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Fluorescence of Petroleum Products V: Three-Dimensional Fluorescence Spectroscopy and Capillary Gas Chromatography of Neat and Evaporated Gasoline Samples

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ABSTRACT: Nine brands and grades of gasoline were analyzed by three dimensional fluorescence spectroscopy (3-DF). Capillary gas chromatograms were also obtained in order to monitor the loss of components during evaporation. All samples were examined neat, then after 50% evaporation, and then after evaporation until only a semi-solid residue remained (nearly evaporated). It was found that the fluorescence technique was capable of distinguishing among the samples in both neat and evaporated conditions and that it showed similarities between neat and 50% evaporated samples. The totally evaporated samples could not be associated with its corresponding neat sample.

KEYWORDS: forensic science, arson, fluorescence, gas chromatography, petroleum products, hydrocarbons

Products derived from petroleum often occur as evidence in criminal and civil cases. These include accelerants such as gasoline or kerosene, charcoal lighters and paint thinners, petrolatum products such as petroleum jelly and even crude oil itself. Although these materials may be encountered in a pristine, uncontaminated form, more often they are weathered or partially evaporated.

In the forensic science laboratory the analyst is normally called upon to determine what type of product (for example, gasoline v. fuel oil) is present. Other times it may be necessary or desirable to show a degree of association between a sample of petroleum product whose source is known with one from a crime scene. The lack of chemical markers in petroleum products normally precludes individualization of an unknown to a particular source.

The technique of choice for the characterization of petroleum products in forensic science laboratories has long been gas chromatography. Originally useful chiefly to categorize a

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petroleum product only by type (for example, gasoline v. kerosene), GC has now demonstrated the ability to differentiate among similar brands and grades of products such as gasoline if high resolution capillary GC is used [1]. Depending upon the circumstances, the hydrocarbon residue may first be concentrated by heated headspace, purge and trap, distillation or solvent extraction.

Many commercial products derived from crude oil exhibit characteristic fluorescence behavior owing to the presence of significant amounts of polynuclear aromatic hydrocarbons (PAH) containing a high degree of conjugation. It is well known that molecular fluorescence is sensitive to the presence and quantity of PAH in a given product. This in turn implies that different products such as gasoline and fuel oil, or different grades of the same product such as regular and high octane gasoline, should exhibit different fluorescence characteristics.

The potential of molecular fluorescence for the analysis of complex hydrocarbons was first recognized by investigators who sought to characterize crude petroleum samples [2-4]. This was later extended to commercial petroleum products [5-8]. Over the past few years, another fluorescence approach was taken by Siegel and coworkers in the analysis of a wide variety of petroleum products. These included gasolines [9], motor oils and lubricants [10], petrolatum-based products such as petroleum jellies [11], and midrange hydrocarbons such as charcoal lighters and paint thinners [12]. The fluorescence method employed a total fluorescence method coined "Three Dimensional Fluorescence" (3-DF), by its developer, the Perkin-Elmer Corp.

Three dimensional fluorescence is a computerized fluorescence technique that permits collection of a large number of fluorescence spectra (25-99) over a large spectral range (200-700 nm). Typically, the set of emission spectra are collected over the same emission range while systematically varying the excitation wavelength over the range of significant fluorescence. It is also possible to collect a set of excitation or synchronous spectra this way. Once collected, the spectra are plotted on a pseudo three dimensional Cartesian system. The resultant plot has the appearance of a mountain range. The spectra can also be plotted in a two dimensional contour array. The overall appearance of 3-D plots are quite sensitive to the number, types and amounts of fluorophores present. In petroleum products such as gasoline, the fluorescence is due chiefly to the presence of PAH, although dyes in the gasoline may also play a role. Because these plots show the significant fluorescence under all conditions of excitation and emission, 3-DF is capable of differentiating among similar products such as different grades and brands of gasoline.

This paper seeks to extend the 3-DF technique to examine the fluorescence behavior of gasolines under conditions that simulate environmental weathering. The samples were allowed to evaporate in air at ambient temperature. Fluorescence plots were obtained after 50% evaporation and after all liquid was evaporated.

One of the goals of this study is to determine if the technique might be of some use in the analysis of fuels that may have been used to accelerate an arson fire. It must be recognized that this study can only be of limited value in simulating the effects of fire on fuels. Partial or nearly complete evaporation is only one of the processes that takes place when a fuel is subjected to extreme heat. In addition, the samples used in this study were taken directly from gasoline pumps at service stations, whereas fuel residues isolated from fires are often contaminated with other materials that may themselves fluoresce, even if the accelerant has been isolated from the matrix by a suitable concentration method. Although the samples used in this study are identified by brand name, it must be recognized that the gasoline distribution system in the US since the 1970's oil embargo is such that there is great variation among samples of the same brand and type taken at different times and from different locations. No attempts were made in this study to compare samples of the same type of gasoline taken from different batches. In any case, the objective here was to compare the fluorescence behavior of the *same sample* of gasoline during the evaporation

process. This study is useful because there are no reports in the literature on the fluorescence behavior of weathered gasoline samples, and because there are cases where relatively intact gasoline samples are obtained from crime scenes and need to be compared with known samples.

Methods, Materials and Instrumentation

Nine brands and grades of gasoline were obtained from service stations in the Lansing, Michigan area. They were tightly sealed and refrigerated until used. The samples were as follows:

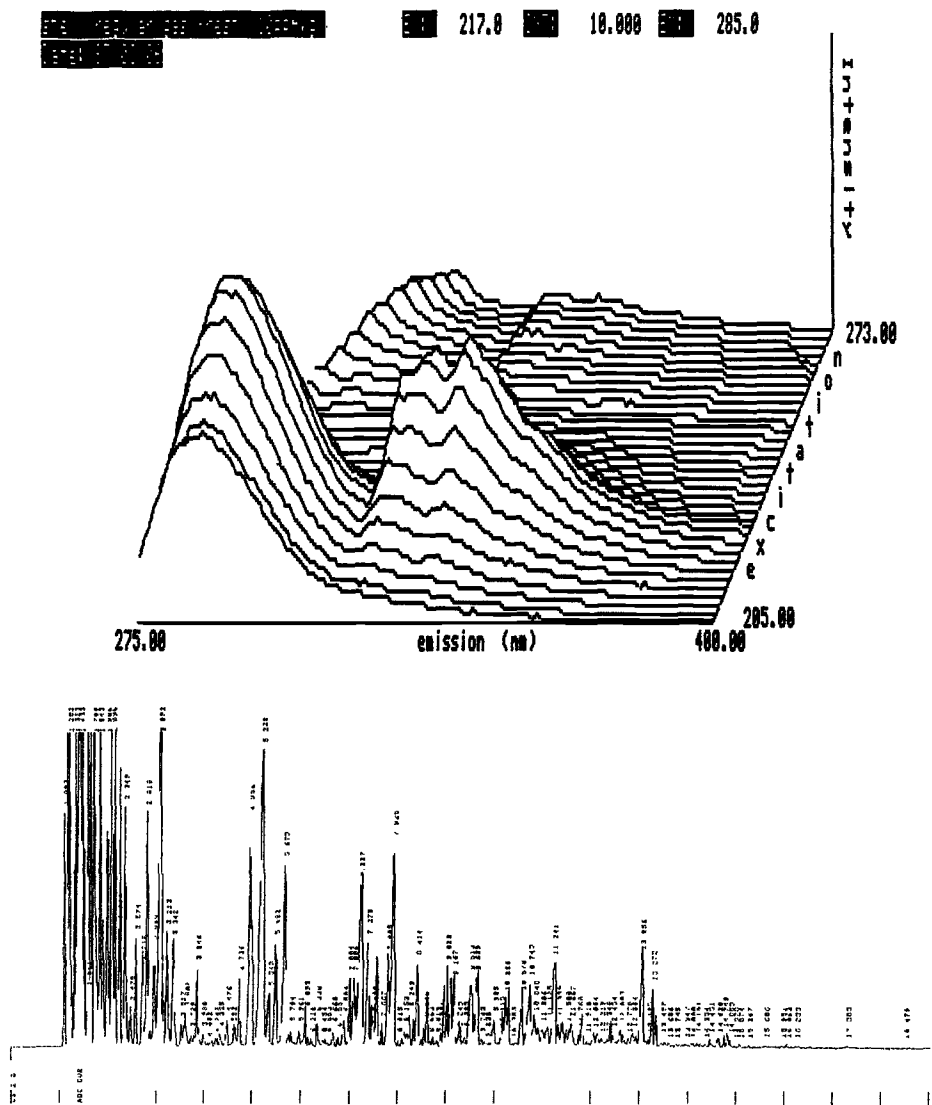


FIG. 1 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of Shell regular leaded gasoline.

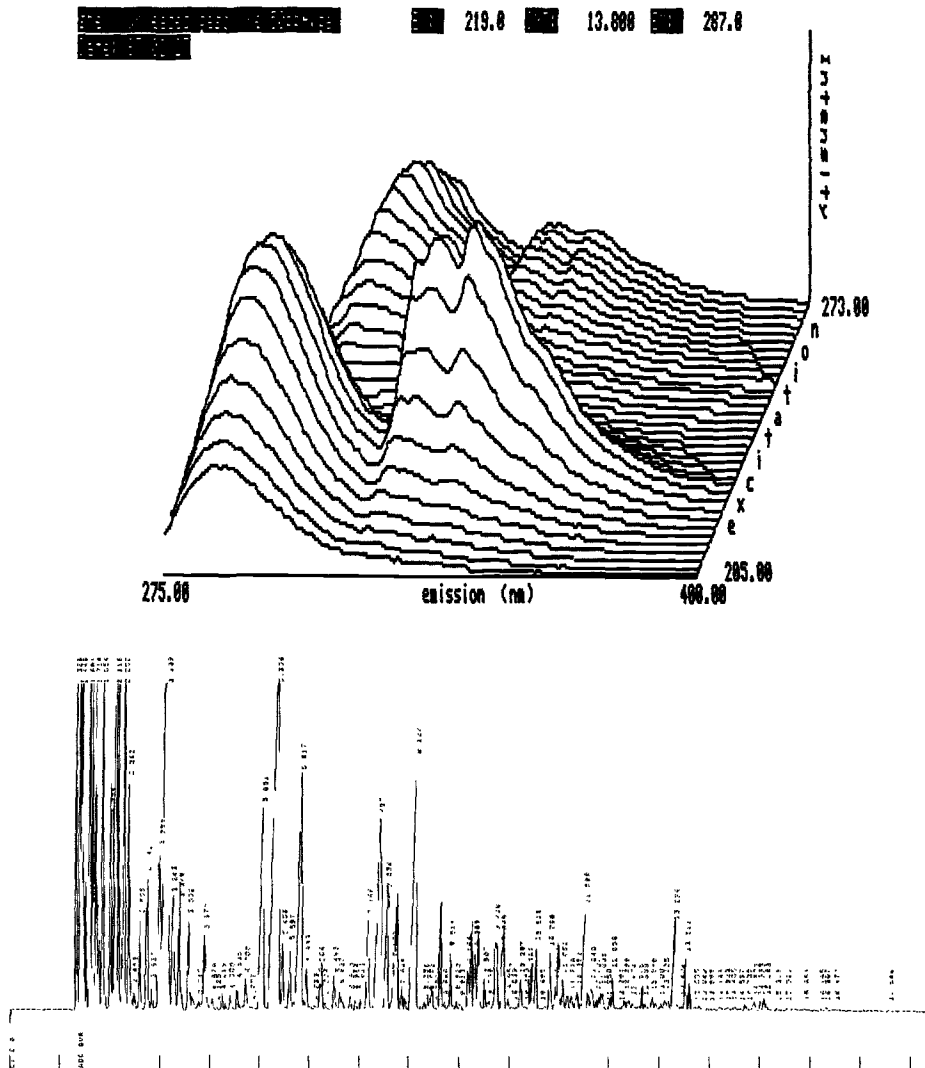


FIG. 2 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of Shell regular unleaded gasoline.

- Mobil regular unleaded
- Mobil super unleaded
- Shell regular leaded
- Shell regular unleaded
- Standard regular leaded
- Standard regular unleaded
- Standard premium unleaded
- Total regular leaded
- Total regular unleaded

Spectrograde cyclohexane (B&J) was used as the solvent for fluorescence without further purification. It showed no interference with fluorescence of the gasolines. The gasoline

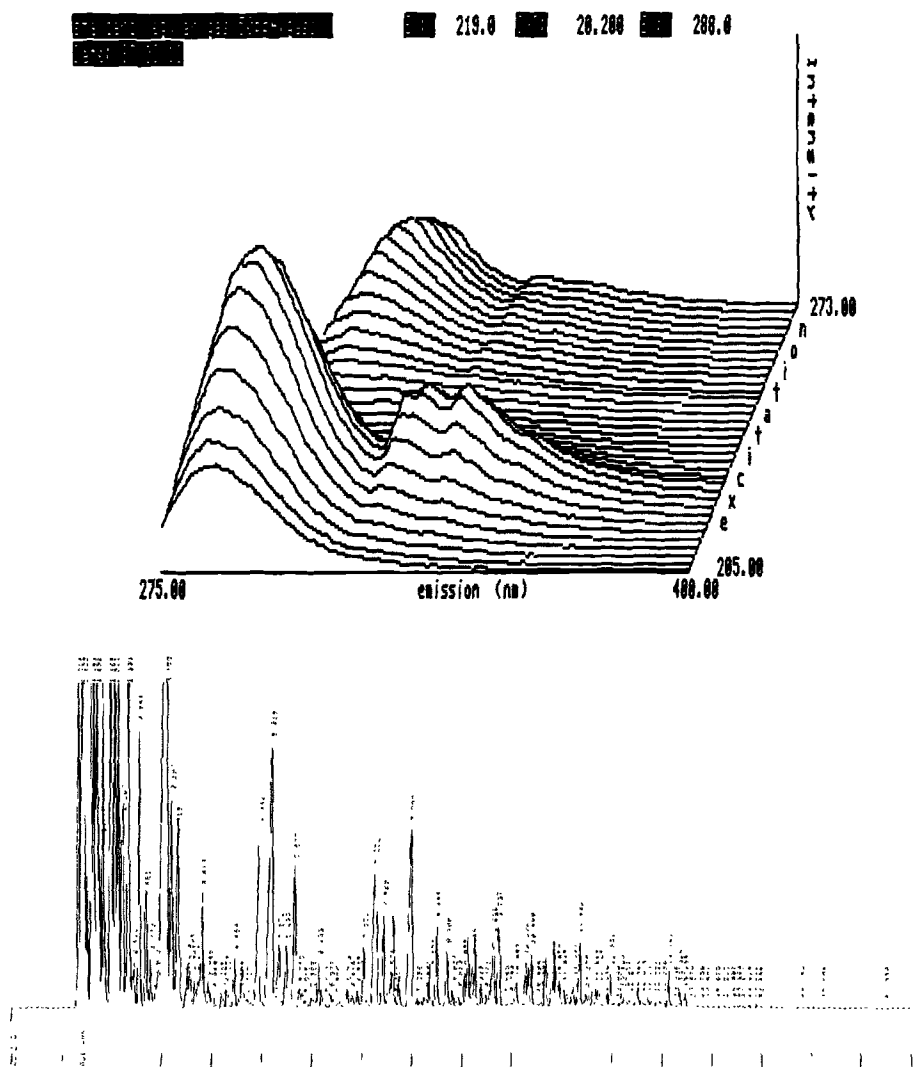


FIG. 3 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of standard regular leaded gasoline.

samples were diluted to 10 ppm for fluorescence. GC samples were run neat except for the nearly evaporated ones, which were reconstituted in cyclohexane.

The fluorimeter was a Perkin-Elmer Model MPF-66 with a Model 7300 data station. Perkin-Elmer's "PECLS" and "TLSM" software packages were used to compile and display spectra. Fluorimeter conditions are given as follows:

Excitation and emission slits: 3 nm

Scan Speed: 240 nm/min

Response: 1

Gain: low

Emission filter: open

Spectra were uncorrected

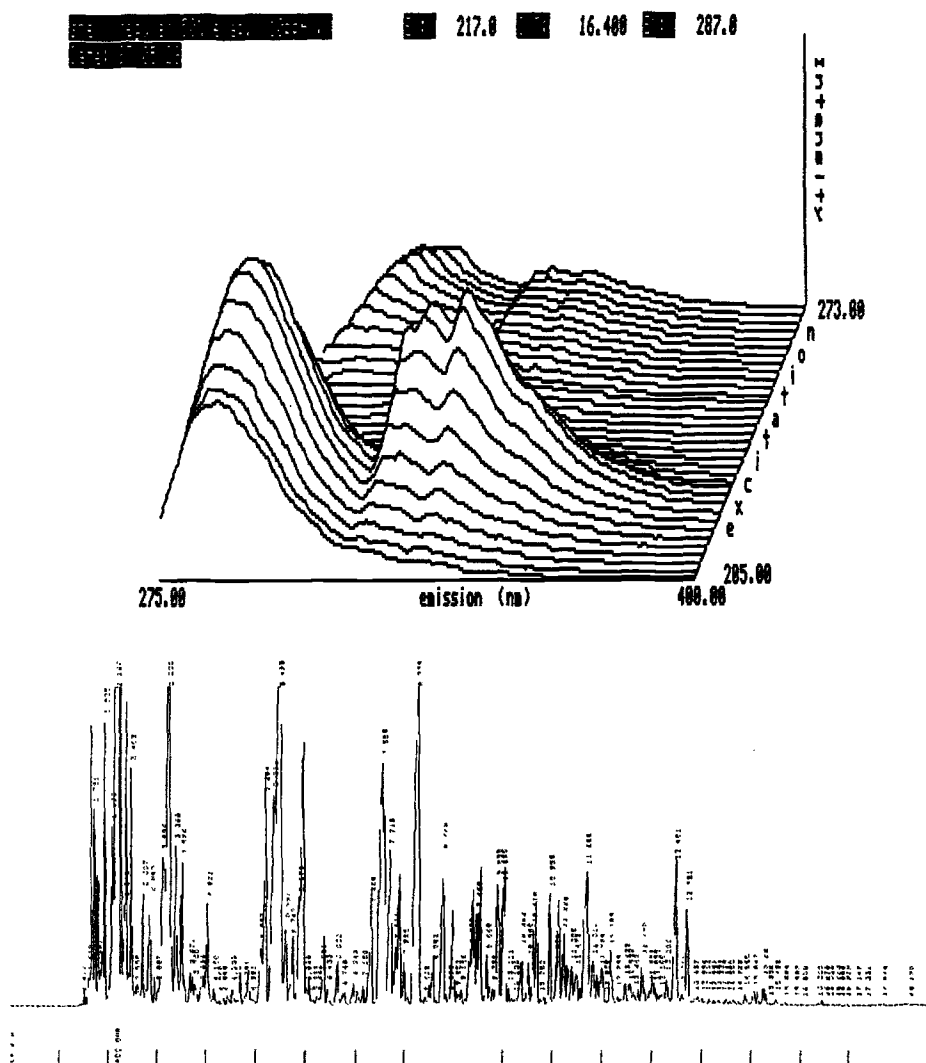


FIG. 5 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of Shell regular leaded gasoline 50% evaporated.

Capillary gas chromatograms were obtained for each sample, chiefly to monitor the loss of components during evaporation. No attempts were made to differentiate the samples on the basis of gas chromatography. The GC was a Varian Model 3300 with a Model 601 data station using Varian software. The column was a J&B, DB-1, 30 meters, 0.25 micron coating. The split ratio was 100:1 and the injection volume was 1 μ l. GC conditions are given below:

Initial column temperature: 50° for 4 minutes

Program rate: 10° per minute

Final column temperature: 200° for 6 minutes

Injector and FID temperatures: 250°

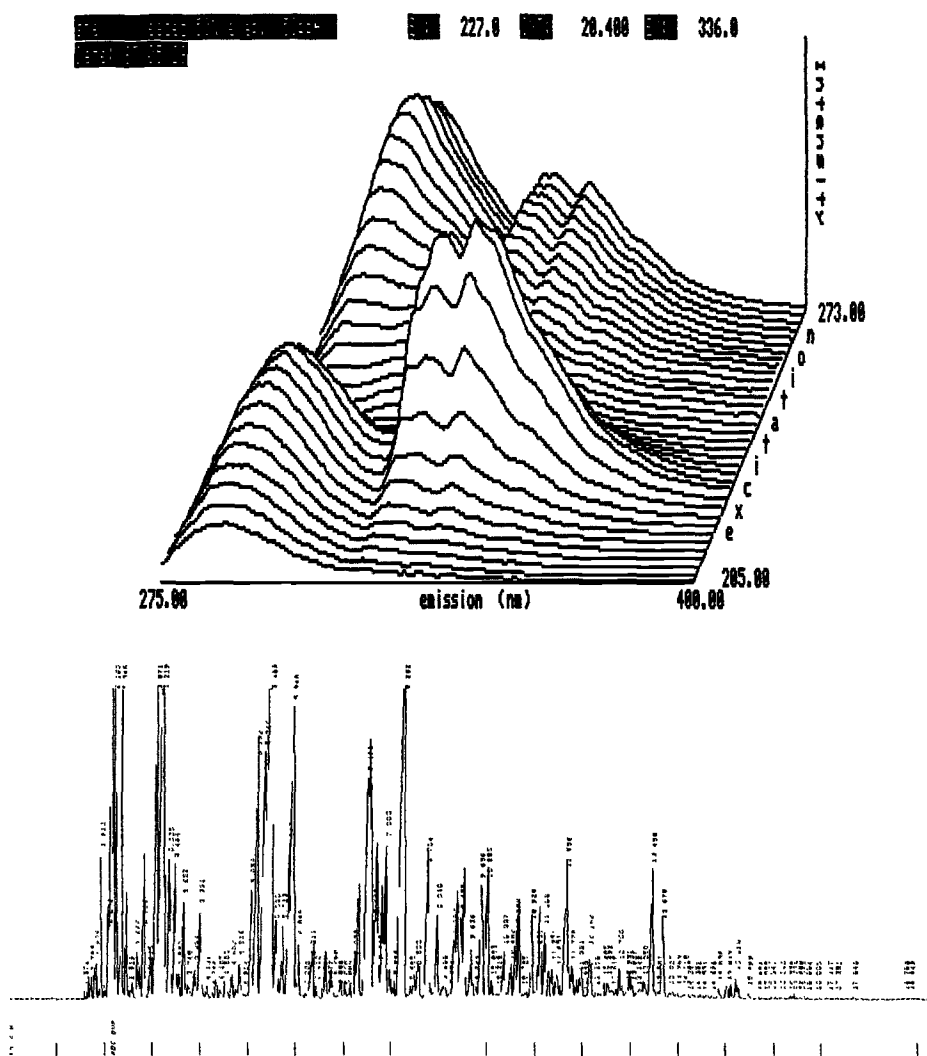
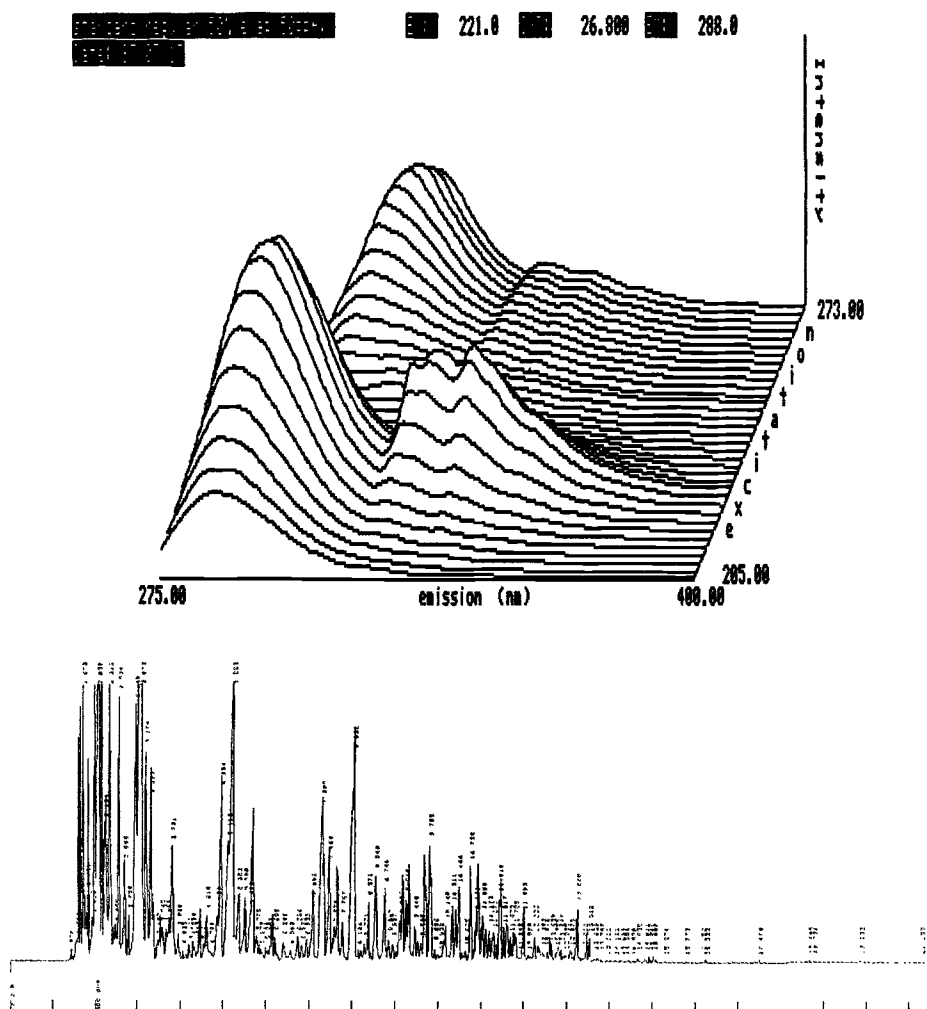
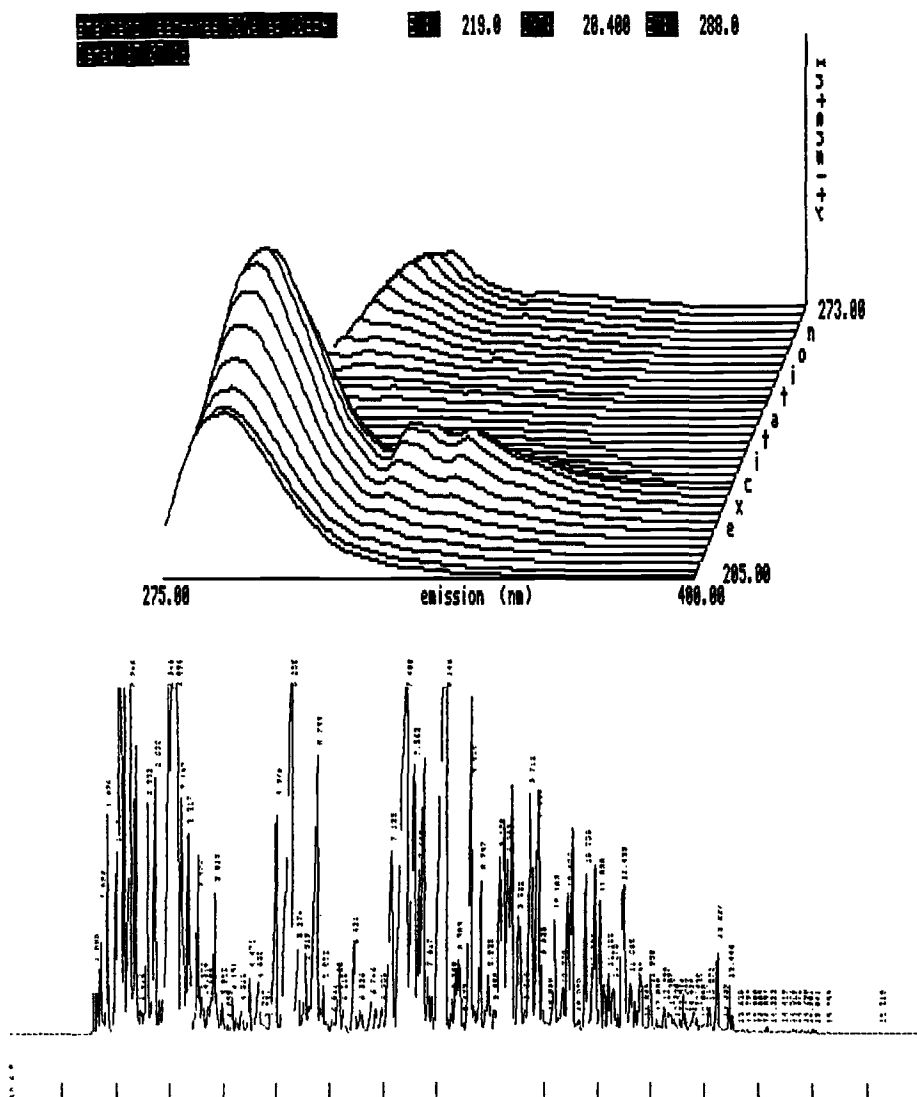


FIG. 6 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of Shell regular unleaded gasoline 50% evaporated.

Results

Representative 3-DF spectra are given below. Figures 1–4 are the 3-DF spectra and gas chromatograms of Shell regular leaded and unleaded, and Standard regular leaded and unleaded gasolines. Figures 5–8 are the 3-DF plots and chromatograms for the 50% evaporated samples of the same gasolines. Figures 9 and 10 are the plots and chromatograms of the nearly evaporated Standard regular and Total unleaded regular gasolines. The chromatograms of the nearly evaporated samples still show some peaks in the midrange area. These are due to some hydrocarbon residues left in the sample after evaporation, which was continued until all visible liquid was gone. Further evaporation of these samples generally proved unavailing.





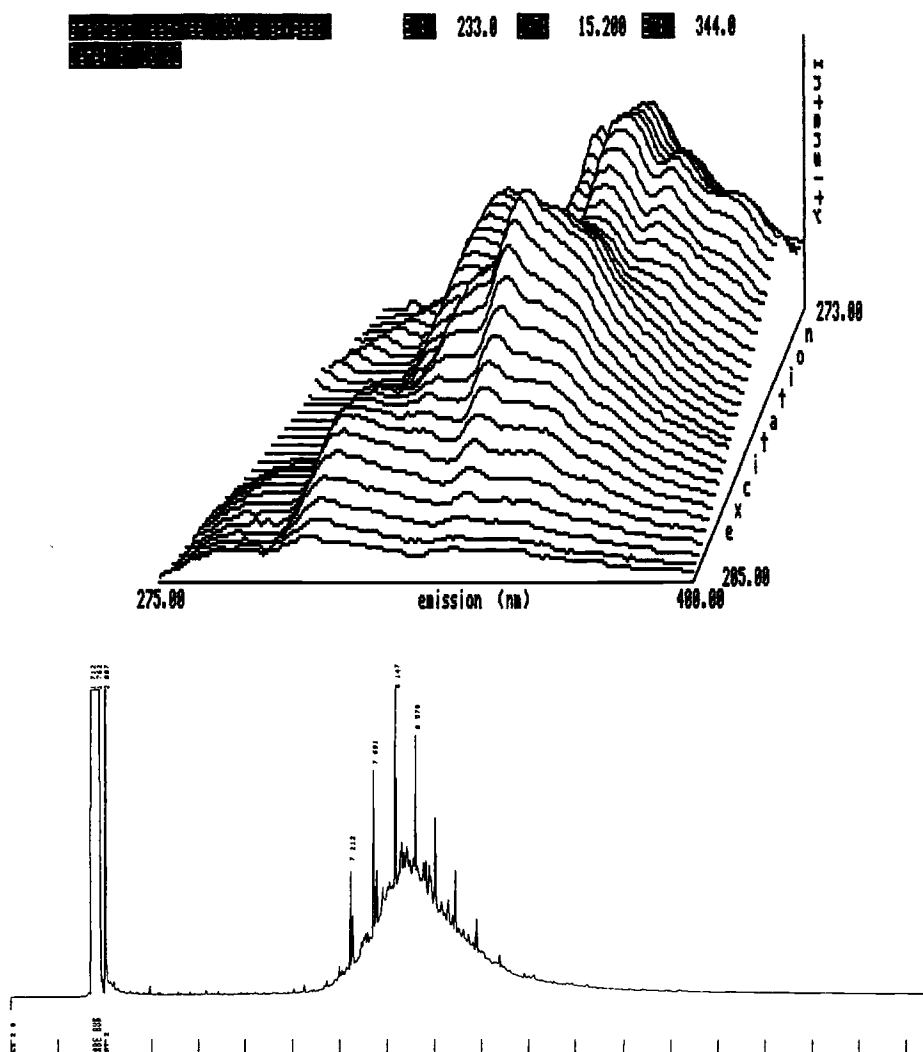


FIG. 9 a, b—Three dimensional fluorescence plot and capillary gas chromatogram of standard regular unleaded gasoline 100% evaporated.

each of the corresponding pairs of plots in Figs. 1 to 4 and 5 to 8 and with the rest of the nine gasolines, no significant differences were found except with the Shell unleaded regular sample where there was an intensity difference between the peaks although they were in the same location. As expected, the main differences in the gas chromatograms of the 50% evaporated samples were the loss of peak intensity in the area of the chromatogram that corresponds to the most volatile components of the gasoline. It is not surprising that the changes in the chromatograms after partial evaporation were more dramatic than the changes in the 3-DF plots. The most volatile components are lost first during evaporation and these would be expected to be mostly straight chain or branched aliphatic hydrocarbons which would not be primarily responsible for the fluorescence seen in the 3-DF plots.

When the gasolines are allowed to evaporate until no liquid remains, the situation changes dramatically. The fluorescence plots are much more complex than those obtained with the

these remaining peaks are due to midrange hydrocarbon residues that are left after all visible liquid has evaporated from the samples.

Conclusions

One purpose of this study was to determine if three dimensional fluorescence plots could be of use in associating partially or completely evaporated samples of gasoline to a similar or unevaporated sample of the same gasoline. Another purpose was to see if partially or nearly evaporated gasolines could be differentiated from one another by 3-DF in the same way that previous work showed that neat samples could. The results of this limited sample size showed that the fluorescence plots changed very little during the process of partial evaporation but, as it proceeded towards dryness, the plots changed dramatically so that they could no longer be compared to plots obtained from fresh samples. As evaporation proceeds, the samples become so rich in high boiling fluorophores that concentration effects such as quenching may be playing a role that causes dramatic shifts in fluorescence positions and intensities.

In this study, no attempts were made to simulate fire conditions that would evaporate and degrade gasoline. In most fires, the gasoline or other fuel is burning within a matrix that will contaminate the sample even if a concentration technique is used. This may be expected to affect the fluorescence plots. As a result, this study probably has little impact on the analysis of gasolines or other hydrocarbon fuels that have been in a fire. Gas chromatography will still be the technique of choice in characterizing accelerants from fires. In those cases, however, where whole or partially evaporated gasoline may be found (for example, Molotov cocktail) or in cases analogous to crude oil spills, 3-DF may have a significant role in characterizing such fuels and relating them back to a known source with some degree of confidence.

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