Journal of Fluorescence, Vol. 10, No. 4, 2000

Multicomponent Determination of a Polyaromatic Hydrocarbon Mixture by Direct Fluorescence Measurements

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Received September 28, 1999; revised May 29, 2000; accepted May 29, 2000

This study deals with an analysis of a mixture of five polyaromatic hydrocarbons (PAHs) with the aim of avoiding any preliminary treatment of the sample such as extraction or concentration, which are time-consuming procedures. To reach this goal we studied a direct multicomponent determination of the PAHs in mixture by applying principal-component analysis and principal-component regression techniques, which are briefly explained in this work. After a calibration procedure we were able to analyze each PAH of the mixture by a simple and direct fluorescence measurement. Moreover, the quantitative results obtained were assessed on some test samples. The results obtained and the further developments of this study will be also discussed.

KEY WORDS: Multicomponent determination; polyaromatic hydrocarbons; principal-component analysis; principal-component regression.

INTRODUCTION

At a time when the public is very concerned with environmental problems, the control of water pollutants is important. Among the different types of pollutants, polyaromatic hydrocarbons (PAHs) are some of the most important because of their proven toxic and mutagenic properties. Consequently, the European Union has brought into force a strict regulation [1]: the total concentration of six reference PAHs is limited to 1 $\mu g \cdot L^{-1}$ in the raw water intended for drinking water production and to 0.2 $\mu g \cdot L^{-1}$ in drinking water; in addition, the benzo[*a*]pyrene concentration in drinking water must be below 0.01 $\mu g \cdot L^{-1}$. On the other hand, the United States of America monitor 16 different PAHs in the water for human consumption [2].

After sampling PAH determination requires long and tedious extraction and concentration steps. Usually, samples are then analyzed by high-performance liquid chromatography [3] on different stationary phases with UV or fluorescence detection [4–6] and more recently by supercritical fluid chromatography [7]. Gas chromatography is also used to analyze PAH and the best results are obtained with mass spectrometry detectors [8,9]. More generally, chromatography allows a good separation of the different PAHs contained in the samples, along with a good sensitivity and interesting limits of detection. However, these techniques are always time-consuming because of the extraction and concentration steps needed prior to the separation.

To save time, new techniques of multicomponent spectrofluorimetric determination [10] have recently been developed. These methods have already been applied to the analysis of different mixtures, e.g., nafcillin and methicillin penicillins [11], and vegetal oils [12]. Some recent works on PAH analysis have also been published, i.e., in micellar media by linear variable angle fluorescence [13],

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1053-0509/00/1200-0393$18.00/0

with the chemometrics spectrum decomposition technique [14–18], and by laser-induced fluorescence [19,20].

In the study reported here we applied a multicomponent analysis based on principal-component analysis (PCA) and principal-component regression (PCR). These techniques require a multivariate calibration procedure with the PAHs under analysis. This calibration consists in first recording the fluorescence spectra of several PAH mixtures of precise compositions, then computing a mathematical model linking the spectra obtained to PAHs concentrations. Once this calibration is achieved, it allows one to get the true concentration of each PAH contained in a mixture through a direct fluorescence measurement without any extraction procedure or separation step.

MATERIALS AND METHODS

PAHs Studied

We studied different mixtures of five PAHs, i.e., naphthalene, fluorene, phenanthrene, fluoranthene and Benzo[*a*]pyrene (all from Supelco Kit 610-N). These PAHs were chosen because of both their solubility in water and their good quantum yield of fluorescence with a linear response in the concentration range given in Table I. For each PAH, first a concentrated mother solution was prepared in acetonitrile (spectrograde from Fisher), then a daughter solution was diluted in the same solvent, then the final dilutions and the mixtures were made in water.

The maximum concentration of each PAH (Table I) in a mixture of the five studied PAHs was determined to avoid the saturation of the spectrofluorimeter detector (Shimadzu RF 1501) while taking into account possible additions of fluorescence intensity. The measurements were made in a 1-cm quartz cell (from Hellma), specially designed with a specific receptacle for a micro stirring bar (2 × 7 mm) at the bottom. Constant stirring clearly improved the repeatability of the spectrum obtained by reducing the risk of PAH microlayer formation at the liquid surface or of PAH adsorption on the cell sides.

Table I. PAHs Composing the Mixture at Their Corresponding Concentration Range, and Conditions of Fluorescence Spectra Recording

PAH	Concentration range (μg/L)	Excitation wavelength (nm)	Fluorescence spectrum (nm)
Naphthalene	0–12.50	224	250–440
Phenanthrene	0–5.00	245	270–480
Fluorene	0–2.43	255	280–500
Benzo[*a*]pyrene	0–1.50	263	290–510
Fluoranthene	0–13.60	275	300–540

For each PAH the excitation wavelength was set to the maximum UV absorption wavelength; the fluorescence spectrum was then recorded between the diffracted excitation signal and the second-order signal (Table I). Consequently, for the different PAH mixtures prepared, five excitation wavelengths were used and five fluorescence spectra were systematically recorded even with mixtures that did not contain all the five PAHs studied.

Multicomponent Analysis

The multicomponent analysis aimed to compute a regression model linking the sample fluorescence spectra to the PAH concentrations in a mixture. The computation of this model required us, first, to carry out a PCA on the fluorescence spectrum, followed by a PCR to relate the PAH concentrations to the spectrum data, and, finally, to evaluate the procedure by predicting the PAH concentrations in some test samples. This three-step procedure is briefly explained in the next paragraph; computations were performed using the Unscrambler (from Camo) software.

Principal-Component Analysis (PCA)

PCA is one of the multivariate analysis techniques used to find correlations between variables and between samples. In spectroscopy, where absorption or emission bands are highly correlated, the goal is to reduce the space dimensions by replacing the correlated variables with new uncorrelated variables called principal components (PCs) [21].

The spectral data are introduced in a matrix *A*, with *n* rows corresponding to the *n* PAH mixtures prepared and *p* columns corresponding to the *p* emission wavelengths of the five fluorescence spectra recorded for each mixture. The PCA algorithm decomposes the *A* matrix into two new matrices, i.e., the score matrix *S*, with *n* rows and *f* columns, the latter corresponding to the number of PCs, and the loading matrix *F*, with *f* rows and *p* columns. The three matrices are related by the equation below, where the matrices are noted with their number of columns as an exponent (superscript) and their number of rows as an index (subscript):

$$A^{p}{}_{n} = S^{f}{}_{n} \times F^{p}{}_{f} \quad (1)$$

The user chooses the number of PCs to explain at least about 95% of the total variance; the first PC contains the maximum percentage of variance and the next ones decreasing percentages of variance. The number of PCs

and the number of compounds in the mixtures are usually about the same. Each mixture sample can be characterized by its coordinates in the subspace of dimensions *f* formed by the PCs.

Principal-Component Regression (PCR)

PCR consists in regressing the concentrations data onto the principal components. As each score calculated by PCA is unique for each spectrum and for each PC, the regression can be built on the score matrix *S*, with only *f* dimensions, instead of the spectrum matrix *A*, with *p* dimensions [22,23]. The matrix equation involved is

$$C^m{}_n = S^f{}_n \times B^m{}_f \tag{2}$$

where *C* is the concentration matrix built with the PAH concentrations in the studied mixtures and composed of *n* rows and as many columns, *m*, as PAHs in the mixtures, and *B* is the regression coefficient matrix sought, composed of *f* rows and *m* columns. To calculate the *B* matrix the following equation, where S^t is the transposed matrix of *S* and $(S^t \times S)^{-1}$ is the inverted matrix of $(S^t \times S)$, must be used:

$$B = (S \times S^t)^{-1} \times S^t \times C \tag{3}$$

Prediction

From the regression coefficients calculated by PCR, one can predict the PAH concentrations in a test sample. This can be achieved by using the last equation set from relations (1) and (2):

$$C = A \times F^t \times (F \times F^t)^{-1} \times B \tag{4}$$

By comparison with the classical regression method, such a PCR prediction has two main advantages: first, the use of a large number of wavelengths to compute the model introduces an averaging effect which reduces the influence exerted by the spectral and apparatus noises; second, the study of complex matrices becomes possible while knowing only the concentration of the compounds of concern. Unfortunately, interpretation of the PCs that do not always correspond directly to the studied compounds may be tricky.

EXPERIMENTAL AND RESULTS

To fit better the conditions of a pollution control, the last dilution of the PAHs to prepare the mixtures for analyses was made in the drinking water supplied by the town water network instead of using Milli-Q extra pure water.

Fluorescence Spectrum Recording

To obtain a good calibration model, one should be cautious in the design of experiments. The best results will be obtained by following an experimental design to minimize the leverage value [24, 25], which indicates the calibration quality. As the PAHs studied have a linear fluorimetric response, we postulated a linear mathematical calibration model. Consequently, to obtain a good calibration in this case we chose a fractional factorial experimental design with a low leverage value. It also had the advantage of minimizing the number of experiments to be performed: indeed, with five compounds and two concentration levels per compound, it is noted 2^{5-1}, which corresponds to only 16 mixtures. Moreover, a central point was added to the calibration to check the linearity of mixture responses; the model predictions were also validated using some test samples. Finally, the 21 mixtures listed in Table II were prepared to compute and evaluate the model used.

The results of the five fluorescence spectra for each of the 21 samples accounted as a whole for 105 spectra; with a mean of 215 fluorescence measurements per spectrum, the data matrix contained approximately 22,500 values. Consequently, the results obtained are illustrated by introducing some short examples extracted from the whole data set. Figure 1 depicts the fluorescence spectra of the five pure PAHs studied (samples 2, 3, 4, 6, and 10, with reference to Table II), at an excitation wavelength of 263 nm. This figure clearly shows that each PAH has a specific emission wavelength at this excitation, but noticeable overlaps of the spectra are also observed. Figure 2 illustrates the fluorescence spectra of the full mixture of the five PAHs at their maximal concentration (sample 17) and of a test mixture containing the five PAHs at lower concentrations (sample 20). According to the overlap of the pure compounds spectra, Fig. 2 highlights that there is no specific area for a given PAH. Consequently, classical analytical techniques such as standard adjusts cannot be applied without a preliminary separation procedure; if so, only the multicomponent analysis procedure will allow us to determine the specific concentration of each PAH in a test mixture.

Calibration Procedure

As explained earlier the calibration procedure started with a PCA.

Table II. Mixtures Prepared to Achieve the Model Calibration and Assess the Predicted Values[a]

Sample		Polyaromatic hydrocarbon concentration($\mu g \cdot L^{-1}$)				
No.	Name	Naphthalene (N)	Fluorene (F)	Phenanthrene (P)	Benzo[a]pyrene (B)	Fluoranthene (Flu)
1	Blank	0.00	0.00	0.00	0.00	0.00
2	Naphthalene	12.50	0.00	0.00	0.00	0.00
3	Fluorene	0.00	2.43	0.00	0.00	0.00
4	Phenanthrene	0.00	0.00	5.00	0.00	0.00
5	N-F-P	12.50	2.43	5.00	0.00	0.00
6	Benzo[*a*]pyrene	0.00	0.00	0.00	1.50	0.00
7	N-F-B	12.50	2.43	0.00	1.50	0.00
8	N-P-B	12.50	0.00	5.00	1.50	0.00
9	F-P-B	0.00	2.43	5.00	1.50	0.00
10	Fluoranthene	0.00	0.00	0.00	0.00	13.6
11	N-F-Flu	12.50	2.43	0.00	0.00	13.6
12	N-P-Flu	12.50	0.00	5.00	0.00	13.6
13	F-P-Flu	0.00	2.43	5.00	0.00	13.6
14	N-B-Flu	12.50	0.00	0.00	1.50	13.6
15	F-B-Flu	0.00	2.43	0.00	1.50	13.6
16	P-B-Flu	0.00	0.00	5.00	1.50	13.6
17	N-F-P-B-Flu	12.50	2.43	5.00	1.50	13.6
18	Center	6.25	1.22	2.60	0.75	6.80
19	Test X	2.23	0.76	2.04	1.25	0.00
20	Test Y	4.02	1.82	2.78	0.50	0.00
21	Test Z	8.93	1.52	3.70	1.00	10.20

[a] Sample 1, the blank, was free of PAH but contained the same residual amounts of solvent as the other solution; Samples 2 to 17 corresponded to the fractional factorial design 2^{5-1}, whereas Sample 18 was an added central point; Samples 19 to 21 were the test samples used to assess the model.

Selection of the Number of Principal Components

Figure 3 shows the evolution of the residual variance versus the number of PCs. The first component explains 42% of the total variance, the second component 30%, and the next one a decreasing percentage of the total variance. The minimum residual variance percentage isobtained with the six first PCs. In this study we decided

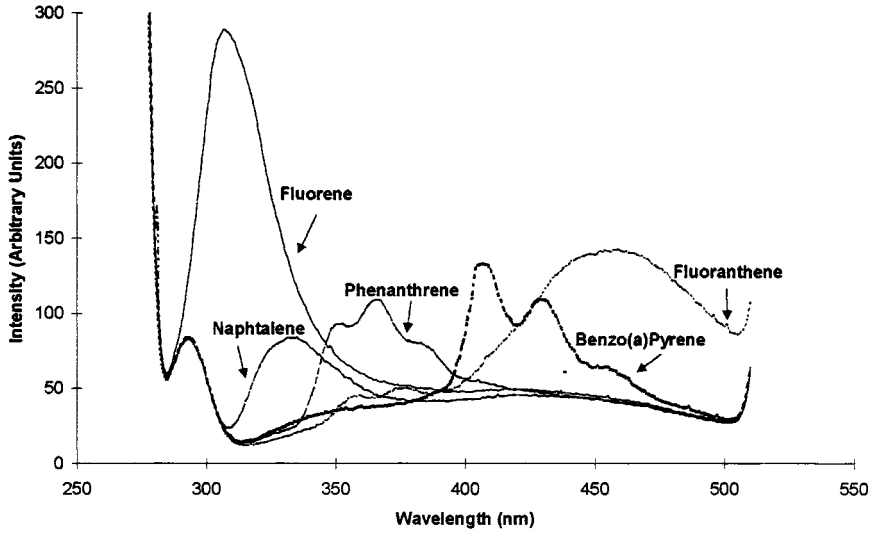

Fig. 1. Fluorescence spectra of the five pure PAHs studied at an excitation wavelength of 263 nm.

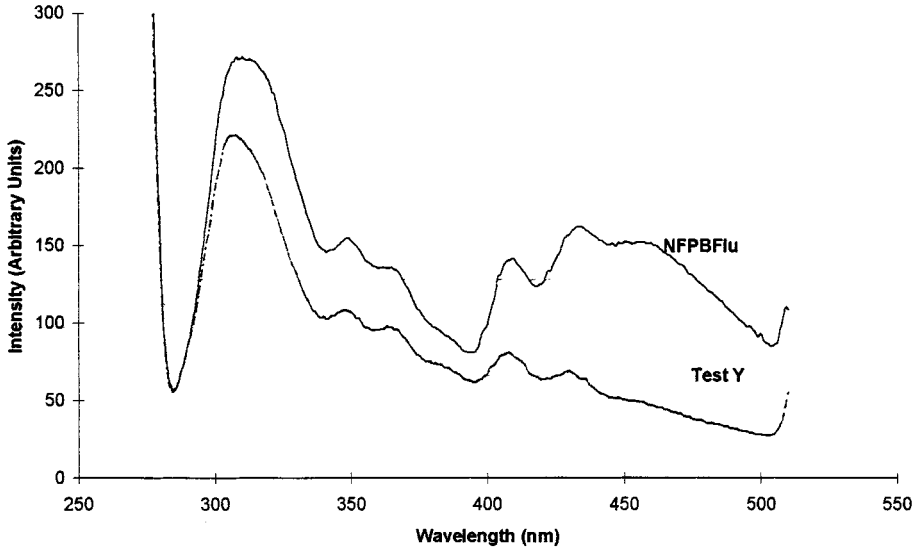

Fig. 2. Fluorescence spectra of two mixtures containing the five PAHs studied at an excitation wavelength of 263 nm. Each PAH is at its maximal concentration in sample NFPBFlu, with lower concentrations than in the previous sample in the test mixture Y.

to keep the six first PCs that explained 99.7% of the total variance, which was highly satisfactory.

Interpretation of the Principal Components

As explained previously, from the PCA each sample has a score value for each of the six PCs and all these scores are contained in the score matrix S^f_n. These scores also correspond to the projections of the samples into the six-dimensional PC space and can be represented graphically by 2- or 3-D cuts of this space. These graphical representations can be used to characterize samples and identify some groups: the samples that have close scores on a same PC are similar, whereas those with opposite scores are totally different.

Figure 4 shows the projections of the samples on a plane formed by PC_1 and PC_2 and explaining 73% of the total variance. The sample score on PC_1 seems propor-

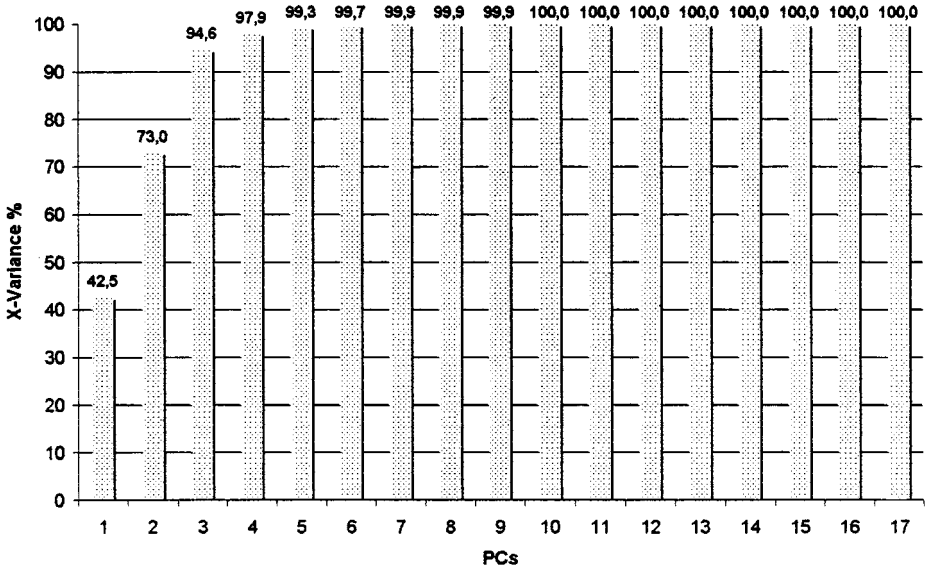

Fig. 3. Evolution of the residual variance versus the number of principal components (PCs) computed.

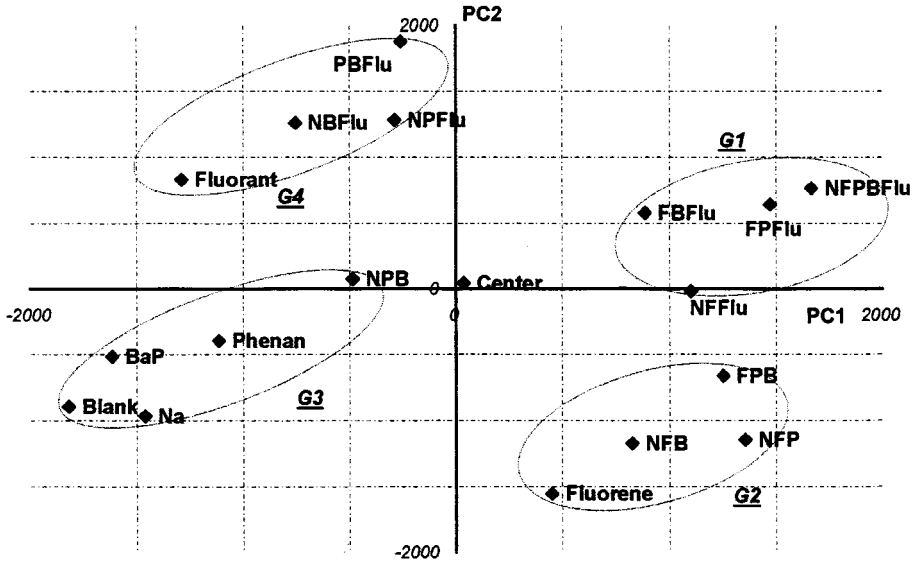

Fig. 4. Projections of the samples in a plane formed by the PC1 and PC2 explaining 73% of the total variance. G1 to G4 highlight samples with similar behavior.

tional to the mean intensity of the fluorescence response. The blank sample (No. 1) has the minimum score, while the full PAH mixture (No. 17) has the maximum one; the other samples are distributed between these two extrema relatively to they global response. Consequently, the pure samples, i.e., benzo[*a*]pyrene-6, naphthalene-2, fluoranthene-10, and phenanthrene-4, have low scores, whereas the central sample has a medium score, close to 0, and the samples containing three PAHs in mixture, e.g., FPB-9, FNP-5, and FPFlu-13, have high scores. This result also depends on the PAH quantum yield of fluorescence: for example, the fluorene (No. 3) characterized by a high response intensity has a higher score than the other pure samples.

The projections of the samples on the PC_2 highlighted a different behavior between two distinct groups of samples: those containing fluoranthene, i.e., PBFlu-16, NBFlu-14, Flu-10, and NPFlu-12, which had high scores, within +1900 and +800 in arbitrary units, and those containing fluorene, i.e., NFP-5, F-3, NFB-7, and FPB-9, which had low scores, between −1600 and −700. This separation into two groups evidenced the lack of common points of the fluorescence spectrum between these two PAHs. One should note that the samples containing both fluorene and fluoranthene, i.e., Centre-18, NFFlu-11, FBFlu-15, FPFlu-13, and NFPBFlu-17, had a medium score, between −900 and +100, like the samples without these two PAHs (Blank-1, N-2, B-6, P-4).

In addition, these properties can also be used as an identification mode for unknown samples by defining groups of samples (Fig 4). For example, a sample with high scores on PC_1 and PC_2 will belong to Group 1 (G1), which indicates a high fluorescence response and proves that it contains fluoranthene, while a sample in G2 will have a high fluorescence response and will thus contain both fluorene and fluoranthene. On the other hand, a sample in G4 will have a low fluorescence response and will contain fluoranthene. Finally, a sample in G3 will have a low fluorescence response and will be free of fluoranthene and fluorene.

Let us now interpret the samples projections on the plane defined by PC_3 and PC_4, which explain 25% of the total variance (Fig. 5). PC_3 indicates opposite behavior between the samples containing phenanthrene with high scores and those free of phenanthrene with low scores. Finally, PC_4 highlights an opposition between the samples containing benzo[*a*]pyrene with high scores and those without this PAH with low scores.

As previously, one can classify the studied samples into different groups (Fig. 5). The samples in G5 have high positive values on PC_3 and PC_4 and contain both phenanthrene and benzo[*a*]pyrene, whereas those in G6 or G8, respectively, contain only phenanthrene (G6) or benzo[*a*]pyrene (G8). Finally, the samples in G7 with high negative values on PC_3 and PC_4 contain neither phenanthrene nor benzo[*a*]pyrene. This reasoning can be also applied to an unknown sample to identify its components.

Calculation of Regression Coefficients and Interpretation

Once the PCA technique has been applied, the PCR technique allows one to compute the coefficients linking

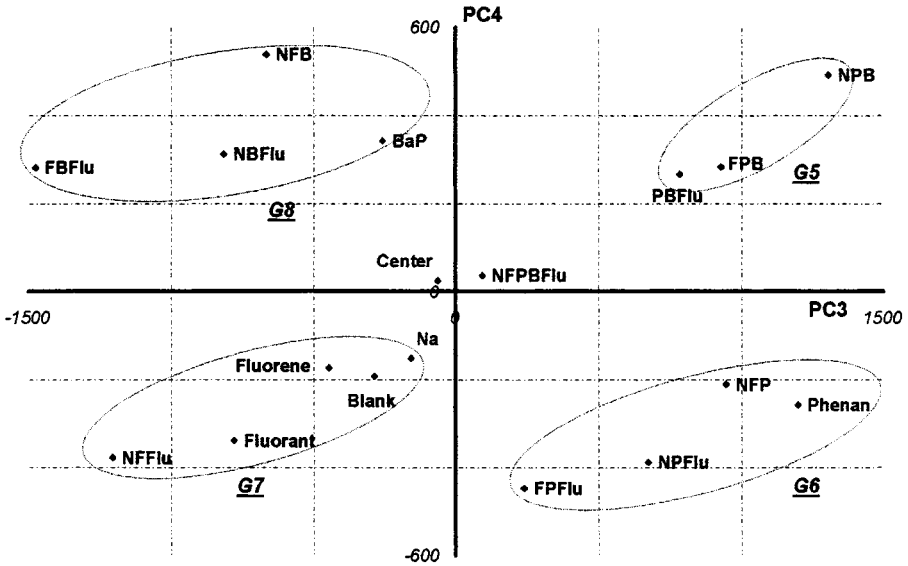

Fig. 5. Projections of the samples in a plane formed by the PC3 and PC4 explaining 25% of the total variance. G5 to G8 highlight samples with similar behavior.

the concentration data to the score data according to the matrix equation (3) already explained. These regression coefficients can be represented graphically for each PAH studied.

As an example Fig. 6 gives the regression coefficients of fluorene versus the wavelengths of the five recorded fluorescence spectra. The highest positive coefficients correspond to the spectral areas characteristic of fluorene, here an emission at 308 $\pm$ 5 nm for excitations at 245, 255, and 263 nm. The zero values of the coefficients correspond to areas without specific emission for fluorene. Finally, the negative coefficients are indicative of an area anticharacteristic to the fluorene, where the fluorescence response probably decreases concomitantly with an increase in fluorene concentration, likely because of interactions with other PAHs. One can also use this graphic representation to select the wavelengths characteristic of a PAH corresponding to the high positive regression coefficients. This will allow one, if necessary, to reduce the number of data collected to only the characteristic ones.

The most specific couples of emission and excitation wavelengths obtained for the different PAHs studied are given in Table III. It should be noted that the highest

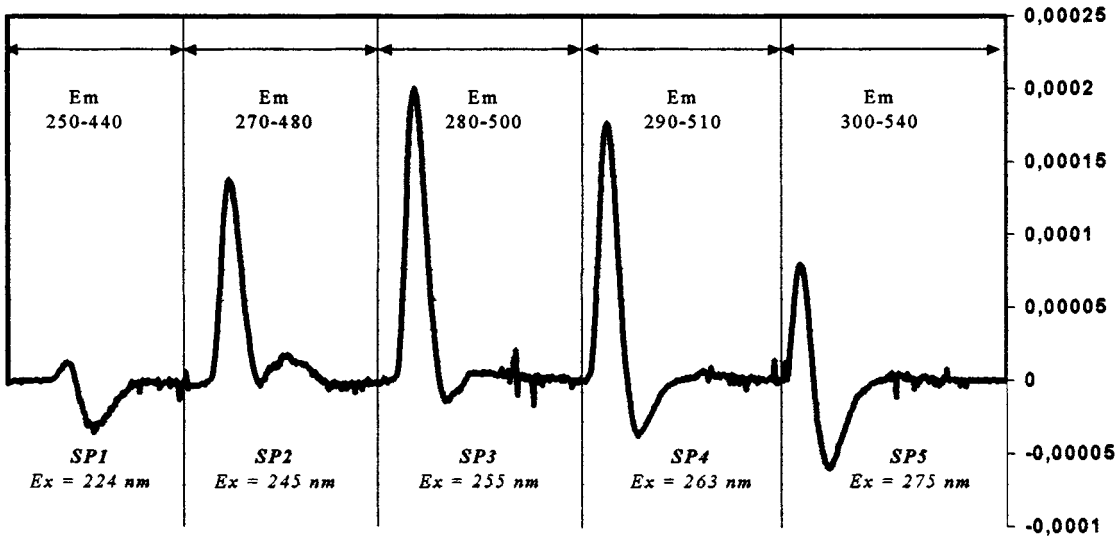

Fig. 6. Regression coefficients of the fluorene versus the wavelengths of the five recorded fluorescence spectra juxtaposed.

Table III. Specific Couples of Emission and Excitation Wavelengths[a]

PAH	Emission wavelength (nm)	Excitation wavelength (nm) 224	245	255	263	275
Naphatalene	338 ± 5			X	X	XX
Fluorene	308 ± 5		X	XX	X	
Phenanthrene	365 ± 5		XX	X		
Benzo[a]pyrene	407 ± 5		X	XX	X	X
Fluoranthene	460 ± 5		X	X	X	XX

[a] A cross indicates high regression coefficients for the corresponding emission/excitation wavelengths couples; two crosses indicate the highest regression coefficients.

regression coefficient corresponds to the spectrum range specific to a given PAH contained in the mixture while taking into account spectrum overlaps with other PAHs or possible interactions between some of them. Consequently, the most specific couple of excitation/emission wavelength in the mixture can differ from that observed with a pure PAH. The case of naphthalene reported in Table III is a good illustration. Indeed, the excitation wavelength of 224 nm was chosen because it induced the highest fluorescence response at 240 nm for pure naphthalene. However, Table III shows that the most characteristic response for naphthalene in mixture with the four other PAHs was obtained at the same emission wavelength, but for an excitation of 275 nm.

We observed more generally that the 224-nm excitation had no characteristic emission for the five PAHs of the mixture. Consequently, the fluorescence spectrum of this mixture recorded at 224 nm (excitation wavelength) did not contain any information of great interest for the model used, so it can be removed from the calibration procedure. This result could be due to the solvent fluorescence or to the presence of some fluorescent impurities, which both have a more intense response at the 224-nm excitation wavelength.

Model Validation and Predictions

Once the calibration has been achieved and the regression coefficient matrix *B* computed, the concentration of each compound of the mixture can be calculated through simple fluorescence measurements carried out at the same five excitation wavelengths as previously and under the same experimental conditions. A way to test and estimate the quality of the predictions obtained is to plot the predicted concentrations against the true ones; if it gives a median straight line, it is, of course, a satisfactory result.

For example, Fig. 7 illustrates the results obtained for fluorene using samples 1 to 18 for calibration and the test samples, Nos. 19 to 21, for assessment. The fluorene-free calibration samples are located at the bottom left in Fig. 7, while the samples containing fluorene at the maximum concentration are situated at the top right. The samples containing fluorene at various concentrations are distributed between these two extrema. One can notice, first, that the center point lies in the middle of the median straight line, thus confirming the correctness of the linearity hypothesis for the fluorescence response of PAHs in mixtures. Second, the three test samples, X, Y, and Z, also are well aligned on the median straight line, confirming the high quality the prediction made for fluorene on the whole concentration range studied.

In conclusion, except for benzo[*a*]pyrene, where uncertainty on the prevision seemed too high, the results obtained for all the PAHs studied were satisfactory. So, carrying out the procedure described to analyze an unknown mixture will allow one rightly to predict the concentrations in naphthalene, phenanthrene, fluorene, and fluoranthene, and to have an approximation of the benzo[*a*]pyrene concentration. Table IV gives the complete set of values obtained for the test samples.

Discussion

The results obtained for the test samples highlight the potentiality of PCA and PCR application to determine quickly the concentrations of five PAHs in mixture without carrying out any preliminary separation steps. These determinations were made in drinking water, which, though being a simple matrix, is a realistic one for many current quality controls performed by water companies. Once the calibration is achieved, the analysis is reduced to the recording of fluorescence spectra and the transfer of data to the computer containing the validated PCR model. Consequently, the whole measurement should not exceed 15 min, which is a very short time for the analysis of five compounds.

However, it is clear that the samples studied did not contain any other fluorescence-inducing substances liable to interfere in the fluorescence measurement. moreover, The interesting progress obtained in terms of specificity for fluorescence analysis of mixtures does not yet allow one to analyze samples from raw water containing, for example, humic and fulvic acids.

CONCLUSIONS

The study reported here has contributed to showing the potential of PCA and PCR methods to increase the

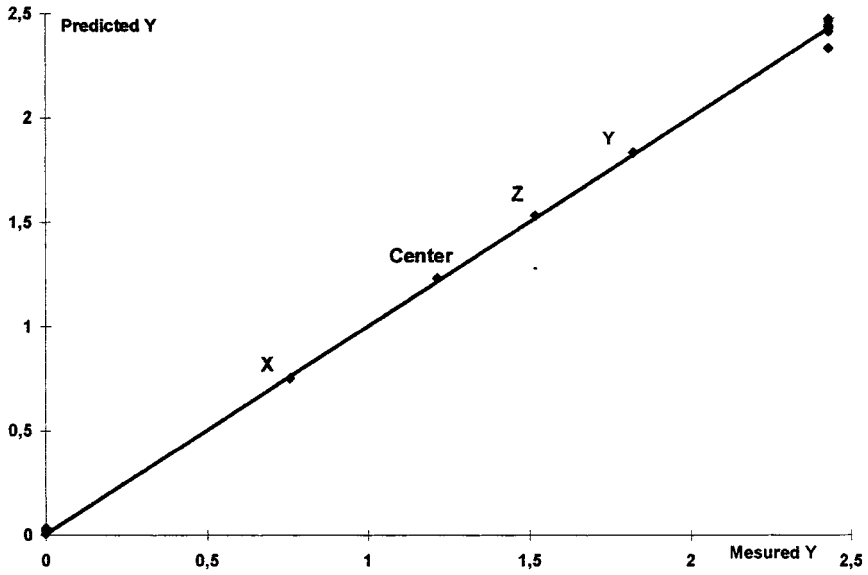

Fig. 7. Plot of the predicted concentrations versus the true ones for fluorene.

specificity of molecular fluorescence analytical techniques. This improvement was clearly demonstrated in the analysis of five PAHs in mixtures carried out without any preliminary concentration or separation step. The good predicted values obtained for the test points evidenced the accuracy of the results. Finally, after the validation of the PCR model, the rapidity of the analytical procedure, less than 15 min, is quite interesting. Coupling a portable fluorimeter with a laptop computer should be of utmost interest in developing a fast technique for *in situ* pollution control. However, to develop this technique, the focus should be on the following three points.

(i) The first aim should be to generalize its application to more complex matrices such as raw, river, or seawaters. This would require setting up and validating a fast extraction method to eliminate all interfering compounds such as fulvic and humic acids or washing agent residues, the source of drawbacks in the baseline measurements.

(ii) The second objective should be to increase the number of compounds analyzed simultaneously. Obtaining this result requires limiting the volume of data to be stored and processed. This led us to select the most characteristic excitation and emission couples as shown in the study reported here. Naturally, to obtain a good calibration the system must remain overdetermined; this implies that the number of excitation and/or emission wavelengths must be greater than the number of compounds studied. Consequently, the search for a compromise to limit the number of data and maintain a good calibration is also of high importance. Moreover, it may also be interesting to test the use of partial least squares (PLS) regression instead of PCR.

Table IV. Comparison of the Predicted Results to the True Values for the Three Test Samples

	Test X (μg/L) value		Test Y (μg/L) value		Test Z (μg/L) value	
PAH	Predicted	True	Predicted	True	Predicted	True
Naphthalene	2.0 ± 0.3	2.2 ± 0.2	3.7 ± 0.3	4.0 ± 0.2	9.0 ± 0.3	8.9 ± 0.2
Fluorene	0.8 ± 0.1	0.76 ± 0.09	1.8 ± 0.1	1.82 ± 0.09	1.5 ± 0.1	1.52 ± 0.09
Phenanthrene	2.1 ± 0.1	2.05 ± 0.09	2.9 ± 0.1	2.8 ± 0.1	3.8 ± 0.2	3.7 ± 0.1
Benzo[*a*]pyrene	1.3 ± 0.1	1.25 ± 0.03	0.5 ± 0.1	0.50 ± 0.03	1.1 ± 0.1	1.00 ± 0.03
Fluoranthene	0.0 ± 0.1	0.00	0.1 ± 0.1	0.00	10.4 ± 0.3	10.2 ± 0.2

(iii) Finally, the sensitivity of this analytical technique should be increased to lower the detection limits or to allow the study of low-quantum yield fluorescence molecules such as benzo [*b*]pyrene. As it remains important to avoid the time-consuming extraction and concentration steps, we plan to use in the future a tunable laser beam, which is a higher energetic excitation source than the classical arc-xenon lamp.

These prospects underline the need for future studies to generalize the use of this technique, which sounds very interesting and promising.

ACKNOWLEDGMENTS

We thank B. Bourgouin, Y. Lijour, and M. P. Friocourt for their constructive contributions to this work.

NOMENCLATURE

$A^p{}_n$	Spectral data matrix, with n rows and p columns
$B^m{}_f$	Regression coefficient matrix, with f rows and m columns
$C^m{}_n$	Concentration matrix, with n rows and m columns
$F^p{}_f$	Loading matrix, with f rows and p columns
$S^f{}_n$	Score matrix, with n rows and f columns
X^{t}	Transposed matrix of X
X^{-1}	Inverted matrix of X
f	Number of PCs
m	Number of PAHs in the studied mixtures
n	Number of samples (PAH mixtures prepared)
p	Number of variables (emission wavelengths)

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