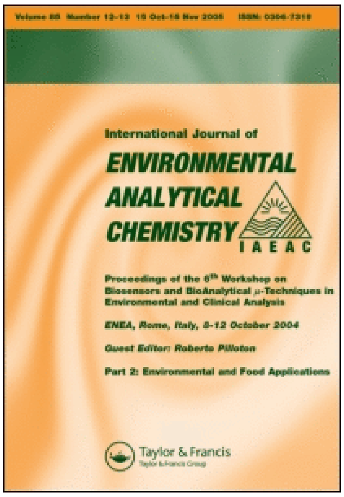

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Quantitative Determination of Polycyclic Aromatic Hydrocarbons in Harbour Sediment via High-Resolution Shpol'skii Spectroscopy

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Polycyclic aromatic hydrocarbons (PAHs) in harbour sediment have been determined by means of Shpol'skii fluorometry. Fundamental aspects of this cryogenic high resolution technique are discussed. It provides characteristic spectra of aromatic molecules that can be successfully employed for identification purposes. Extra selectivity is obtained by making use of selective excitation, even with a broad-banded light source. Highly specific quantitative determinations can be achieved, due to the quasi-linear character of the spectra. Deuterated PAHs are suitable as internal standards. Calibration curves with linearity from $10^{-5}-10^{-6}$ M down to the detection limit are found, yielding a dynamic range from 2 to 4 decades for the compounds investigated. The reproducibility of the quantitative experiment lies between 6 and 20 per cent. The results obtained with Shpol'skii spectroscopy are in good agreement with data found by a standard method of analysis employing fluorescence detected HPLC.

KEY WORDS: Shpol'skii fluorometry, polycyclic aromatic hydrocarbons, sediment.

INTRODUCTION

Luminescence methods are widely applied for the identification and quantificiation of Polycyclic Aromatic Hydrocarbons (PAHs). Especially fluorometric analysis affords low detection limits (in the sub-ppb range) for many PAHs that are commonly encountered as trace-level environmental contaminants in effluents associated with combustion, pyrolysis and other thermal degradation processes.[1] A severe disadvantage of room temperature luminescence techniques is their relatively low selectivity. Like absorption spectra, emission spectra of PAHs in liquid solutions tend to have broad bands (up to hundreds of cm^{-1}) due to collisional broadening processes. Differences in spectral appearance between the various PAHs can be very slight, especially when isomeric molecules are compared; hence selective excitation offers only limited relief. Thus, unless complete chromatographic resolution is achieved, interference from other organic compounds or PAHs in luminescence spectrometric detection cannot be excluded.

The selectivity of luminescence methods can be strongly improved by application of high resolution optical techniques. Considerable narrowing of the spectral lines can be achieved by making use of special solid state techniques. The width of the spectral bands of amorphous solid samples (see Figure 1a) is determined by a sum of—narrow—vibronic transitions that are slightly shifted in the spectrum with respect to each other, due to different interactions of the solute molecules with their non-uniform surroundings. However, the hidden fine structure of such heterogeneously broadened spectra can be made visible by employing laser excitation at low temperatures ($T < 30\,K$, depending on the sample) as a means to optically select the molecules that luminesce. This, so called Fluorescence Line Narrowing technique, has been applied to a number of different amorphous matrix materials, such as glasses,[2] polymer films[3] and TLC-plates.[4]

The width of the spectral bands can also be reduced by making use of more ordered solid samples. In the mixed-crystal technique a final bandwidth of approximately $1\,cm^{-1}$ FWHM (full width at half maximum) can be reached. This is accomplished by incorporating the analyte in a single crystal of another hydrocarbon with approximately the same molecular dimensions, so that the molecules

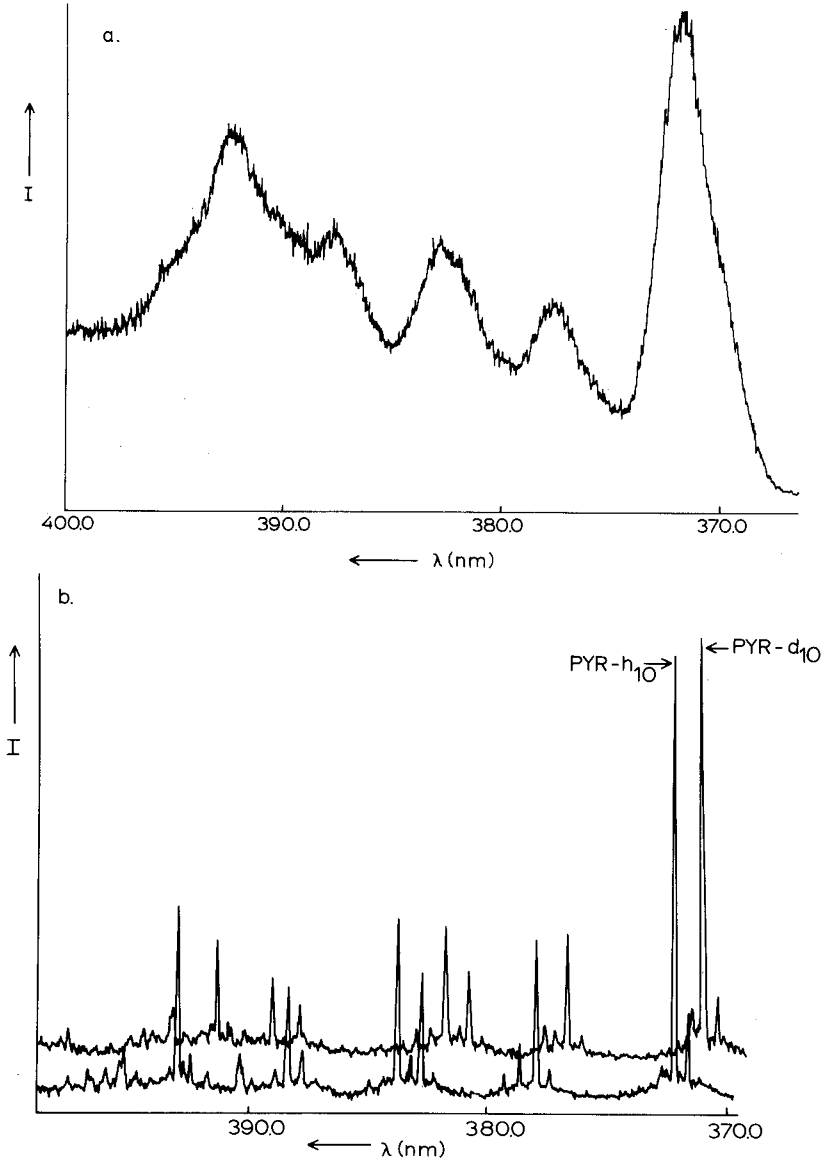


FIGURE 1(a) Fluorescence spectrum of 1 μg pyrene on a t.l.c. plate at 20 K (λ_{exc} = 320 nm). (b) Fluorescence spectra of 10^{-5} M solutions of pyrene and pyrene-d_{10} in *n*-octane at 20 K (λ_{exc} = 338 nm).

occupy nearly identical sites within the host lattice.[5] Recently Thornberg and Maple reported the determination of methylnaphthalene derivatives in shale oil via fluorescence spectrometry in a low-temperature durene cyrstal.[6] Since the appearance of the narrow spectral lines in the mixed-crystal technique depends critically on the compatibility of the geometries of guest and host molecules, and the preparation of the samples involves a tedious process of crystal growing, its analytical applications seem limited.

Fortunately there is another technique which also produces considerable decrease in the inhomogeneous bandwidth by a suitable choice of the matrix material but does not have the severe experimental limitations of the mixed crystal method, the so-called Shpol'skii method.

In 1952 the Russian scientist Shpol'skii reported the observation of narrow spectral lines in the emission spectra of aromatic molecules dissolved in *n*-alkanes and measured at low temperatures ($T \lesssim 77\,\mathrm{K}$)[7]. Since then numerous applications of the Shpol'skii technique have appeared in the literature (the most recent general review was, as far as we know, published in 1969 by Nurmukhametov[8a]; recently D'Silva and Fassel authored a review with emphasis on laser-excited Shpol'skii spectrometry, a new development in this field[8b]). A thorough evaluation of conventional Shpol'skii fluorometry for analytical purpose has been carried out by Kirkbright and coworkers.[9–11] By now analytical applications of conventional Shpol'skii luminescence methods have been published concerning the qualitative and/or quantitative determination of PAHs in a number of environmental samples, e.g., coal and coal tar pitch,[12] water,[13] automobile exhaust and ambient air,[14] carbon black,[15] petroleum and marine sediments[16–18] and crude oils.[19,20] The technique has been applied both with [14,15,20] and without [12,13,16–19] prior chromatographic separation.

The present study will be devoted to several aspects of the application of low temperature Shpol'skii fluorescence spectroscopy to environmental analysis. The quantitative determination in harbour sediment of a number of PAHs occurring on the Priority Pollutant list of the Environmental Protection Agency will be described. The results will be compared with fluorescence detected HPLC data obtained with a standard method at the Dutch Governmental Institute for Sewage and Wastewater Treatment (RIZA).

THE SHPOL'SKII EFFECT

Theoretical aspects

As was mentioned above the Shpol'skii effect is a matrix effect, i.e. due to a reduction in the non-uniformity of the micro-environment experienced by the guest molecules, the heterogeneous broadening of the spectral bands in emission as well as absorption is strongly diminished. Under conditions where heterogeneous broadening plays no role, the spectral band shapes are determined by homogeneous broadening processes. Two factors are important, i.e. the lifetime of the excited state involved in the spectral transition and the coupling of the electronic transition of the guest molecule to the vibrations of the host matrix (electron-phonon coupling).

The homogeneous broadening $\Delta\bar{\nu}$ (in cm^{-1}) caused by the limited lifetime of the excited state τ is given by the Heisenberg uncertainty principle[21]:

$$\Delta\bar{\nu}\,.\,\tau \geqq \frac{1}{4\pi c}. \tag{1}$$

This explains why transitions to and from higher excited electronic states are usually broad, since they have very short lifetimes, due to the high efficiency of radiationless decay processes; for instance $\tau = 10^{-13}\,\mathrm{s}$ gives $\Delta\bar{\nu} \geqq 30\,\mathrm{cm}^{-1}$. On the contrary, the lowest excited electronic state has a typical lifetime of 1–100 ns; rendering linewidths ranging from $10^{-2}-10^{-4}\,\mathrm{cm}^{-1}$.

As a result of the electron-phonon coupling the spectral bands are composed of two parts: a sharp line, the zero-phonon line (ZPL), and a broad band, the phono wing (PW), as depicted in Figure 2. This coupling is in general expressed as an adiabatic potential, which describes the difference of the phonon hamiltonian of a crystal with the guest molecule in the initial and final electronic state, respectively.[22] Because the displacements from equilibrium along any normal coordinate of the matrix are small, the potential can be expanded in a Taylor series in the ground state normal coordinates, which is truncated after the second term, so that only linear and quadratic electron-phonon coupling have to be considered. The latter affects the position and width of the ZPL. For the systems under

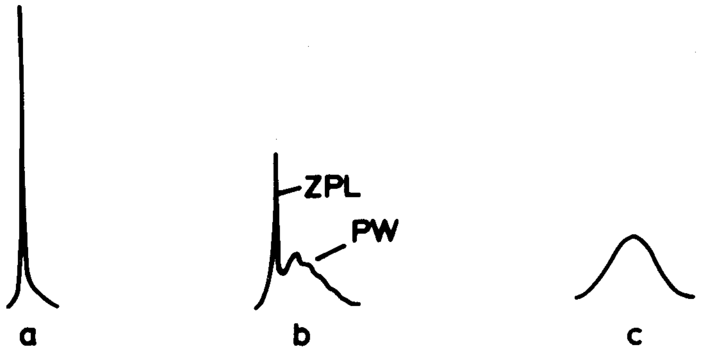


FIGURE 2 Typical shapes of vibronic lines observed in low temperature Shpol'skii matrices for weak (a), intermediate (b) and strong (c) electron-phonon coupling. ZPL denotes the zero-phonon line, PW the phonon-wing.

consideration it is small enough to be neglected. The linear term determines the relative intensities of the ZPL and the PW, generally designated as the Debije-Waller factor α:

$$\alpha = I_{\mathrm{ZPL}}/(I_{\mathrm{ZPL}} + I_{\mathrm{PW}}) \qquad (2)$$

The quality of the spectra is optimal if α is close to one, which is the case for weak coupling (i.e. small values of the displacement from the equilibrium positions of the matrix vibrations during the electronic excitation of the guest molecule) and at low temperatures. For organic guest-host systems, like Shpol'skii matrices, the electron-phonon coupling is relatively weak so that even at relatively high temperatures as 77 K, reasonably well resolved spectra can be recorded as is shown in Figure 3 for tetracene in *n*-nonane. The bandwidth observed in the spectrum recorded at 20 K is 10 cm^{-1} FWHM, which is quite typical for low temperature Shpol'skii spectra. This is at least one or two orders above the limiting homogeneous bandwidth of the zero-phonon line, which strongly suggests the presence of residual heterogeneous broadening. This has been demonstrated directly by Abram *et al.*, who induced line narrowing in the fluorescence spectrum of perylene in *n*-octane by making use of laser excitation.[23]

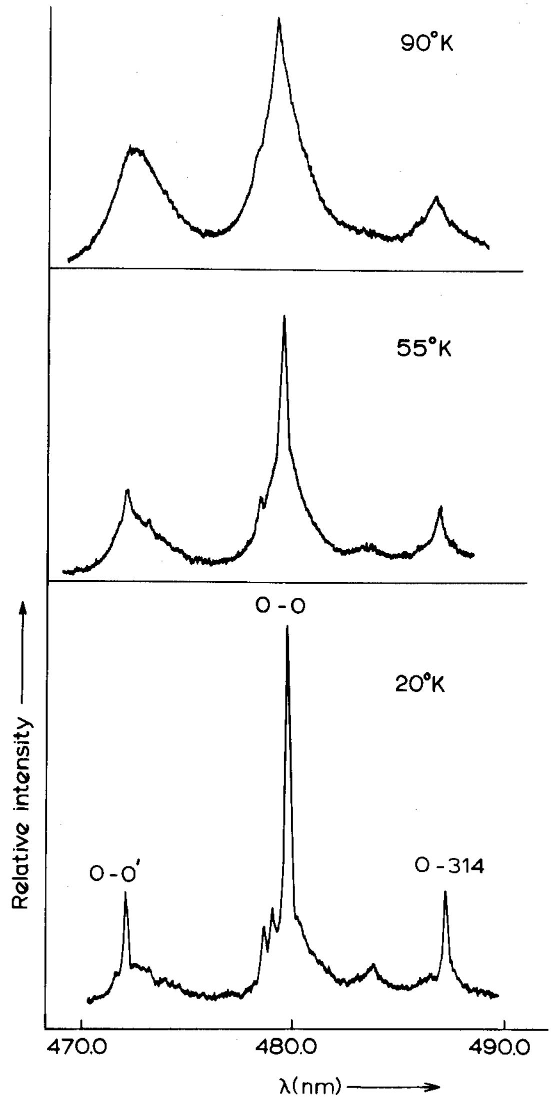


FIGURE 3 The 0–0 transition region of the fluorescence spectrum of tetracene in *n*-nonane at different temperatures. Two sites are visible, with 0–0 transitions indicated as 0–0 and 0–0′. Also one vibronic band, at 314 cm^{-1} from the origin, is depicted.

Summarizing, it can be stated that well resolved Shpol'skii spectra are obtained for guest–host combinations with weak electron-phonon coupling and not too large inhomogeneous broadening.

Experimental aspects

In this paragraph several experimental factors that influence the final appearance of a Shpol'skii spectrum will be discussed, i.e. solvent choice, multiplet structure, rate of cooling and concentration.

Solvent choice The nature of the solvent and the preparation of the sample have a strong influence on the spectra that are recorded. The best spectral resolution is generally observed when there is a close match between the longest dimension of the guest molecule and the length of the host *n*-alkane.[24,25] However, for instance polyacenes form an exception to this "key-and-hole" rule.[26] The general validity of this rule-of-thumb suggests that the solute molecules occupy substitutional sites in the *n*-alkane lattice, which is polycrystalline when rapidly frozen, an assumption which is supported by several experiments.[27–30]

Multiplet structure Often Shpol'skii spectra are composed of several identical spectra which are displaced with respect to one another over a slight energetic distance (generally not more than $100\,\mathrm{cm}^{-1}$). Several experiments indicate that the multiplet structure is due to molecules inserted in different substitutional sites in the host lattice, experiencing different microenvironments.[31,32]

Rate of cooling and concentration. In Shpol'skii spectroscopy the samples are generally cooled in a closed cycle helium cryostat at 8–10°/min or via immersion in liquid nitrogen or helium. In both cases one may obtain metastable, polycrystalline solids, since the speed of the cooling process is too high to maintain thermodynamic equilibrium. Thus it is not surprising that the thermal history of the sample frequently has a profound influence on the final appearance of the spectra. Furthermore during the cooling of a binary system one has to reckon with the possibility of segregation, a process that, of course, also strongly depends on the speed of cooling.

At present, it seems that roughly two types of aromatic compounds can be discerned.[33] The first type consists of guest molecules whose dimensions require the substitution of two or more *n*-alkane molecules. The bigger PAHs belong to this group, where the Shpol'skii effect is observed independent from the cooling rate, at concentrations which are low enough to preclude formation of solute aggregates (generally a concentration lower than $10^{-5}-10^{-6}$ M suffices).[34] At higher concentrations broad bands due to aggregates[35] or excimers[36] are observed next to narrow quasi-lines.

The second type contains compounds as polyacenes and linearly ortho-condensed aromatics, which give rise to both quasi-line and broad-banded spectra, depending on cooling rate and concentration. The molecular dimensions of these guest molecules are not easily compatible with the host matrix, so that segregation effects are expected to play an important role. Dekkers *et al.*, suppose that non-equilibrium solutions give rise to quasi-line spectra, while broad-banded spectra are correlated with thermodynamic equilibrium situations.[37] This point of view is supported by Rima *et al.*[33] These studies indicate that for elucidating the mechanism of the Shpol'skii effect for second type molecules especially attention should be paid to the thermodynamic aspects of the formation of the low-temperature solid solution. From the experimental work done so far the conclusion can be drawn that quasi-linear Shpol'skii spectra are obtained for type 2 molecules if very fast cooling by immersion in liquid nitrogen or helium is employed for samples with guest molecule concentrations of 10^{-6} M or less.[33]

Analytical aspects

Advantages and disadvantages As far as the advantages of the application of Shpol'skii spectroscopy in analytical chemistry are concerned, it is obvious that the high resolution of the spectra obtained ensures impressive selectivity. Since the Shpol'skii effect is a matrix effect, both emission as well as absorption (of the lowest energy electronic transition) spectra are quasi-linear. Extra selectivity can be obtained via selective excitation of the molecules of interest; this can be done most effectively by making use of a tunable dye laser as excitation source. Yang *et al.*[38,39] have applied the "laser-excited Shpol'skii spectoscopy" (LESS) technique with success in several studies of environmental samples.

Another advantage of the Shpol'skii technique is the fact that the role of inner-filter effects and fluorescence (phosphorescence) quenching are expected to be not so important as in fluorescence (phosphorescence) spectroscopy in liquid solutions. Of course, short range (collisional) energy transfer plays no role in a low temperature matrix. Moreover, also inner filter effects and (Förster) long range energy transfer are minimized because the amount of overlap between the absorption spectrum of the acceptor and the emission spectrum of the donor is small due to their quasi-linear character.[40,41] Hence the Shpol'skii method has an inherent high quantitative reliability.

An important advantage of the Shpol'skii method as compared to the other high resolution low temperature techniques is on the one hand the relatively low cost of the equipment (versus Fluorescence Line Narrowing spectroscopy), on the other hand the relative ease of sample preparation (versus mixed crystal techniques). High resolution Shpol'skii spectra in the conventional mode are obtained by making use of simple broad-band lamp excitation. The samples can be cooled with liquid nitrogen to 77 K or, preferably, to 10 K in a closed-cycle helium refrigerator, which does not involve the consumption of expensive liquid helium. For measurement of the emission spectra a relatively simple monochromator, affording resolution of 0.1–0.2 nm, may be employed. It must be noted, that the efficiency of stray light rejection is strongly dependent on the quality of the monochromator. The detection can be performed very effectively with d.c. integration of the voltage generated across a load resistor on the output of the photomultiplier.[10]

Of course, the Shpol'skii technique also has several disadvantages. One of the most important is the dependence of the spectra on the rate of cooling of the sample and the concentration of the guest molecules. Presumably, these problems can be dealt with adequately by employing very fast cooling rates and concentrations lower than 10^{-6} M for type 2 molecules, as discussed above, while these effects do not play such an important role for the type 1 molecules. The formation of aggregates can also be avoided by making use of matrix-isolation deposition techniques.[42] The dependence of the resolution of the spectra of a certain guest molecule on the host *n*-alkane necessitates the use of several solvents to determine all the components in a complex sample. On the other hand this dependence provides an extra means of selectivity.

As was noted before, after cooling polycrystalline solid samples are formed. These samples are opaque, so preferentially use should be made of front-surface illumination. Furthermore, they produce severe scattering. Scattering problems in detection can be reduced by employing X-ray[43,44] or mercury arc[9] excitation. However, then one loses the possibility of selective excitation, while in the case of X-ray excited luminescence one also should reckon with the possibility of radiolysis. The most serious disadvantage of Shpol'skii spectroscopy is that several especially polar and ionic compounds, do not dissolve in *n*-alkanes, so that this method cannot be applied to all kinds of compounds. However, quasi-linear spectra of polar heterocyclic PAHs have been obtained in low temperature tetrahydrofuran solutions.[45,46] Furthermore the Shpol'skii method is, as all low temperature solid state techniques, very suited for the study of instable reactive species.[47]

Quantitative aspects Finally, the application of the Shpol'skii technique to the quantitative determination of PAHs in environmental samples will be discussed. Due to the dependence of the appearance of the spectra on experimental conditions (rate of cooling, nature of the solvent) empirical standardization is necessary. Generally use is made of either an internal standard or a standard addition approach or a combination of both techniques.[9] Deuterated PAHs are very suited as internal standards since they produce spectral lines distinct from the PAHs of interest, and thus do not interfere with the measurement, but experience the same interaction with the *n*-alkane solvent as their non-deuterated analogues. Recently, also the use of the scattered component of the mercury excitation line as reference was reported.[48] If sufficient care is taken, quantitative determinations with relative standard deviations lower than 10 per cent can be obtained in analyses by Shpol'skii spectroscopy.[49]

Wehry and Mamantov in their 1981 review[50] mentioned as one of the main disadvantages of the Shpol'skii method as an analytical tool, the rather limited dynamic range reported for the calibration curves in quantitative studies (2.5 decades or less). Several papers, however, claim calibration curves with linearity over 3,[10,39] 4[51] or even 5[52] decades. In the latter study use is made of laser excitation of samples prepared via matrix isolation procedures. Comparison of the literature data suggests that the linear range of the calibration curves in

Shpol'skii fluorometry is limited at the upper side at approximately 1 μg/ml and at the lower side by the detection limit.

Detection limits of the Shpol'skii technique, where the luminescence of the guest molecules is completely concentrated in a number of narrow spectral lines, can be almost as low as in conventional liquid solution emission measurements. In liquid solutions a detection limit of 0.008 ng/ml for benz(a)pyrene was reported by Jurgensen *et al.*[53] Detection limits for benz(a)pyrene in *n*-octane with conventional lamp excitation can be as low as 0.05 ng/ml.[54] Conrad *et al.*[52] report detection limits of 0.01 ng/ml for methyl-derivatives of benz(a)pyrene in laser-excited matrix-isolated solutions in *n*-octane. Both experiments have been performed at 10–15 K. Winefordner's group[49, 55] contends the possibility to achieve the same low detection limits in Shpol'skii spectroscopy as in room temperature emission measurements. Their measurements, however, were performed at 77 K, where the zero-phonon lines are broadened with respect to the width observed at 20 K and less. On the other hand the possibility to record moderately high resolution Shpol'skii spectra at liquid nitrogen temperatures brings this selective and relatively simple analytical technique into scope for any reasonably well equipped laboratory.

EXPERIMENTAL

Sample preparation

PAHs were isolated from harbour sediment by means of a standard procedure developed at the RIZA. In the isolation procedure 20 g of homogenized wet sediment was dried with $MgSO_4.H_2O$; subsequently the PAHs were extracted by refluxing the dried homogenate during 4 hours with 250 ml dichloromethane in a Soxhlet-apparatus. The extraction efficiency has been established to be better than 90% for the PAHs concerned. The dry weight of the sediment sample was determined by drying a homogenate of the wet sample at 103°C to constant weight. For the sample investigated in this study the percentage dry weight was 31.2%.

Low-temperature Shpol'skii measurements

The dichloromethane extract was evaporated and the residue dissolved in an equal amount of *n*-octane. Quantification was achieved by comparison with calibration curves, using NBS standard reference material 1647 (PAHs dissolved in acetonitrile). Acetonitrile was evaporated and different concentrations were obtained by dissolving the residue in *n*-octane. Deuterated compounds were employed as internal standards. No clean-up of the samples was performed.

Low-temperature fluorescence emission and excitation spectra were recorded at 20 K in a model 20 Cryocooler of Cryogenic Technology Inc. The final temperature was reached in approximately 30 minutes. The samples were contained in approximately 0.2 mm pathlength cuvettes consisting of two quartz plates separated by an indium ring and contained in a gilded copper sample holder, which was mounted on the cold stage of the refrigerator. For excitation the radiation of a 450 W xenon lamp was passed through a 0.5 m Bausch and Lomb monochromator, equipped with a grating of 600 lines/mm. Front surface illumination was applied. The fluorescent light was detected at an angle of approximately 30° of the exciting radiation and separated by a 1 m Jobin-Yvon HR 1000 monochromator (grating 1200 grooves/mm). An Ortec–Brookdeal 5C1 photon counting apparatus was used to process the signal from an EMI 9558 QA photomultiplier cooled to $-20°C$. The spectra were recorded on a Kipp BD 5 recorder. In the emission experiments the excitation bandwidth was 10 nm, the emitted light was measured with a resolution of 0.1 nm for the quantitative experiment, and with resolutions between 0.02 and 0.08 nm for the determination of the reference spectra of the pure compounds. The excitation measurements were performed by monitoring the most intense vibronic band in the fluorescence spectrum at a bandwidth of 2.0 nm. The resolution in the excitation experiment was 0.1 nm. The excitation spectra were not corrected for wavelength dependency of the exciting radiation.

Chromatographic measurements

The dichloromethane extract was evaporated and the residue dissolved in methanol. The methanol solution, filtered through a Millex SR 0.5 μ filter, was introduced via a 50 μl Rheodyne injection loop into a HPLC system consisting of a Pye-Unicam LC-XPS pump, a Pye-Unicam LC-FL fluorescence detector equipped with a 360 nm band-pass filter on the excitation side and a 418 nm cut-off filter on the emission side, and a Hewlett–Packard HP 3390 A integrator. For separation a Perkin–Elmer 250 × 2.6 mm I.D. ODS-HCSIL-X-1 analytical column was used, protected by a Brownlee Spheri-10 RP 18 guard column. The analytical column was thermostated at 25°C. As eluent 100% methanol, continuously deaerated with helium, was employed. The flow-rate was 1 ml/min.

Materials

Chrysene (puriss., Aldrich), pyrene (Gold Marke, EGA-chemie), benz(b) fluoranthene, benz(k)fluoranthene, benz(a)pyrene, benz(ghi)perylene, indeno(1, 2, 3-cd)pyrene (all Certified Reference Materials from the Community Bureau of Reference of the Commission of the European Communities), pyrene-d_{10}, perylene-d_{12} (both from Merck, Sharp and Dohme, >98%) and NBS Standard Reference Material 1647 (PAHs in acetonitrile) were used as received. The solvents, *n*-hexane (Aldrich, 99+%), *n*-heptane and *n*-octane (Baker analyzed, 99+%), dichloromethane and ethanol (both Baker analyzed HPLC), were also used without further purification. $MgSO_4 . 7H_2O$ (Baker grade) was washed with dichloromethane and dried at 103°C. Schleicher and Schüll 33 × 94 mm glass fiber thimbles were glowed at 200°C before use.

RESULTS AND DISCUSSION

It is the purpose of the present investigation to determine the six PAHs designated by the World Health Organization as pollution indicators for surface water,[56] which are routinely determined at the RIZA, i.e., benz(a)pyrene, fluoranthene, benz(ghi)perylene, benz(k)-fluoranthene, benz(b)fluoranthene and indeno(1, 2, 3-cd)pyrene. In addition two other important priority pollutants, namely chrysene and pyrene, will be determined. As the Shpol'skii effect is strongly solvent dependent, it is necessary first to determine the optimal solvent for the PAH of interest. Furthermore, attention should be paid to the effect of the cooling process on the spectra.

Optimization of the experimental conditions

For all these compounds fluorescence spectra were recorded of 10^{-5} M in the *n*-alkanes supposed to be appropriate regarding the key-and-hole rule,[24,25] i.e., *n*-hexane, *n*-heptane and *n*-octane. The solutions were frozen at a speed of 8–10°/min in a closed cycle helium cryostat. Comparison with spectra obtained for quickly frozen solutions (sample immersion in liquid nitrogen followed by cooling in the closed cycle refrigerator) indicates that for the compounds under study the appearance of the Shpol'skii spectra is hardly influenced by the cooling procedure. This is not surprising since, in view of their shape, most of these PAHs (with chrysene and fluoranthene as possible exceptions) are expected to belong to type 1.

For chrysene, pyrene, benz(b)fluoranthene, benz(k)fluoranthene and benz(a)pyrene the optimal spectrum is observed in *n*-octane. Fluoranthene, unfortunately, does not produce a quasi-linear spectrum in this solvent; a quasi-linear spectrum is found in *n*-hexane. Benz(ghi)perylene gives a good, highly resolved, spectrum in both *n*-hexane and *n*-octane. The best spectrum for indeno(1,2,3-cd)pyrene is observed in *n*-heptane. The spectrum obtained in *n*-octane is also well resolved but shows a second site of medium intensity. All other compounds except fluoranthene and pyrene, however, yield many sited quasi-line spectra in *n*-heptane. The presence of many sites in Shpol'skii spectra is not only detrimental to the detection limits, but can also cause problems due to the increased possibility of band-overlap for different species. Therefore we applied *n*-octane, which is the optimal solvent for all compounds involved except fluoranthene and, to a much lesser extent, indeno(1,2,3-cd)pyrene. The fact that fluoranthene does not give a quasi-line spectrum in *n*-octane precludes the sensitive detection of this compound in the present investigation. Spectra of the 0–0 transition area of benz(k)-fluoranthene and benz(a)pyrene in *n*-hexane and *n*-octane are depicted in Figure 4. The spectrum of benz(a)pyrene in *n*-hexane shows more sites than in *n*-octane. The spectral bands of benz(k)fluoranthene in *n*-hexane are much broader than in *n*-octane; furthermore in the first solvent they appear on a broad, diffuse background. The two internal standards, pyrene-d_{10} and perylene-d_{12}, both show one sited, highly resolved spectra in *n*-octane. The

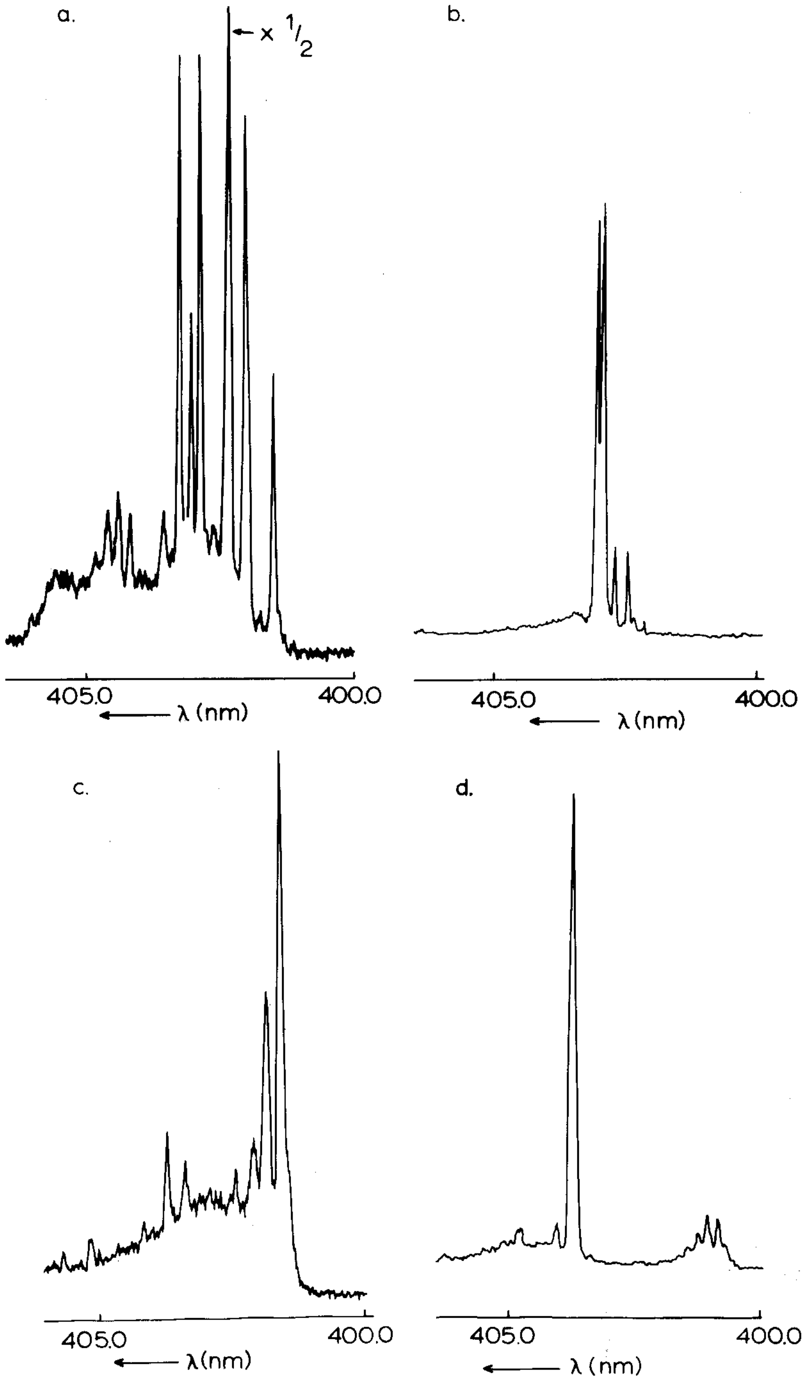


FIGURE 4 The 0–0 transition region of the fluorescence spectrum of (a) benz(a)pyrene in *n*-hexane ($\lambda_{exc} = 300\,nm$); (b) benz(a)pyrene in *n*-octane ($\lambda_{exc} = 300\,nm$); (c) benz(k)fluoranthene in *n*-hexane ($\lambda_{exc} = 310\,nm$); (d) benz(k)fluoranthene in *n*-octane ($\lambda_{exc} = 310\,nm$). All spectra were recorded at 20 K for 10^{-5} M solutions.

spectra of pyrene-h_{10} and pyrene-d_{10} in *n*-octane are shown in Figure 1b.

The optimal excitation wavelength for each compound was determined by varying the excitation wavelength while monitoring its most intense vibronic emission band. In Figure 5 the fluorescence excitation spectra of benz(a)pyrene and benz(k)fluoranthene are depicted. From this figure the potential of selective narrow line laser excitation is clear: the S_1-state vibronic lines appear with bandwidths of 0.1–0.3 nm in the spectrum. Unfortunately, to get enough intensity from the xenon-lamp, broad-band excitation with a bandwidth of 10 nm had to be used. To minimize scattering problems a difference of at least 15–20 nm between emission and excitation wavelengths was taken.

In Table I the optimal excitation and emission wavelengths for the PAHs investigated are collected. To illustrate the influence of the excitation wavelength, in Figure 6 fluorescence spectra recorded for an academic mixture of the seven PAHs and the two internal standards with concentrations as given in Table I at excitation wavelengths of 300, 304, 310, 338 and 391 nm, respectively, are depicted. In the figure the most prominent lines for the compounds of interest are indicated. The strong excitation and wavelength dependence of the intensity of the lines for benz(k)fluoranthene and

TABLE I

Optimal excitation and emission wavelengths for the PAHs in *n*-octane with xenon-lamp excitation.

Compound	Concentration in artificial mixture (M)	Optimal excitation wavelength (nm)	Optimal emission wavelength (nm)
Chrysene (CHR)	$1.6 . 10^{-6}$	272	360.6
Pyrene (PYR)	$1.4 . 10^{-7}$	339	372.0
Benz(b)fluoranthene (B(b)F)	$1.7 . 10^{-6}$	304	397.8
Benz(a)pyrene (B(a)P)	$1.0 . 10^{-7}$	300	403.0
Benz(k)fluoranthene (B(k)F)	$6.2 . 10^{-8}$	310	403.5
Benz(ghi)perylene (B(ghi)P)	$1.5 . 10^{-6}$	304	406.3
Indeno(1, 2, 3-cd)pyrene (IP)	$4.0 . 10^{-6}$	380	462.7
Pyrene-d_{10} ($PYR_{d_{10}}$)	$1.6 . 10^{-7}$	338	371.0
Perylene-d_{12} ($PER_{d_{12}}$)	$6.0 . 10^{-7}$	391	443.6

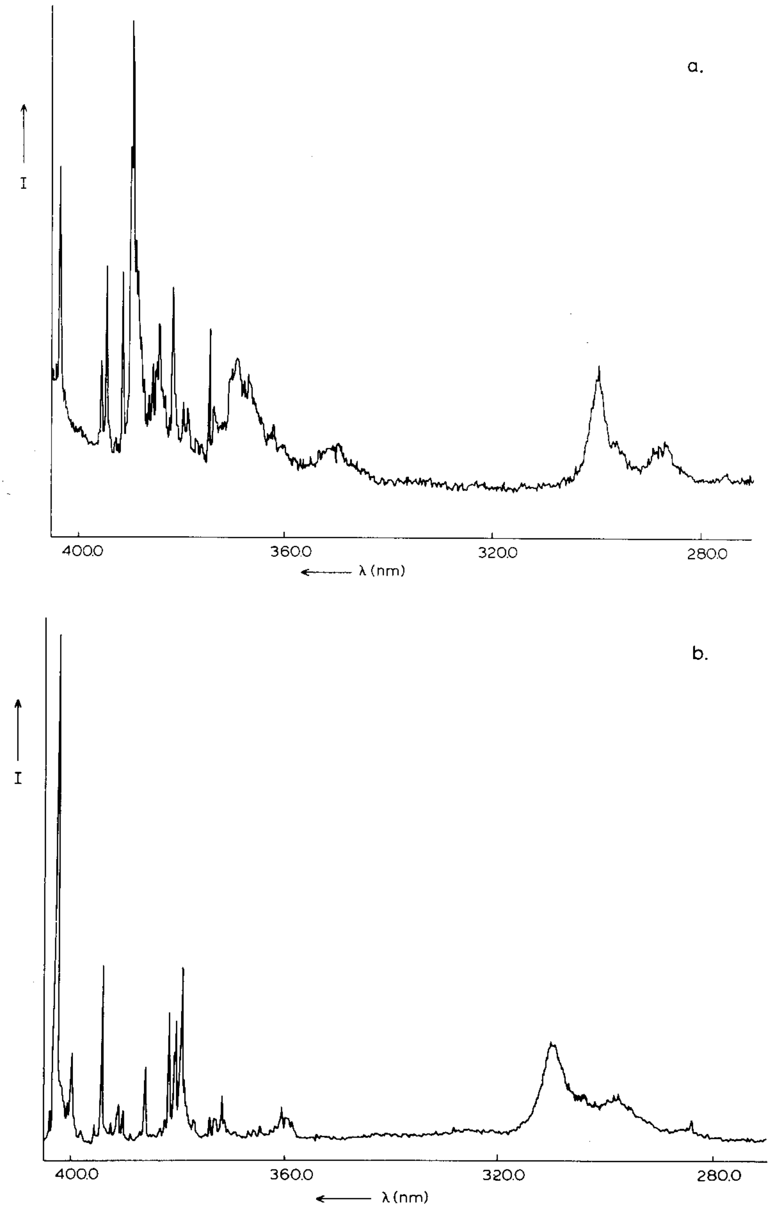


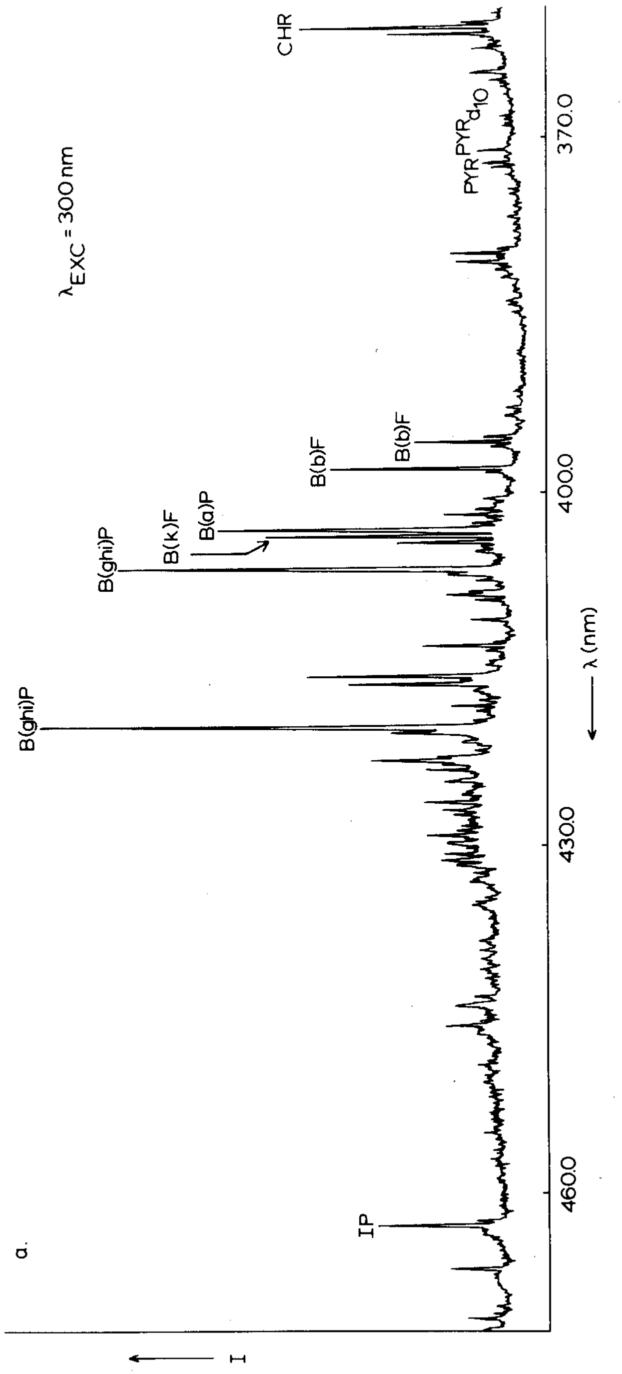
FIGURE 5 Excitation spectra of 10^{-5} M solutions of (a) benz(a)pyrene ($\lambda_{em} = 408.5$ nm); (b) benz(k)fluoranthene ($\lambda_{em} = 428.6$ nm). The spectra were recorded at 20 K.

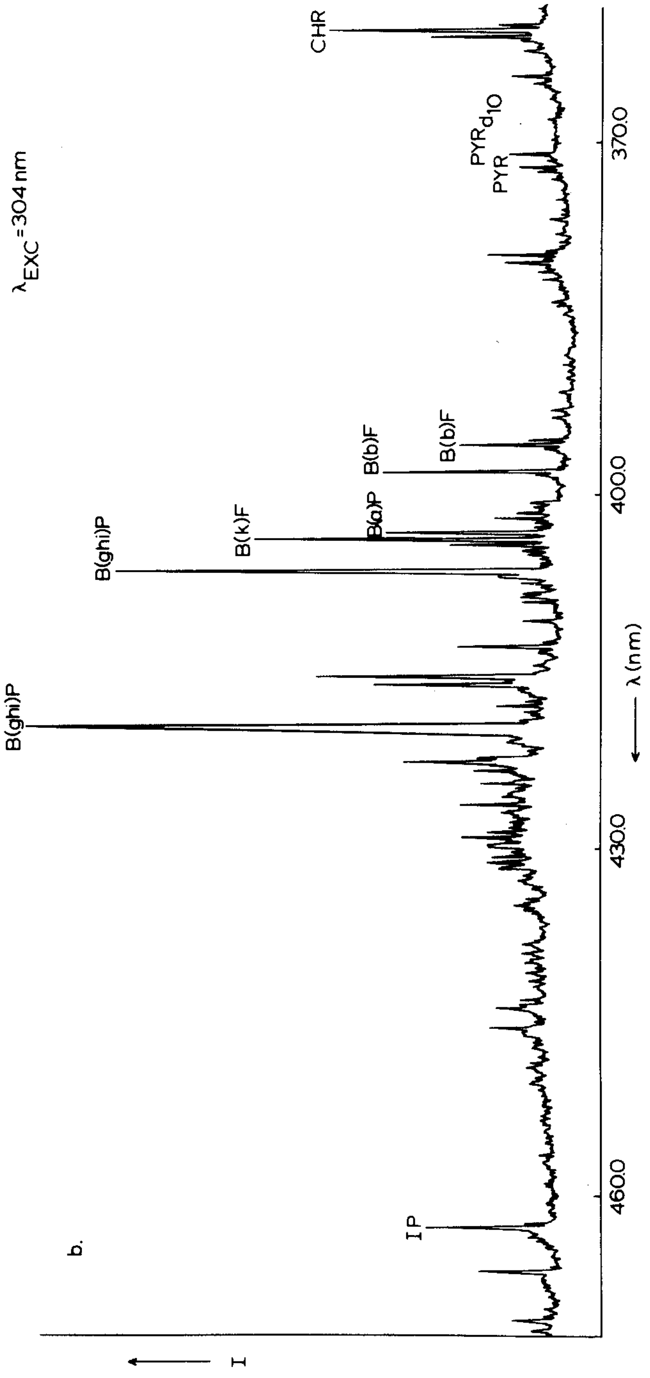
benz(a)pyrene is striking. This can be effectively used to discriminate the two most prominent bands of these two compounds which are situated very close together, i.e., at 403.5 nm and 403.0 nm, respectively. Fortunately, for excitation at 310 nm almost no fluorescence from benz(a)pyrene is recorded, whereas the fluorescence signal for benz(k)fluoranthene is optimal. The reverse effect is observed for excitation at 300 nm.

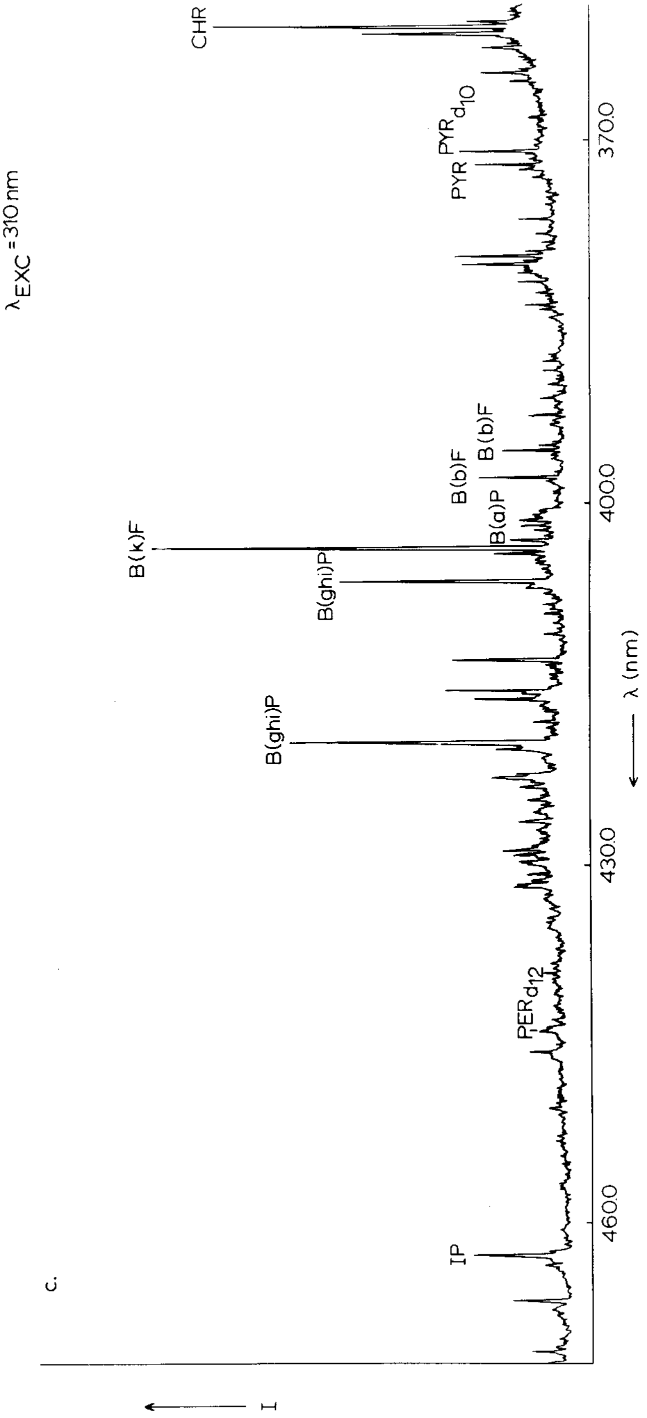
Quantitative determination of PAHs

Academic solutions For quantitative determination of the PAHs calibration curves had to be measured. Use was made of a NBS certified reference material, SRM 1647, containing 16 PAHs in acetonitrile, amongst whom the seven involved in this investigation, at concentrations ranging from 10^{-5} to 10^{-6} M. Acetonitrile was evaporated and *n*-octane added to form the various concentrations. The internal standards, pyrene-d_{10} and perylene-d_{12}, were added resulting in concentrations ranging from $6.3 . 10^{-8} - 2.5 . 10^{-7}$ M and $2.0 . 10^{-7} - 8.0 . 10^{-7}$ M, respectively. The optimal emission and excitation wavelengths as given in Table I were used. In addition, for pyrene also 339 nm as excitation and 392.6 nm as emission wavelengths were employed, for benz(a)pyrene 389 nm and 408.5 nm, and for benz(k)fluoranthene 310 nm and 412.8 nm. All intensity measurements of the spectral lines were repeated five times and averaged; the reproducibility was found to be better than 1% for the higher concentrations and to increase to approximately 10–15% near the detection limit. The results for the calibration curves are given in Table II (with pyrene-d_{10} as internal standard) and Table III (with perylene-d_{12}).

In Figure 7 and 8 calibration curves for benz(a)pyrene and benz(k)fluoranthene are depicted. All compounds appear to give good, linear calibration curves from approximately 5.10^{-6} M downward to their respective detection limits. At higher concentrations the curves deviate from linearity due to energy transfer processes or inner-filter effects. Below 5.10^{-6} M no reabsorption of emitted S_1–S_0 0–0 transition light occurs, as can be judged from the fact that the calibration curves for pyrene, benz(a)pyrene and benz(k)fluoranthene with the emission signal detected in a vibronic emission band have exactly the same slope as with detection in the 0–0 emission band. In


a.
λ$_{EXC}$ = 300 nm
CHR
PYR
PYR
PYR$_{d_{10}}$
B(b)F
B(b)F
B(a)P
B(k)F
B(ghi)P
B(ghi)P
IP
370.0
400.0
430.0
460.0
λ (nm)
I


b.
λ$_{EXC}$=304 nm
CHR
PYR$_{d10}$
PYR
B(b)F
B(b)F
B(a)P
B(k)F
B(ghi)P
B(ghi)P
IP
370.0
400.0
430.0
460.0
λ (nm)
I


c.
λ_{EXC} = 310 nm
CHR
PYR
$PYR_{d_{10}}$
B(b)F
B(b)F
B(a)P
B(k)F
B(ghi)P
B(ghi)P
$PER_{d_{12}}$
IP
370.0
400.0
430.0
460.0
λ (nm)
I

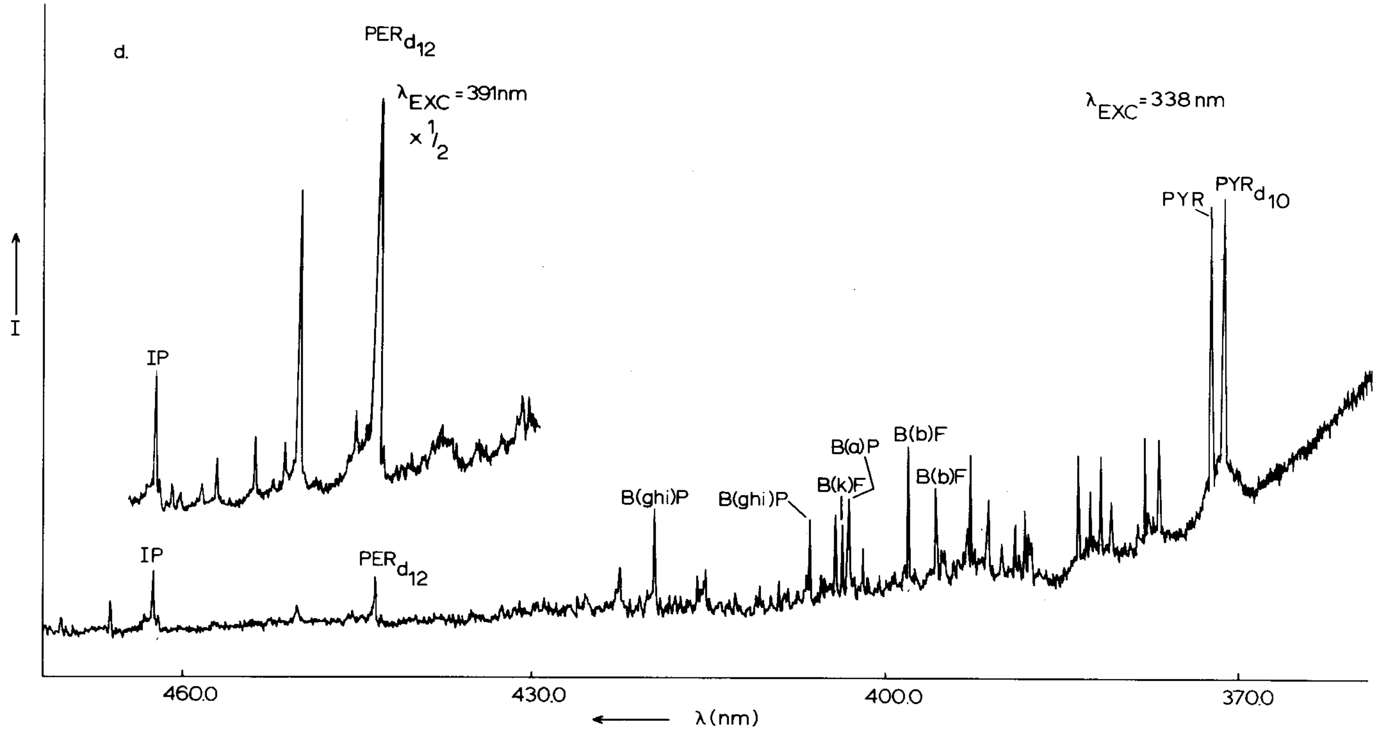


FIGURE 6 Fluorescence spectra of an artificial mixture containing the seven PAHs and the two internal standards at concentrations as indicated in Table I. Several excitation wavelengths were employed: (a) $\lambda_{exc} = 300$ nm; (b) $\lambda_{exc} = 304$ nm; (c) $\lambda_{exc} = 310$ nm; (d) $\lambda_{exc} = 338$ nm; insert $\lambda_{exc} = 391$ nm. The most important peaks in the spectra were assigned with abbreviations as given in Table I. The steadily increasing background in the short wavelength region of Figure 6(d) is caused by scattered excitation light. The spectra were recorded at 20 K.

TABLE II

Calibration curves for the PAHs with pyrene-d_{10} as internal standard.

Compound	λ_{exc}(nm)	λ_{em}(nm)	Slope	Standard deviation	Intercept	Standard deviation	*n*	*r*
Chrysene	272	360.6	0.893	0.014	5.490	0.089	24	0.9975
Pyrene	339	372.0	0.868	0.025	6.169	0.166	13	0.9954
	339	392.6	0.896	0.017	5.958	0.108	23	0.9962
Benz(b)fluoranthene	304	397.8	0.837	0.019	4.726	0.122	20	0.9953
Benz(a)pyrene	300	403.0	0.907	0.019	6.478	0.148	13	0.9977
	389	408.5	0.906	0.011	6.188	0.071	21	0.9986
Benz(k)fluoranthene	310	403.5	0.947	0.014	7.099	0.106	25	0.9975
	310	412.8	0.952	0.013	6.435	0.086	26	0.9977
Benz(ghi)perylene	304	406.3	0.891	0.029	5.476	0.189	7	0.9974
Ideno(1, 2, 3-cd)pyrene	380	462.7	0.598	0.022	3.033	0.138	14	0.9923

TABLE III

Calibration curves for the PAHs with perylene-d_{12} as internal standard.

Compound	λ_{exc}(nm)	λ_{em}(nm)	Slope	Standard deviation	Intercept	Standard deviation	n	r
Chrysene	272	360.6	0.952	0.015	6.106	0.097	23	0.9975
Pyrene	339	372.0	0.983	0.018	7.130	0.121	13	0.9981
	339	392.6	0.987	0.015	6.760	0.097	13	0.9975
Benz(b)fluoranthene	304	397.8	0.893	0.019	5.331	0.121	18	0.9965
Benz(a)pyrene	300	403.0	0.934	0.027	6.885	0.211	14	0.9951
	389	408.5	0.983	0.012	6.915	0.076	24	0.9984
Benz(k)fluoranthene	310	403.5	0.990	0.011	7.615	0.079	26	0.9986
	310	412.8	1.050	0.009	7.320	0.059	27	0.9991
Benz(ghi)perylene	304	406.3	0.942	0.018	6.061	0.117	7	0.9991
Indeno(1, 2, 3-cd)pyrene	380	462.7	0.652	0.018	3.645	0.113	12	0.9964

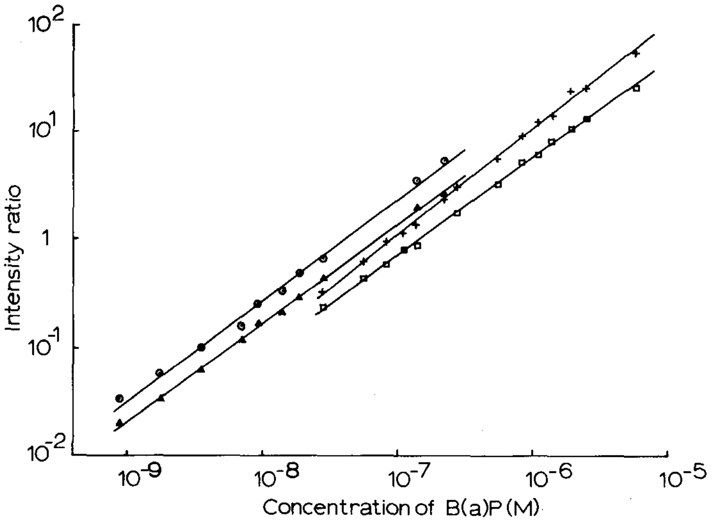


FIGURE 7 Calibration curves for benz(a)pyrene: ⊙ $\lambda_{exc} = 300$ nm, $\lambda_{em} = 403.0$ nm; perylene-d_{12} as internal standard. ▲ $\lambda_{exc} = 300$ nm, $\lambda_{em} = 403.0$ nm; pyrene-d_{10} as internal standard. + $\lambda_{exc} = 389$ nm, $\lambda_{em} = 408.5$ nm; perylene-d_{12} as internal standard □ $\lambda_{exc} = 389$ nm; $\lambda_{em} = 408.5$ nm; pyrene-d_{10} as internal standard. The statistical information is incorporated in Tables II and III.

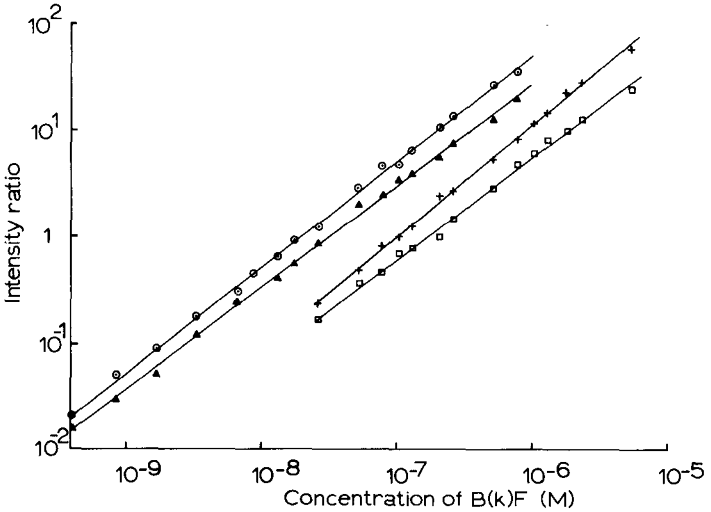


FIGURE 8 Calibration curves for benz(k)fluoranthene. Excitation was performed at 310 nm. ⊙ $\lambda_{em} = 403.5$ nm; perylene-d_{12} as internal standard. ▲ $\lambda_{em} = 403.5$ nm; pyrene-d_{10} as internal standard. + $\lambda_{em} = 412.8$ nm; perylene-d_{12} as internal standard. □ $\lambda_{em} = 412.8$ nm; pyrene-d_{10} as internal standard. The statistical information is incorporated in Tables II and III.

TABLE IV
Linear dynamic range and detection limits for the quantitative determination of PAHs by Shpol'skii fluorometry.

Compound	Linear dynamic range (in decades)	Detection limit (in 10^{-9} M)
Chrysene	2.5	10
Pyrene	3	5
Benz(b)fluoranthene	2.5	25
Benz(a)pyrene	4	0.8
Benz(k)fluoranthene	4	0.4
Benz(ghi)perylene	2.5	10
Indeno(1, 2, 3-cd)pyrene	2	60

the applied experimental set-up (front surface illumination and relatively short pathlength cuvettes) inner-filter effects are minimized. As can be seen in Table IV the linear dynamic range varies from two decades for indeno(1, 2, 3-cd)pyrene to four decades for benz(a)pyrene and benz(k)fluoranthene; detection limits vary from 4.10^{-10} M for benz(k)fluoranthene to 6.10^{-8} M for indeno(1, 2, 3-cd)pyrene. The detection limit is taken as the signal plus three times the peak-to-peak noise of the blanc. For the data in Table IV the optimal excitation and emission wavelengths given in Table 1 were used.

The statistics from the calibration curves determined with perylene-d_{12} as internal standard appear to be somewhat better than with pyrene-d_{10}. This is probably due to the fact that the pyrene-d_{10} emission occurs in a more crowded part of the spectrum.

Real samples For the quantitative determination of PAHs in a harbour sediment sample nine aliquots of the dichloromethane extract were submitted to a procedure, which involved evaporation of the solvent and subsequent solution in an equal amount of *n*-octane. Without any preliminary clean-up step the internal standards were added, the *n*-octane solution cooled and the fluorescence detected at suitable excitation and emission wavelengths for each compound. A typical Shpol'skii fluorescence spectrum obtained with 304 nm excitation is shown in Figure 9. Even in the complex mixture the fluorescence signals can be easily assigned to the PAHs of interest. The band positions are exactly the same as in the pure

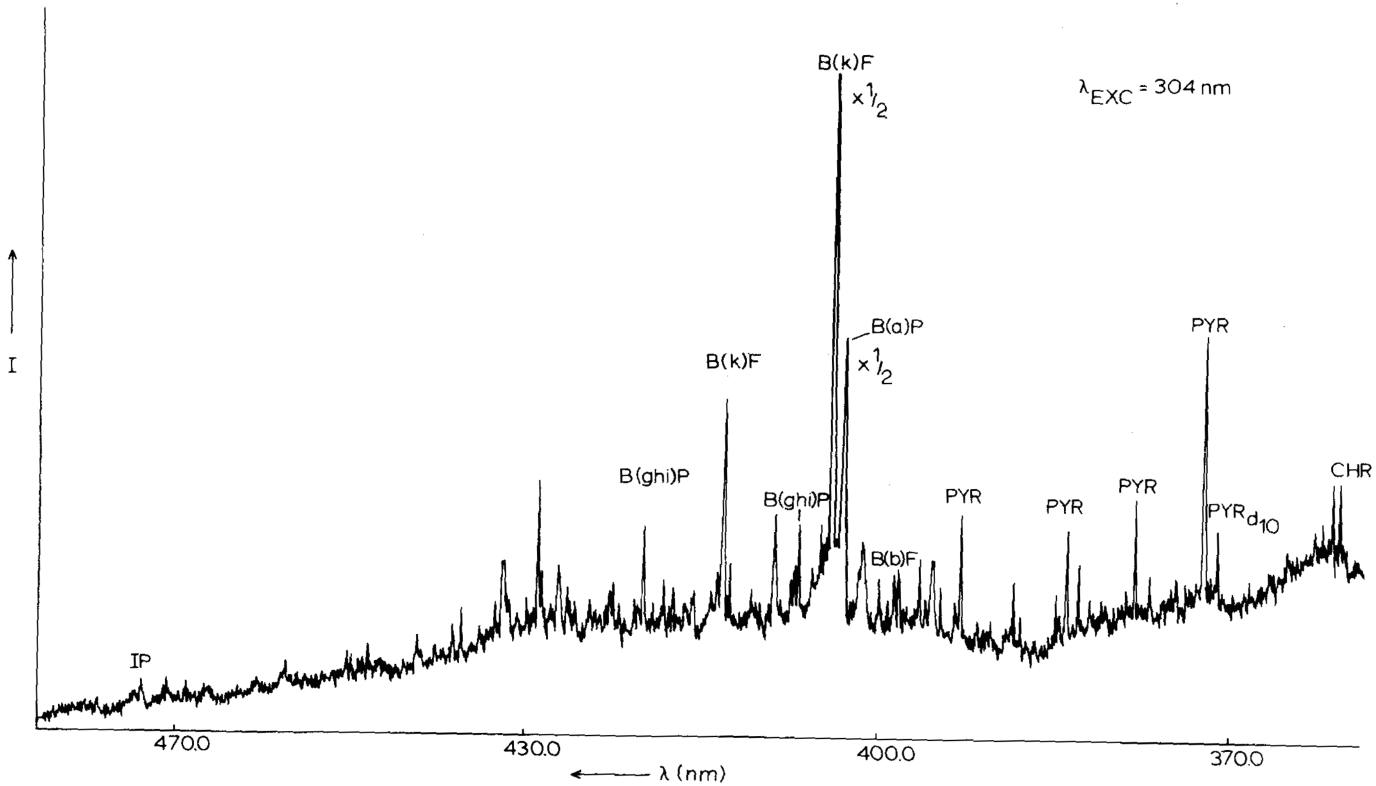


FIGURE 9 Fluorescence spectrum of the real sample, excited at 304 nm. The main peaks in the spectrum were assigned with abbreviations as given in Table 1. The spectrum was recorded at 20 K.

reference samples, so that the PAHs can be identified unambiguously. This is especially clear when, apart from the 0–0 transitions, also a number of vibronic lines are taken into account. Several intense vibronic bands from pyrene, benz(k)fluoranthene and benz(ghi)perylene are indicated in Figure 9 next to the, generally most intense, 0–0 transition band, illustrating the potential of the Shpol'skii technique as a "fingerprinting" method.

The concentrations of the PAHs in the octane solution measured varied from 6.10^{-8} M to 3.10^{-7} M. The amounts in the sediment sample per kilogram dry weight were determined with reference to the best calibration curves determined before (see Table II and III). The results of the nine measurements were averaged and the standard deviations determined. In Table V the results of the quantitative determination of the seven PAHs in the sediment are summarized. The amounts determined with pyrene-d_{10} and perylene-d_{12} as internal standard are denoted separately. Despite the fact that these compounds emit at strongly different wavelengths, the results in Table V correspond within their confidence intervals. This provides strong evidence that, for the present sample, the quantification can be done without taking recourse to elaborate standard addition procedures. The precision of the results obtained with perylene-d_{12} as internal standard appears to be better than that with pyrene-d_{10}. With perylene-d_{12} the relative standard deviation from the mean ranges from 6% for chrysene and benz(b)fluoranthene to 14% for indeno(1,2,3-cd)pyrene, with pyrene-d_{10} the highest precision is obtained for pyrene (9%), the lowest for indeno(1,2,3-cd)pyrene (20%).

The same sample was also investigated at the RIZA by means of a routine procedure based upon HPLC with fluorescence detection; only the six WHO water pollution indicators are determined. Chromatograms for the standard reference sample and for the sediment sample are given in Figure 10; the retention times have been incorporated in Table V. Quantification is achieved with an integrator by comparison of the summed sample intensity with the summed intensity of the NBS standard reference sample for each compound (see Table V).

Comparison of the two methods reveals that the amounts determined lie in the same range; a satisfying result in view of the relatively low specificity and precision of the HPLC method used. In the latter method for excitation a 360 nm band-pass filter is utilized,

TABLE V

Results of the determination of PAHs in harbour sediment by Shpol'skii fluorometry and fluorescence detected HPLC.

Compound	λ_{exc}(nm)	λ_{em}(nm)	Amount determined with pyr. d_{10} as standard (mg/kg sediment)	Amount determined with per. d_{12} as standard (mg/kg sediment)	Amount determined with HPLC (mg/kg sediment)
Chrysene	272	360.6	1.23 ± 0.13	1.20 ± 0.07	—
Pyrene	339	392.6	2.73 ± 0.24	2.64 ± 0.29	—
Benz(b)fluoranthene	304	397.8	1.58 ± 0.19	1.50 ± 0.09	2.1 (4.5)[a]
Benz(a)pyrene	389	408.5	1.10 ± 0.17	1.12 ± 0.11	0.9 (6.1)[a]
Benz(k)fluoranthene	310	412.8	0.72 ± 0.09	0.72 ± 0.05	0.6 (5.5)[a]
Benz(ghi)perylene	304	406.3	0.86 ± 0.10	0.83 ± 0.06	0.5 (8.6)[a]
Indeno(1, 2, 3-cd)pyrene	380	462.7	0.75 ± 0.15	0.70 ± 0.10	1.3 (10.6)[a]

[a] Retention time in minutes.

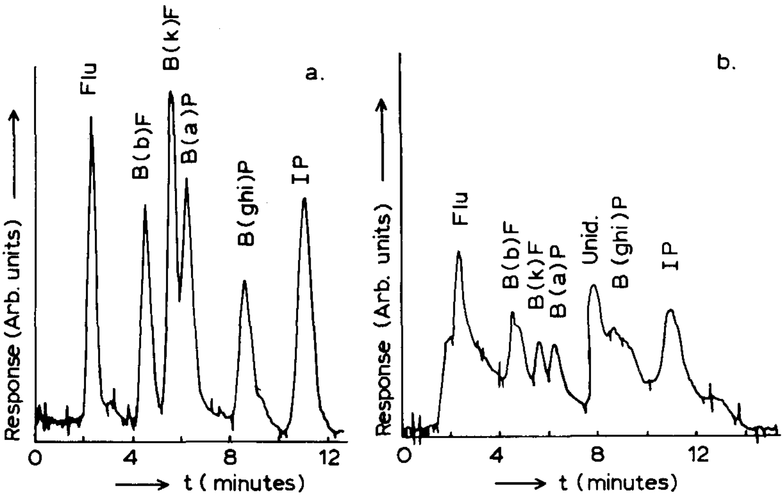


FIGURE 10 Chromatograms for the NBS standard reference material (a) and the real sample (b) recorded at the RIZA. Abbreviations as given in Table I. Flu = fluoranthene, Unid = unidentified.

while a cut-off filter affords registration of all emission above 418 nm. Of course, this configuration provides optimal sensitivity for the detection of PAHs absorbing and fluorescing at longer wavelengths, but the selectivity is almost exclusively determined by the efficiency of the separation. For instance, judging the shape of the peak at a retention time of 4.5 minutes (benz(b)fluoranthene) the separation was not optimal for this compound, which might explain its higher value in Table V.

CONCLUSIONS

Shpol'skii fluorometry is an appropriate analytical method for the quantitative and qualitative determination of PAHs in sediment. The technique affords comparable low detection limits as a standard procedure based on HPLC with fluorometric detection, but offers much more selectivity. Since the Shpol'skii effect is a matrix effect, the selectivity of the method can be significantly increased by making use of selective excitation, even with a conventional broadband light source.

Application of Shpol'skii spectroscopy to this harbour sediment sample does not require preliminary clean-up or chromatographic separation for the determination of the priority pollutant PAHs investigated. Quantification can be successfully done with deuterated PAHs as internal standards. Linear calibration curves are obtained for concentrations of 10^{-5}–10^{-6} M down to the detection limit of the compounds studied (ranging from 10^{-7}–10^{-10} M). The precision is reasonably high; a relative standard deviation from the mean of 6% was attainable with perylene-d_{12} as internal standard.

The results obtained underline the applicability of the conventional Shpol'skii technique as an analytical method to a limited but important class of compounds. In its conventional form it is not appropriate for ionic or polar molecules. Furthermore the opaqueness of the solid samples causes scattering problems and obstructs the recording of absorption spectra. It should be realized, however, that these problems will be overcome or at least strongly reduced by recent developments as matrix-isolation sample deposition techniques and X-ray or laser excitation. Therefore the potential of the Shpol'skii method in analytical chemistry seems promising.

Acknowledgement

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