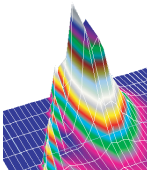
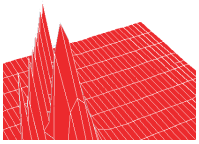
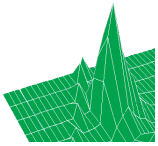
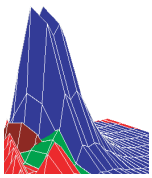






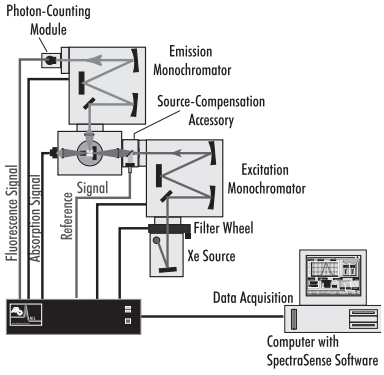


Measurement of Environmental Contaminant Hydrocarbons by Fluorescence Spectroscopy

Polycyclic aromatic hydrocarbons (PAH) and related chemicals are the largest known class of mutagens and carcinogens. They are frequent components of environmental contamination in water and soil. Contamination levels often occur in the ppm range, well above current EPA standards for acceptable levels, which are in the ppb range. This note describes the novel combined use of standard UV spectroscopy and fluorescence excitation-emission spectroscopy to measure low-ppm levels of PAH and other hydrocarbons. Standard Roper Scientific™/Acton Research spectroscopy components were used in a unique single system for both types of measurements. The results demonstrate that the two methods are complementary and that analysis of fluorescence excitation-emission matrices (EEM) of environmental contaminant hydrocarbons can sometimes provide greater sensitivity than UV spectroscopy.

Experimental Methodology

The work reported in this note was conducted by James Brasch of JB Labs in Columbus, Ohio for Acton Research. The instrumentation consisted of a 75-W xenon source, a filter wheel, and Acton Research SpectraPro® spectrometers. A universal sample chamber with 0-degree and 90-degree exit ports permitted both the absorption and fluorescence measurements. A source-monitoring detector mounted at the monochromator exit at the 0-degree port was used to compensate for variations in the xenon source at each measurement. For the absorption studies, an Acton Research SpectraPro 150 served to illuminate the samples and a silicon detector in the 0-degree port of the sample chamber was employed. For the fluorescence measurements, the aforementioned SpectraPro 150 served as the excitation monochromator and a second SpectraPro 150 with a photon-counting detector was attached to the 90-degree port as the emission monochromator (**Figure 1**). To control the system and acquire data from the detectors, an Acton Research NCL™ acquisition package and SpectraSense™ software were utilized. The EEM were evaluated using Grams® 5.0 and 3-D software (Galactic Industries Corp.).



Fluorescence Absorption Configuration

***Figure 1**. Experimental setup.*

Three PAH were used in the study – anthracene, naphthalene, and pyrene. The non-PAH, stilbene, was also included because of its intense fluorescence spectrum. Ethanol stock solutions of the individual chemicals and mixtures of all four were prepared at 2-ppm and 20-ppm concentrations. All samples were subjected to both absorption and fluorescence measurements to allow comparison of the techniques for low-concentration samples. Absorption measurements were collected in 2-nm increments at wavelengths between 200 nm and 660 nm using an integration time of 50 msec. Fluorescence readings were taken with excitation in 20-nm increments between 220 nm and 400 nm and emissions collected in 10-nm increments between 250 nm and 600 nm. EEM acquisition time was approximately 4 min using a 2-nm bandpass.

UV and Fluorescence Measurement of Hydrocarbons

The four chemicals each had a distinct UV-absorbance spectrum at 20-ppm concentration (see **Figure 2**). However, **Figure 3** shows that at 0.2-ppm concentrations, the three PAH were barely distinguishable and stilbene could not be visualized, even with first and second derivatives of the spectra.

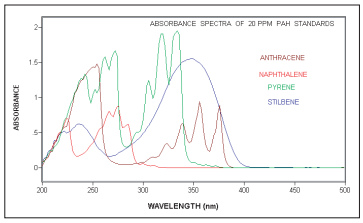


Figure 2

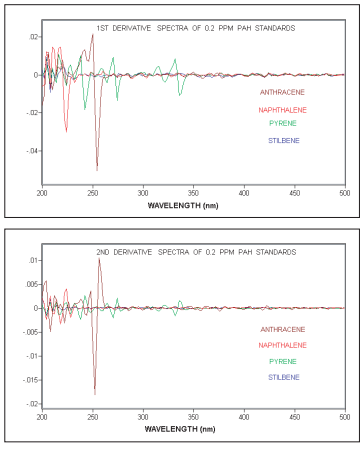


Figure 3

***Figure 2**. Absorbance spectra of 20-ppm samples.*
***Figure 3**. Absorbance spectra first derivative (top tracing) and second derivative (bottom tracing) of 0.2-ppm samples.*

With fluorescence measurements in which EEM were created, each of the four chemicals had a distinct EEM at the 2-ppm level (refer to **Figures 4 - 7**). **Figure 8** shows a combined overlay of the EEM for all four chemicals (0.2 ppm) on the same intensity scale. By this method, there was a distinctive characteristic of each component that could be used for identification. In **Figure 9**, an EEM is shown for a 0.05-ppm mixture of all four hydrocarbons. All except pyrene were readily discernible at 0.05 ppm by the fluorescence methodology using two Acton Research SpectraPro 150 instruments.

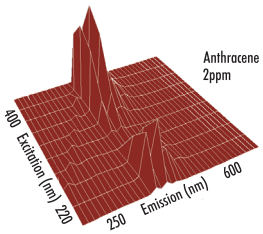


Figure 4

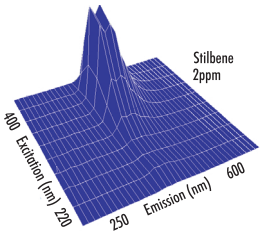


Figure 5

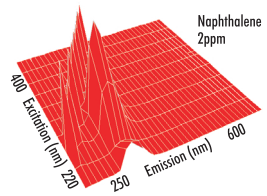


Figure 6

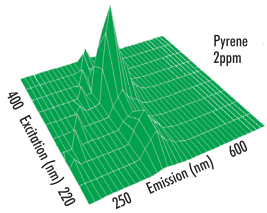


Figure 7

***Figure 4**. EEM of 2 ppm anthracene.*
***Figure 5**. EEM of 2 ppm stilbene.*
***Figure 6**. EEM of 2 ppm naphthalene.*
***Figure 7**. EEM of 2 ppm pyrene.*

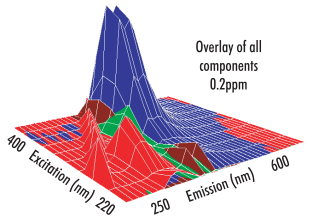


Figure 8

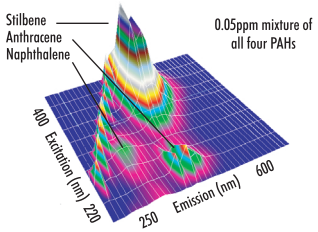


Figure 9

***Figure 8**. Combined overlay of EEM for all four chemicals at 0.2 ppm.*
***Figure 9**. EEM of mixture of all four chemicals at 0.05 ppm.*

In conclusion, fluorescence spectroscopy with EEM construction and analysis is a sensitive method that complements standard UV spectroscopy for low concentrations of hydrocarbons. Furthermore, this method of fluorescence spectroscopy can detect some chemicals at concentrations that are below the detection limits of standard UV absorption spectroscopy (e.g., stilbene at 0.2 ppm). This method could greatly facilitate the detection and monitoring of environmental contaminant PAH and other hydrocarbons.

SpectraPro Monochromators and Spectrographs

Acton Research SpectraPro monochromators and spectrographs from Roper Scientific are recognized as industry standards for rugged high-performance operation and versatility. Each features an automated multiple-grating turret for extended spectral coverage. Four standard focal lengths and a host of unique customized features make SpectraPro spectrometers ideal for environmental, industrial, educational, and research applications. Through innovative engineering, these monochromators and spectrographs can be incorporated into completely integrated spectroscopy systems customized to suit a specific application. The SpectraPro advantages are as follows:

High Throughput – All SpectraPro monochromators and spectrographs feature high-aperture optics, corrected and computer-optimized to reduce astigmatism.

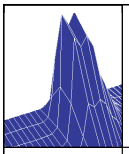
High Resolution – In high-aperture imaging spectrographs, the off-axis aberrations can compromise system performance. Only SpectraPro offers interchangeable focal-plane adapters optimized for particular needs.

Positrack Grating Interchange – The advantage of a multiple-grating turret is to be able to quickly change gratings. The wavelength of the spectrometer from grating-to-grating interchange should be maintained with the same precision as that expected with a single grating. The entire SpectraPro line meets this stringent stability requirement.

Exclusive High-Reflectivity Coatings – All SpectraPro monochromators and spectrographs feature enhanced UV-to-VIS reflective coatings with 90% or better average reflectance. Specialized gold and silver reflective coatings for IR and NIR wavelengths are available as options.

Versatility – Some models of SpectraPro can be configured with multiple exit and entrance ports for extended spectral coverage or a CCD/single-channel detector combination. There are over 100 gratings from which to choose. RS232C and IEEE488 communications capabilities and LabView drivers are included. Optional 68 x 84-mm gratings for constant full aperture are available, as are optional interchangeable turrets and high-precision motorized slits.

Control and Integration Solutions – SpectraSense spectral-acquisition and manipulation software seamlessly integrates interactive control of your system. It provides real-time interactive control of all experimental parameters, as well as real-time data manipulation. An intuitive interface allows easy access to any system components, including switching between multichannel and single-channel detection. A unique process-monitoring interface employing real-time chemometrics makes SpectraSense the most versatile spectral-acquisition software available.



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Double Monochromators – Double monochromators are also available in both additive and subtractive models in 300-mm, 500-mm, and 750-mm configurations. Additive models feature a triple-grating turret and provide twice the dispersion of single monochromators of the same focal length. They also have stray-light rejection in the 10^{9} range. Double additives are designed for high-resolution, high-purity applications. Double subtractive systems are supplied with single-grating kinematic mounts. They provide zero dispersion and an extremely pure homogenous bandpass of light at the exit. All doubles can be ordered with exit ports on the first monochromator for single-spectrometer operation or dual exit ports for multiple detectors.

Vacuum Monochromators – Roper Scientific is the premier manufacturer of vacuum monochromators and spectrographs for the industrial and scientific markets. Models are offered with focal lengths between 0.2 m and 1.3 m. The exclusive VM504 is the only triple-grating-turret vacuum monochromator/ spectrograph available. It is capable of making *in vacuo* measurements from the UV to the far IR without breaking vacuum.

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Roper Scientific offers a full line of accessories for SpectraPro instruments. These include light-input devices, light sources, universal sample chamber and sample holders, filter wheel assemblies, single-channel detector assemblies, and fiberoptic bundles and adapters. Spectroscopy components and accessories from Roper Scientific are the solutions for your Raman, fluorescence, emission, or absorption application needs.

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