

Fingerprinting Petroleum Contamination Using Synchronous Scanning Fluorescence Spectroscopy

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Abstract

Synchronous scanning fluorescence spectroscopy is a simple, cost-effective method for fingerprinting many petroleum contaminants in ground-water and soil samples. The extraction of contaminated ground-water and soil samples with water and cyclohexane followed by the synchronous scanning fluorescence spectrophotometry of the organic extract is described for over 20 petroleum product standards and actual samples. This method allows for the classification and identification of aromatic-containing products such as: gasoline, kerosene, diesel oil, various grades of fuel oil, and asphalt. This analytical method is more efficient than chromatographic methods typically used for quantitative analysis of petroleum contaminants and its spectra are easier to interpret for fingerprinting purposes. Several case studies of its use in determining among alternate sources of contamination are presented.

Introduction

Synchronous scanning fluorescence spectroscopy allows for simple cost-effective fingerprinting analysis of contamination by petroleum products in ground water and soil. Fingerprint identification is used when one is interested in the source of a contamination rather than its concentration. One usually can find a variety of sample locations that could be the source of pollution but, as is described in the case studies, the closest underground tank is not always the pollution source.

Other methods have been used for the fingerprinting of petroleum products. These include sample preconcentrations steps using purge and trap at ambient temperatures (Bellar and Lichtenberg, 1974) and higher temperatures (Betz, Hazard, and Brown, 1991) combined with gas chromatography for separation and analysis. The Purgeable Aromatic Method 602 (EPA, 1979) is also in this category. A flame ionization detector (FID) or a mass spectrometer (MS) are the detectors of choice. The cost of a GC-MS instrument is about four to six times greater than a fluorescence spectrophotometer, and one must also include the cost of a capillary column and a purge and trap. Even without the time required for purge and trap preconcentration, the GC-MS analysis of gasoline takes at least 30 minutes. From start to finish, SSF analysis takes between 5 and 20 minutes.

Chromatographic methods present difficulties for fingerprinting analysis because many of the same compounds are found in varying amounts in all five types of lightweight petroleum products that were studied. The chromatograms of regular and super gasoline appear similar because there are over 200 peaks present on their respective chromatograms and the differences in the grades many not be found in the larger peaks. It is also possible for some aromatic and aliphatic compounds to have the same retention times, thus making identification difficult. To simplify the process using a gas chromatography-mass spectrometry method, Webb (1987) attempted to distinguish between gasoline samples using the more volatile aromatic components of benzene, xylene, and naphthalene but only with limited success. A final limitation is that chromatographic methods are unable to handle samples that vaporize above 200°C, thus excluding some of the heavier petroleum products.

Although the Total Recoverable Oil and Grease Method (EPA, 1974) is less expensive than the chromatographic methods previously described, it also has significant limitations for fingerprinting analysis. This method was developed for the analysis of aliphatic hydrocarbons containing compounds such as vegetable oils, animal fats, soaps, waxes, and greases. The petroleum sample is extracted with Freon at a pH less than 2.0; then the infrared absorbance spectrum of the sample is obtained, and a comparison is made with standards. Lightweight petroleum products that volatilize at temperatures below 70°C such as gasoline and fuel oil No. 2 exhibit a substantial or complete loss of organic compounds in the solvent removal operation. Also, some heavy fuel oils or crude oils may contain a significant percentage of higher molecular weight compounds that are not soluble in Freon. A final limitation of this method is the

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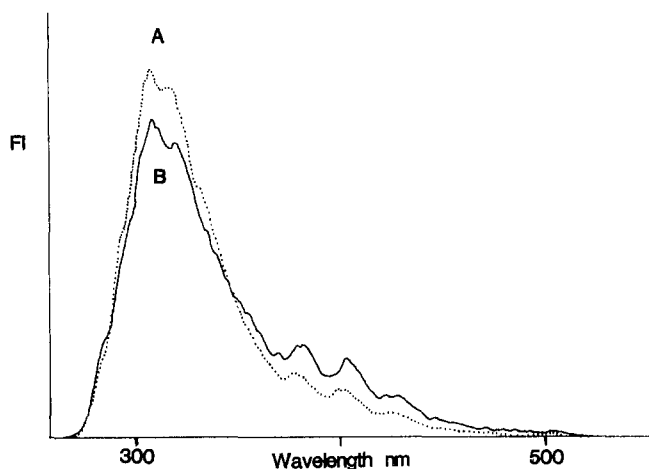


Fig. 1. The normal fluorescence emission spectra of two different gasoline samples, plotting fluorescence intensity vs wavelength using $\lambda_{ex} = 254$ nm. A is EN-92-octane gasoline (dotted line); and B is SL-87-octane gasoline.

relative insensitivity of infrared spectroscopy which is 10 to 100 times less than that of UV-visible spectroscopy, while fluorescence spectroscopy is 1,000 to 10,000 times more sensitive than UV-visible spectroscopy.

Complex mixtures of petroleum products contain examples of two major chemical classifications: aromatic hydrocarbons and aliphatic hydrocarbons. When two or more aromatic rings are fused together, the aromatic systems are called polyaromatic hydrocarbons (PAH). Since aromatic compounds undergo some fluorescence while aliphatic compounds do not, fluorescence analysis has been used successfully for the detection, identification, and quan-

tification of a number of pollutants as well as the determination of dyes added to water for flow studies.

In normal fluorescence of complex samples like gasoline, the sample is excited at 254 nm, with the resulting fluorescence emission spectrum consisting of a rather large and indistinct peak. This makes it impossible to identify one gasoline sample from any other grade or brand of gasoline (see Figure 1). However, SSF spectroscopy may be used to simplify the spectrum by reducing the spectral bandwidth as seen in Figure 2. This results in a spectrum that has more individual peaks for use in distinguishing among the different grades and brands of gasoline.

Synchronous scanning fluorescence which is more selective in its spectral profile than regular fluorescence has been used for the analysis of gasoline engine exhaust (Winefordner et al., 1986), aromatic compounds (Patterson and Taylor, 1987), mixtures of polyaromatic hydrocarbons (Winefordner and Inman, 1982), workplace air particulate samples (Vo-Dinh et al., 1981) and oil weathering processes in sea water, and sediments (Wakeham, 1977). An excellent discussion of the theoretical aspects of SSF was presented by Vo-Dinh (1978).

Synchronous spectroscopy involves the simultaneous scanning of both the emission and excitation monochromators at a fixed wavelength difference ($\Delta\lambda$). The intensity of the signal $[I(em-ex)]$ at a given pair of wavelengths (λ_{ex} , λ_{em}) is described by:

$$[I(em-ex)] = k C d E_x(\lambda_{ex}) E_m(\lambda_{em})$$

where k = a constant; C = concentration of the fluorophore(s); d = cell pathlength; $E_x(\lambda_{ex})$ = intensity of the excitation spectrum at λ_{ex} ; and $E_m(\lambda_{em})$ = the intensity of

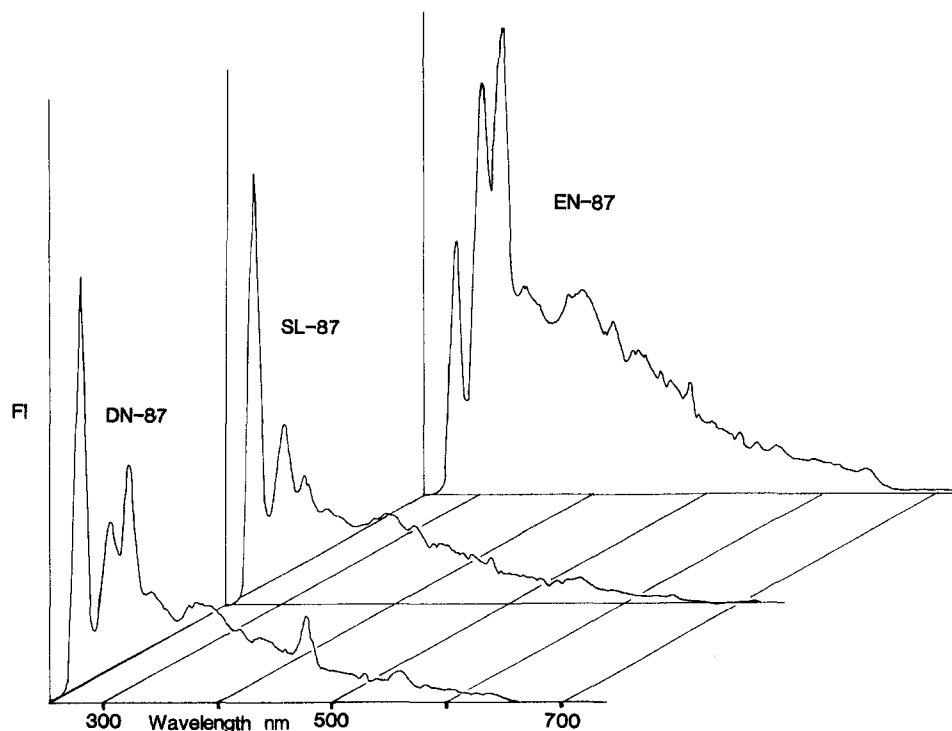


Fig. 2. Synchronous scanning fluorescence spectra using $\Delta\lambda = 5$ nm for three different brands of 87-octane regular gasoline: A is EN-87; B is SL-87; and C is DN-87.

the emission spectrum at λ_{em} . The synchronous spectrum is therefore a function of both the excitation and the emission spectrum of the compound of interest. The value of $\Delta\lambda$ has a significant impact on the nature of the spectrum (Vo-Dinh, 1978). The advantages of SSF compared to fluorescence are: (1) simplification of the spectral profile, (2) sharper peaks resulting from spectral bandwidth reduction, and (3) less background because of a reduction of scattered light.

For example, tetracene has a normal fluorescence emission spectrum which covers a range of 460 to 600 nm with peaks at 473, 507, and 546 nm. In the spectrum obtained from a synchronous scan where $\Delta\lambda = 5$ nm, only one narrow peak is seen at 473 nm (Vo-Dinh, 1978). The width of the synchronous spectrum can be expanded by increasing the value of $\Delta\lambda$.

With this simplification of the spectral signal, one can construct some type of general classification of polycyclic aromatic compounds based upon the maximum wavelengths obtained from the compounds typically found in petroleum products. The magnitude of excitation depends upon the size, rigidity, and number of conjugated double bonds in the compound. Monocyclic aromatic compounds such as benzene, toluene, xylenes, phenols, and their substituted analogs exhibit a peak between 250-290 nm when $\Delta\lambda = 3$ nm. Aromatic compounds with two rings like naphthalene have a peak between 310-330 nm, phenanthrenes (three-ring system) between 345-355 nm, and the more condensed ring systems would exhibit peaks at even higher wavelengths. For a mixture of polycyclic aromatic hydrocarbons, the spectra becomes a mixture of distinct peaks, one for each type of aromatic system. The intensity of the peaks is affected by both the concentration and fluorescence efficiency.

Experimental Methods

Twenty-one petroleum product samples given in Table 1 were obtained directly from service station tanks locally and used without further purification. A library of SSF's spectra was developed from these samples by making "contaminated" aqueous samples using 100 ml of distilled deionized water spiked with 10 μ l of the petroleum product. These samples and actual water samples described in the case studies were extracted with HPLC grade cyclohexane or hexane (Fisher Scientific) using a ratio of 1:20 or 1:5. Cyclohexane proved to be the solvent of choice because in the blank studies it exhibited very little spectral interference.

Soil samples from the case studies were first extracted with distilled deionized water (2 grams of soil to 10 ml water or a similar ratio), and then the aqueous phase was extracted with cyclohexane like the water samples. This approach reduced the large amount of naturally occurring organic material that may be found in soils from being extracted into the cyclohexane and thereby causing a significant interference. Some clay soil samples and storm drain-water samples required filtering through Whatman #41 filter paper because much of the suspended material would not settle out. Inner filter effects were avoided by using low concentrations (below 200 ppm) in all studies. Oxygen may be removed by bubbling the organic solvent with nitrogen gas prior to extraction. Although this had been recommended

by Patterson and Taylor (1987), no significant difference was found between the extractions done with deoxygenated solvent and regular cyclohexane. This was probably due to the length of time for the extraction. Patterson allowed 10 days, while typically extraction times of less than one to two minutes were used for this study.

SSF measurements can be made on any commercially available fluorescence spectrophotometer in which the excitation and emission monochromators can be interlocked. For this study a Perkin-Elmer spectrofluorometer (Model LS-5, Perkin-Elmer, Norwalk, CT) was used throughout. The printer was a Perkin-Elmer GP-100 Graphics Printer. The following parameters were used for the $\Delta\lambda = 3$ nm, 5 nm, and 20 nm analysis using hexane or cyclohexane for the extraction: response = 1, fixed-scale expansion factor = 1.0, recorder offset = 0, excitation limits = 250 nm to 700 nm, Ex-Em speed = 120 nm/min, and recorder speed = 20 nm/cm. The emission and excitation slit widths were kept at 5 nm.

Results and Discussion

Figure 1 shows the normal fluorescence emission spectra obtained from two different gasoline samples using 254 nm as the excitation wavelength. The spectra do not exhibit enough spectral differences to readily distinguish the EN-92 octane from the SL-87 octane gasoline. The difference in height of fluorescence intensity is concentration dependent. Figure 2 compares three different regular 87 octane gasoline brands using SSF with $\Delta\lambda = 5$ nm. It can be seen that there are enough peaks in the spectra to distinguish among the three brands of regular gasoline shown. Figure 3 illustrates how differences among different grades of the same brand of gasoline can be distinguished from one another.

Table 1 presents the library of SSF spectral peaks obtained from cyclohexane extractions of the 21 product samples mentioned above for $\Delta\lambda = 5$ nm. The tabulated wavelengths (± 1 nm) correspond to a value for the highest fluorescence intensity normalized at 100 units, and the other peaks in the spectrum are in relation to that value for that specific spectrum. This allows for an easier comparison of spectra and is acceptable because fluorescence intensity is a relative rather than an absolute number. Some of the latter peaks occur along a sloping base line of peaks which are also characteristic of that particular petroleum product but which are difficult to tabulate. A solid line is used in Table 1 to represent this type of spectral information and the fluorescence intensity value given is the total height of the peak, including the height of the sloping base line. For example, in Figure 2C (the DN-87 octane), the sloping baseline from 345 nm to 640 nm has three small peaks at 384, 440, and 480 nm.

The spectral library was produced to show that each of the spectra is unique. The easiest identification occurs when a comparison of an unknown and standards are those of different types of petroleum products are analyzed such as gasoline, kerosene, used motor oil, fuel oil No. 2, and fuel oil No. 5. Table 1, while useful, would not always be an adequate substitution for an actual spectrum when used for fingerprint identification purposes. Specific trends may be seen within brands of gasoline but generally not when

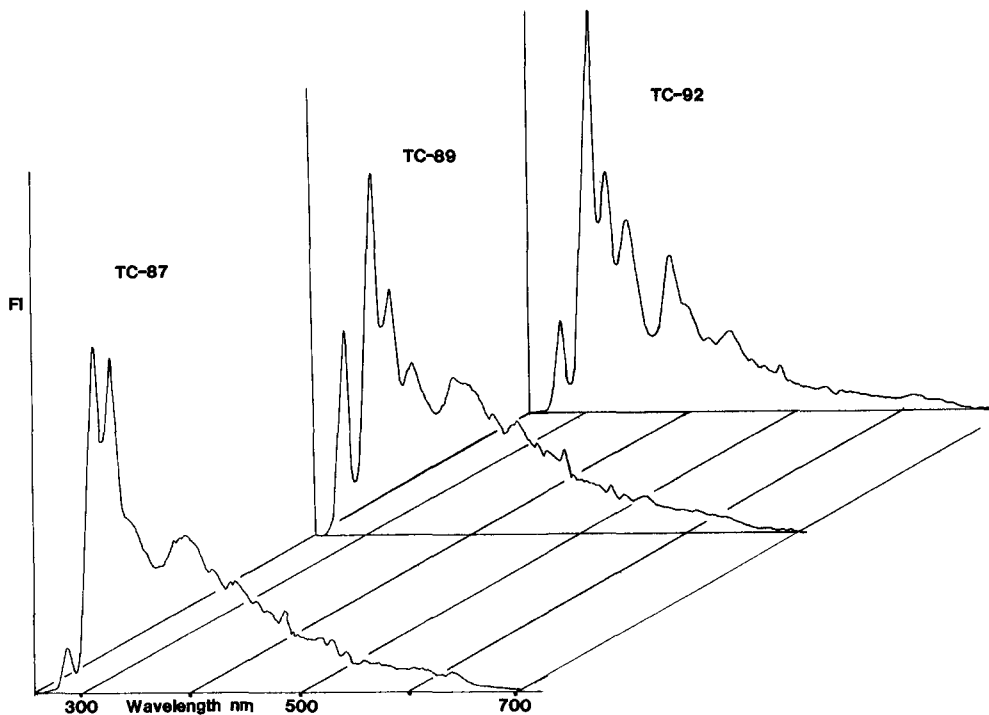


Fig. 3. Synchronous scanning fluorescence spectra $\Delta\lambda = 5$ nm of all three grades of the same brand of gasoline: A is TC-92-octane; B is TC-89-octane; and C is TC-87-octane.

Table 1. Synchronous Scanning Fluorescence Spectral Characteristics of Petroleum Products Using $\Delta\lambda = 5$ nm

Wavelength (nm) ($\pm 1 \lambda$ nm)	275	279	284	294	303	307	310	322	325	328	342	345	381	384	391	395	402	419	432	438	440	481	486	
AC-87	100				69			49									29							
AC-89	100				31			24									16							
AC-92	100				26			24									21							
CN-87	100					37			32			21	17											
CN-89	100					40			30			19	16											
CN-93	100					54			27			21	18											
DN-87	100				42			55			26		23									14	20	
DN-92	86				100			56			45		41									19	9	
EN-87	55				88			100			49	43				44		37	31					
EN-89	61				100			79			34	21							19					
EN-92	40				100			32			27	22					15	15						
SL-87	100					35			22			14	11				12							
SL-89	100					68			49			43	37				37	29				26	21	
SL-92	100					60			28			22					16					12		
SN-87		100				76			61								20							
SN-92		44				100			45		35						29					14		
TC-87			13	100					99			50						46						
TC-89			57	100					68			46						43						
TC-92			22	100					59			47					39	26				20		
Diesel						58		100						24										
Kerosene		6				100					59													

The tabulated wavelengths correspond with a normalized fluorescence intensity of 100 for the highest peak, and the other peaks are in relation to that value for that specific spectrum. The solid line indicates a sloping base line and the peaks bracketed by these lines have a fluorescence intensity that includes the height of the sloping base line.

octane ratings of different manufacturers are compared to one another due to formulation differences.

It should also be remembered that petroleum companies reformulate their gasolines at different times of the year (especially winter/summer), and a local distributor may actually sell gasoline to more than one service station, each of which may therefore sell the same 87-octane gasoline under a different name. Once a major oil company sells its product to a distributor, it no longer has control of the product in most states. The 89-octane gasolines may be a special formulation petroleum product or a mixture of the regular 87-octane and the super 92-octane gasolines by the distributor.

In order to study aging effects, six of the gasoline samples studied were newly obtained and analyzed along with the three-month-old samples using SSF. The resulting spectra were the same as the original library spectra. Lot to lot variations, as well as variations of a product with time, may be a factor in spectral identification. In the case studies, the samples from possible nearby petroleum sources and suspected water or soil samples were collected at the same time. The knowns and unknowns were then compared in a qualitative identification.

Case Studies

The following case studies illustrate problem solving using SSF spectroscopy. Not only was this technique useful in identifying the petroleum tank that was polluting but also in discovering the possible types of polluting petroleum product.

1. Mr. Woody of the Lexington Public Works Office requested help in tracking down an organic chemical smell that was occurring in the storm drains near Cameron Hall on the VMI campus. The storm drain proved inaccessible for the removal of a water sample, so a sample was obtained

from another storm drain near the Buildings and Grounds Office which was 320 meters downstream from Cameron Hall. The next nearest storm drain upstream of Cameron Hall was 900 meters away from the sample site and lacked any indication of fumes. Between the clean storm drain and Cameron Hall, there were two service stations: the "AC" station which was 650 meters away from the sample site and the "SL" station which was 850 meters away. Samples were obtained for each of the petroleum products sold by the two stations and these were compared to the unknown by SSF. Prior to this analysis, the service station owners were asked to check for gasoline losses from their tanks based on their inventory volume and to do a water test on their storage tanks. Both tests yielded negative results.

"Fingerprint" comparisons of the SSF spectra of the seven petroleum products from the two service stations and the unknown aqueous extract identified the SL-87 octane gasoline as the contaminant. This first case actually was the basis of the SSF study, and the seven products analyzed served as the start of the spectral library in Table 1.

2. The second case study was also performed for Mr. Woody. It involved the analysis of soil samples collected after the removal of an underground storage tank. One sample exhibited a positive SSF test result with a range from 400 to 680 nm using $\Delta\lambda = 5$ nm. This was an indication, based on the library spectra, of a heavyweight petroleum product and not the No. 2 weight heating oil that had been stored in the underground tank (see Figure 4). Upon closer inspection of the soil sample, it was found that small pieces of the parking lot asphalt or tar had been knocked down into the hole where the sample was taken. When the sample tested contained only soil, a negative result was obtained.

3. The "DX" Gas and Oil Company requested an analysis when a thin oil slick appeared on the small creek behind their establishment. Their underground storage

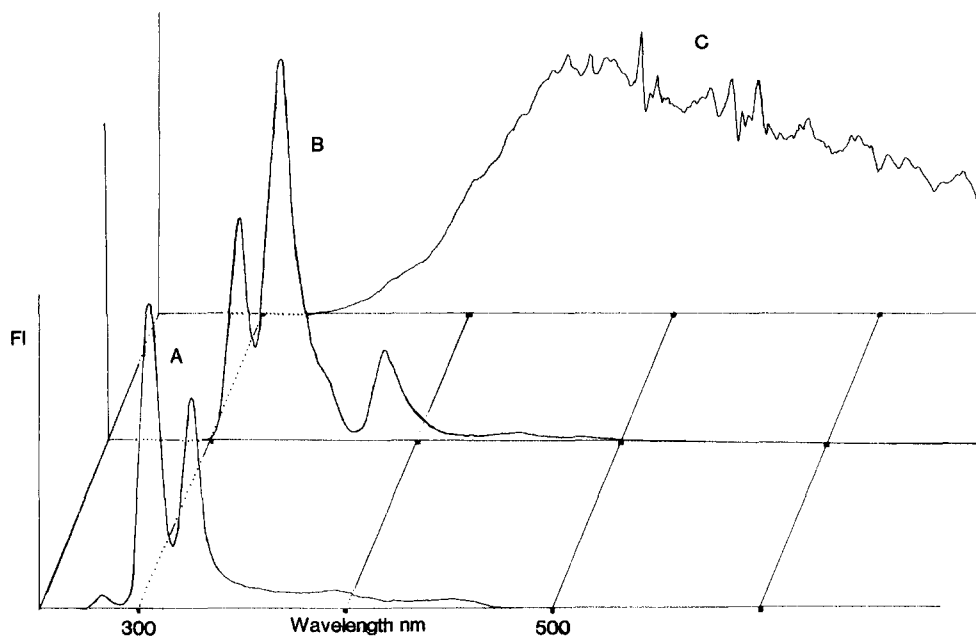


Fig. 4. Synchronous scanning fluorescence spectra $\Delta\lambda = 5$ nm: A is kerosine; B is fuel oil No. 2; C is asphalt from a soil sample.

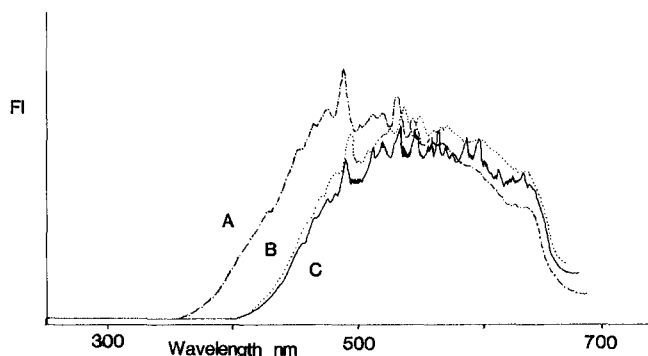


Fig. 5. Synchronous scanning fluorescence spectra of heavier weight petroleum products $\Delta\lambda = 5$ nm: A is used motor oil from waste storage tank (· - · - ·); B is unknown oil extract from stream (dotted line); and C is fuel oil No. 5 (solid line).

tanks had been checked recently for losses based on inventory and a water test of their tanks was negative. A water sample, samples of the company's petroleum products, and a sample of oil from an underground waste oil tank were obtained. The water sample's SSF spectrum ($\Delta\lambda = 5$ nm) had peaks in a range from 420 to 680 nm with small peaks at 485, 522, 530, and 548 nm as shown in Figure 5B. The underground waste oil storage tank sample had the spectrum closest to this sample, but its peaks ranged from 370 to 660 nm with small peaks at 420, 456, 470, 480, 530, and 540 nm (Figure 5A). This was not considered a close enough match because the oil spectrum started 50 nm before the water sample spectrum, that is, at 370 nm compared to 420 nm. Because the water spectrum started at such a high wavelength, a higher weight fuel oil was indicated as the probable contaminant. DX Gas and Oil did not sell such a product but volunteered to determine if someone else in the area did. They sent a sample of fuel oil No. 5 from a storage tank located across the street (Figure 5C). This oil sample's SSF was found to match the unknown's SSF identifying the other business as the source of contamination.

4. In another analysis, some suspect well water exhibited no SSF peaks but had a total petroleum hydrocarbon, TPH, analysis result of 13 ppm hydrocarbons. These results are not inconsistent because the TPH test is for grease, fats, and oils, many of which are aliphatic hydrocarbons (naturally occurring products), while the fluorescence method is a screening identification test for aromatic hydrocarbons which usually occur in petroleum products. It was possible that the contamination in the well water occurred because the well was located 10 feet from the back door of the house and the grease trap leading to the septic tank was less than seven feet away from the well; however, this could not be confirmed because the owners were not interested in further testing.

Conclusions

Qualitative fingerprint identification using SSF can be accomplished with a series of spectral knowns of petroleum products extracted from water by cyclohexane and analyzed using $\Delta\lambda = 3$ nm or 5 nm. A direct comparison of known and unknown peak positions, relative intensities, and baseline slopes results in a fingerprint identification of not only one type of petroleum product to another, but also differentiation of grades of gasoline from the same manufacturer. SSF is a sensitive (low ppm to ppb) and selective (only aromatic compounds) method of analysis with a relatively short extraction and analysis time when compared to other methods.

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