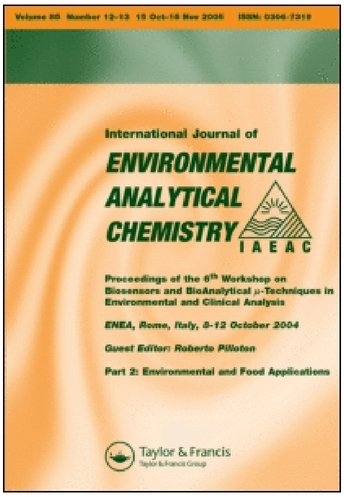

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Application of High Resolution Shpol'skii Luminescence Spectroscopy to the Analysis of Polycyclic Aromatic Hydrocarbons (PAH) in the Environmental Samples[†]

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High resolution spectrofluorometry (HRS) in *n*-alkane matrices (Shpol'skii effect) has been applied to the analysis of several methylated-PAH series, aromatic biogeochemical markers, and common PAH in environmental samples (sediments, aerosols, crude oils, liquid fuels). Analytical results obtained by HRS on crude samples have been also compared with those obtained by other analytical methodologies.

KEY WORDS: Shpol'skii effect, polycyclic aromatic hydrocarbons (PAH), monomethylchrysenes (MC), monomethylphenanthrenes (MP), biogeochemical aromatic markers, quantitative analysis, sediment, crude oil, aerosol, liquid fuel.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are common trace components of environmental samples. In the past ten years, analytical techniques characterized by high sensitivity and selectivity have been

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developed or improved for the identification and the quantitative analysis of PAH, partly due to the mutagenic and carcinogenic character of some aromatic compounds.

Besides the classical analytical methodologies, (gas capillary chromatography coupled or not with mass spectrometry (GC-MS), and high performance liquid chromatography (HPLC)), high resolution spectrofluorometry (HRS) at low temperature *n*-alkane matrices (Shpol'skii effect) has recently attracted much attention.[1,2,3]

Since the first observation in the early fifties,[4] this method has been widely applied to the analysis of common PAH (i.e. pyrene, benzo(a)pyrene...) in crude samples or in chromatographic samples fractions (from air, automobile exhausts, crude oils, sediments).[5,6]

Our purpose in this paper is to demonstrate the potential of HRS by a few studies of several specific PAH series of geochemical interest:

- observation of the relative distribution of phenanthrene and chrysene compounds in different natural samples,
- detection of biogeochemical aromatic markers related to natural precursor series (amyrines, hopane).

The ability of quantitative analysis of selected PAH by HRS on a crude liquid fuel is also demonstrated and the results are briefly compared with those obtained by other analytical techniques.

High resolution Shpol'skii spectrometry

Fluorescence and phosphorescence spectra of aromatic compounds are quite broad at room temperature, having full widths at half-maximum (FWHM) of the order of a few nanometers. A sharpening of the luminescent spectra is observed when PAH are incorporated into an appropriate *n*-alkane matrix frozen at low temperature ($T \ll 77$ K) (Figure 1).

The low temperature luminescence spectra exhibit a 0–0 transition with several sharp peaks ("quasi-lines") having FWHM about 0.1 nm called multiplet structure and related to different substitution sites of the aromatic molecule in the *n*-alkane lattice.[7]

Some experimental requirements must be observed for obtaining high resolution spectra:

(a) only certain solute-solvent combination provide quasi-linear

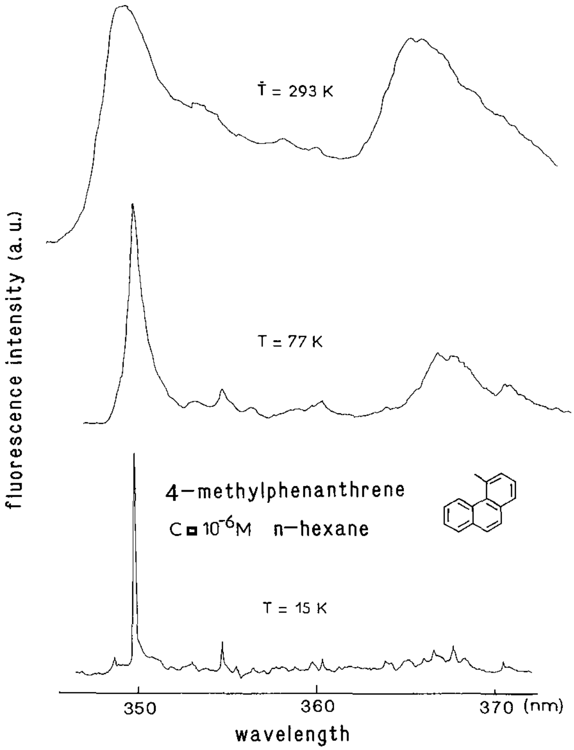

FIGURE 1 Effect of the temperature on the fluorescence spectrum of 4-methylphenanthrene in *n*-hexane.
Excitation wavelength: 299 nm. $C = 5 \times 10^{-6}$ M.

spectra.[8] This "key and hole" rule is based on the dimensional and geometric similarities between the solvent and the solute molecules.

(b) a preliminary fast freezing of the samples in liquid nitrogen is essential to avoid aggregate formation[9] and to assure sample reproducibility,[10]

(c) the analysed samples should be very dilute (concentration $\approx 10^{-6}$ M) to minimize the possible formation of aggregates or microcrystallites[11] which can alter the reproducibility of fluorescence intensity.[2,10]

Virtually any neutral, polar (such as PAH metabolites, compound No. 1), or heterocyclic aromatic compound (compound Nos. 2, 3, and 4) should exhibit quasilinear luminescence spectra in an appropriate *n*-alkane solvent, as shown in Figure 2. HRS has been recently also applied to the detection of sulfur[12] or nitrogen[13,14] aromatic heterocyclic compounds in natural samples.

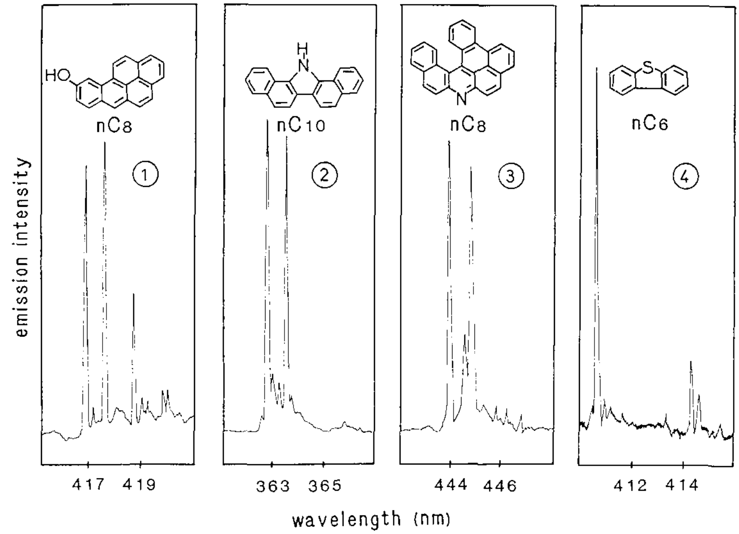

FIGURE 2 High resolution fluorescence (compounds 1, 2, 3) and phosphorescence (compound 4) spectra of different polycyclic aromatic compounds. Concentration about 2×10^{-6} M for each compound. $T=15$ K.

EXPERIMENTAL SECTION

Low temperature spectrofluorometry

Low temperature luminescence experiments at 15 K were performed with a home-made spectrofluorometer previously described,[10,15] using a lamp excitation source.

Sample preparation

Preliminary HPLC separation of PAH from natural samples is sometimes required for specific identification of aromatics by HRS.

This HPLC procedure has been reported elsewhere[3,14,15] and includes two steps: first to isolate compounds according to the degree of aromaticity (level I) and second, to separate parent compounds according to the degree of alkylation (level II). The chromatographic fractions suspected of containing the studied PAH were then analysed at different levels of fractionation (level I for detection of biogeochemical markers, level II for analysis of methyl-PAH).

Origin of the samples

The estuarine sediment was collected in the Gironde estuary and the PAH extracted according to the Institut Français du Pétrole (IFP) method.[17] The air particulate matter originates from the Washington D.C. area and was extracted as reported previously.[18] The deltaic sediment was cored during MISEDOR operations in the Mahakam delta area (Indonesia). The crude oil was drilled from a well in China.

RESULTS AND DISCUSSION

Observation of phenanthrene and chrysene compounds in different natural samples

As previously claimed[19,20] the abundance and relative distribution of alkylated-PAH to their respective parent compound could be an indicator of the source of the organic sedimentary matter.

In the sedimentary environment, both combustion (pyrolysis of fossil fuels and wood) and fossil sources (recent and ancient organic matter, petroleum) produce the same aromatic compounds. For the phenanthrenic series, the values of MP/P (i.e. ratio of the total concentration of monomethylphenanthrenes to the concentration of the parent compound) measured in natural samples from these two distinct sources were characteristically different.[19] Such a ratio is useful as an indicator of the relative level of contamination of the studied sediments. For instance, the ratio MP/P may range from 2 up to 6 in fossil fuels whereas samples generated by high temperature combustion processes display MP/P values of 0.5–1.0.[20]

However methylated PAH are often difficult to quantify by GC or

GC-MS due to coelution problems with numerous isomers. In these cases, HRS has demonstrated its ability to analyse such complex methylated PAH mixtures[3] and to lead to a true determination of the relative distribution of methylated PAH series.[21]

The identification of phenanthrene and methyl-phenanthrenes, chrysene and methyl-chrysenes has been performed by HRS on three different natural extracts (Figures 3 and 4). The 4,5-methylene-phenanthrene (4,5 MP) was absent in the crude oil (as previously reported for other crude oils[14]). This aromatic compound of pyrolytic origin was observed in the Washington air particulate matter and also in the estuarine sediment (Figure 3).

The values of MP/P and MC/C ratios have been calculated and are reported in Table I. These values suggest a pyrolytic origin for the sedimentary matter in the estuarine sediment which presents values for the both ratios closer to those of air particulate matter than those of crude oil.

TABLE I

Phenanthrene and chrysene ratios determined in the studied environmental samples Σ MP/P (Σ MC/C) = ratio of the sum of concentrations of monomethylated phenanthrenes (chrysenes) over the concentration of phenanthrene (chrysene).

Sample	Σ MP/P	Σ MC/C
Gironde sediment	1.17	0.37
Aerosol	0.72	0.20
Crude oil	2.40	2.30

Such results demonstrate the analytical capability of HRS to correctly identify methylated PAH isomers, leading to their relative quantification in natural matrices and allowing hypotheses on the origin of the sedimentary organic matter.

DETECTION OF AROMATIC BIOGEOCHEMICAL MARKERS

Molecular markers are organic compounds with specific chemical structure which can be correlated to biological precursors. Such

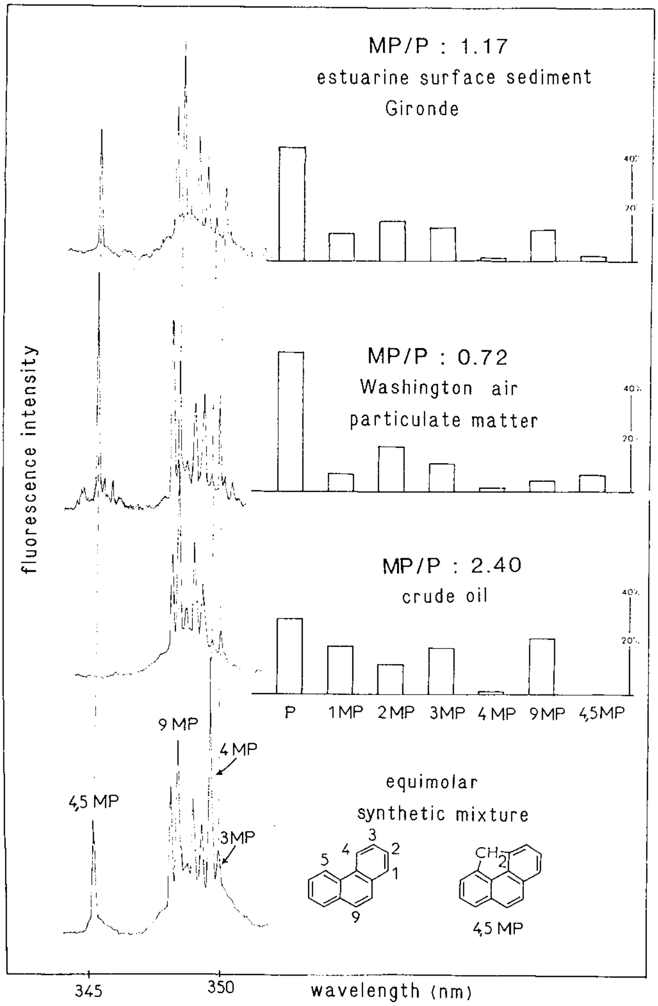

FIGURE 3 High resolution fluorescence spectra in *n*-hexane and relative distribution of phenanthrenic compounds extracted from different matrices. P, 1 MP and 2 MP were identified by phosphorescence spectra (non-pictured). $C = 2 \times 10^{-7}$ M for each component in the synthetic mixture.

Excitation wavelength: 299 nm. $T = 15$ K.

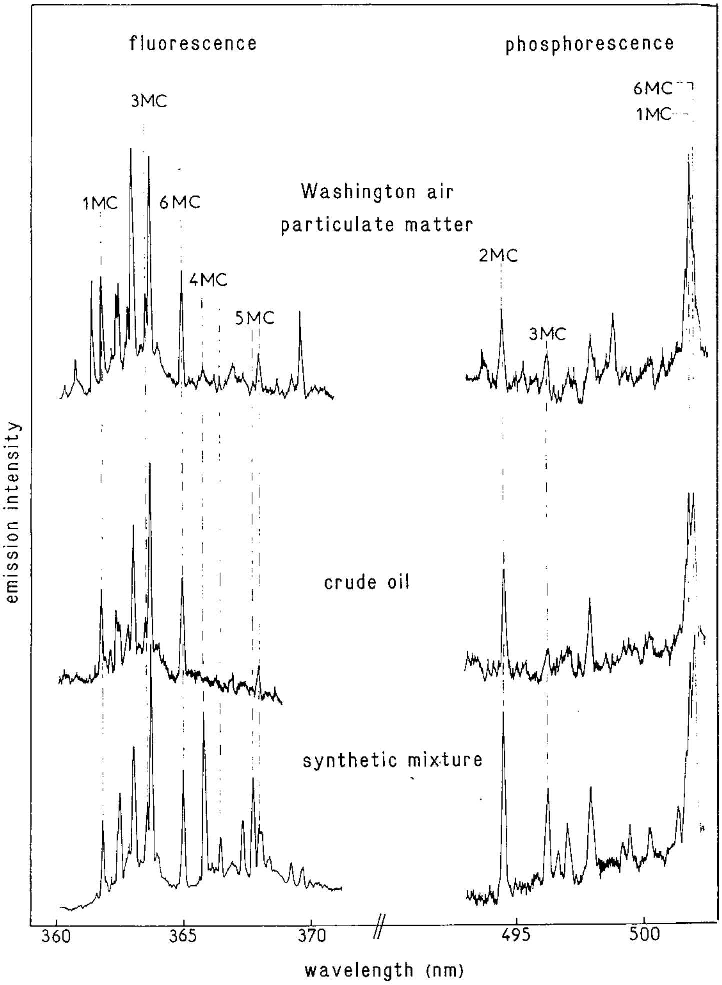

FIGURE 4 High resolution fluorescence (right) and phosphorescence (left) spectra in *n*-octane of monomethylchrysenes extracted from different matrices. Note the lack of 4 MC and 5 MC. $C = 10^{-7}$ M for each component in the synthetic mixture. Excitation wavelength: 327 nm. $T = 15$ K.

markers can be utilized as indicators of sources, environmental conditions, geologic maturity, and product precursor relationships. Some of these molecules are related to the hopane series derived from bacteria or blue algae, and others are derived from triterpenoid compounds (amyrines) of higher plants. The conversion of precursors into partially aromatized species would occur at a very early stage of diagenesis, presumably by a dehydrogenation mechanism.[22, 23]

Pentacyclic chrysenes have been identified in a deltaic sediment extract by comparison with an equimolar synthetic mixture of reference compounds, deriving from the hopane series (bacterial origin) and β-amyrine series (terrestrial origin) (Figure 5).

Similar identifications have been previously obtained for deep sea marine sediments.[24] The presence of bulky substituents on the

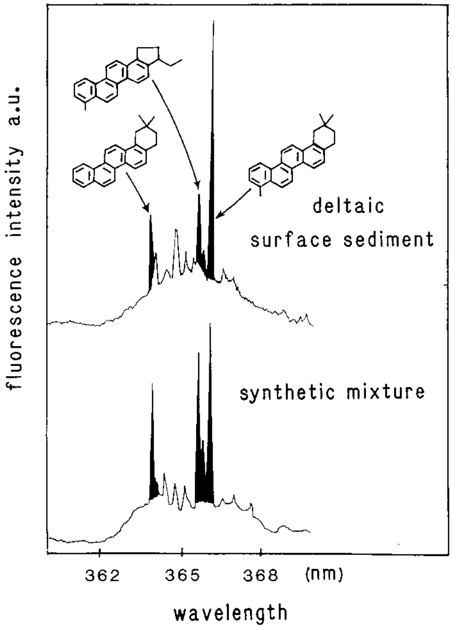

FIGURE 5 High resolution fluorescence spectra in *n*-decane of biogeochemical markers in a tetraaromatic fraction of a deltaic surface sediment extract. $C = 10^{-6}$ M for each compound in the synthetic mixture.

Excitation wavelength: 273 nm. $T = 15$ K.

aromatic skeleton does not, in most cases hinder the inclusion of the aromatic solute in the *n*-alkane crystal. Due to the large size of these molecules, *n*-decane was the most appropriate matrix for obtaining sharp emission spectra according to the precited "key and hole" rule.

QUANTITATIVE ANALYSIS OF SELECTED PAH

The applications of HRS to quantitative analysis of PAH in environmental samples have been limited until recently to a few examples only. This is certainly due to the necessity of internal standard and standard addition combined methods which are not convenient for rapid analyses. A relatively simple method has been introduced recently by the use of deuterated aromatic compounds as internal reference standards.[25] Deuterated PAH exhibit a similar Shpol'skii emission spectra to the parent compound but with a spectral line shift of about 1 nm for the quasi-lines of the 0–0 transition (Figure 6).[25]

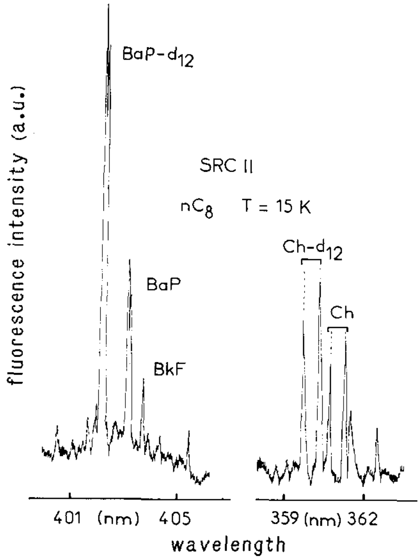

FIGURE 6 High resolution fluorescence spectra of benzo(a)pyrene (BaP), benzo(k)-fluoranthene (BkF) and chrysene (Ch) in the crude coal liquid (SRC-II) dilute in *n*-octane. Deuterated BaP and Ch spiked as internal references.
Excitation wavelength: 300 nm for BaP and BkF.
Excitation wavelength: 275 nm for Ch.

TABLE II

Results of the direct determination of selected PAH (Figure 9) in the SRC-II sample by different analytical techniques (Figure 9).

	HRS	Synchronous fluorescence[a]	NBS data (HPLC)[b]	LESS[c]
Chrysene	66	—	—	—
Benzo(a) anthracene	24	—	—	—
Benzo(a) pyrene	160	130	134	145
Benzo(k) fluoranthene	92	—	62	—
Perylene	26	20	26	29

[a] Reference 27.
[b] Reference 26.27.
[c] Reference 25.26; LESS = Laser Excited Shpol'skii Spectroscopy.

To evaluate the ability of this method, we have analysed a liquid fuel which has been used in the U.S.A. for an interlaboratory comparison exercise.[26] Typical fluorescence of chrysene and benzo(a)pyrene and their deuterated analogues spiked in the dilute crude liquid fuel are shown in Figure 6. In Table II, the preliminary analytical results (only one analysed aliquot) are compared with values obtained by other analytical methodologies (HPLC, spectrofluorometric methods).[26,27] The results obtained by HRS are found to be in quite good agreement with the other techniques, thus demonstrating the reliability of HRS for quantitative analysis.

CONCLUSION

The various results presented in this paper show the analytical capability of high resolution spectrofluorometry in Shpol'skii matrices for the detection of different aromatic compounds and their quantification in fractionated or crude samples.

Further analytical developments are in progress in our laboratory for a fast and precise measurement of PAH series in environmental matrices, particularly the detection of the priority pollutants recommended by the U.S. Environmental Protection Agency (EPA).[27] Such results will give information about the origin and the transport of organic matter in the environment.

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