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Fluorescence of Petroleum Products II. Three-Dimensional Fluorescence Plots of Gasolines

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ABSTRACT: The technique of three-dimensional fluorescence, first used in the forensic science analysis of motor oils and auto lubricants, is evaluated in the study of gasoline samples taken straight from the pump. The study includes ten samples of different grades and brands. No common spectral features attributable to brand or grade type could be shown. A program designed to determine the similarities or differences between two three-dimensional plots is employed to determine if two samples of gasoline could have a common source.

KEYWORDS: criminalistics, arson, gasoline, luminescence, petroleum products, fluorescence

The determination of gasoline in the forensic science laboratory has long been of interest. Although there are a number of civil or criminal case types where gasoline could be of prime importance as evidence, it is most often found as an accelerant in incendiary (arson) fires. The final determination of whether a given fire is arson usually depends upon the skill and experience of the fire scene investigator; however, the forensic science laboratory can assume an important backup role by determining the identity of an accelerant which is recovered from the fire. Gasoline is, by far, the most often encountered accelerant in fires today.

Depending upon the circumstances surrounding the fire, gasoline (or other accelerants) may be found in any of a number of forms in a variety of locales. For example, a sample of gasoline may not be directly involved in the fire and suffer relatively little heat effects. Such evidence would essentially be "whole" and would be fairly easy to analyze. Other times, some of the accelerant may be impregnated in a porous material such as carpeting, bed-clothes, seat cushions, and so forth. Such a sample may be partially or almost totally burned or evaporated. The remains would then be in the form of a residue which must be isolated from the surrounding matrix before analysis.

To a certain extent, the condition of the accelerant will dictate the methods used by the laboratory to isolate and identify it. Relatively few samples of gasoline from a fire arrive at

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the laboratory in a pristine state. They are most often absorbed into a matrix in a highly impure state. This is often complicated by the fact that the matrix itself may be derived from petroleum like the accelerant impregnating it. This can certainly hamper an analysis as can the fact that the fire department often uses thousands of gallons of water to put out a fire which can cause large disbursement of the accelerant. This state of affairs severely limits the amount and types of analysis that the forensic science laboratory can do.

Another limitation on the types of analysis that the laboratory will usually perform on gasoline residues is the lack of a sample of known origin with which to compare the residue. Because of this, identification of the type of accelerant present is performed rather than the degree of association possible with a sample of known source. Unfortunately, when such a comparison is called for, the methods normally used in forensic science laboratories for analysis are generally inadequate to the task of determining the certainty with which two samples may be associated.

The classical method of identification of the accelerant type in arson cases is gas liquid chromatography, usually after some form of concentration. This is practically the only technique that can reliably identify the type of accelerant present when it consists of a partially burned residue. The concentration methods mentioned above include room temperature or heated headspace methods or both, purge-and-trap, solvent extraction, and steam distillation. Although packed column gas chromatography (GC) is still most often employed, the resurgence of capillary GC with its attendant increase in resolution and sensitivity is rapidly taking over in this area. Even capillary GC lacks the discriminating power, however, to determine reliably the brand of gasoline or even whether it is leaded or unleaded, regular or high octane.

Many other tests have been used in the analysis of such petroleum products. These include infrared (IR) spectrophotometry [1], thin-layer chromatography [2], and lead analysis by atomic absorption, the common technique used in the analysis of lead. These methods are dependent upon the availability of a relatively intact sample with which to work and do not generally provide as much information as GC.

In the analysis of petroleum-based products in general, attention has recently been focused on the method of fluorescence spectroscopy. The previous article in this series contains references to the application of fluorescence to these substances, and focuses specifically on the analysis of motor oils and other automobile lubricants [3]. That study involves the use of a new technique called by the authors "three-dimensional fluorescence spectroscopy" because the printed output has a three-dimensional appearance to it. This method basically involves the collection of a large number of fluorescence spectra (excitation, emission, or synchronous excitation), each taken under different conditions. This collection of spectra is then plotted on a single graph resulting in a complete picture of the fluorescence characteristics of the sample; far more information than would be available from a single fluorescence plot. If all three types of fluorescence are run, the two possible views of each plot result in a total of six different three-dimensional views of the spectrum. When applied to motor oils and lubricants, the method yielded fluorescence plots that were so characteristic of the sample run, that all twenty-one of the lubricants tested could be differentiated. In addition, a computer program was developed by the authors that permitted the comparison of one plot with another by subtraction of the plots spectrum by spectrum. A preliminary test was done on this program using two of the lubricants.

The present paper is the second in this series and comprises a study of the three-dimensional fluorescence spectra of ten gasoline samples taken straight from the pump. The purposes of the study were first, to determine the range of fluorescence for gasoline samples; second, to determine if different brands and grades of gasoline could be differentiated by three-dimensional fluorescence; and third, to test the comparison program much more thoroughly using blind testing on more samples.

Experimental Methods

Samples and Reagents

For this study, the following ten brands of gasoline were used. They were all taken straight from the pump and were used without further treatment except dilution:

Amoco regular,
Amoco lead free,
Amoco premium lead free,
Mobil regular,
Mobil lead free,
Mobil super unleaded,
Shell regular,
Shell regular unleaded,
Total regular, and
Total lead free.

All samples were diluted to 20 ppm in ultraviolet (UV) grade cyclohexane (Burdick-Jackson). The solvent was determined to contribute negligible fluorescence to the spectra. The glassware was treated as described in the previous article in this series [3].

Instrumentation and Software

The Perkin-Elmer Model LS-5 Spectrofluorimeter was employed as described in the previous article [3]. The same is true with the software used in this study (Perkin-Elmer PECLS and PLOT and Siegel's SY3D and DF3D programs). The procedures for obtaining and plotting the spectra were also as previously described.

Results and Discussion

All of the gasoline samples exhibited all of their fluorescence peaks in the same general areas. For excitation, this is 200 to 300 nm and for emission, 250 to 400 nm. These are approximately the same regions where the previously studied motor oils and lubricants had their fluorescence maxima. This is not surprising since the same types of polynuclear aromatic hydrocarbons are present in all of these petroleum distillates. Figures 1 through 3 show single excitation, emission, and synchronous excitation spectra for one of the gasoline samples. Figures 4 through 6 show three-dimensional excitation, emission, and synchronous plots of the same sample.

After examining the three-dimensional plots for all ten gasolines, it was determined that the emission plots provided the best intersample discrimination. Figures 7 through 16 contain the emission plots of the ten gasolines studied. If these plots are examined side by side, it is very difficult to discern marked differences between them, although they all contain three distinct regions of emission fluorescence. It is because of this difficulty that the subtraction program was developed. This program shows graphically whether or not two plots are truly different.

The emission plots were further studied to determine if there were any features common to either different grades of gasoline of the same brand (for example, Shell regular and unleaded) or within a group of gasolines of the same grade (for example, Shell, Mobil, and Amoco regular). No major common features were found, evidently because the differences within brands or grades are not the moieties primarily responsible for their fluorescence.

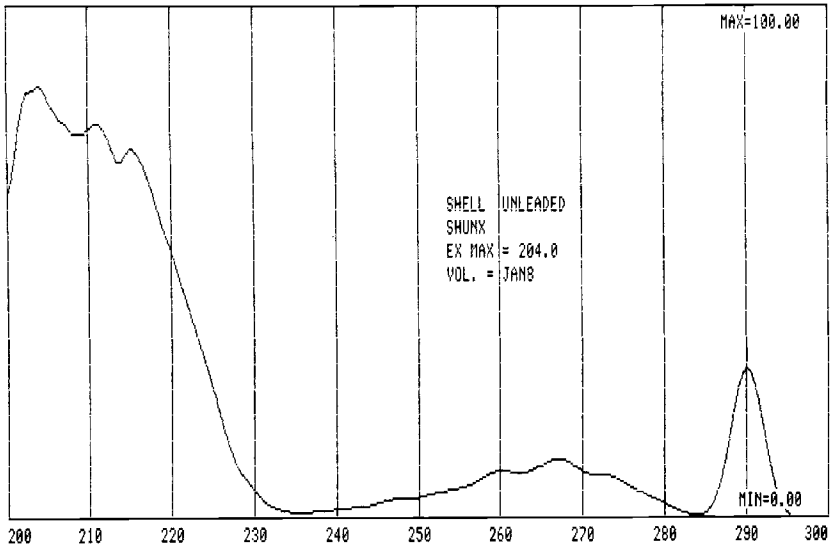


FIG. 1—Single excitation fluorescence spectrum of Shell regular unleaded gasoline.

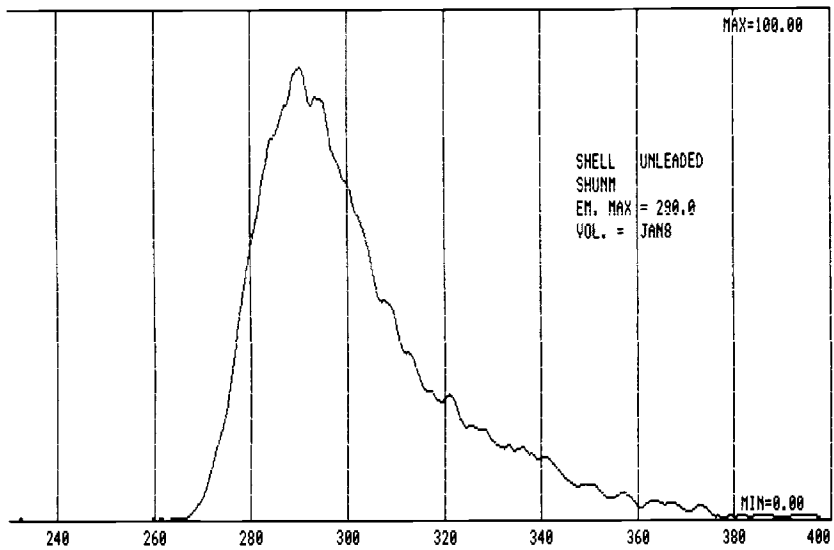


FIG. 2—Single emission fluorescence spectrum of Shell regular unleaded gasoline.

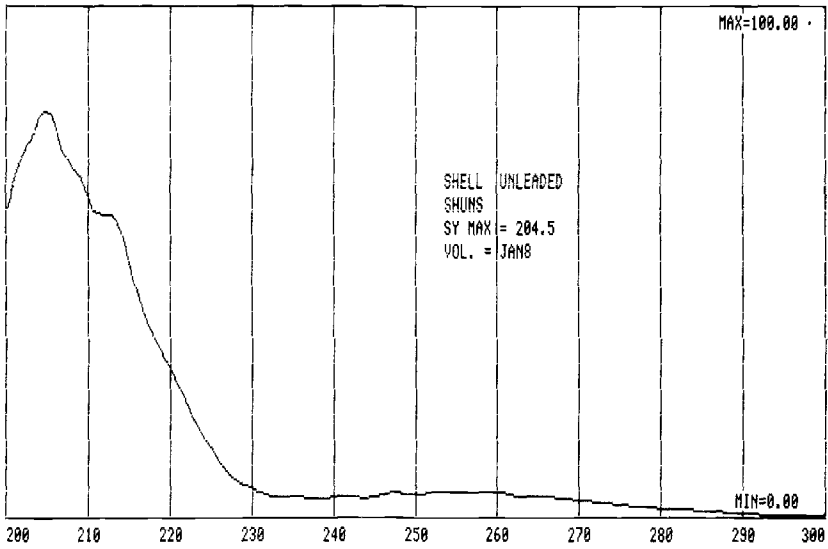


FIG. 3—Single synchronous fluorescence spectrum of Shell regular unleaded gasoline.

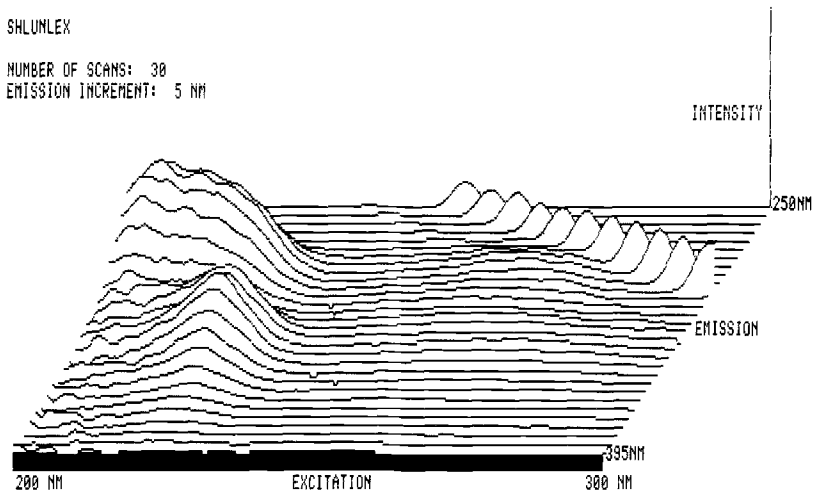


FIG. 4—Three-dimensional excitation plot of Shell regular unleaded gasoline.

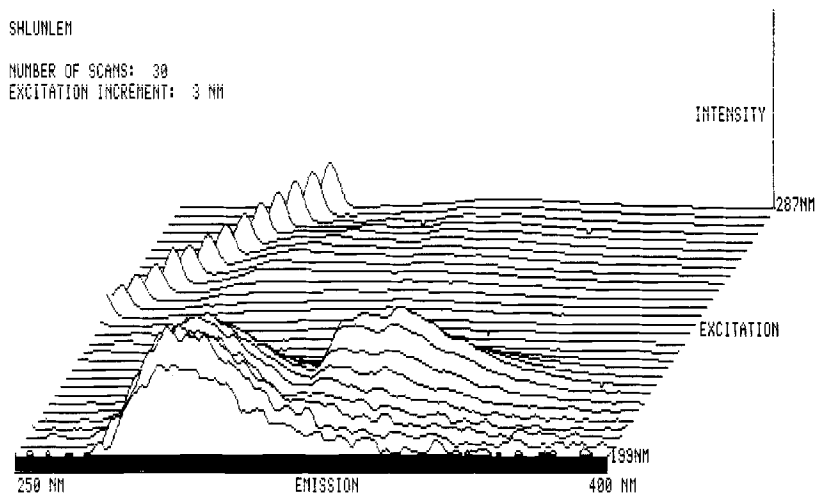


FIG. 5—Three-dimensional emission plot of Shell regular unleaded gasoline.

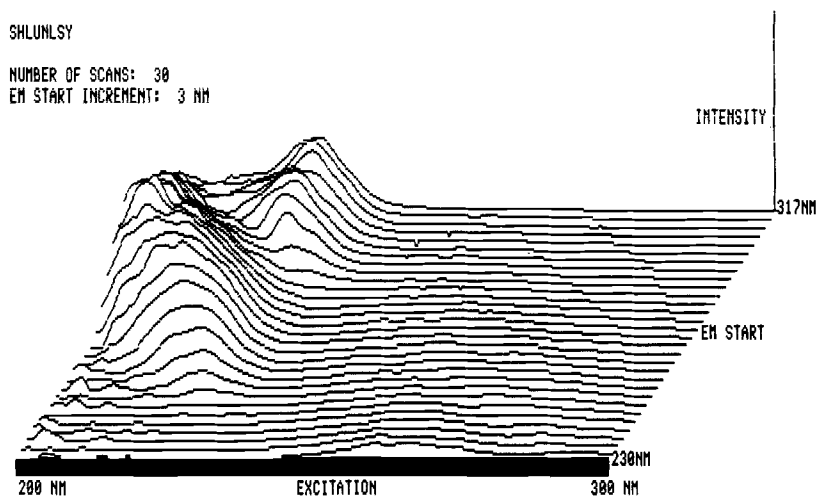


FIG. 6—Three-dimensional synchronous plot of Shell regular unleaded gasoline.

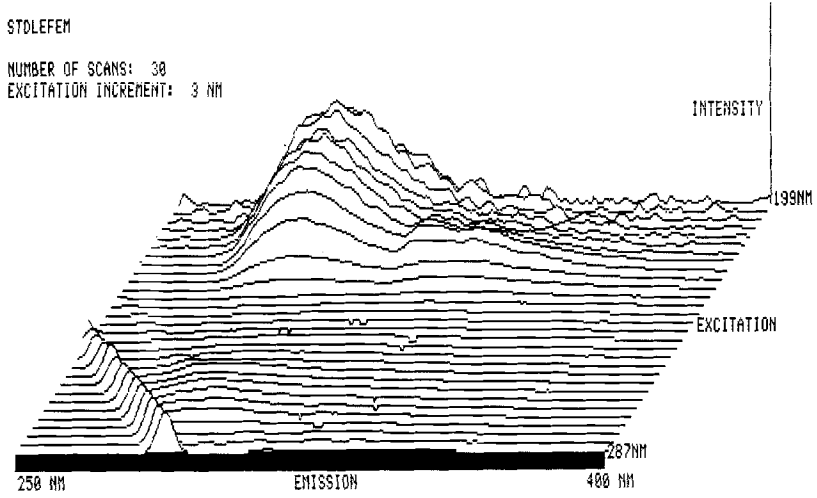


FIG. 7—Three-dimensional emission spectrum of Amoco lead free.

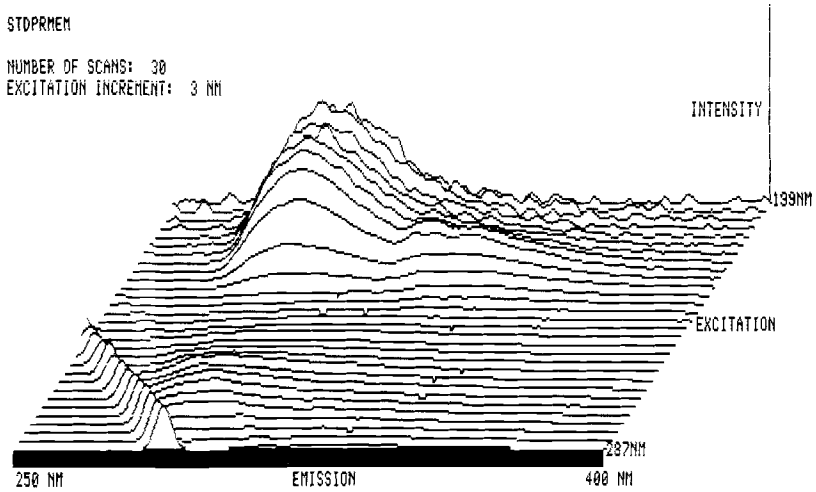


FIG. 8—Three-dimensional emission spectrum of Amoco premium lead free.

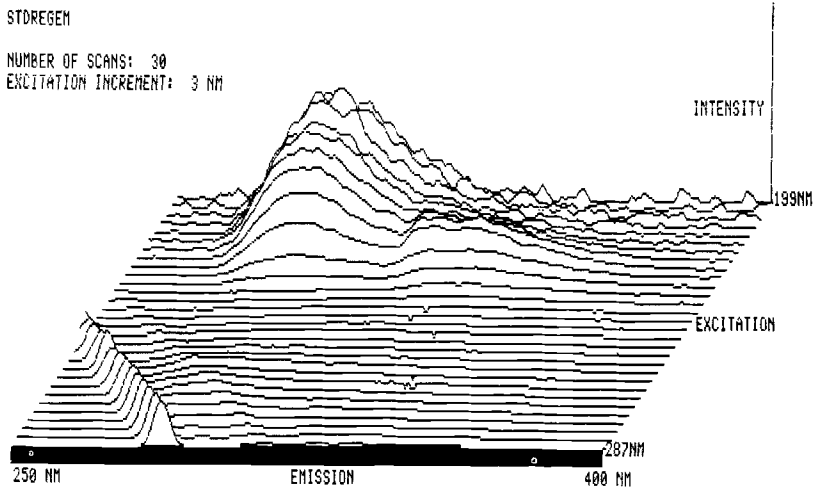


FIG. 9—Three-dimensional emission spectrum of Amoco regular.

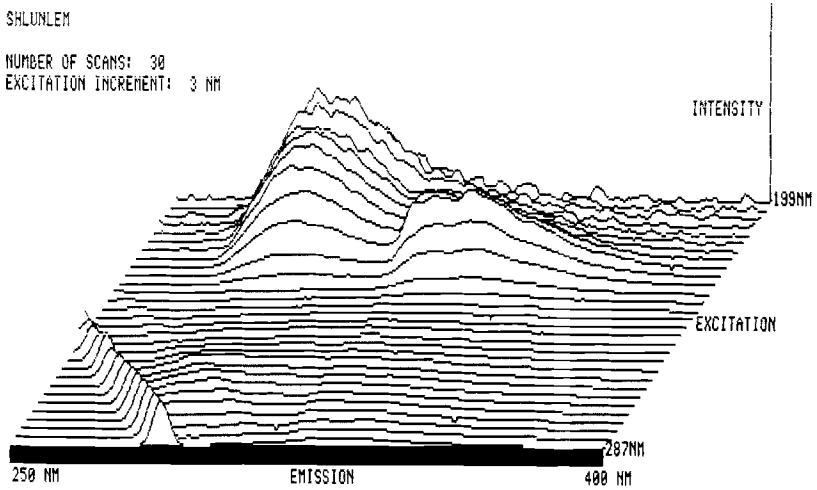


FIG. 10—Three-dimensional emission spectrum of Shell regular unleaded.

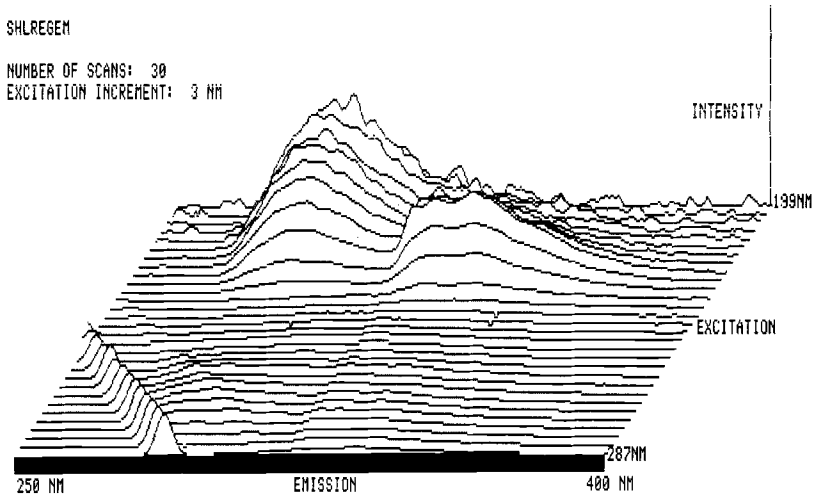


FIG. 11—Three-dimensional emission spectrum of Shell regular.

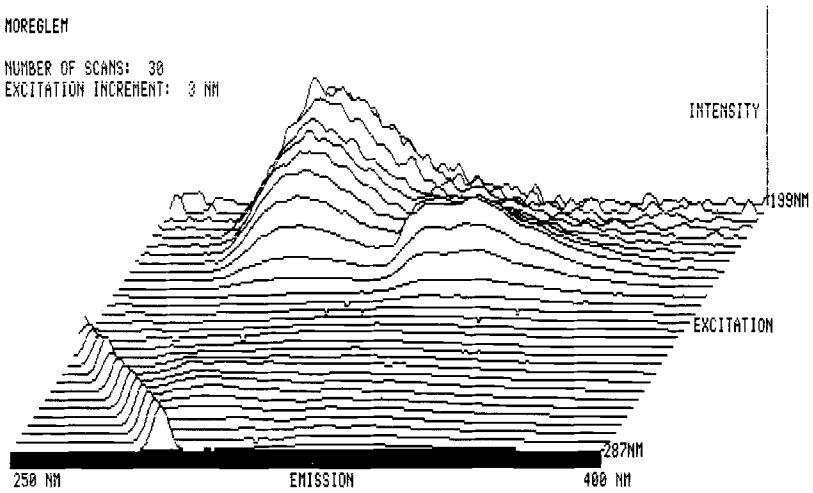


FIG. 12—Three-dimensional emission spectrum of Mobile regular.

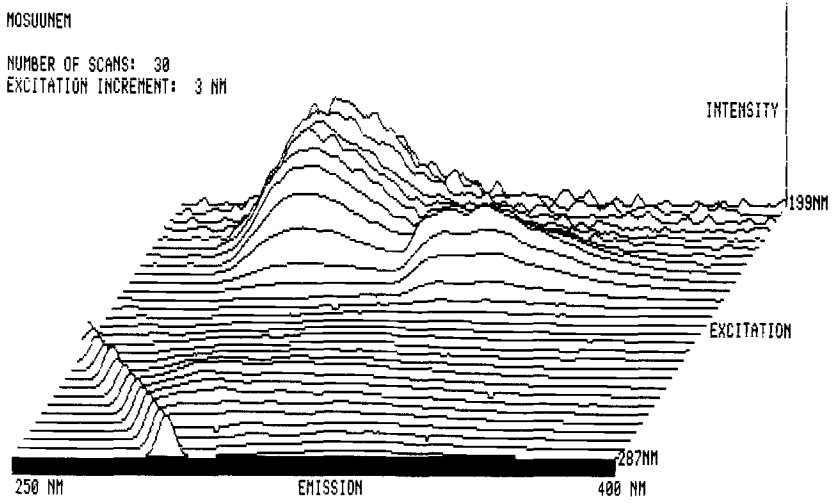


FIG. 13—Three-dimensional emission spectrum of Mobil super unleaded.

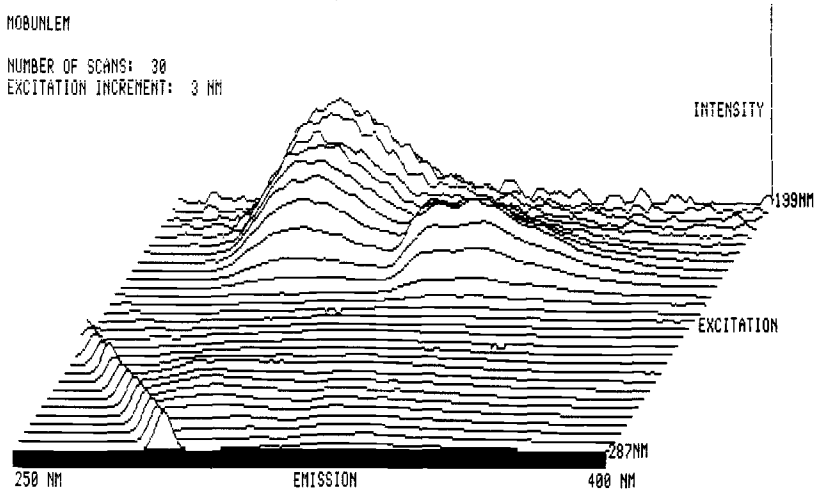


FIG. 14—Three-dimensional emission spectrum of Mobil lead free.

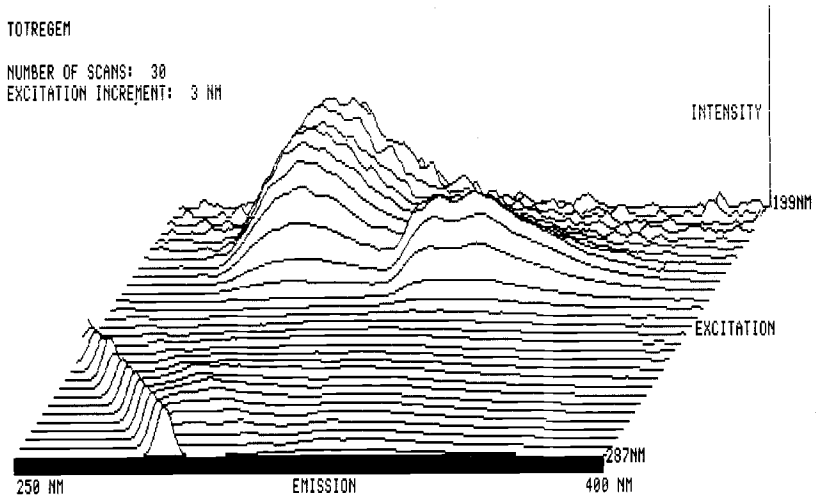


FIG. 15—Three-dimensional emission spectrum of Total regular.

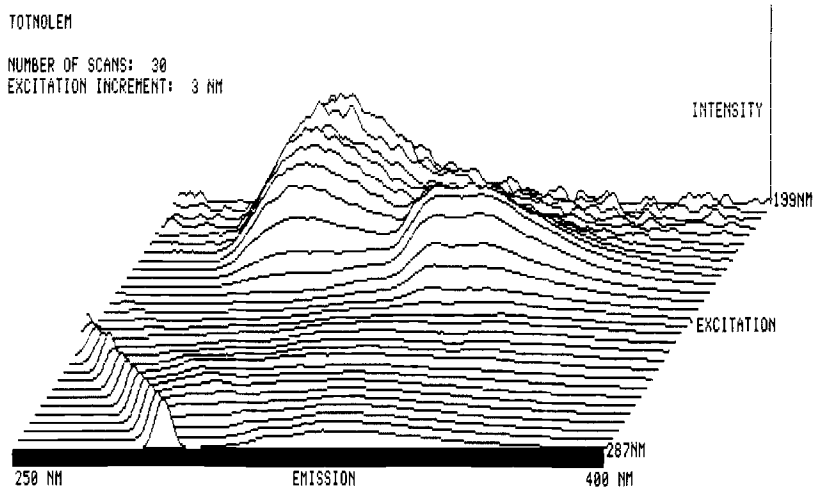


FIG. 16—Three-dimensional emission spectrum of total lead free.

The Subtraction Program

To determine if the spectrofluorimeter and data system employed in this study could reliably determine if two samples of gasoline could have a common source, Siegel's subtraction program was employed in a blind study. Note that the object of this study is not to be able to conclude that two samples of gasoline definitely have a common source to a standard of reasonable scientific certainty, but only to show that it is possible to conclude from this method that two samples could have had (or could not have had) a common source.

The evaluation of the subtraction program was performed as follows. A total of twelve samples of gasoline taken from those previously studied were presented to the analyst in pairs. The object of the exercise was to use three-dimensional fluorescence and the program which subtracts one plot from another to determine if each member of a pair could have a common source. For each sample, a three-dimensional emission plot was generated. Each plot was obtained over the same spectral range, both samples were "auto-concentrated" at their peaks of maximum excitation and emission, and the same number of spectra (thirty) were obtained from each.

After obtaining the emission plots, one member of a pair was subtracted from the other, spectrum by spectrum, and the resultant three-dimensional subtracted plots were printed. Figures 17 through 22 contain the six resultant plots. It is hypothesized that such a resultant plot should be essentially flat (except for noise which was present at excitation wavelengths below 230 nm) if the two samples could have had a common source. If the plot showed any appreciable "humps," then the conclusion is that the samples had to have different sources. On this basis, the analyst concluded that Samples 3-4, 7-8, and 9-10 each could have had a common source with the other of the pair. It was further concluded that members of the other pairs, namely 1-2, 5-6, and 11-12 had different sources. The actual compositions of the pairs were as follows:

- 1-2 Mobil regular - Amoco regular,
- 3-4 Mobil unleaded - Mobil unleaded,
- 5-6 Shell regular - Shell unleaded,
- 7-8 Total regular - Total regular,
- 9-10 Mobil supreme - Mobil supreme, and
- 11-12 Amoco unleaded - Amoco unleaded + total unleaded.

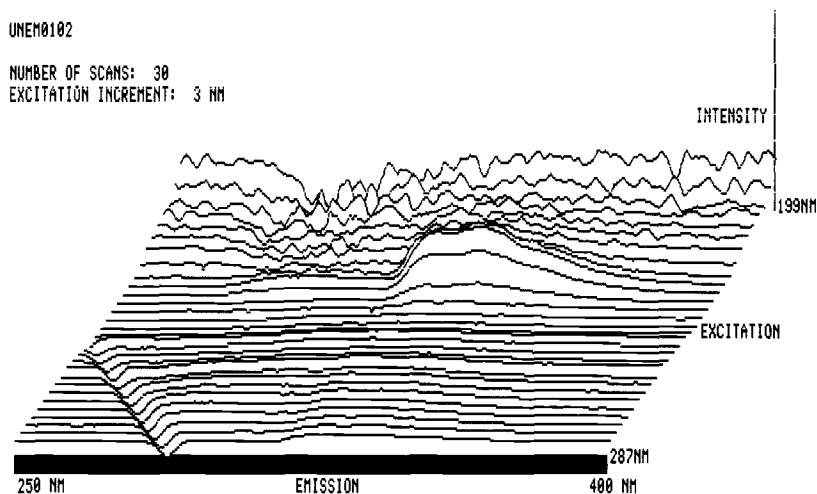


FIG. 17—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 1 and 2 — Mobil regular and Amoco regular.

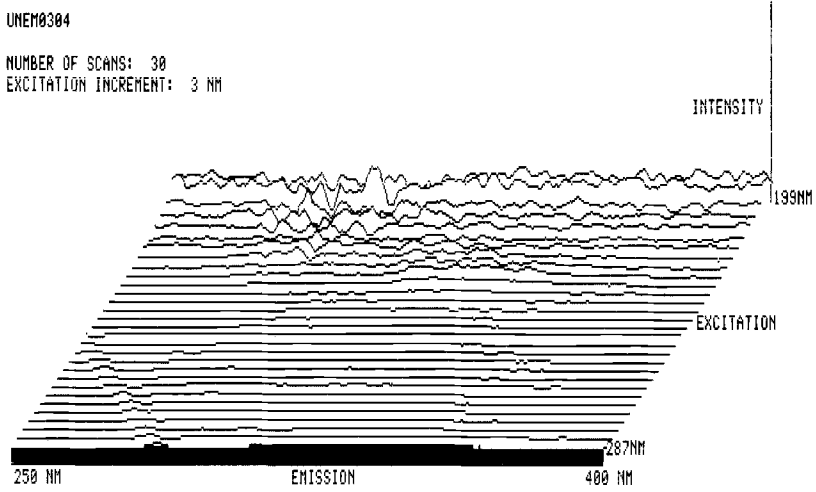


FIG. 18—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 3 and 4 — both Mobil unleaded.

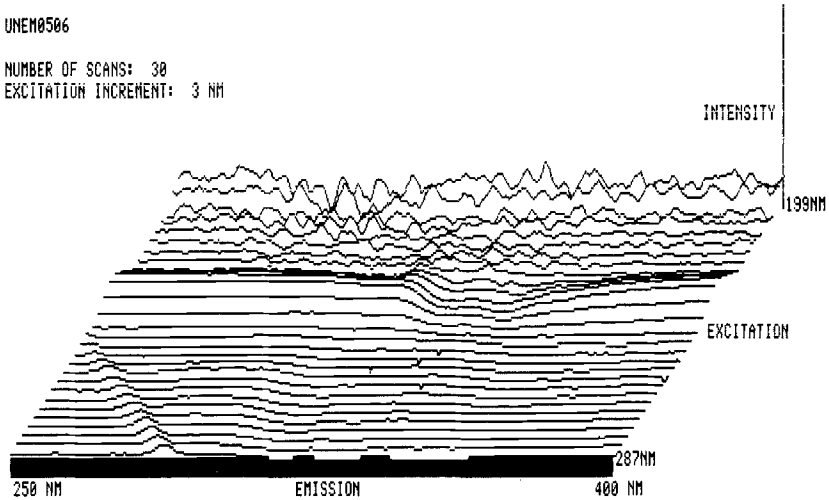


FIG. 19—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 5 and 6 — Shell regular and Shell unleaded.

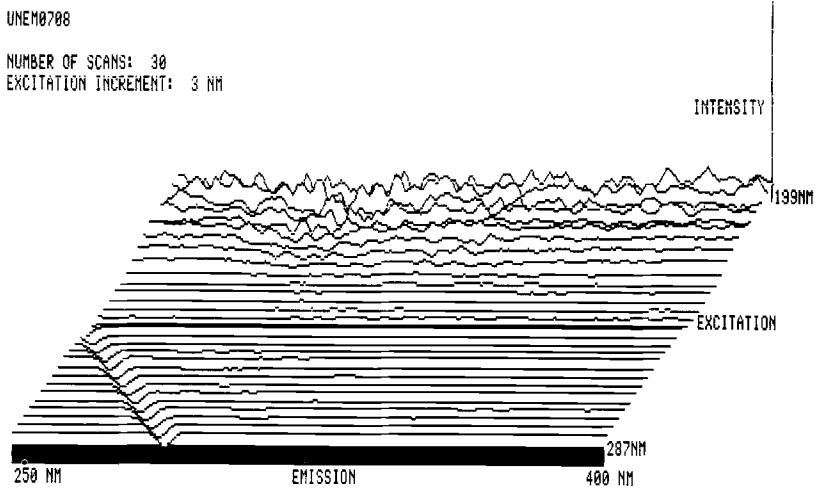


FIG. 20—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 7 and 8 — both total regular.

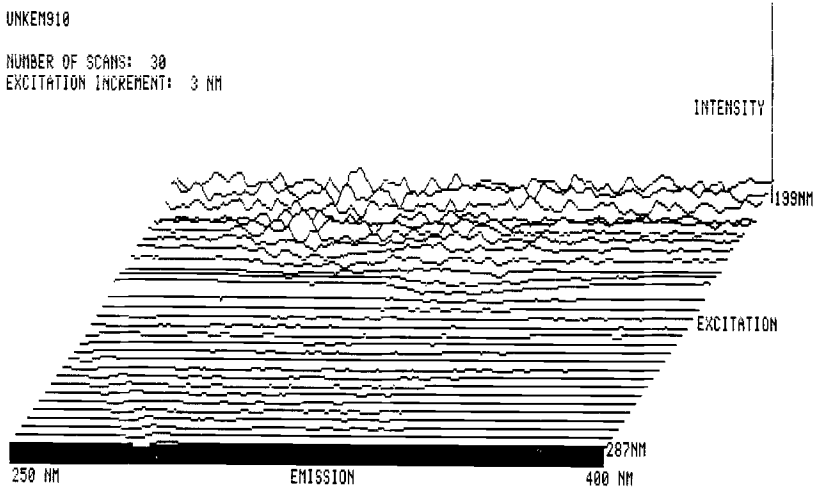


FIG. 21—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 9 and 10 — both Mobil supreme.

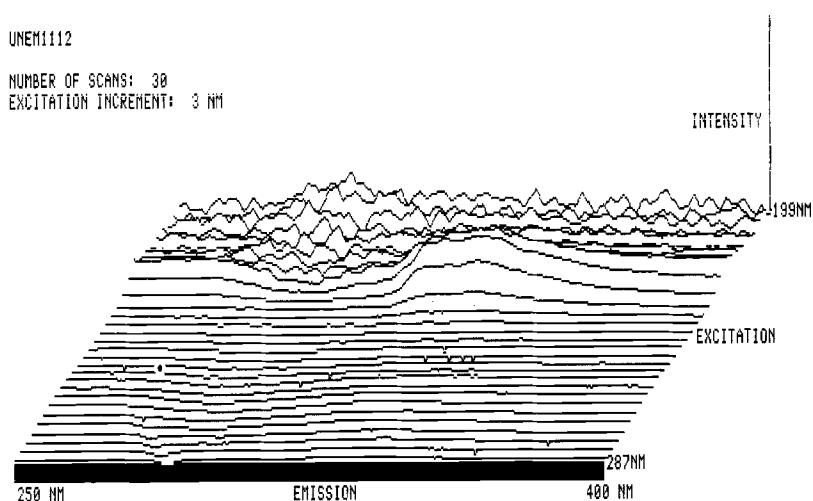


FIG. 22—Plot resulting from subtraction of one three-dimensional emission plot from another—Unknowns 11 and 12 — Amoco unleaded and Amoco unleaded.

As can be seen from examination of the subtracted plots, those pairs with different sources had clear areas of net fluorescence in them and were easily distinguishable from those whose plots were essentially planar. The noise in regions where the excitation monochromator is below 230 nm is not the fault of the specific instrument, but is due to the fact that this model is not designed to run at these low wavelengths although it can be forced to.

Summary

The technique of three-dimensional fluorescence has been employed in the determination of whole gasoline samples. The areas of maximum fluorescence in gasolines are similar to those in other petroleum distillates studied previously. Three-dimensional emission plots provide enough discrimination to permit determination of whether two samples could have had a common source. This is accomplished by subtracting one emission plot from the other and examining the resultant three-dimensional plot.

The effects of evaporation (weathering) and controlled combustion on the three-dimensional fluorescence of gasolines are presently being studied. In addition, the contribution of the dye packages present in commercial gasolines to their fluorescence is also being investigated.

References

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