



## Project Summary

# Analysis of Polynuclear Aromatic Hydrocarbons in Particulate Matter by Luminescence Techniques

W. A. Ivancic, L. L. Brown, R. M. Riggin, and R. H. Barnes

Fluorescence, phosphorescence, and heavy-metal activated room temperature phosphorescence spectra were obtained for ten polycyclic aromatic hydrocarbon (PAH) reference compounds individually and in mixtures on quartz plates and particulate matter. The results indicate that multicomponent analysis of PAHs on airborne particulate matter may be possible with the development of appropriate multicomponent spectral deconvolution procedures. The direct analysis approach in combination with the use of solvent extraction followed by fluorescence analysis can provide a rapid means of analysis for PAHs both within and on the surface of particulate matter. Direct phosphorescence was too weak to be useful at 5-10  $\mu\text{g/g}$  levels found in many types of particulate samples. Heavy-metal activated room-temperature phosphorescence appears more sensitive to matrix and substrate effects and less amenable to multicomponent analysis than fluorescence.

The fluorescence spectrum of benzo(a)pyrene was found to be affected by exposure to low levels of ozone. However, the fluorescence spectrum retains characteristic features that enable identification of the benzo(a)pyrene.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same*

*title (see Project Report ordering information at back).*

### Introduction

This project involved an exploratory study to evaluate the potential of optical fluorescence and phosphorescence techniques for the direct analysis of polycyclic aromatic hydrocarbons (PAHs) in urban particulate samples. Current chemical procedures for the analysis of PAHs in particulate samples are both time consuming and expensive. If the luminescence techniques without involved chemical extractions were available for PAH particulate analysis, it would greatly extend the capabilities for the study and survey of carcinogen-bearing particulate materials in the environment.

The facts that PAHs tend to be highly luminescent with characteristic spectra for individual compounds suggest the possible use of fluorescence and phosphorescence for particulate analysis. These techniques simply involve irradiating a sample with ultraviolet light and analyzing the timing and intensities of the spectral components of the luminescence. Fluorescence emissions for PAHs generally decay with emission lifetimes less than 10  $\mu\text{s}$  while phosphorescence is characterized by lifetimes extending from about 100  $\mu\text{s}$  to minutes. Through selective wavelength excitation coupled with temporal and spectral analysis of the emitted luminescence, it is often possible to apply multicomponent analysis procedures to identify and quantify individual species in complex mixtures.

As a basis for these studies, ten major PAHs typically found in urban particulates were selected as reference compounds. The selected compounds are listed in Table 1. These compounds were used individually and in mixtures of various complexities on quartz substrates and on particulate samples to generate luminescence data for evaluating the utility of the fluorescence and heavy-metal-activated room-temperature phosphorescence (RTP) techniques for the direct analysis of PAHs on particulate materials.

Also investigated as part of this study were the effects of low-level ozone exposure on fluorescence from benzo(a)pyrene and the use of supercritical fluid CO<sub>2</sub> to extract PAHs from particles for fluorescence analysis.











## Procedure

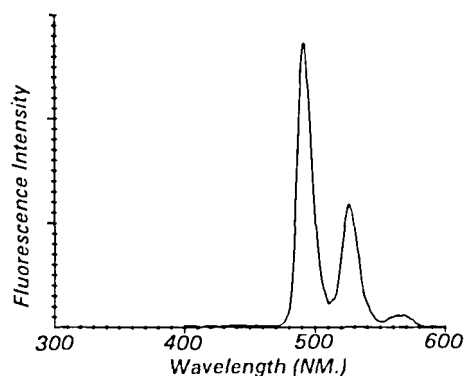
A Molelectron® frequency doubled Model DL14 pulsed dye laser pumped by a nitrogen laser was employed as the excitation source for the luminescence measurements. Samples of the reference compounds were deposited in solvents onto S1-UV quartz plates or particle samples and then evaporated to dryness. The beam from the dye laser was focused onto the surface of the samples at an angle 70° from the normal and the luminescence collected with f/4 optics in a direction normal to the sample and spectrally analyzed using a f/9 1.26-m spectrometer with a low-noise photomultiplier tube. The signal from the photomultiplier was processed with a dual photon counting system to allow both fluorescence and phosphorescence spectra to be recorded simultaneously. The photon counting system was synchronized to the laser pulse and the dual detection channels gated with separate delays and variable time windows. Output from the dye laser was monitored and used to normalize the luminescence to compensate for variations in the output of the dye laser.

## Results and Discussion

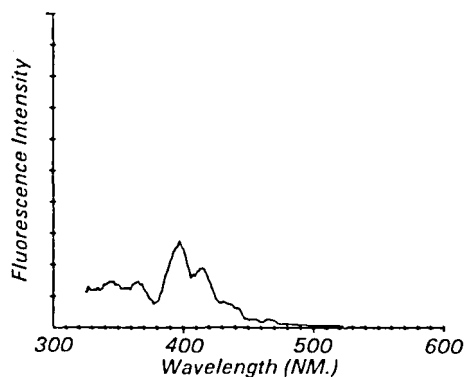
Typical fluorescence spectra are shown in Figures 1 and 2 for benzo(a)anthracene on quartz and on particulate standard reference material NBS SRM 1633. For the quartz sample, 4 μL of 100 ppm acetone solution was deposited as a 2 mm diameter spot, while for the particulate sample, 50 μL of 100 ppm solution was deposited on 5.8 mg of NBS SRM 1633. In the case of all the reference PAHs, the type of substrate influenced the spectra; however, the individual

**Table 1.** Polycyclic Aromatic Hydrocarbons Used as Reference Compounds

Polycyclic Aromatic Compounds	Formula	Structure
<i>Benzo(b)fluoranthene</i> (3,4-Benzofluoranthene)	C <sub>20</sub> H <sub>12</sub>	
<i>Benzo(k)fluoranthene</i> (11,12-Benzofluoranthene)	C <sub>20</sub> H <sub>12</sub>	
<i>Benzo(a)pyrene</i> (3,4-Benzopyrene)	C <sub>20</sub> H <sub>12</sub>	
<i>Benzo(e)pyrene</i> (4,5-Benzopyrene)	C <sub>20</sub> H <sub>12</sub>	
<i>Benzo(a)anthracene</i> (1,2-Benzanthracene)	C <sub>18</sub> H <sub>12</sub>	
<i>Chrysene</i> (1,2-Benzophenanthrene)	C <sub>18</sub> H <sub>12</sub>	
<i>Benzo(ghi)perylene</i> (1,12-Benzoperylene)	C <sub>22</sub> H <sub>12</sub>	
<i>1,2,3,4-Dibenzanthracene</i>	C <sub>22</sub> H <sub>14</sub>	
<i>1,2,5,6-Dibenzanthracene</i> (Dibenz[a,h]anthracene)	C <sub>22</sub> H <sub>14</sub>	
<i>Fluoranthene</i> (1,2-Benzacenaphthene)	C <sub>16</sub> H <sub>10</sub>	



**Figure 1.** Fluorescence reference spectrum excited at 292 nm for benzo(a)anthracene on quartz.



**Figure 2.** Fluorescence spectrum excited at 295 nm for chrysene on NBS SRM 1633.

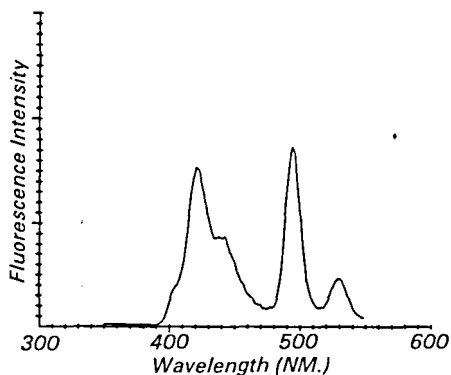
compounds still retained their characteristic features.

Fluorescence spectra for an equal mixture of all ten reference compounds on quartz and NBS SRM 1633 are presented in Figures 3 and 4. The quartz sample was deposited as 10 μL of a 100 ppm solution made up of 10 ppm of each reference PAH. For the particulate sample, 50 μL of the mixture solution was deposited on 5.5 mg of NBS SRM 1633.

Detection limits for the PAHs on the particulate were about 2.5 ng. cursory examination of the mixture spectra indicated that it should be possible to analyze for the individual PAHs in the ten-component mixtures using multicomponent analysis procedures.

Experiments using a J&W Scientific (Orangevale, CA) high-pressure supercritical CO<sub>2</sub> Soxhlet extractor showed that organic constituents in particulate materials could easily be extracted and transferred to quartz plates for fluorescence analysis.

For the heavy-metal activated RTP studies the time windows were set to separate the long-lived phosphorescence from fluorescence. PAHs on quartz, NBS SRM 1633 and filter paper were activated with lead acetate. The phosphorescence measured was found to be extremely sensitive to the type of substrate and degree of drying of the sample, making it difficult to obtain reproducible results.



**Figure 3.** Fluorescence spectrum excited at 292 nm for equal part mixture of all 10 PAH reference compounds on quartz.

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Nancy K. Wilson is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Polynuclear Aromatic Hydrocarbons in Particulate Matter by Luminescence Techniques," (Order No. PB 84-181 882;

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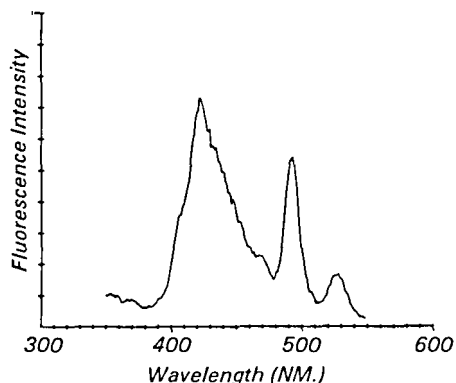
The EPA Project Officer can be contacted at:

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**Figure 4.** Fluorescence spectrum excited at 292 nm for equal part mixture of 10 PAH reference compounds on NBS SRM 1633.

Also, the intensity of the heavy-metal-activated RTP was weaker than direct fluorescence with a detection limit of about 160 ng.

The ozone studies were conducted by exposing benzo(a)pyrene deposited on a quartz plate to 1 ppmv of ozone for various periods of time, after which fluorescence measurements were made and compared with a control sample that had not been exposed to ozone. Changes in the fluorescence spectrum for benzo(a)pyrene were produced by the ozone exposure; however, the characteristic spectral features were still retained after a 42-hour exposure.