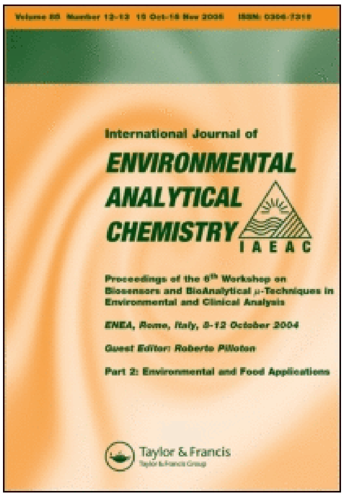

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P. Garrigues[a]; M. Ewald[a]; M. Lamotte[a]; J. Rima[a]; A. Veyres[a]; R. Lapouyade[b]; J. Joussot-dubien[a]; G. Bourgeois[c]
[a] Laboratoires de Chimie Physique A et de Chimie Organique, Talence Cedex, France [b] ERA du CNRS no. 167-Université de Bordeaux 1, Talence Cedex, France [c] Centre d'Etude Structurale et d'Analyse des Molécules Organiques, Université de Bordeaux 1, Talence Cedex, France

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Low Temperature Spectrofluorimetry of Complex Mixtures of PAH, Application to the Analysis of Isomeric PAH Extracted from Environmental Samples (Petroleum, Marine Sediments)†

P. GARRIGUES,‡ M. EWALD,¶‡ M. LAMOTTE,‡ J. RIMA,‡
A. VEYRES,‡ R. LAPOUYADE§ and J. JOUSSOT-DUBIEN‡
Laboratoires de Chimie Physique A‡ et de Chimie Organique,§ ERA du CNRS no. 167— Université de Bordeaux I, 351 Cours de la Libération 33405 Talence Cedex, France

and

G. BOURGEOIS
Centre d'Etude Structurale et d'Analyse des Molécules Organiques, Université de Bordeaux 1, 351 Cours de la Libération, 33405 Talence Cedex, France

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Spectra obtained by High Resolution Spectrofluorimetry (HRS) in *n*-alkane matrices are more resolved and more structured than those obtained in nitrogen matrix. Analysis of petroleum and marine sediment fractions obtained by a two steps HPLC procedure allow us to identify and quantify the five isomers of the monomethylphenanthrene by HRS in *n*-hexane at 15 K. Some results are compared with those obtained by GC-MS analysis.

KEY WORDS: Polycyclic-aromatic-hydrocarbons (PAH), monomethyl-phenanthrene isomers (MP), monomethyl-chrysene isomers (MC), petroleum, marine sediment, high-resolution-spectrofluorimetry (HRS), high-performance-liquid-chromatography (HPLC), gas-chromatography-mass-spectrometry (GC-MS).

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¶To whom correspondence should be addressed.

INTRODUCTION

During the last ten years, two methods with high resolution spectrofluorimetric detection at low temperature ($T \ll 77\,K$) have been developed: the *n*-alkane frozen solutions of PAH (Shpolskii matrices)[1] and the matrix isolation spectroscopy in inert gas matrix.[2] Our purpose was to choose the best method for the analysis of isomeric PAH in environmental samples. Qualitative studies on synthetic mixtures show that the Shpolskii matrices method is the most convenient one. This method was applied to the analysis of monomethylphenanthrenes (MP) in petroleum and marine sediment fractions.

Quantitative determinations are made by combined internal-standard and standard addition methods. Results are briefly compared with those of GC-MS analysis and further developments are under way to obtain quantitative determination with standard deviations for the two techniques (HRS and GC-MS).

EXPERIMENTAL

Authentics of the monomethylphenanthrenes have been synthetized in the laboratory,[3] except the 2-methylphenanthrene (2 MP) (K and K Fine Products). Purity of these compounds have been tested by GC-MS. Authentics of methyl-chrysene have been provided by Dr. A. Colmsjö of Arrhenius Laboratory (Stockholm, Sweden). Results presented in this work have been obtained with a crude petroleum from North Sea (marine origin) and with a marine sediment from Cariaco Trench (Orgon II Cruise).[4,5] Two other petroleums[6] and three different marine sediments were examined which lead to the generality of the informations presented here.

(a) Fractionation

The chromatographic procedure has been described in previous papers.[7,8] After adsorption chromatography of crude samples on Florisil (SiO_2 and MgO) with pentane elution to eliminate aliphatics and very polar compounds, two HPLC steps allow us to isolate first the triaromatic compounds on μ-silica-NH_2, secondly the monomethylated triaromatics on μ-silica-C_{18}. Elution of the aromatic compounds was monitored at 254 nm with UV-VIS monochromatic absorption detector (LDC Spectromonitor III).

(b) High resolution spectrofluorimetry (HRS)

A home made high resolution spectrofluorimeter has been previously described.[9] For the frozen solution method, quartz tubes containing *n*-alkane solutions of PAH were attached to the cold head of a closed cycle helium cryogenerator (CTI Cryodyne 21S) operating at 15 K. Preliminary fast freezing of solutions at 77 K in liquid nitrogen is necessary to obtain sharp emission spectra. For matrix isolation spectroscopy, PAH were sublimed and mixed with N_2 gas before trapping on a cold surface attached to the head of the cryogenerator.[2]

The light of the excitation source (Xenon lamp XBO Osram, 450 W) was dispersed by a monochromator (Jobin Yvon HR 20) and focused on the analyzed samples. Fluorescence emission was observed at 90° through a high resolution monochromator (Jobin Yvon HR 1000, resolution 0.8 Å).

RESULTS AND DISCUSSION

(a) Qualitative experiments on artificial mixtures

We have compared emission spectra obtained for artificial mixtures of isomeric PAH in *n*-alkane frozen solutions and in nitrogen matrix.

The first mixture was composed of the five monomethylphenanthrene isomers. In Shpolskii matrices, very sharp emission bands (bandwidth about 0.1 nm) are observed. Each compound can be detected by a specific emission band for selective excitation wavelength, by comparison with emission spectra of authentic compounds. With an excitation wavelength centered at 298.5 nm (bandwidths about 2.5 nm) (Figure 1), characteristic emission bands belonging to 9 MP, 4 MP and 3 MP are observed. In nitrogen matrix on the contrary, only one very intense broad band (bandwidth about 1.2 nm) is observed for any excitation wavelength, indicating clearly that monomethylphenanthrene individual emissions cannot be distinguished by this method.

A mixture of the six monomethylchrysene isomers was also analyzed. Each isomer is well detected in *n*-heptane frozen solutions by characteristic sharp fluorescence peaks (Figure 2). In nitrogen matrix, some isomers are only detected as shoulders on more intense fluorescence bands. A change in excitation wavelength conditions, does not allow a better observation of these compounds.

In conclusion, emission spectra of PAH in *n*-alkane matrices are more resolved and more structured than those obtained in nitrogen matrix and allow the identification of each compound in a complex mixture of isomers.

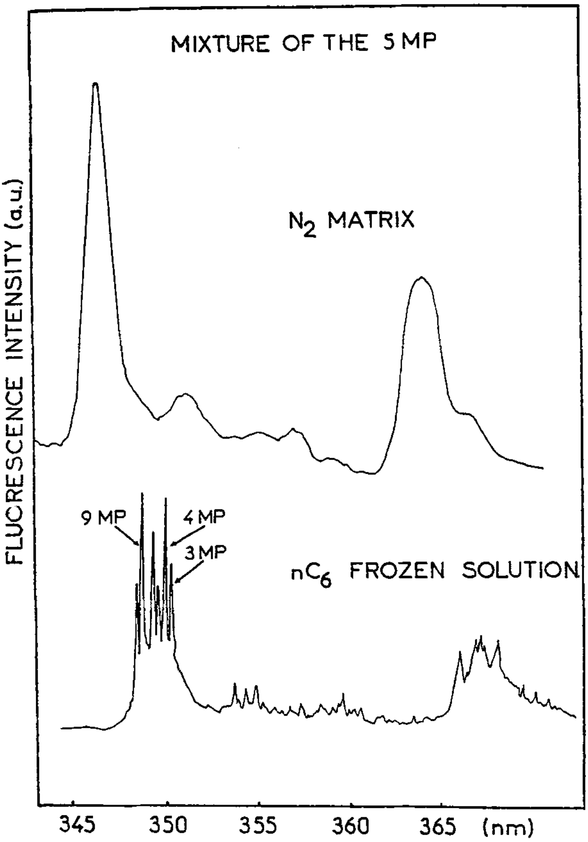

FIGURE 1 Fluorescence spectra at 15 K of monomethylphenanthrenes (MP) in a synthetic mixture:

— in nitrogen matrix: 200 ng of each isomer, excitation wavelength at 292 nm, molecular ratio $N_2/MP > 10^6$.

— in nC_6 frozen solution: $c = 2.10^{-7}$ M for each isomer, excitation wavelength at 298.5 nm.

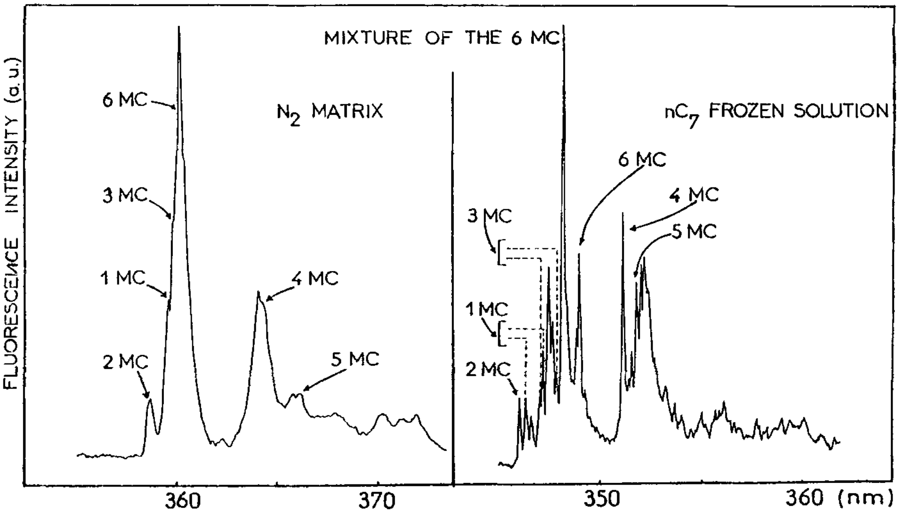

FIGURE 2 Fluorescence spectra at 15 K of the six monomethylchrysenes (MC) in a synthetic mixture:

— in nitrogen matrix: about 100 ng for each isomer, excitation wavelength at 261 nm, molecular ratio $N_2/MC > 10^6$.

— in nC_6 frozen solution: $c \sim 2.10^{-6}$ M for each isomer, excitation wavelength at 266 nm.

(b) Identification of monomethylphenanthrenes in natural samples

We have analyzed the monomethylphenanthrenes contained in fractions of petroleum and of marine sediment, obtained by a two step HPLC procedure. The optimum conditions for the characterization of each isomer were first defined by using a synthetic mixture with a judicious choice of the excitation wavelength and by recording either the fluorescence (for 9 MP, 4 MP and 3 MP) or the phosphorescence (for 2 MP and 1 MP). The spectra of natural samples compared with those of synthetic mixtures indicate the small amount of 4 MP both in petroleum and in marine sediment fractions (Figure 3). The fact that natural samples emission spectra are similar to those of synthetic mixtures, (i.e. good signal/noise ratio, no detectable interference from others solutes), points out the selectivity of the chromatographic separations and of the spectrofluorimetric analysis.

(c) Quantitative determination in the petroleum fraction

Due to different kinds of solute aggregations in Shpolskii matrices

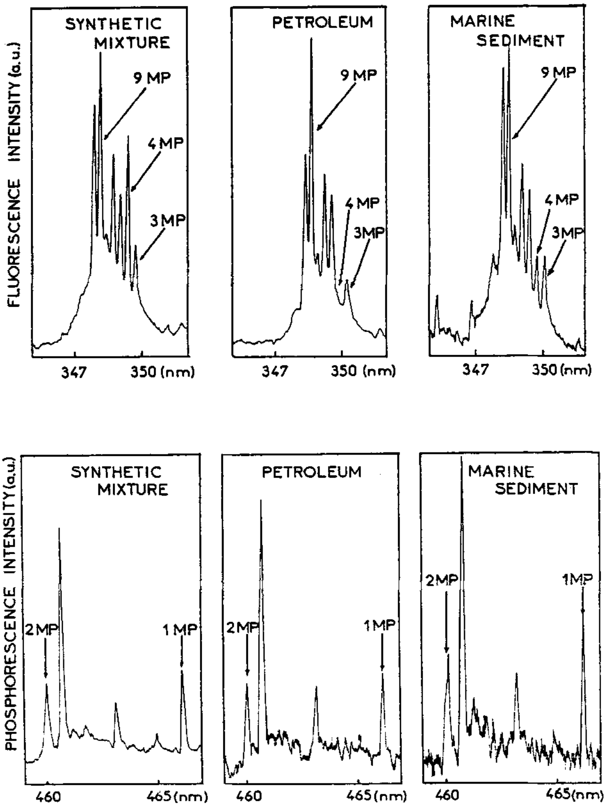

FIGURE 3 Emission spectra of monomethylphenanthrenes (MP) in a synthetic mixture (each MP isomer at 2×10^{-7} M) and in petroleum and marine sediment fractions, frozen in polycristalline *n*-hexane at 15 K. Excitation at 299 nm for fluorescence spectra. Excitation at 296.5 nm for phosphorescence spectra. Each isomer is identified by one characteristic emission peak.

occurring at high concentration ($c > 10^{-5}$M), fluorescence intensity depends linearly in concentration only below $c = 10^{-6}$ M.[10,11]

Quantitative determinations have been carried out by the combined standard addition-internal standard calibration procedure.[12]

This method has been discussed for the analysis of monomethylphenanthrenes extracted from natural samples.[13]

This method has been extended here to the quantitative analysis of a North Sea petroleum fraction. The standard addition calibration curve is calculated for each isomer by a mean square method and the concentration of each compound in the sample is determined by extrapolation. Analyses have been also carried out by GC-MS which allows an identification of each monomethylphenanthrene.[14] Preliminary results on the relative distribution of MP isomers obtained respectively by these two methods are in good agreement (Figure 4). Works are in progress to determine concentration of each isomer with standard deviations in several natural samples analyzed both by HRS and GC-MS.

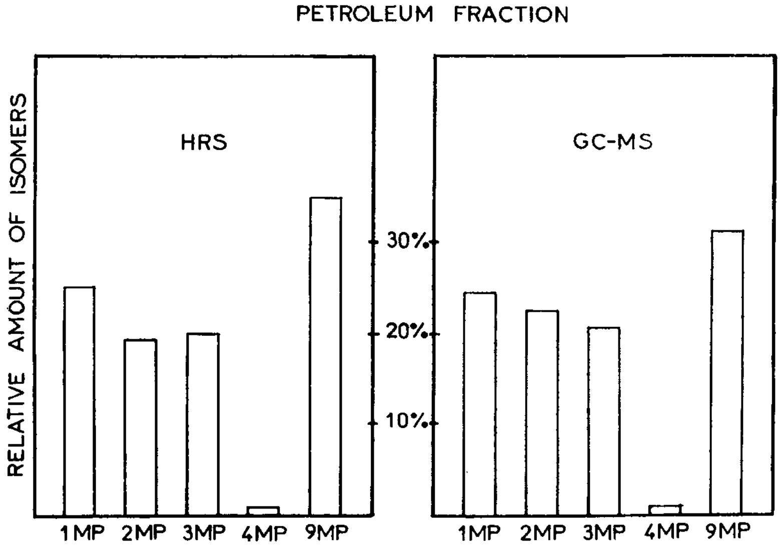

FIGURE 4 Relative distribution of monomethylphenanthrene isomers in North Sea petroleum fraction, determined by HRS and by GC-MS (fragmentographic detection at $m/z = 192$). (Standard deviations on the results obtained with several different samples are under examination and will be published later, including a discussion on the relative accuracy of the two methods HRS and GC-MS).

In conclusion, results presented in this paper demonstrate the capability of the high resolution spectrofluorimetry in Shpolskii matrices at 15 K in solving identification and quantification problems occurring in complex mixtures of isomeric PAH. Further quantitative applications of this technique will be done on biogeochemical markers of the phenanthrene and chrysene series, derivatives of triterpenoid compounds, which have been also identified by HRS in marine sediments.[8,14]

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