

Screening and Classifying Hazardous Waste Samples with Fluorescence Spectroscopy

Introduction

Timely and accurate analysis of hazardous materials is fundamental to environmental protection. In addition to the obvious necessity of identifying a suspected contaminant, a detailed analytical profile can help trace the source of a dangerous material and contribute to selecting the best containment and cleanup strategy.

A substantial body of research has clearly established the efficiency and economy of fluorescence spectroscopy as a technique for characterizing many hazardous substances. One recent effort in this area involved the use of a SPEX® FLUOROLOG® spectrofluorometer for detecting, classifying, and quantifying samples containing petroleum oils or chemicals like polychlorinated biphenyls (PCBs) and aromatics.

The project was conceived and carried out by US Army Corps of Engineers affiliates DeLyle Eastwood and Russell Lidberg. Their aim was to enlarge the use of spectroscopic pattern recognition for environmental projects conducted by the Department of Defense under the Defense Environmental Restoration Account. The two researchers successfully applied fluorescence, low-temperature luminescence, and, for comparative purposes, Fourier-transform infrared spectroscopy to the analysis of hazardous waste samples for sites in Alaska and Kansas. Their work was also intended to augment the library of spectral references available for analysis of petroleum oils and fluorescent hazardous chemicals.

Eastwood and Lidberg used standard emission methods as well as excitation and synchronous scanning techniques at both room and liquid-nitrogen temperatures. With appropriate reference standards and emission methodology, samples can be quantified over a range from 100 ppb to a few ppb, even where extraction is from difficult matrices such as river sediments. The experimental results compiled by Eastwood and Lidberg emphasize how spectrofluorometry can easily accomplish

what is much harder to achieve via conventional approaches using gas chromatography and mass spectrometry.

Experimental Procedures

Computerized search routines for classifying spectra based on feature sets and similarity measures were developed. For fluorescence, pattern recognition factors encompassed spectral area, peak positions, and angular distance between spectra.

For all fluorescence spectra, The FLUOROLOG® research spectrofluorometer system included a single-grating excitation monochromator and a double-grating emission monochromator. The excitation source was a 150-W xenon lamp. Both emission and reference detectors contained photomultiplier tubes.

Twenty-nine reference oil samples were obtained from the Environmental Protection Agency and the U.S. Coast Guard Research and Development Center. These references were chosen to be representative of the principal types of petroleum oils: light fuels, heavy fuels, and crude oils. Standard solutions were prepared from the reference oils at a concentration of 20 µg/g in cyclohexene. Reference solutions for polychlorinated biphenyl (PCB) analysis were prepared by dilution to concentrations of 10–30 µg/g in cyclohexene. Real-world samples obtained for analysis were divided into three groups: contaminated soil samples, “neat” samples that appeared to be pure oils, and liquid samples (many of which contained a water phase) that were not pure oils.

All spectra presented herein were taken with the excitation bandpass at 4.5 nm, and emission bandpass at 0.9 nm. Excitation was at 254 nm.

Results and Discussion

The 29 reference oils were characterized by their emission spectra as well as by data obtained from synchronous scanning. Eastwood and Lidberg tabulated all of this information, categorizing the

results of their experiments according to spectral features like maximum peak wavelengths, wavelengths for distinctive secondary peaks and shoulders, and the relative areas under corrected spectral curves.

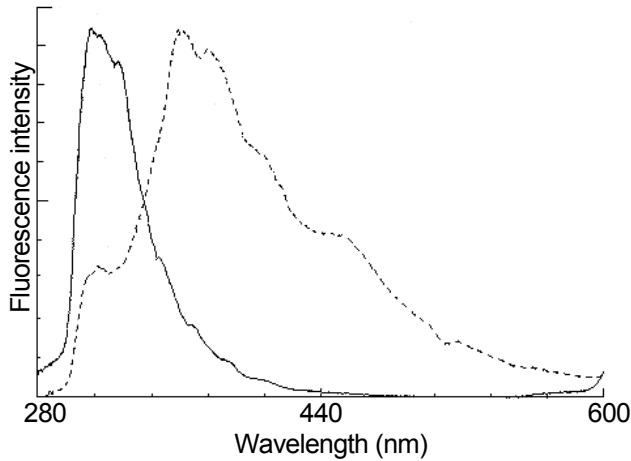


Figure 1. Emission spectra of a No. 2 fuel oil (solid line) and a No. 6 fuel oil (dashed line).

Figure 1 shows emission spectra for a typical No. 2 fuel oil and a typical No. 6 fuel oil. The differences are clear, permitting easy classification. The differences between two No. 6 oils illustrated in Figure 2, however, are slight. Furthermore, in Figure 3, note that the Prudhoe Bay crude oil spectrum is very similar to the data shown in Figure 2. Such close correspondence in emission spectra is common, and can lead to classification errors.

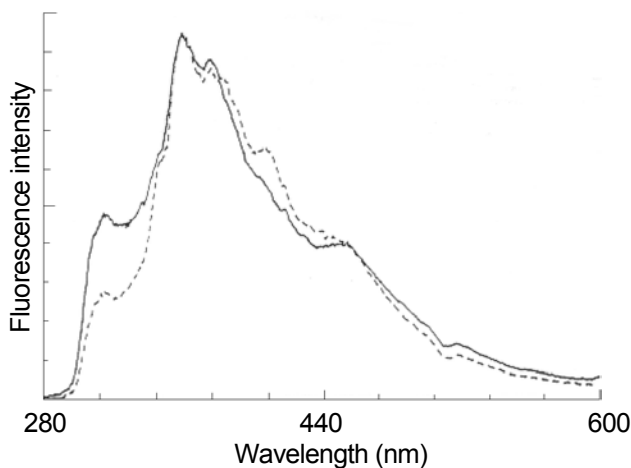


Figure 2. Emission spectra of two No. 6 fuel oils.

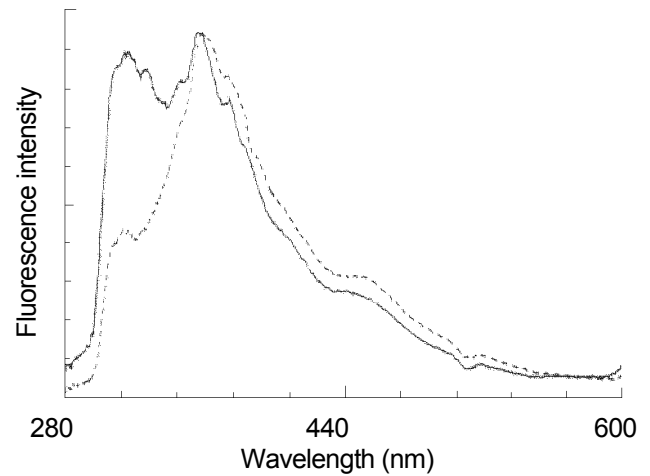


Figure 3. Emission spectra of South Louisiana crude oil (solid line) and Prudhoe Bay crude oil (dashed line).

When emission data are not sufficient for conclusive sample identification, *synchronous scanning* can provide significantly more useful spectral structure. Synchronous scanning entails simultaneous scanning of the excitation and emission monochromators with a constant offset between them. The recorded intensity is proportional to the product of the observed excitation and emission intensities. Accordingly, a significant difference could then be discerned between the maximum peak wavelengths of the No. 6 fuel oils in Figure 4 and the Prudhoe Bay crude oil in Figure 5. Whereas the maximum peak positions were identical for the samples' emission spectra, synchronous scanning increases the difference in position by around 50 nm.

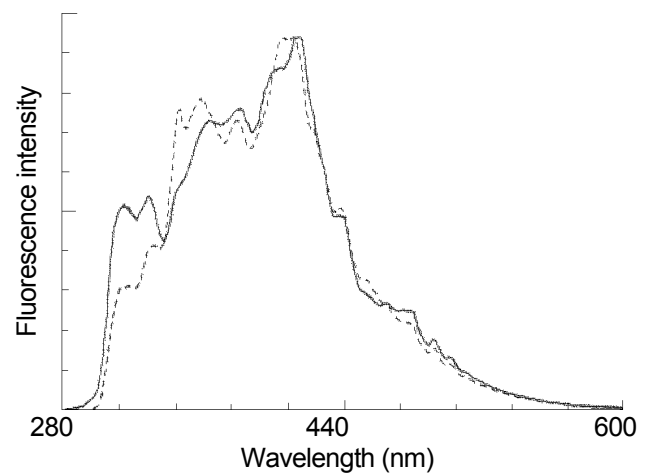


Figure 4. Synchronous spectra of two No. 6 fuel oils. Both monochromators scanned simultaneously with a 25-nm offset.

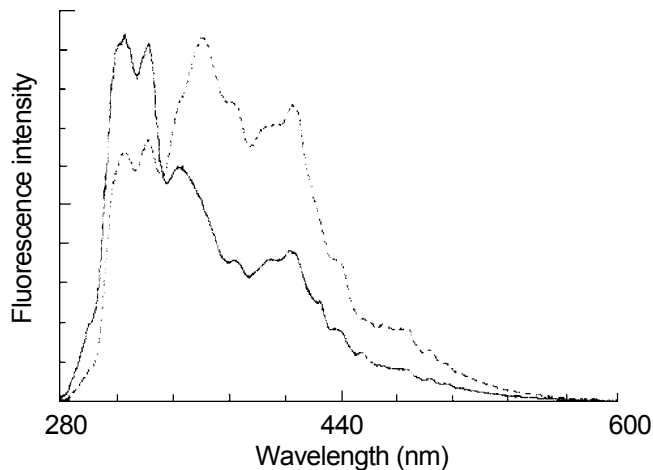


Figure 5. Synchronous spectra of South Louisiana crude oil (solid line) and Prudhoe Bay crude oil (dashed line). Both monochromators scanned simultaneously with a 25-nm offset.

Figures 6, 7, and 8 provide practical examples comparing emission spectra of unknown oil samples and library references. Figure 6 shows that an analytical sample extracted from soil yields recognizable and useful spectra. Figure 7 reveals a close correspondence between a known Prudhoe Bay crude oil and an unknown sample received in isopropanol. Figure 8 is interesting because it compares a weathered real-world sample with a known JP-4 jet fuel. Fluorescence analysis of samples weathered in a thin film or water is less common because of potential data distortion. From research, the correct analytical approach reveals distinguishable spectra even after periods of weathering ranging from two days to several weeks.

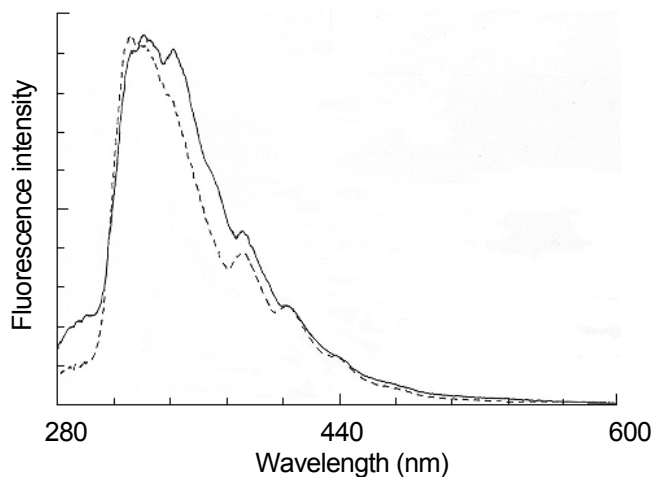


Figure 6. Emission spectra of an unknown sample extracted from soil (solid line) and a No. 2 fuel oil (dashed line).

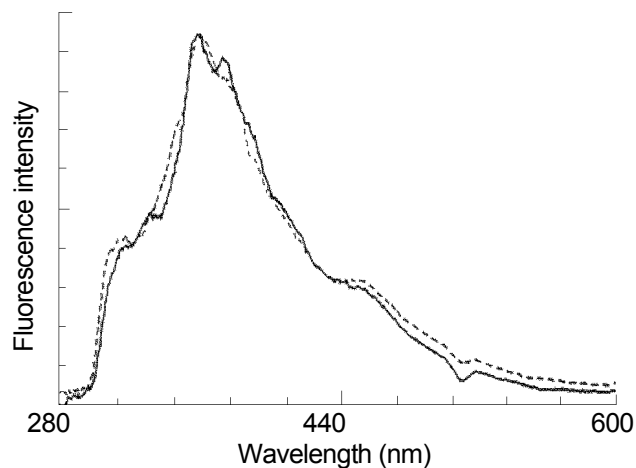


Figure 7. Emission spectra of an unknown sample in isopropanol (concentration unknown, solid line) and Prudhoe Bay crude oil (dashed line).

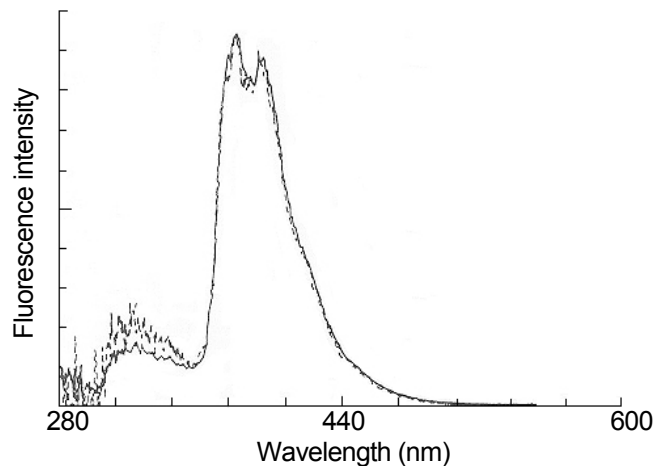


Figure 8. Emission spectra of a neat unknown sample (solid line) and JP-4 jet fuel (dashed line). Excited at 230 nm.

With regard to hazardous chemicals, a 1979 Coast Guard report lists approximately 90 substances that can be readily identified by their room-temperature fluorescence spectra. Eastwood and Lidberg indicated that this list could be extended to about 250 hazardous materials if low-temperature luminescence/phosphorescence spectra were included.

Figure 9 shows a spectral comparison of PCB samples acquired at 77 K, where the emission intensity is greater for phosphorescence than fluorescence. Low-temperature analysis is considerably more sensitive, allowing quantification in the ppb

range. For field-screening in the ppm range, room-temperature fluorescence appears satisfactory, for fluorescence quenching by the internal heavy-atom effect is incomplete.

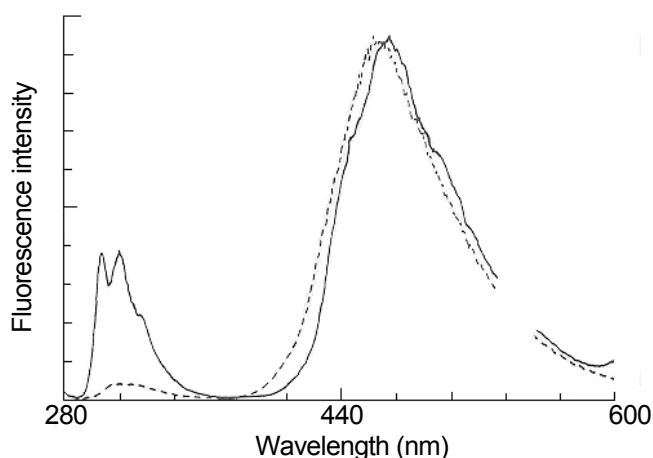


Figure 9. Low-temperature (77 K) luminescence spectra, excited at 270 nm, showing fluorescence and phosphorescence of two PCB samples: 10 µg/g (solid line) and 27 µg/g (dashed line), both in methylcyclohexane. Blanks in spectra indicate where second-order emission has been deleted.

In the future, Eastwood and Lidberg intend to use their SPEX system to expand the library of spectral references for petroleum oils and hazardous chemicals. The exceptional sensitivity of their FLUOROLOG® system also will be applied to developing a more comprehensive system of classifying spectra: one that would encompass subclasses based on spectral characterization rather than just API categories or physical properties. Information about the geographical origin of oils could also be integrated into such a framework.

In addition, preliminary PCB measurements need to be expanded and refined to ensure better detection, identification, and quantification for these ubiquitous chemicals, especially in field work. The same holds true for other important classes of fluorescing hazardous chemicals, among them organochlorine pesticides, dioxins, and polynuclear aromatic molecules.

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