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## Fluorescence of Petroleum Products

### I. Three-Dimensional Fluorescence Plots of Motor Oils and Lubricants

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**REFERENCE:** Siegel, J. A., Fisher, J., Gilna, C., Spadafora, A., and Krupp, D., "Fluorescence of Petroleum Products. I. Three-Dimensional Fluorescence Plots of Motor Oils and Lubricants," *Journal of Forensic Sciences*, JFSCA, Vol. 30, No. 3, July 1985, pp. 741-759.

**ABSTRACT:** The technique of three-dimensional fluorescence is employed in the analysis of unused motor oils and selected machine lubricants. This technique provides much more spectral information than is available from conventional forms of fluorescence spectroscopy. A method for direct comparison of three-dimensional plots to determine if a common source exists is also presented.

**KEYWORDS:** petroleum products, criminalistics, luminescence, fluorescence

A wide variety of commercial products refined from crude petroleum exhibit characteristic fluorescence behavior owing to the presence of polycyclic aromatic hydrocarbons (PAHs) containing a high degree of conjugation. Because of the sensitivity of molecular fluorescence to differences in the types and amounts of various PAHs, this technique has shown great promise in helping to determine the source of a particular petroleum-based product. A technique for comparing two such samples to determine whether they come from a common source would be especially useful in several areas of criminalistics.

The use of fluorescence in criminalistics has received much attention within the past few years. For example, oil spills have been successfully characterized by the Coast Guard [1]. Similarly, crude oils have also been subjected to fluorescence [2,3], as have fuels [4]. Petro-latum-based lubricants have been studied by using synchronous fluorescence combined with gas-liquid chromatography [5]. More recently, a modified synchronous fluorescence technique called variable separation synchronous excitation (VSSE) was used in conjunction with normal emission and synchronous excitation fluorescence to individualize both used and unused motor oils [6, 7].

In the present work another form of contour fluorescence plot is evaluated for its ability to individualize unused motor oils, with an emphasis on comparative analysis to determine whether two samples have a common source. The technique is called three-dimensional fluorescence (3-DF) and it generates a great deal of information about the luminescence properties of a sample in a form that is easy to understand and interpret.

Normal excitation or emission fluorescence spectra are obtained by scanning either the

Presented at the 36th Annual Meeting of the American Academy of Forensic Sciences, Anaheim, CA, 21-25 Feb. 1984. Received for publication 1 Aug. 1984; revised manuscript received 26 Oct. 1984; accepted for publication 29 Oct. 1984.

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emission or excitation monochromator through the ultraviolet-visible electromagnetic spectrum while holding the other monochromator constant, usually at a wavelength where significant luminescence is known to occur. Such normal fluorescence spectra are illustrated in Fig. 1, which contains the excitation-versus-intensity plots of two motor oils.

Normal fluorescence spectra yield information about the luminescence properties of a sample under only a single set of conditions. Since petroleum products generally have a number of different types of PAH, much of the available luminescence information is not obtained.

When the normal fluorescence spectra such as those depicted in Fig. 1 are qualitatively different, they can be compared directly and the differences can be shown clearly, as in Fig. 2. With normal fluorescence spectra of many similar motor oils, however, such differences will be minimal and comparison of normal fluorescence spectra may not be adequate.

The technique of synchronous fluorescence can be employed when solvent scattering (Rayleigh scattering) or the presence of luminescence from impurities can interfere with the interpretation of the luminescence of the substance of interest. In synchronous fluorescence, both the excitation and emission monochromators are scanned simultaneously at a fixed wavelength increment  $\Delta\lambda$ . The result is generally a somewhat simplified excitation spectrum. If the  $\Delta\lambda$  is chosen carefully, luminescence from interfering substances can be eliminated. This technique, then, can offer a significant improvement over normal excitation or emission fluorescence. However, it still exhibits only a small portion of the available luminescence information, and comparison of such spectra is still inadequate for individualization. Figure 3 depicts the synchronous excitation spectrum of a motor oil sample.

Three-dimensional fluorescence represents a great improvement over normal fluorescence because 3-DF is capable of providing spectral information about the total luminescence of the petroleum product instead of a single narrow region. In excitation or emission 3-DF, a series of excitation or emission scans (up to 30 with the present software configuration) are generated under computer control. During each scan, the scanning monochromator covers the same wavelength range while the fixed monochromator is incremented by a fixed amount with each successive scan over the entire range of luminescence. The process is automated so that the operator need not be present except to load the samples. The resultant spectra are saved by the

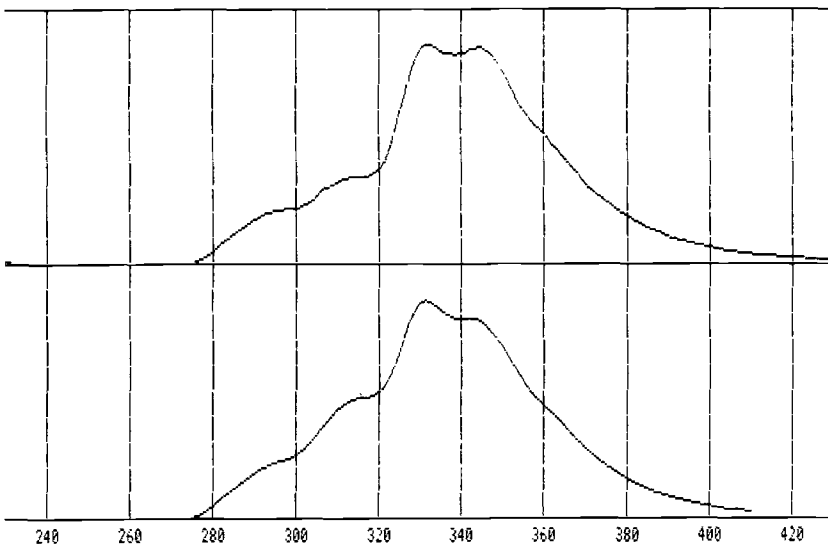


FIG. 1—Normal emission fluorescence spectra of Quaker State 10W-40 (top) and Pennzoil 10W-40 motor oils.

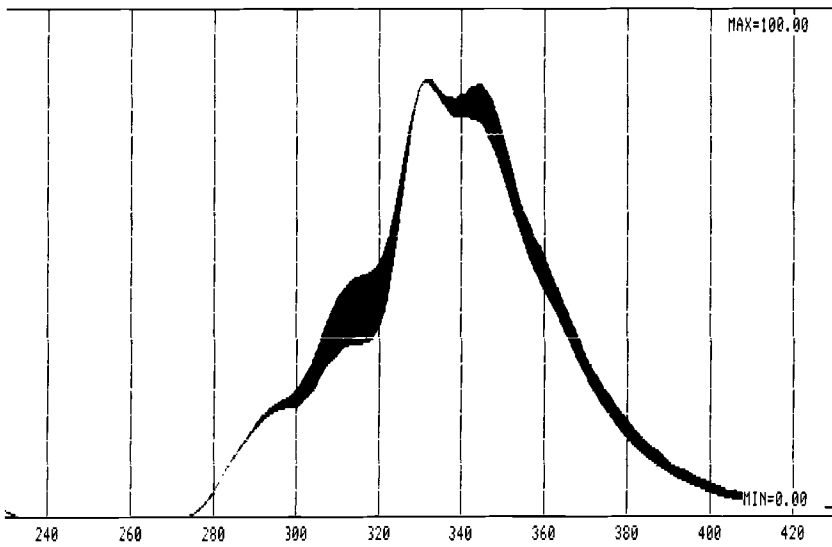


FIG. 2—Plotted difference fluorescence spectrum of Quaker State and Pennzoil shown in Fig. 1.

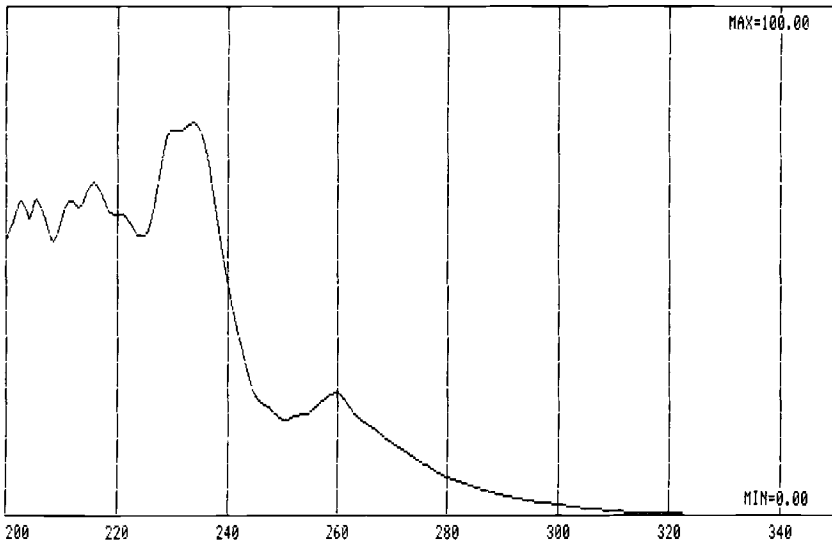


FIG. 3—Normal synchronous fluorescence spectrum of Pennzoil 10W-40 motor oil.

computer on disk and then subsequently plotted on a three-dimensional Cartesian system with the scanning monochromator wavelength on the  $x$ -axis, the fixed monochromator wavelength on the  $y$ -axis, and the fluorescence intensity on the  $z$ -axis. The contour plot so obtained is a profile of all of the major areas of fluorescence of the sample. As many as four different views of the contour plot may be obtained by generating both excitation and emission 3-DF plots and by plotting the fixed monochromator response from either high to low or low to high wavelength. Figure 4 presents the four views of the 3-DF plots for a motor oil sample.

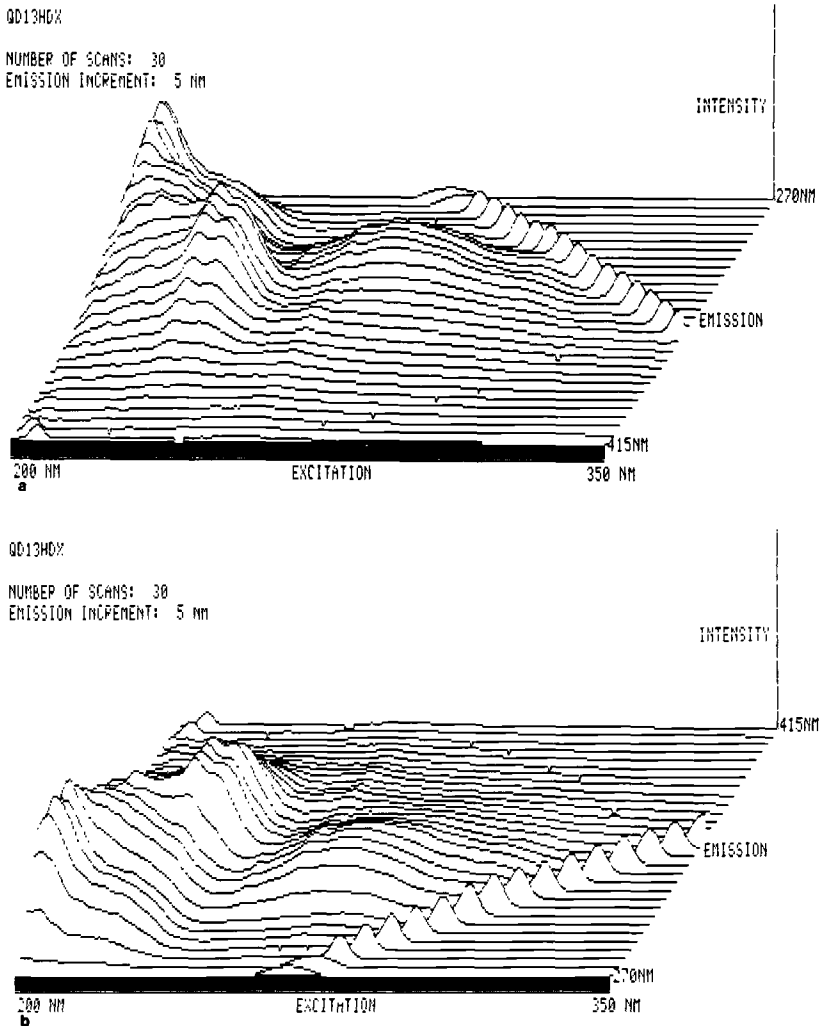


FIG. 4—Four different views of the three-dimensional stacked plot fluorescence spectrum (3-DF) of Quaker State Deluxe 10W-30 motor oil.

The software used to control the spectral collection process has been modified by the authors to collect three-dimensional synchronous excitation plots (3-DSEF). In this case, both monochromators are scanned first at fixed  $\Delta\lambda$ . For each succeeding scan,  $\Delta\lambda$  is increased by a fixed amount. The resultant spectra are plotted as excitation wavelength ( $x$ -axis) versus starting wavelength of the emission monochromator ( $y$ -axis) versus the fluorescence intensity ( $z$ -axis). Plotting the  $y$ -axis from high to low or low to high wavelength then gives two views of the synchronous fluorescence profile, making a total of six different views of the fluorescence of the sample, as shown in Fig. 5.

In many cases involving scientific evidence, the goal of the analysis of the evidence is not so much to identify something (say, to identify a motor oil as Quaker State 10W-40), but to compare a sample of unknown origin to one whose source is known. One of the objects of the pres-

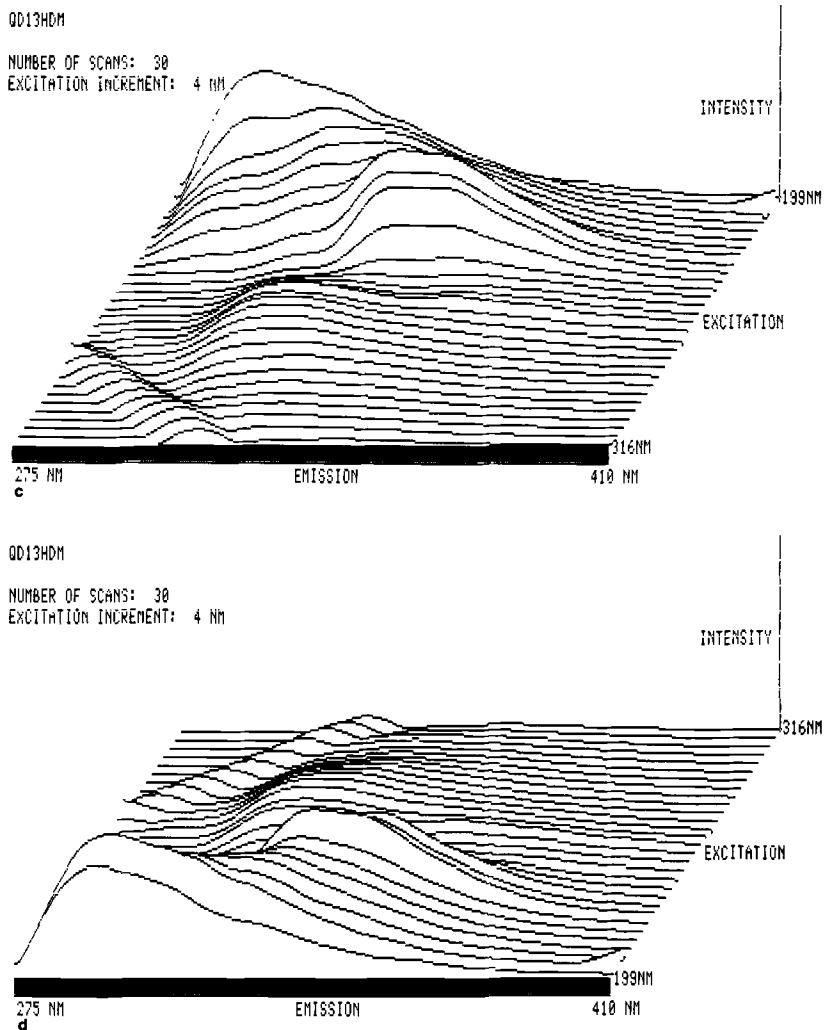


FIG. 4—Continued.

ent study is to see if this process of comparative analysis could be facilitated by the computer that originally generated the data. Taking advantage of the power and versatility of the operating system, the authors have created a program that has the capability of evaluating two 3-DF or 3-DSEF plots obtained under the same conditions and subtracting them from one another spectrum by spectrum. After compensation for negative fluorescence generated by the subtraction process, the resultant spectra are compiled and plotted in a manner similar to that used for the 3-DF or 3-DSEF plots. A flat "plane" plot would indicate that there is essentially no resultant fluorescence, thus suggesting that there may be a common source for the two samples. Such a plot is shown in Fig. 6a, where two different samples of the same brand and type of motor oil are compared. If the two samples being compared were of different sources, the differential plot would be expected to show contours in those areas where the fluorescence profiles differed. This shown in the plot in Fig. 6b, where two different motor oils are compared.

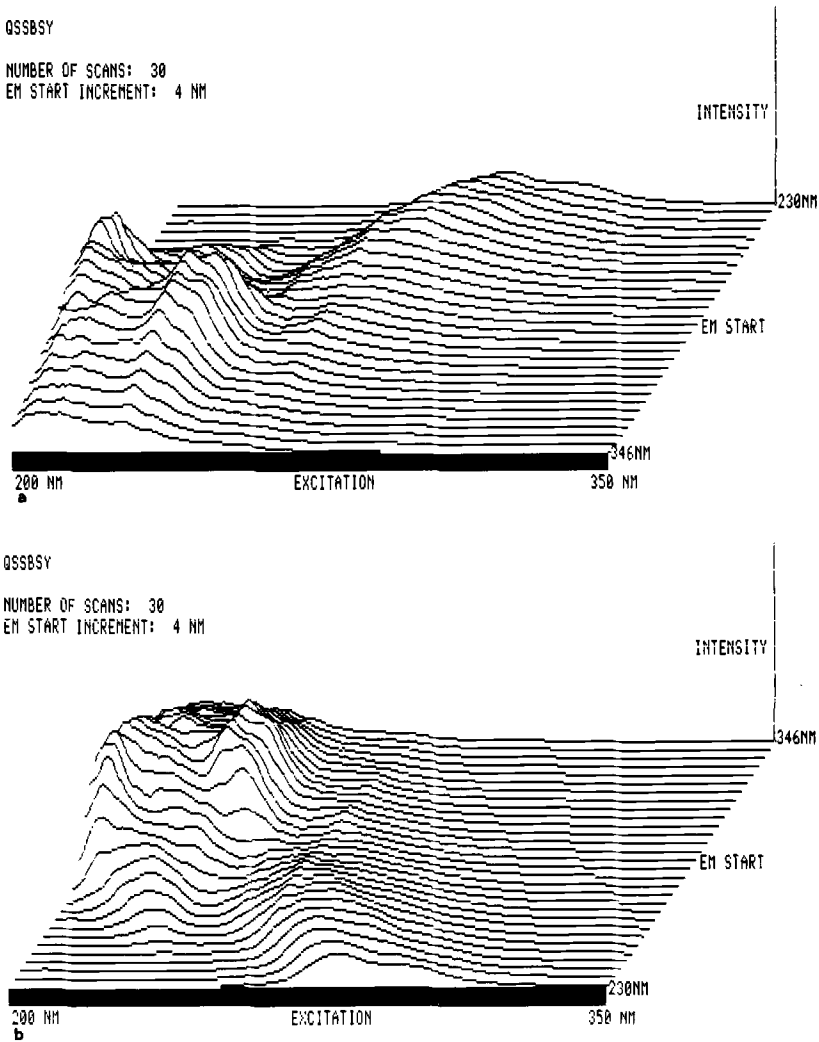


FIG. 5—Two different views of the three-dimensional stacked plot synchronous fluorescence spectrum (3-DSEF) of Quaker State Super Blend motor oil.

**Experimental Procedure**

*Reagents and Samples*

Motor oils and lubricants were taken straight from the container. Each sample was diluted to the optimum concentration, which was determined to be 25 ppm in hexane (Burdick-Jackson, high-performance liquid chromatography grade). Background fluorescence spectra of the hexane were taken under all experimental conditions. With the exception of Rayleigh scatter peaks, no fluorescence of consequence was noted from the solvent.

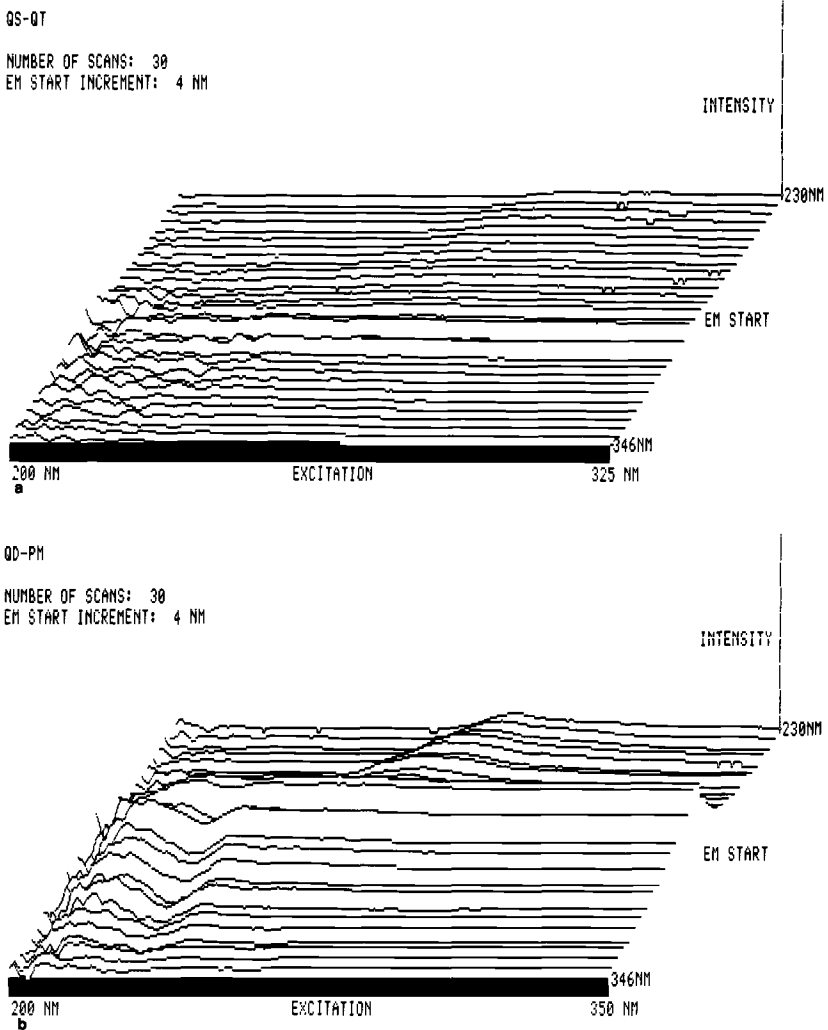


FIG. 6—Plotted differential synchronous stacked plot fluorescence spectrum of (a) two different samples of Quaker State 10W-40 motor oil and (b) Quaker State 10W-40 and Pennzoil 10W-40 motor oils.

A total of ten motor oil samples obtained from the Michigan State Police were analyzed. They were as follows:

- Meijer
  - Heavy-duty 30W 10W30
- Mobil Special 10W-30
- Pennzoil
  - Multivis 10W-40
  - Multivis 10W-30
  - 30W with Z-7

Quaker State  
20W-20  
30W  
Deluxe 10W-40  
Super blend

In addition, a total of eleven lubricating oils of various types, also obtained from the Michigan State Police, were tested:

Antirust oil 26 (brand unknown)  
Artex oil 11  
Cutting oil (brand unknown)  
Etna oil  
Hydraulic oil (brand unknown)  
Sears gear oil  
Sparvis oil 52, 47, and 65  
Stanicoil oil 5  
Total Leonard mineral seal oil

To minimize contamination by stray fluorescence, all glassware and cuvettes were cleaned after use with hexane, acetone, distilled water, and concentrated nitric acid. After a final wash with distilled water, the glassware was dried in an oven at 60°C.

#### *Instrumentation and Software*

The fluorimeter was a Perkin-Elmer Model LS-5 interfaced with a Model 3600 data station. The software used to control spectral data collection was Perkin-Elmer PECLS II. The plotting program, also Perkin-Elmer, was PLOT operating under PETOS. The spectrofluorimeter slits were set at 3 nm.

Each sample was prescanned to determine the wavelengths of maximum excitation and emission. Then normal and synchronous fluorescence plots were obtained by using the parameters determined by the prescan. From these data, conditions were selected to run the 3-DF (using Perkin-Elmer's LU3D program) and a 3-DSEF (using Siegel's SY3D program). Selected plots were compared by using Siegel's DF3D spectral subtraction program (see note on software at end of this article).

#### **Results and Discussion**

To avoid undue consumption of space, representative three-dimensional spectra are shown here. There are, of course, other views of the same plots, which are not given. Figure 7 contains one view of the 3-DF emission plots of the ten motor oil samples and Fig. 8 contains one of the 3-DSEF views of these motor oils. Figure 9 contains one of the 3-DSEF views of each of the other eleven lubricants.

Motor oils in general contain three distinct classes of PAH. This can be seen by examining any of the three-dimensional spectra shown here, all of which contain three separate areas of fluorescence. Although the motor oil samples studied exhibit similar fluorescence spectra, they can all be differentiated by at least one of several means, owing to the wealth of spectral information available.

Some of the motor oil samples can be distinguished by their normal fluorescence spectra. An example of this is shown in Fig. 1. The differences between these spectra are quite significant, especially considering that both samples are of the same grade (10W-40 high detergent). The subtracted spectrum in Fig. 2 emphasizes the differences between these spectra.



Examination of the ten 3-D emission spectral plots shows that most of the samples can be differentiated by careful examination of the plots. The broad peaks characteristic of the emission spectra of motor oils make comparisons of these plots somewhat more difficult than would otherwise be the case. Figures 7c (Mobil Special 10W-30) and 7j (Quaker State Deluxe 10W-40) are the easiest to distinguish from the others. Examination of other views of these spectra, as in Fig. 4, enable one to distinguish the other samples. The reader is directed to especially note the excitation spectra in Fig. 4 in comparison to the emission spectra. The excitation spectra have peaks which are generally sharper and easier to characterize.

The ten motor oil synchronous spectra shown in Fig. 8 also show the three major PAH regions. All of these plots can be differentiated by careful examination, although some of the differences are subtle. One problem that arose with the synchronous 3-D spectra as well as the 3-D excitation spectra should be noted. The two most intense excitation regions in motor oils occur between 200 and 230 nm. The instrument employed in the study is capable of scanning excitation wavelengths as low as 200 nm but does not maintain its high level of stability below 230 nm. As a result, the important spectral region below 230 nm tends to be somewhat noisy. This is especially true in those spectra where the fluorescence is significant in this region. The result is a loss in reproducibility in the spectra when the same sample is run repeatedly.

Most of the miscellaneous lubrication oils shown in Fig. 9 are somewhat similar to motor oils in their fluorescence characteristics but are easily differentiable from the motor oils. The reader is directed to especially note Fig. 9b (cutting oil), 9d (hydraulic oil), 9e (gear oil), and 9i (Sparvis 65). These exhibit especially unique 3-D plots.

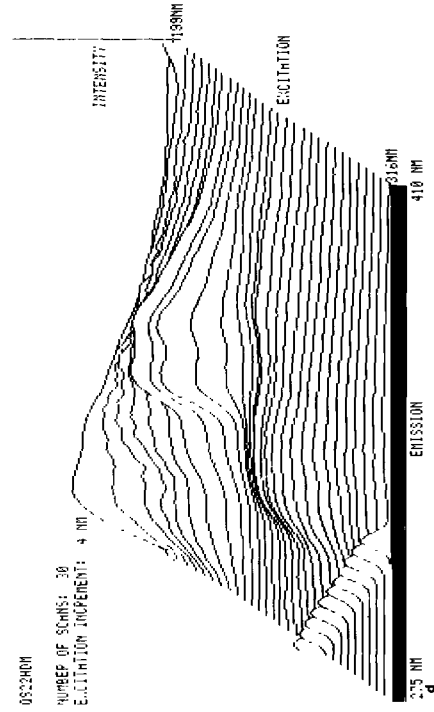
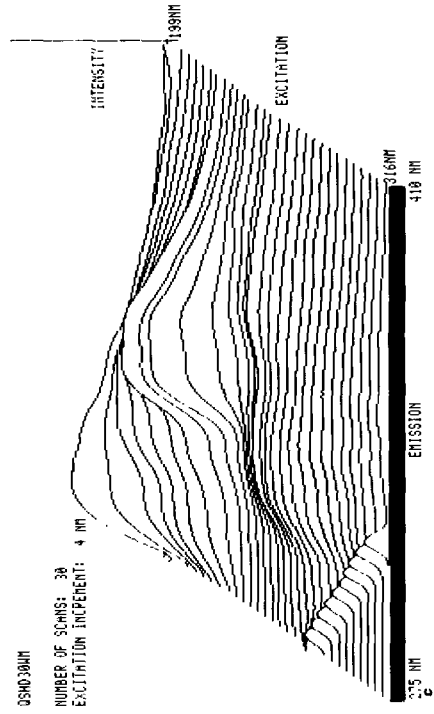
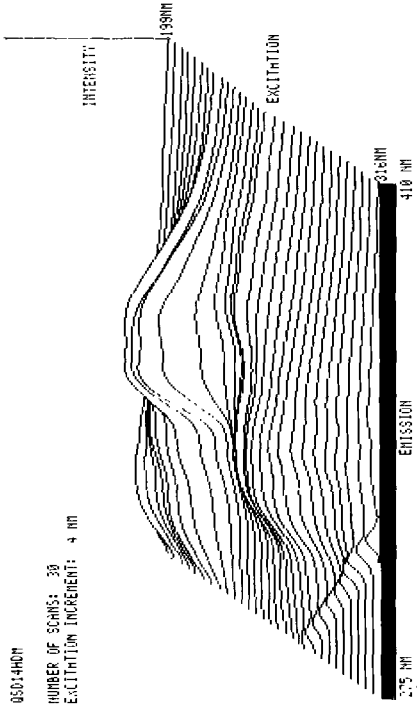
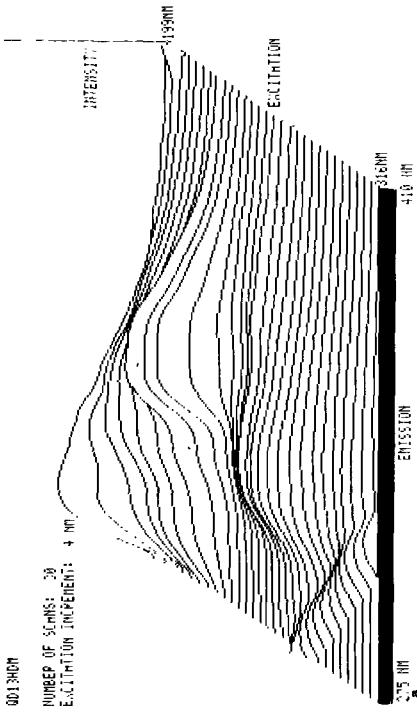
Without question, the most useful characteristic of the technique of 3-D stacked plot fluorescence spectroscopy is its ability to compare directly the spectra of two samples. The direct comparison of a sample of known source or origin with one whose source is unknown is a fairly common analysis in criminalistics. The method of subtracting stacked plots presented here is an effective way of directly comparing two samples of motor oil. This is shown in Figs. 6a and b. The only drawback to this particular technique is the noise level below 230 nm in the excitation or synchronous modes.

### Summary

The technique of three-dimensional stacked plot fluorescence spectroscopy has been evaluated for its ability to differentiate among a group of unused motor oils. The technique is capable of providing a large amount of spectral information concerning the total fluorescence of the sample and can present this information in a variety of ways with a minimum of operator intervention. The computer control of the operation also allows for direct comparison of two samples to help whether they could have a common source. The authors are at present exploring the possibility of investigating used motor oils using the methods presented here. The results of this investigation will be presented in a future paper.

### Note on Software

The software used in this work is available only from the Perkin-Elmer Corp. and is made to work only in conjunction with Perkin-Elmer spectrofluorometers and data stations. The OBEY programs for synchronous 3-D spectral plots generated in this work was written by Dr. Jay A. Siegel, although the authors understand that a similar program is available through Perkin-Elmer. Likewise the program for subtracting two 3-D plots was written by Dr. Siegel. This program has been made available to Perkin-Elmer to distribute with the other programs in the package and is due to be published in their *Fluorescence Newsletter*. For those who own the requisite hardware and software from Perkin-Elmer, the SY3D and DF3d programs written by Dr. Siegel may also be obtained by writing to him.



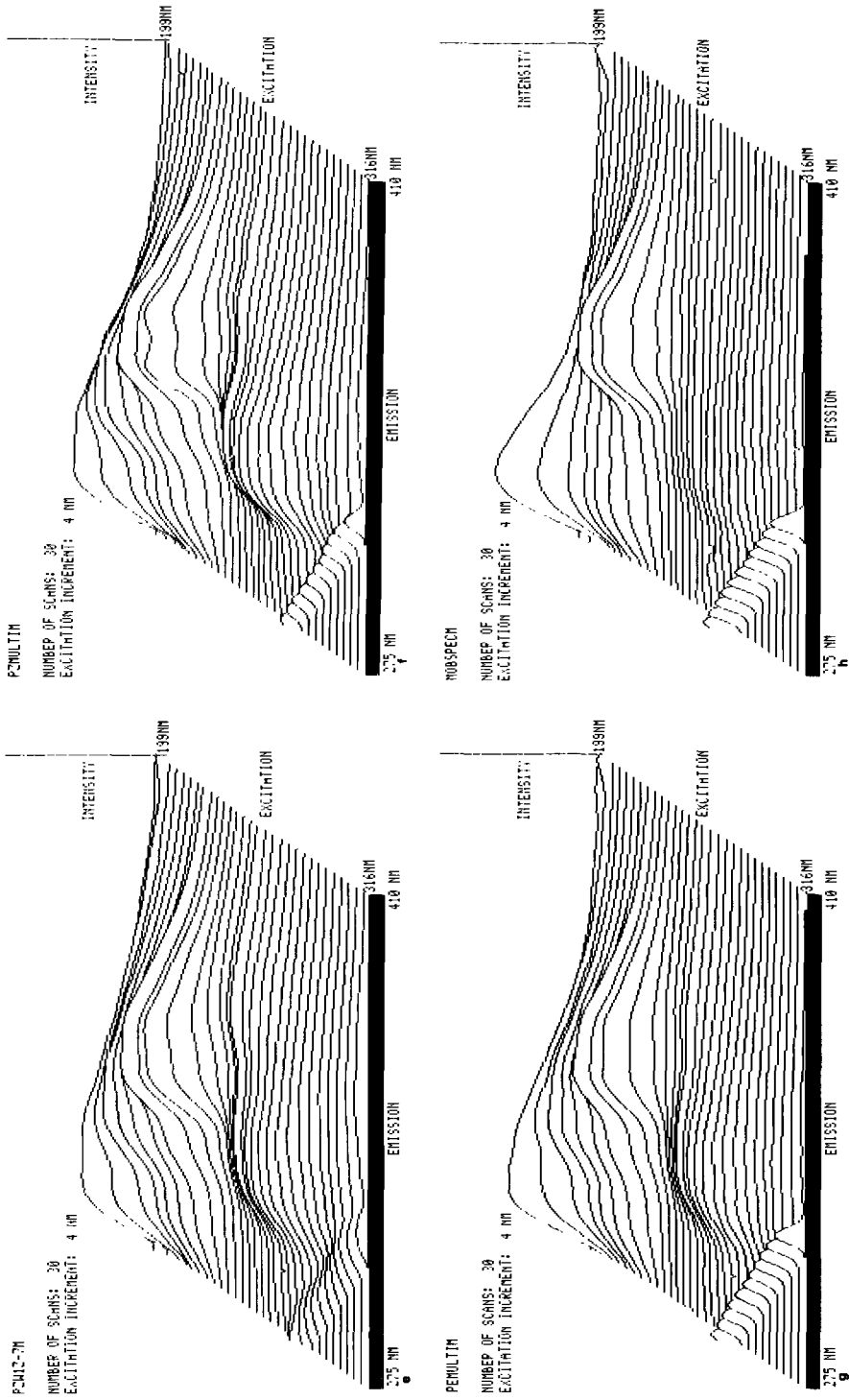


FIG. 7—3-D emission fluorescence spectra of ten motor oils.

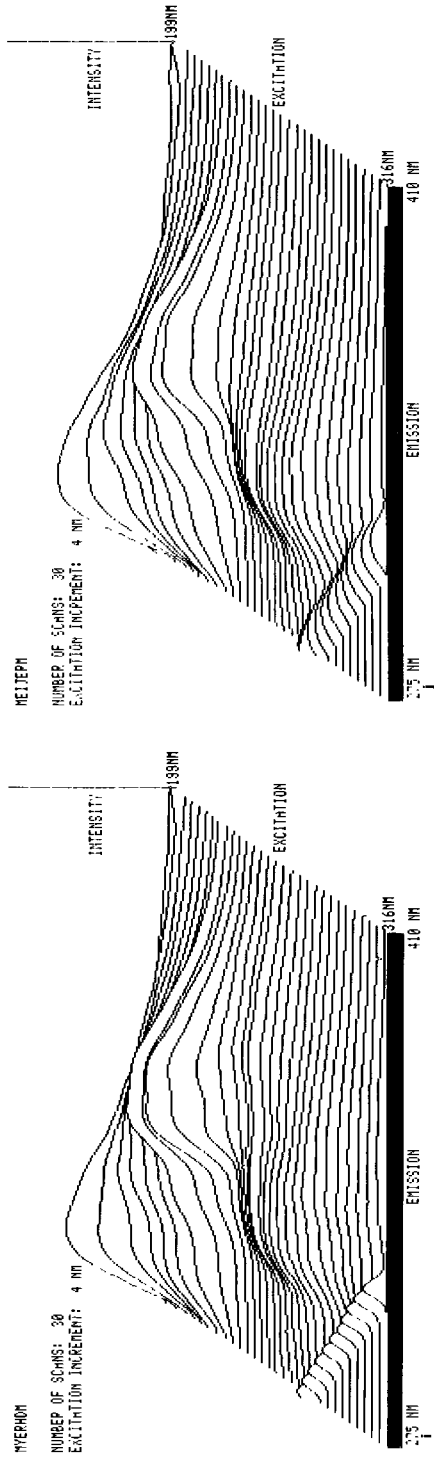


FIG. 7—Continued.

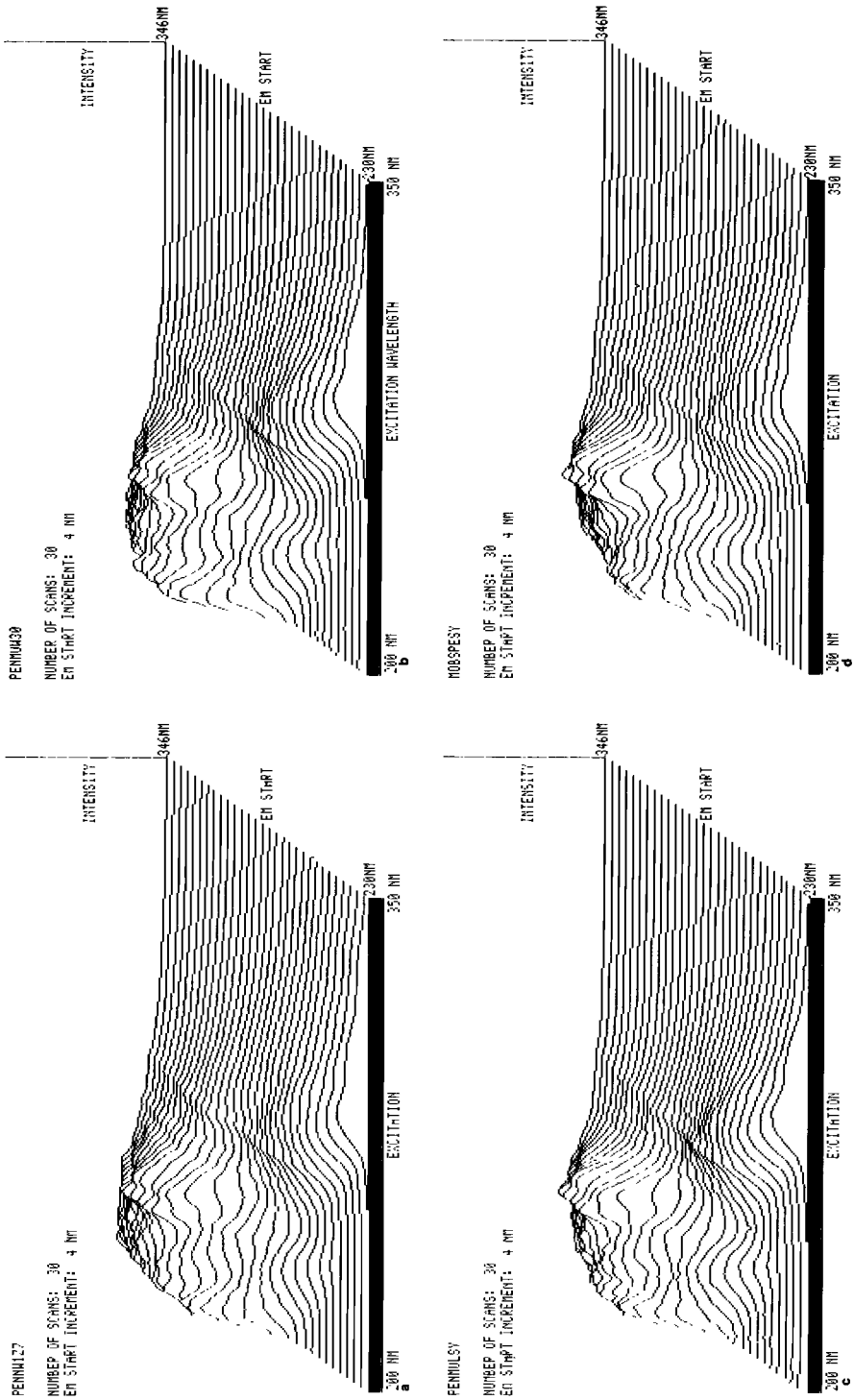
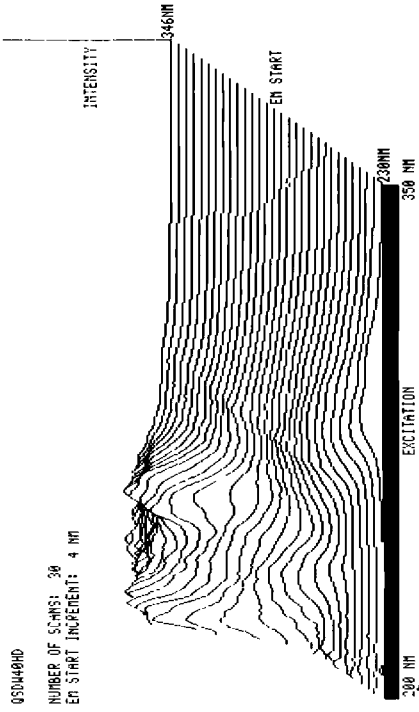
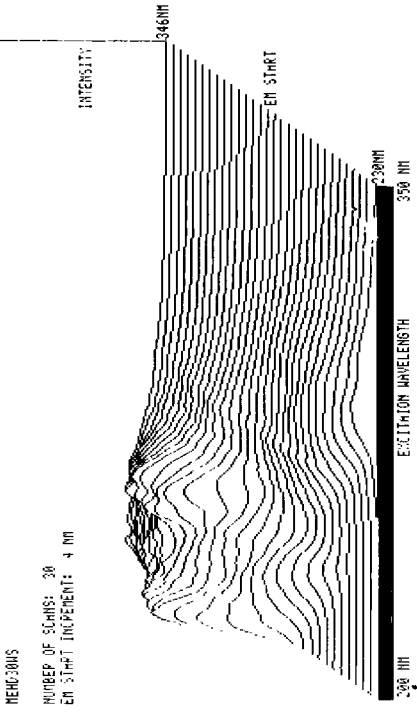
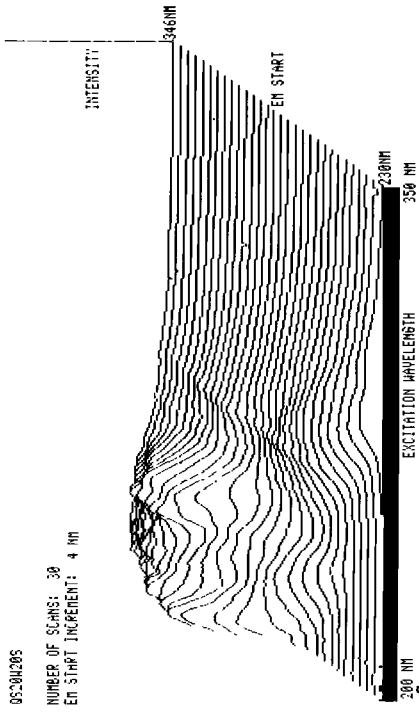
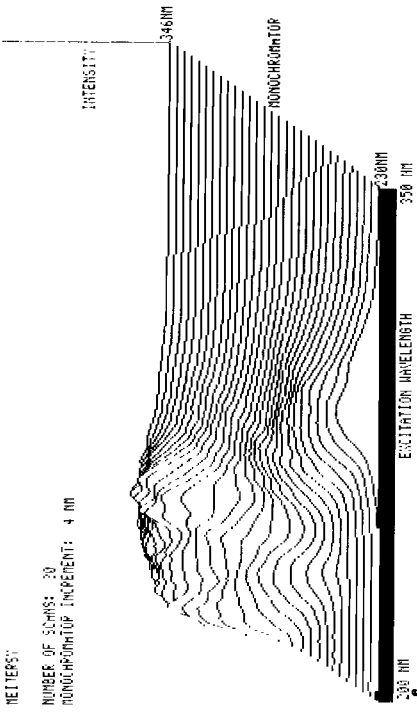


FIG. 8—3-DSEF fluorescence spectra of ten motor oils.



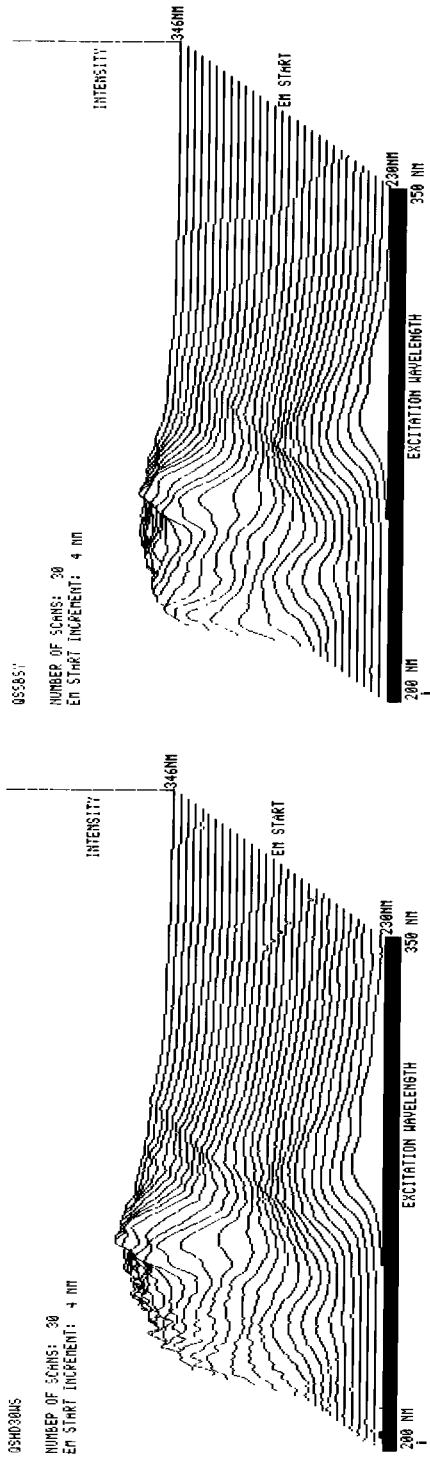
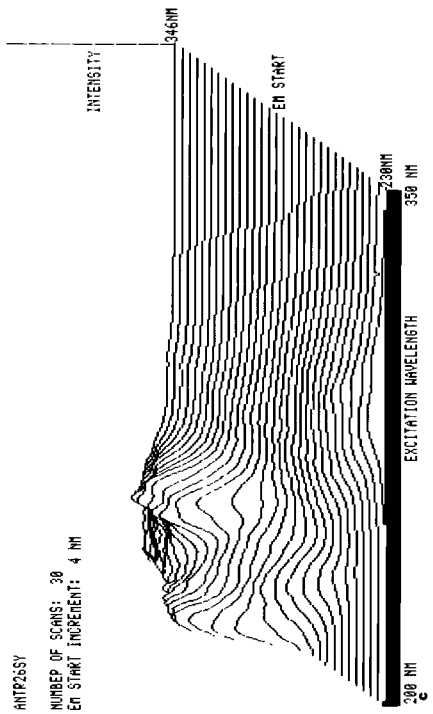
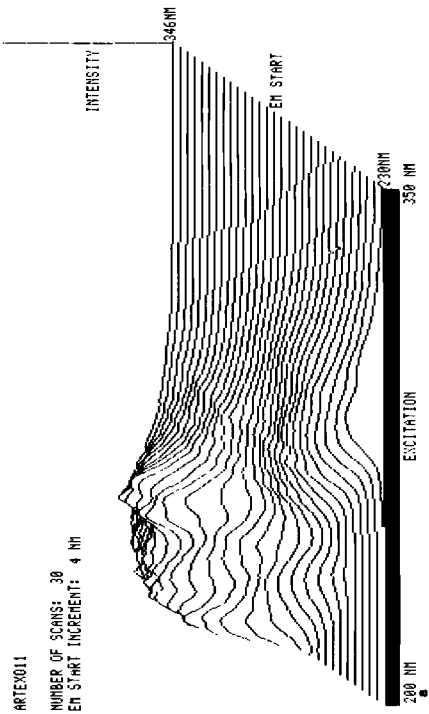
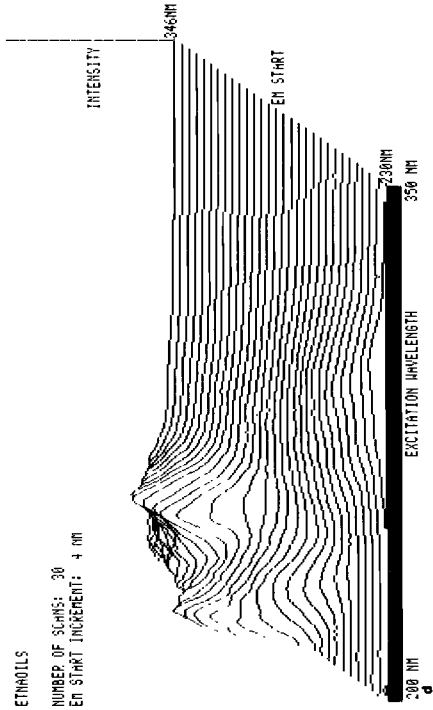
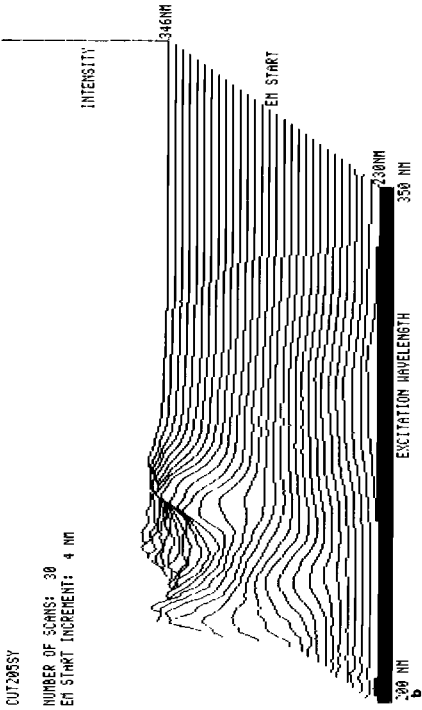


FIG. 8—Continued.





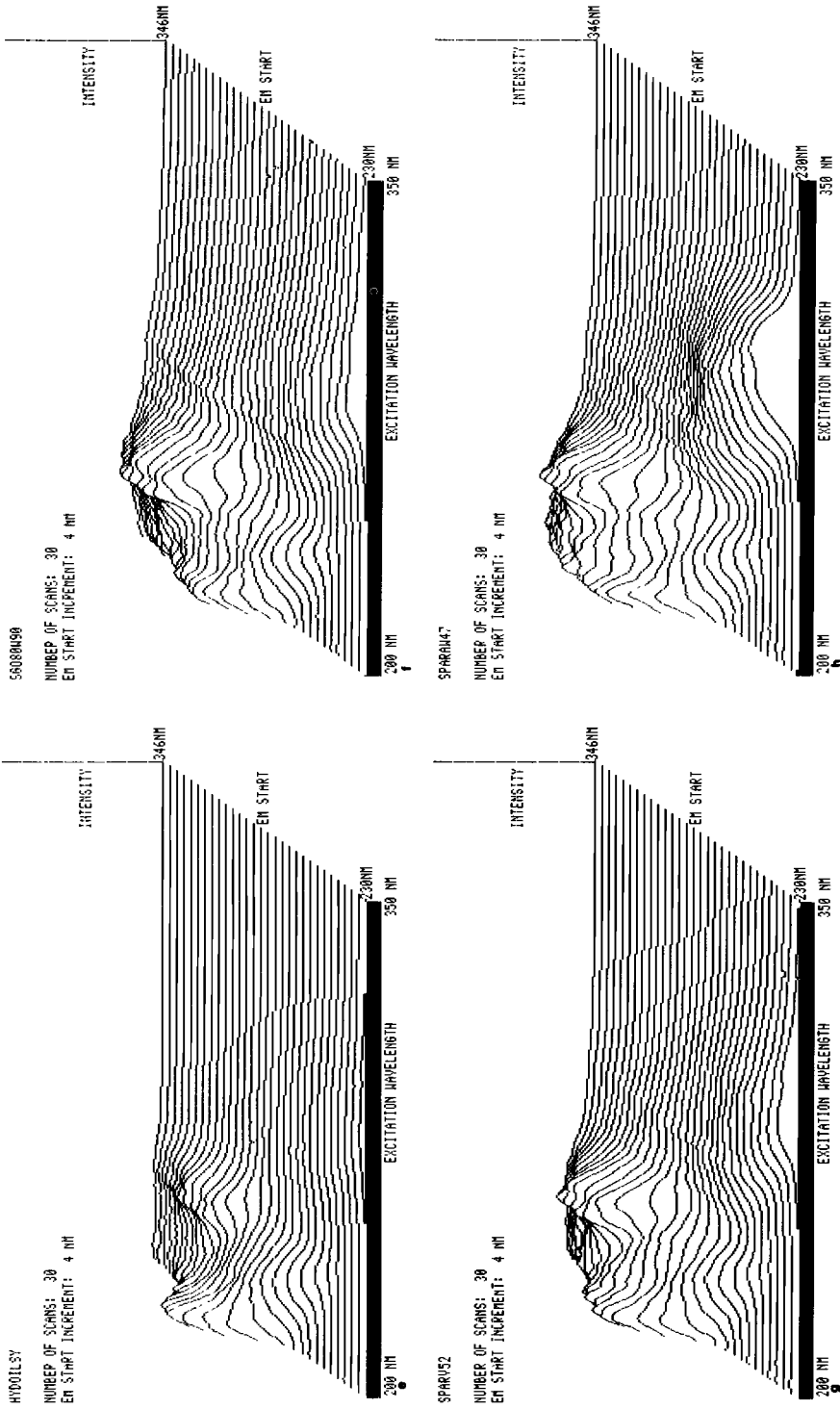


FIG. 9—3-DSEF fluorescence spectra of eleven miscellaneous lubricating oils.

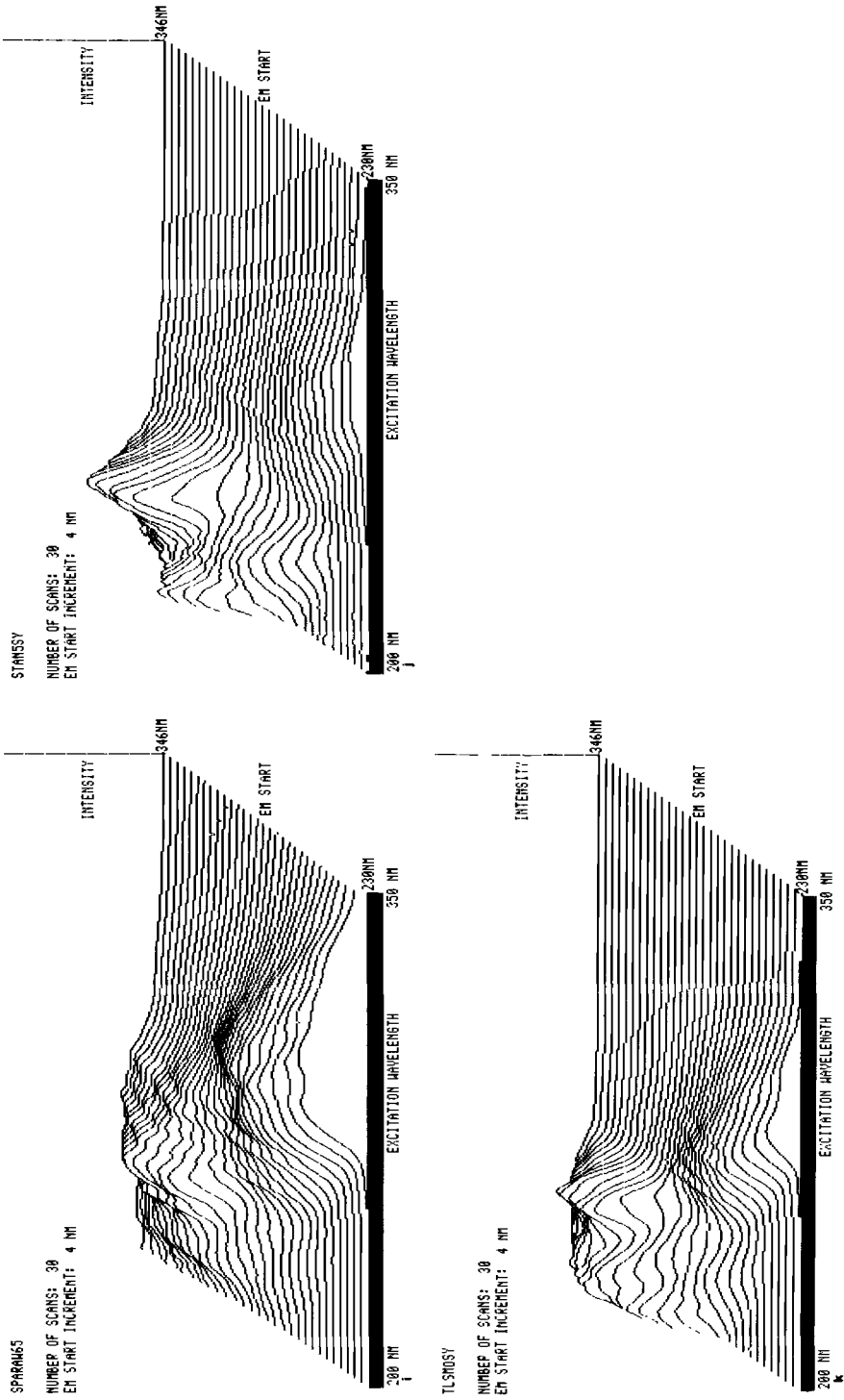


FIG. 9—Continued.

### Acknowledgments

The authors wish to express their appreciation to the Michigan State Police for the motor oil and lubricant samples used in this study.

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