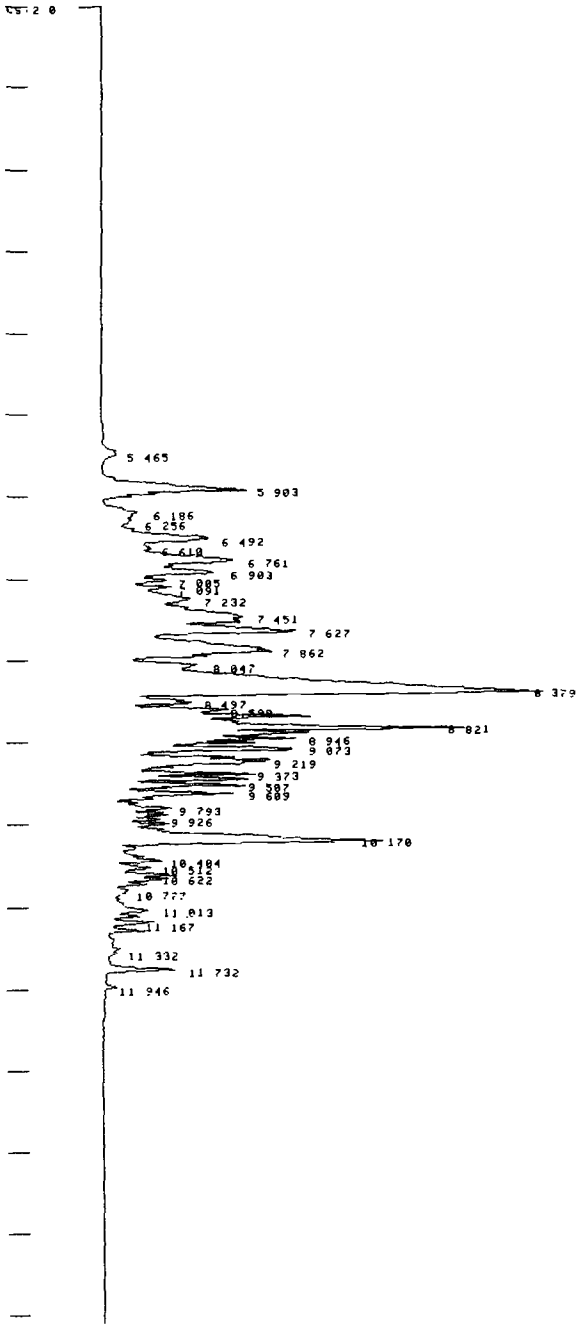


FIG. 5—*Capillary GC of Sample CL02: unevaporated.*

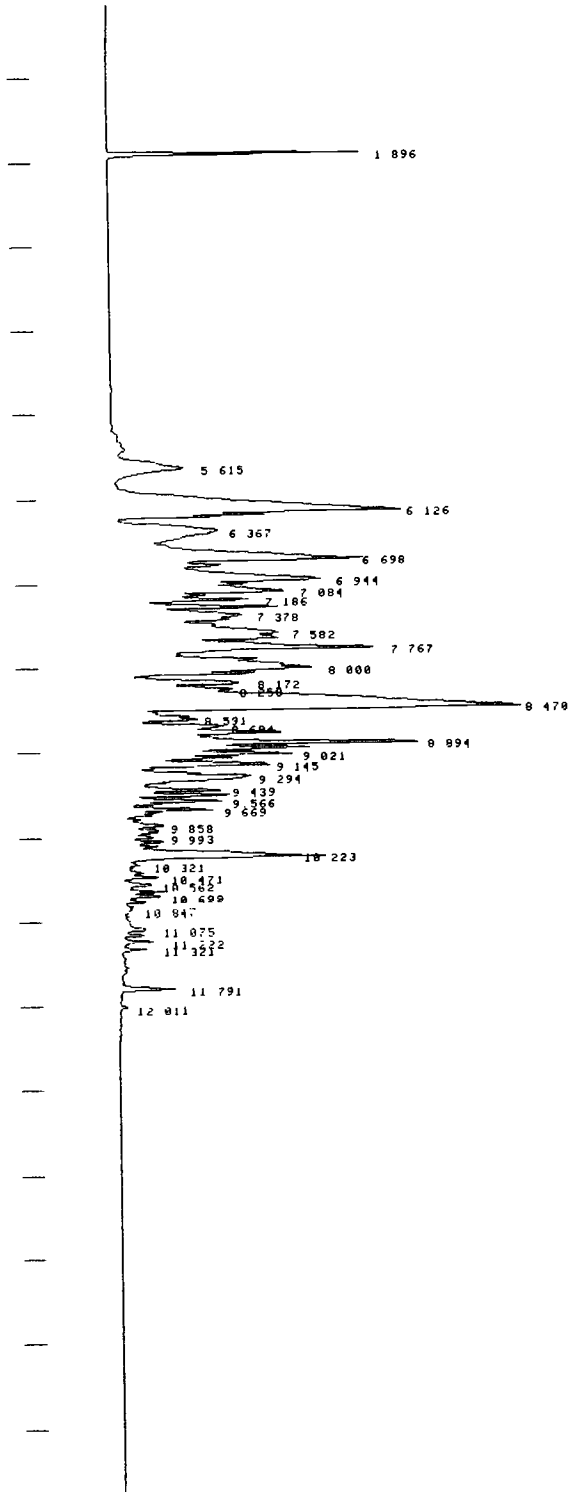


FIG. 6—*Capillary GC of Sample CL02: 50% evaporated.*

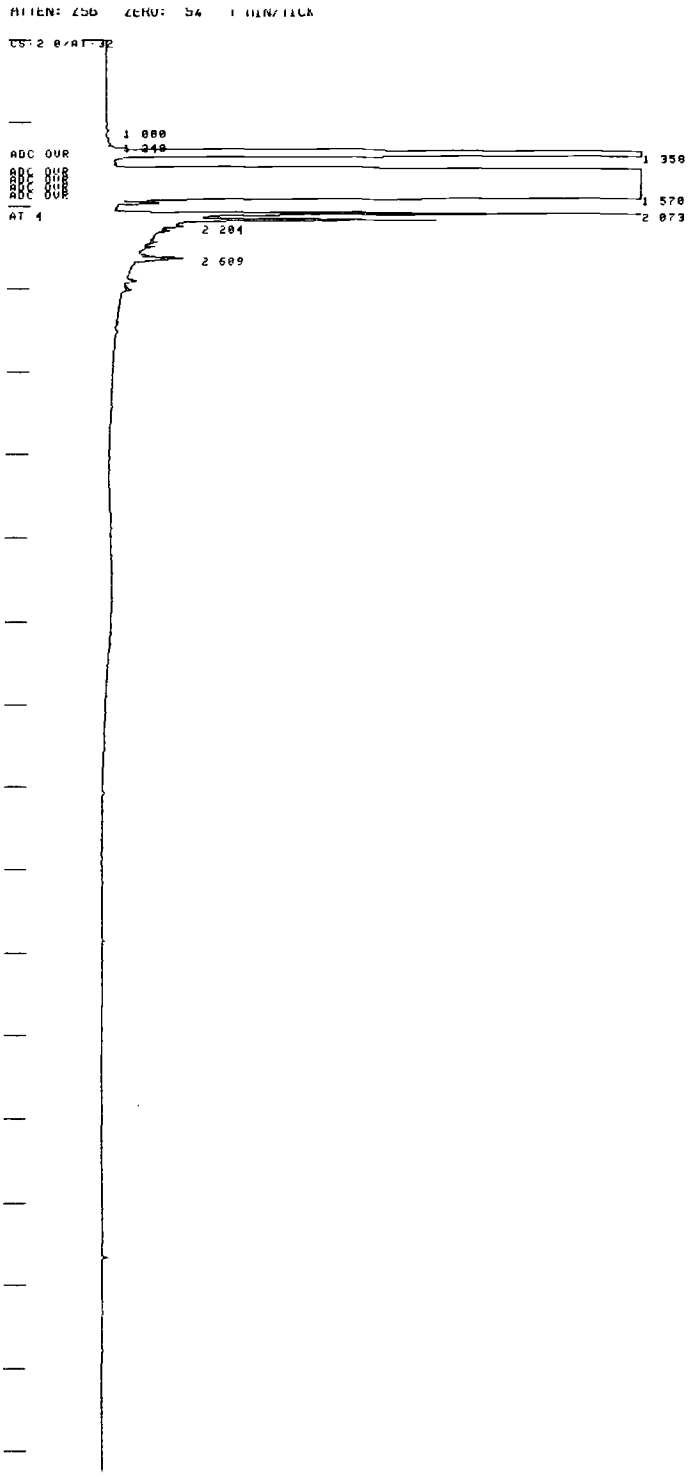


FIG. 7—*Capillary GC of Sample CL02: 100% evaporated (no liquid remains).*

In the case of fluorescence, 3-D plots were obtainable for all the 50% and totally evaporated samples. The plots are dramatically different from those of the neat samples, however. This means that a "weathered" sample could probably not be matched back to a neat sample of the same material unless the degree of evaporation was known, an unlikely situation in a real case. The spectra of a given evaporated sample are consistent; that is, the spectra are the same each time a given sample is evaporated to the same degree. Figure 8 *a* through *c* show the 3-D contour plots for a neat sample and 50 and 100% evaporation.

Burned Samples

Combustion is an extremely complex process, and even the most rigorous attempts to control the conditions of a combustion often lead to inconsistent results. Nevertheless, it is necessary to attempt to study the GC and fluorescence behavior of the midrange petroleum products under controlled combustion conditions to get a more complete picture of the behavior of these materials in actual fire situations.

For this study, the same eight samples were chosen as in the evaporation experiment. Of each sample 50 mL was put into a clean 1-gal (3.8-L) paint can with a 44- by 20-cm piece of cheesecloth which was folded into a 7.5- by 7.5-cm square. The can was put in a fume hood and the fuel ignited. Within 5 to 7 min, the fire stopped, the can was allowed to cool, and then 100 mL of cyclohexane was poured in. After 10 min, the solution was filtered by gravity and evaporated to dryness; it was then reconstituted in 3.5 mL of cyclohexane, and fluorescence measurements were taken. Then the solution was evaporated to dryness and reconstituted in 20 μL of cyclohexane for GC analysis.

The samples were evaporated to dryness so as to approximate the weathering process as closely as possible and to use a worst-case scenerio. In the case of these samples, "dryness" meant that there was no visible liquid left. It did not mean that there was no residue. In almost all cases, some nonvolatile residue was left, as is generally the case with products

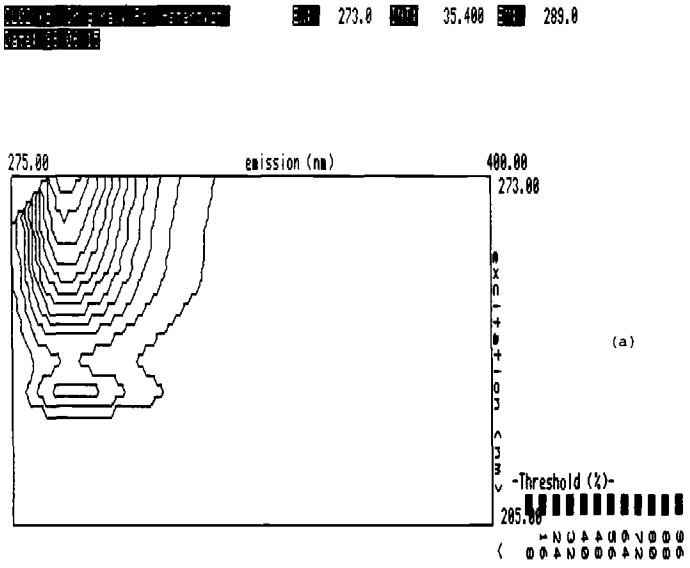


FIG. 8—*Contour 3-D plots of sample CL02. Same conditions as in Fig. 5.*

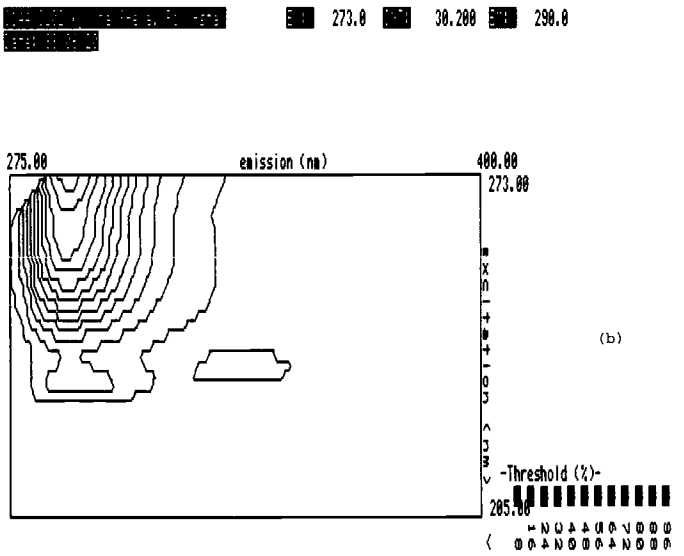


FIG. 8—*Continued.*

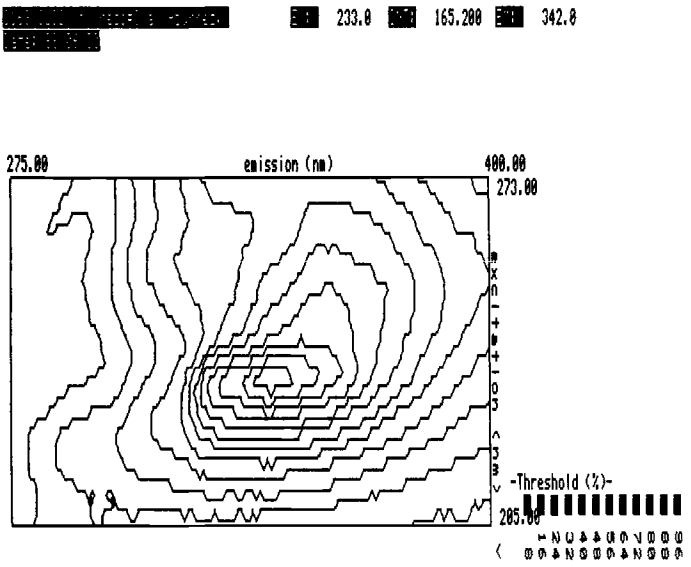


FIG. 9—*Contour plot of sample CL02 after combustion.*

derived from petroleum. This residue gave rise to the weak fluorescence and resulted in the very weak chromatograms.

As in the GCs of the fully evaporated samples, the GCs of these burned samples were quite nondescript and weak. This indicates that the combustion consumed nearly all of the hydrocarbon. It was possible to obtain 3-D fluorescence plots for all of the samples. They were substantially different than the plots for the neat samples. In addition, when the burning was repeated on the same sample a number of times under the same conditions, the fluorescence spectra were all different, indicating that the combustion was somewhat different each time, in spite of attempts to control conditions. In a real case, the situation would be even worse, since the combustion conditions would not even be known, let alone reproducible. Hence, combusting a known sample suspected to be involved in a fire and comparing the spectrum to that of the unknown would probably be futile.

It is possible that, had the combustion been cut short by putting out the fire with water or by smothering it, more of the residue of the hydrocarbon would have remained, perhaps increasing the chances for reproducibility. There are, however, reasons to believe that would not be the case. First, introducing water to the mixture increases the chance for contamination of the fluorescence owing to impurities in the water. Although this will be the case for most real fires, it was not desirable to add this variable in this initial study. Second, smothering the fire by cutting off oxygen would not introduce any contamination, but at the same time, is not the way real fires are generally extinguished. Finally, the evaporation study showed that, when a portion of the sample is lost, the 3-D plot changes and can no longer be matched to the neat sample. Nonetheless, it is encouraging to know that a 3-D plot can be obtained even from severely burned samples of midrange hydrocarbons. Figure 9 shows 3-D contour plots for a sample after combustion.

Summary

Twenty-two midrange petroleum products, including charcoal lighters, paint thinners, and synthetic solvents, were studied by capillary GC and 3-D fluorescence. It was found that

3-D fluorescence is far better at discriminating among similar products than was GC, which could only put the products into broad classes. When partially or totally evaporated, the 3-D fluorescence plots were altered enough that they could not be matched with those of neat samples. A similar situation exists when they are burned. Also, when burned even under controlled conditions, these compounds do not yield consistent fluorescence patterns.

A blind test on neat samples showed that 3-D fluorescence can be a reliable technique for determining whether or not two samples were of the same brand.

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