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ORIGINAL PAPER

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Detection and quantification of PAH in drinking water by front-face fluorimetry on a solid sorbent and PLS analysis

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Abstract The direct determination in drinking water of perylene, chrysene, pyrene, benzo[*a*]pyrene, and benzo[*k*]fluoranthene, by front-face synchronous fluorimetry on a commercial SPE disk, has been evaluated. Sorbent treatment, influence of humic substances, and pH effect are discussed. In pure water the detection limits were estimated to be in the range 0.03–0.01 μg L^{-1}. A working pH in the range 10–11 was found to minimize the fluorescence quenching effect of humic substances. The proposed method combined with a partial-least-square (PLS) treatment was tested for quantitative analysis of mixtures of four PAH in a spiked drinking water.

Keywords Solid-phase extraction · Synchronous fluorescence · Polycyclic aromatic hydrocarbons · Drinking water

Introduction

Among a wide variety of anthropogenic chemicals, polycyclic aromatic hydrocarbons (PAH) are of particular concern as widespread, persistent and toxic contaminants [1, 2]. In addition to their increasing presence in oceans, lakes, and rivers, there is much evidence they are carcinogenic and mutagenic in living species in aquatic systems. For this reason there still great interest in developing a simple and sensitive method to detect these pollutants in natural waters [3, 4].

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The methods most widely used for the detection and quantification of PAH in aqueous matrices are based on separative techniques such as high-performance liquid chromatography (HPLC) with fluorimetry [5–7], gas chromatography (GC) with FID or MS detection [5, 8, 9], supercritical-fluid chromatography (SFC) [5, 10] or capillary electrophoresis [11]. These methods normally include an extraction step (liquid–liquid or solid-phase extraction) which, besides making necessary a complex calibration process, because of appreciable loss of analytes [12, 13], requires use of organic solvents, for example halogenated solvents, whose use is subject to limitation by government regulations [14]. As an alternative, non-invasive simpler methods based mostly on luminescence techniques has been proposed for the direct detection of PAH in aqueous media. These include conventional, synchronous [15, 16] or laser-excited fluorimetry [17–20] or room-temperature phosphorimetry [21, 22], both combined with use of an enhancement agent, for example micelles [15, 23, 24] or cyclodextrins [25, 26]. Another approach based on front-surface fluorimetric detection on a solid sorbent after solid-phase extraction was early proposed some time ago by Poziomek et al. [27, 28], who used C_{18} Empore membranes. Carr and Harris [29] using an alkylated silica adsorbent and Vilchez et al. [30] using Sephadex G-25 gel have also demonstrated the potential of this type of technique for direct detection of PAH in water. More recent applications combining solid-phase extraction and spectrofluorimetry have also been evaluated by Dmitrienko et al. [31], Campiglia and co-workers [32, 33], Fernandez-Sanchez et al. [34] or Algarra et al. [35, 36]. A similar approach has also been applied to the detection of BTEX [37, 38] and PCB [33, 35].

In previous work, among the various possibilities for the choice of the solid sorbent and the spectroscopic technique for detection, we paid particular attention to the use of tab-shaped fiber glass C_{18} extraction disks combined with synchronous fluorimetry and a common commercial instrument. It seemed that this choice could satisfy conditions for a simple, rapid, and inexpensive

Table 1 Fluorescence data for PAH adsorbed on C_{18} Envi-Disk solid phase

Structure					
Name	Benzo[*a*]Pyrene	Benzo[*k*]Fluoranthene	Chrysene	Perylene	Pyrene
$\lambda_{ex}/\lambda_{em}$ (nm)	285,298/404,428,455	294,308/406,420	269/362,382,403	408/438,468	335/372,383,393
Applied offset (nm)	37	112	112	37	37

analytical method for detection of PAH [39] and PCB [36, 39] in water and PAH metabolites in the urine of PAH-exposed persons [40, 41] at sub-ppb levels. However application to detection of PAH in natural and drinking waters requires that several points are examined ro reduce as far as possible the limit of detection at values close to or below the legal regulation limits. In this paper we report on three of these points, which were not precisely considered in previous work. These are:

1 research to determine the optimum operating conditions for the preparation of the phase and for the adsorption procedure;
2 suppression, or at least the diminution, of the interaction with naturally present natural organic matter responsible for fluorescence signal reduction [42]; and
3 verification that there is no competition nor interaction between the PAH which could be present simultaneously, and thus that the method can be applied to PAH mixtures.

Materials and methods

Chemicals and materials

Polycyclic aromatic hydrocarbons: benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), chrysene (Chr), perylene (Per) and pyrene (Pyr) (Table 1) were purchased from Aldrich (Milwaukee, WI, USA). Suwannee River humic acid from the IHSS (International Humic Substance Society) was used for testing interference with PAH. Stock concentrated PAH solutions were initially prepared in acetonitrile (SupraSolv; Merck, Darmstadt, Germany). Fresh aqueous working solutions were subsequently prepared by appropriate dilution either with pure water (Milli Q/Milli-Q2 system, Millipore, Bedford, MA, USA) or drinking water. In all cases, the volume content in acetonitrile did not exceed 0.3%.

The solid phase was prepared as 5 mm×10 mm rectangular tab-shaped elements cut from an SPE disk made of octadecyl silica phase enmeshed in a fiber glass support (C_{18} Envi-Disk from Supelco). Because the adsorption capacity of the extraction disk may differ from one piece to another, all the measurements described in this work were made using sorbent elements cut from the same 90-mm diameter disk.

Special attention was devoted to avoiding adsorption on to the flask walls [43] by using only stainless steel equipment, which simply comprises a 200 mL beaker, the sorbent holder, and a rod-like agitator driven by a small motor set above the beaker as shown schematically in Fig. 1.

The drinking water was collected from the laboratory water supply. The concentration of dissolved organic carbon (DOC) in the water samples was determined with a Shimadzu organic carbon analyzer (TOC-Vcsm/csn).

Front-face fluorescence spectra measurements

Fluorimetric measurements were performed with a commercial Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp and interfaced to a microcomputer for instrument operation and spectra processing. The slit-widths were adjusted to 2.5 nm for both excitation and emission and the photomultiplier (PMT R-3788) voltage was set at 950 V. The synchronous fluorescence spectra were corrected for variations with wavelength of lamp intensity and photomultiplier sensitivity. After adsorption the sorbent holder was placed in the sample compartment for front-face fluorescence measurement with the sorbent surface oriented at 45° to the excitation and emission beams.

Analytical procedure

Aliquots of PAH solution in acetonitrile (10–30 μL) were transferred to a stainless steel flask containing 150 mL water. Working solutions always contained less than 0.1% acetonitrile. The rectangular sorbent tab attached to the stainless steel holder was immersed in the PAH-spiked aqueous solution for a fixed period of time with stirring (Fig. 1). It was observed that at the low concentrations at which we worked, well below

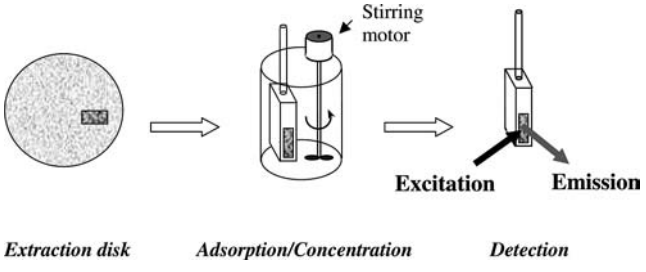

Fig. 1 Schematic diagram of the procedure used for direct front-face fluorimetric detection of PAH after adsorption from a spiked water solution on to a tab-shaped element cut from an Envi-Disk extraction disk

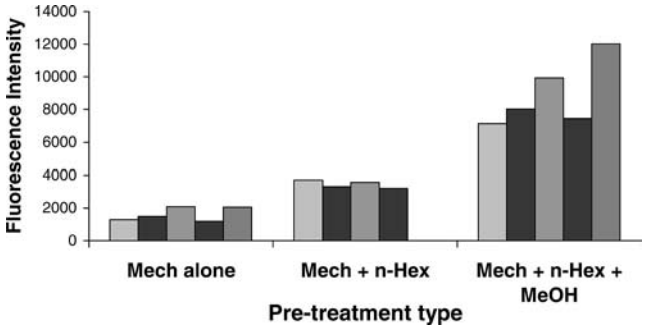

Fig. 2 Fluorescence intensity and reproducibility of Envi-Disk tabs after different types of pretreatment applied before adsorption of Pyr from water *Mech* mechanical treatment by stirring for 30 min, *n-Hex* wetting with *n*-hexane and drying for 1 min, *MeOH* wetting with methanol

saturation concentrations for most of the PAH we tested, the time for adsorption equilibrium is very long. For this reason, a fixed optimum immersion time of 60 min was chosen as a compromise between sensitivity and a reasonable time for analysis [22].

After adsorption, the sorbent holder is placed into the sample compartment of the spectrofluorimeter to measure its synchronous fluorescence signal. The PAH fluorescence spectrum is obtained by subtracting from this signal the blank signal recorded from the sorbent tab previously immersed in a pure water sample during mechanical treatment (vide infra).

The corrected synchronous fluorescence signals (sample and blank) were recorded in an excitation scale between 240 and 400 nm with the following wavelength offsets: $\Delta\lambda_1 = \lambda_{em} - \lambda_{ex} = 37$ nm for Pyr, BaP, and BkF and $\Delta\lambda_2 = 112$ nm for BkF and Chr.

Pretreatment of the sorbent phase

To guarantee suitable precision and reproducibility of the measurements, it was necessary to optimize the operating conditions. Two of these are of importance—the constancy of the stirring conditions and sorbent pretreatment. Satisfactorily stable stirring conditions were satisfied by using always the same stirrer and using 1.5 V batteries for a constant rate of rotation of the stirring motor [41].

It was initially observed during the bath adsorption process that fibers were released from the surface of the extraction disk during stirring, with the consequence of poor reproducibility of the signal. This problem was solved by previously subjecting the phase, attached to its sampler holder, to vigorous stirring in pure water for 30 min, to eliminate the most fragile fibers from the surface. This is the mechanical pre-treatment step referred to above. Estimation of signal reproducibility on application of this treatment for five identically concentrated Pyr solutions yielded a relative standard deviation of approximately 26%. Wetting with *n*-hexane for 10 min followed by gentle drying for 1 min with a hair drier was subsequently applied. Such a phase impregnation with *n*-hexane was supposed to achieve disentanglement of C_{18} alkyl chains, thus increasing contact between the sorbent surface and the analyte molecules. As shown in Fig. 2, this treatment leads both to better sensitivity and to better reproducibility, as evidenced by a relative standard deviation of approximately 7% obtained for four consecutive measurements.

In normal use of the C_{18} extraction disks, wetting with a polar organic solvent, for example methanol or acetonitrile, is recommended for PAH extraction [6]. We observed that subsequent wetting with methanol improves the efficiency of the Pyr extraction on the sorbent surface by a factor of appproximately 2 (Fig. 2). This pretreatment leads to less reproducible results, however (relative standard deviation ~23%), probably because of non-uniform and uncontrolled modification of the sorbent surface, and it was not used in this work.

Results and discussion

Synchronous fluorescence conditions

Good conditions for synchronous fluorescence (largest signal) are normally fulfilled when the wavelength offset ($\Delta\lambda$) is made equal to the wavelength difference between the absorption maximum and the fluorescence maximum. In principle, the best offset, satisfactory for both intense and narrow single synchronous signals, is different from one PAH to another. Nevertheless, with the mixture used in this work even choice of the best $\Delta\lambda$ for each PAH may lead to the observation of a complex signal in which the signal of a selected PAH, although dominating, could not be totally isolated and may contain a contribution from the fluorescence of other PAH. It could then be sufficient to simplify the analytical

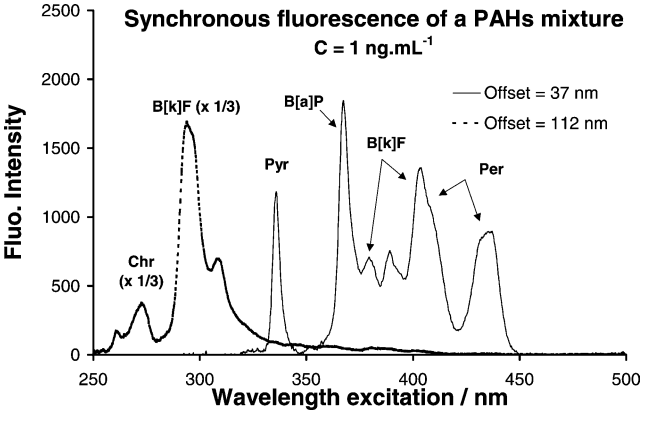

Fig. 3 Synchronous fluorescence spectra of a mixture of five PAH adsorbed on a tab-shaped piece of solid sorbent cut from a C_{18} Envi-Disk (Supelco) extraction disk from aqueous solution all at a concentration of 1 μg L^{-1} (1 ppb). The two wavelength offsets, 37 and 112 nm, were selected to enable the detection of all compounds with good sensitivity

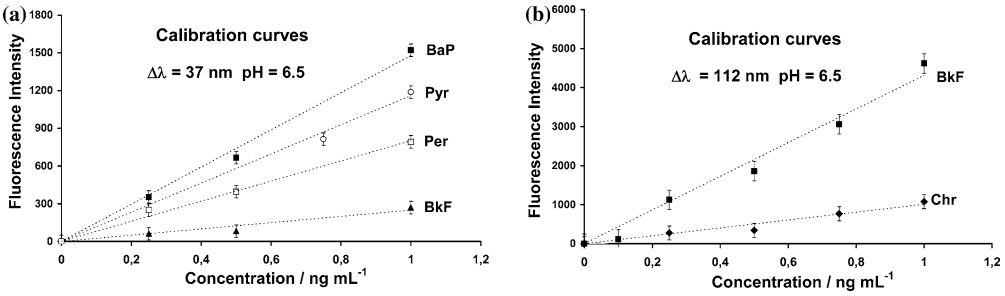

Fig. 4 Dependence of synchronous fluorescence intensity on concentration for the selected PAH using two wavelength offsets: **a** 37 nm and **b** 112 nm

procedure by combining a minimum number of offsets with an appropriate statistical analytical method to circumvent signal overlapping.

For the PAH mixture containing Pyr, BaP, BkF, Chr, and Per, two wavelength offsets were selected as good compromise for their detection. An offset $\Delta\lambda = 37$ nm seems to be suitable for simultaneous detection of Pyr, BaP, BkF, and Per whereas an offset $\Delta\lambda = 112$ nm enables detection of Chr and BkF. Table 1 lists the offsets used for each PAH adsorbed on C_{18} solid phase, together with their main absorption and fluorescence spectrum maxima. As an example, Fig. 3 shows the synchronous fluorescence spectra obtained from a C_{18} solid phase after immersion for 30 min in a mixture containing 1 μg L^{-1} of each PAH, with offsets of 37 and 112 nm.

Analytical figures of merit of the method

To estimate the potential of the method for detection of the selected PAH in water we individually evaluated, for each PAH, their limits of detection (LOD) and their linear dynamic ranges (LDR) in pure water. The LOD were estimated from the slopes of the calibration plots (Fig. 4) and the lowest detectable signals equal to three times the rms value of the noise signal. Each point plotted in the calibration plots was the average of three intensity measurements. The lowest limits for the LDR was arbitrarily taken equal to two times the LOD values, while the upper limits correspond to concentrations close to the PAH solubility in water at room temperature [44, 45], except for Pyr, for which it corresponds to the limit of the linearity of the dependence of fluorescence intensity on concentration (Table 2). For BaP, our estimate leads to an LOD of approximately 0.03 μg L^{-1}, which is close to the upper limit of 0.01 μg L^{-1} imposed by the European Union regulation in drinking water [46]. For BkF the best sensitivity is obtained with an offset of 112 nm. These LOD values are highly dependent on fluorimeter performance and the efficiency of the extraction disk. Increased sensitivity could be achieved by using a more sensitive fluorimeter on the one hand and possible improvement of the surface adsorption capacity of the extraction disks, which were not specially designed for this type of application.

Negative effect of humic substances

Humic substances (HS) are ubiquitously present in all natural waters. Their interaction with PAH is a matter of interest in environmental chemistry because PAH–HS association has been shown to be important in PAH transport and fate in the global environment [47, 48]. Such interaction has also a negative effect on solid-phase extraction because of the competitive adsorption of PAH by these substances [49, 50].

To estimate the extent to which the presence of humic substances in water can affect the results of this method, we tested the effect of Suwannee River humic acid (SRHA) on the Pyr fluorescence signal of a sorbent element immersed in pure water solution spiked at a concentration of 1 μg L^{-1}. As expected, a decrease of

Table 2 Calibration plots, linear dynamic range (LDR), and limits of detection (LOD)[a] at λ_{sfs}[b] for each of the five selected PAH in pure water

PAH	$\Delta\lambda_{(nm)}$	λ_{sfs} (nm)	$I_F \propto a$ [PAH]		LDR (μg L^{-1})	LOD (μg L^{-1})
			Slope a[c]	R^2		
Pyr	37	335.6	1160	0.9899	0.1–10	0.04
B[*a*]P	37	367.2	1661	0.9942	0.06–4.0	0.03
Per	37	436.6	801	0.9922	0.15–3.5	0.06
Chr	112	271.2	1011	0.9780	0.06–1.0	0.03
B[*k*]F	37	380.8	250	0.9468	0.15–0.8	0.08
B[*k*]F	112	295.0	4317	0.9901	0.02–0.8	0.01

[a]LOD have been estimated from the slope of the calibration plots and the lowest detectable signal taken equal to three times the rms value of the noise signal

[b]λ_{sfs} = wavelength of the synchronous fluorescence maximum (wavelength excitation scale)

[c]In Fluo unit. μg^{-1} LR^2 is the determination coefficient

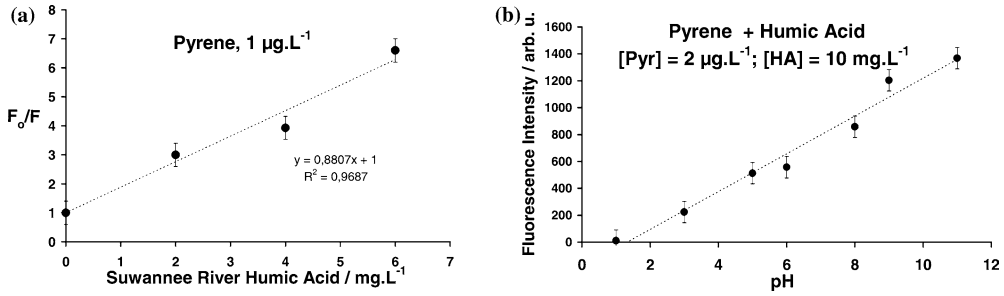

Fig. 5 **a** Stern–Volmer-type plot for Pyr fluorescence signal decrease on increasing the concentration of Suwannee River humic acid in pure water (initial pH 6.5). **b** effect of pH on the fluorescence intensity signal of Pyr adsorbed from a water solution ($c = 2$ µg L^{-1}) in the presence of 10 mg L^{-1} Suwannee River humic acid

Table 3 Model and test sample concentrations in drinking water (µg L^{-1}) prepared for PLS analysis of PAH mixtures

Sample No.	Pyrene (Pyr)	Benzo[*a*] pyrene (BaP)	Benzo[*k*] fluoranthene (BkF)	Perylene (Per)
1	0.15	0.15	0.075	0.90
2	0.05	0.15	0.225	0.45
3	0.15	0.05	0.45	0.45
4	0.30	0.15	0.45	0.15
5	0.30	0.30	0.075	0.45
6	0.05	0.30	0.45	0.90
7	0.30	0.05	0.225	0.90
8	0.15	0.30	0.225	0.15
9	0.05	0.05	0.075	0.15
10	0.30	0	0	0
11	0	0.30	0	0
12	0	0	0.9	0
13	0	0	0	0.45
Test 1	0.20	0.10	0.60	0.60
Test 2	0.10	0.20	0.15	0.60
Test 3	0.25	0.10	0.30	0.60
Test 4	0.15	0.06	0.36	0.30

signal intensity with increasing concentration of HS was observed (Fig. 5a). Assuming that the signal observed reflects the concentration of free Pyr molecules, from the Stern–Volmer plot shown in Fig. 5a a value of 1.6×10^6 L kg^{-1} is estimated for the apparent association constant, K_{OC}, of Pyr with SRHA. For this estimate we used a SRHA carbon weigh proportion of 54.2% [51]. The K_{OC} value estimated in this way is significantly higher than K_{OC} values evaluated so far for association of Pyr with various humic substances, which have been found to be in the range $0.1–0.18\times10^6$ L kg^{-1} [48, 52, 53] at natural pH. This overestimate of K_{OC} may indicate that, besides complexing Pyr, humic acids have other side-effects, for example blocking some of the adsorption sites on the sorbent surface. This is, however, a hypothesis and further studies are needed for confirmation. Interestingly, as shown in Fig. 5b, and in agreement with the pH effect reported by Kumke et al. [48] and Algarra [54], an increase of pH results in reduction of the negative effect of the humic acids on the Pyr fluorescence intensity. For Pyr in the presence of 10 mg L^{-1} of SRHA almost no signal is obtained at pH 2 whereas approximately 60% recovery of the signal intensity expected in pure water at normal pH (~6.5) is obtained at pH 11. This effect may be because of a decrease of the hydrophobic character of the HS as a result of deprotonation of carboxyl and hydroxyl functionality [55, 56]. Such a modification is expected to reduce the affinity of SRHA for Pyr on the one hand, and, if any, for the sorbent, on the other hand.

Application of the method to drinking water

PAH mixture analysis

In the event of accidental contamination of drinking water, not only one but a mixture of PAH might be present. In that case it must be verified that there is neither preferential adsorption nor mutual interference in the detection of mixtures of the compounds adsorbed on the solid sorbent surface (e.g. inner filter effect, energy transfer). As a test, we analyzed several drinking water samples artificially contaminated with Pyr, BkF, BaP, and Per in different proportions all at sub-ppb concentrations and at the natural pH of the drinking water, which was in the range 6.5–7. Chr, which gives a weak signal with a 112 nm offset and cannot be detected with a 37 nm offset, was not considered.

For this study, we applied partial-least-square analysis (PLS 2) of the data using Simca-P software from Umetrics. As a first step we built a set of calibration spectra (model data) with 13 mixtures. To minimize the number of mixtures in the model, we prepared a set of nine mixtures with, for each of the four PAH, three different concentrations combined in each mixture in accordance with Plackett–Burman coefficients [57]. As a supplement, we added to the model spectra of drinking water samples spiked with each PAH alone. This model was then used to predict the concentrations in the four test solutions. The PAH concentrations in the mixtures prepared for calibration and testing are indicated in Table 3. The statistical analysis was found to require five components and the calibration model we used was found to predict 99.5% of the variation (R^2Ycum) of the concentrations according to cross validation, a value which is an indication of its suitable validity.

Results from prediction of PAH concentrations in the four test samples are shown in Figs. 6 and 7. In Fig. 6 the scatter plot of predicted values against expected values for all the concentrations determined in the four test solutions led to a determination coefficient larger than 0.98. In Fig. 7 the predicted concentrations are compared with the expected concentrations for each test

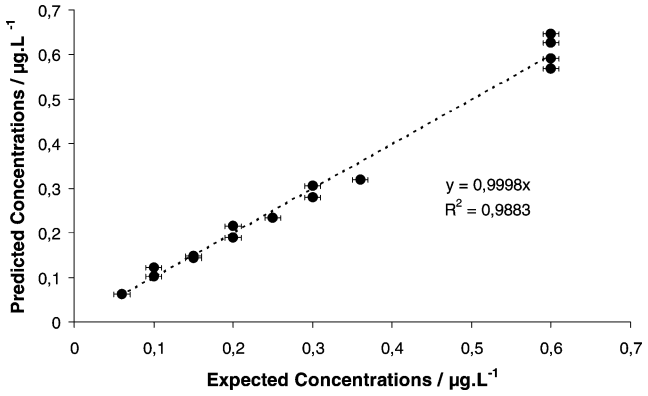

Fig. 6 Scatter plot of predicted against expected concentrations for the four test solutions. Regression analysis leads to a slope very close to unity and a coefficient of determination (R^2) of 0.988

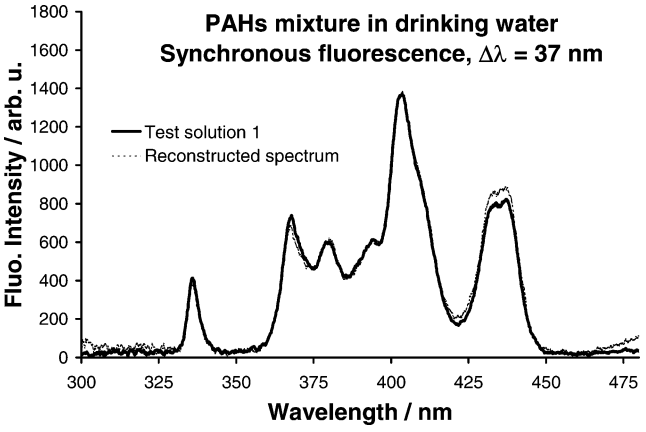

Fig. 8 Experimental synchronous fluorescence spectrum observed for the test 1 sample and the reconstructed spectrum obtained by combining reference pure compound spectra each multiplied by weight factors proportional to their respective concentrations derived from the PLS analysis

solution. The predicted values are usually within the uncertainty domains estimated for the expected values. The good correspondence between expected and predicted values shows there is no evidence of the presence of interferences of any type between the PAH analytes.

As an illustration of the reliability and precision of the method, in Fig. 8, are superimposed the experimental fluorescence spectrum observed for the test 1 sample and the reconstructed spectrum obtained by combining reference pure compound spectra each multiplied by weight factors proportional to their respective concentrations in the mixture, as derived from PLS analysis.

Interference from natural organic matter

Because all measurements including calibration were performed using the same drinking water, it was not necessary to take into account the presence of natural organic matter (NOM) of which humic substances are a major component [51]. Nevertheless, an upper limit of 0.3 mg L^{-1} was determined for the DOC concentration in the drinking water we used. Moreover, all measurements were performed in the pH range 6.5–7, i.e. at a pH at which the presence of natural organic matter (NOM) and particularly humic substances may affect the PAH fluorescence signal. It follows that PAH signal attenuation cannot be neglected, because the limit of detection of the method, in particular for BaP, is close to the maximum tolerated concentration in drinking water.

Indeed, an important reduction of BaP signals ($c = 0.3$ ppb) was observed in drinking water compared with those in pure water. The fact that, as observed for pure water spiked with humic substances, the signal in the tap water was found to increase on increasing the pH to 11 indicates that, among other possible interferences, NOM can be thought to be responsible for much of the BaP signal reduction. This result indicates that the reliability and accuracy of the method can be questioned if

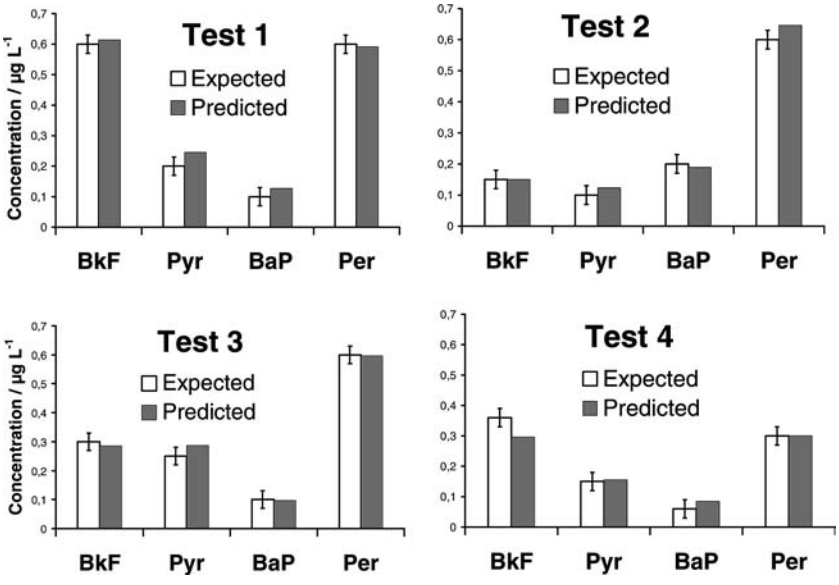

Fig. 7 Expected and calculated concentrations determined by applying PLS treatment to data recorded from drinking water solutions containing mixtures of benzo[*k*]fluoranthene (*BkF*), pyrene (*Pyr*), benzo[*a*]pyrene (*BaP*) and perylene (*Per*). Data are from front-face synchronous fluorescence spectra recorded with 37 nm offset on a tab-shaped C_{18} Envi-Disk after adsorption

the NOM content of the water is not taken into consideration. In fact this is a very common problem in solid-phase extraction of non-polar organic pollutants from water. Destruction of the NOM before extraction seems an attractive solution. A simple and efficient method which is worth consideration is oxidation of the NOM with potassium permanganate, as described by Bonifazi et al. [58]. It is thus of interest to explore whether previous destruction of the humic substances by this method is compatible with the analytical technique described in this paper. Such a study is in progress.

Conclusions

This paper is a contribution to the development of simple technique for determination of PAH in drinking water by a combination of solid-phase adsorption and front-face synchronous fluorimetric detection [27–35].

Optimized conditions for good sensitivity and reproducibility include previous mechanical conditioning, *n*-hexane impregnation followed by a mild air drying, and highly constant stirring conditions Evaluation of the potential of the method demonstrated that it leads to a limit of detection for BaP in pure water ($\leq 0.03\ \mu g\ L^{-1}$) very close to the limit of concentration recommended by European legislation.

We expect sensitivity can be significantly increased if new phases with more homogeneous surface specially adapted to optical detection could be devised by manufacturers and if a more sensitive system for fluorescence detection is used.

Naturally present natural organic matter has been shown to be responsible for significant attenuation of the fluorescence signal even in drinking water, in which its concentration is usually rather low. Although a satisfactory solution would be to destroy these substances before the analysis, we have no evidence that this treatment is compatible with the method. As an alternative to this treatment, increasing the pH to high values seems to be a simple way of minimizing the negative effect of humic substances.

Application of the method to a four-component PAH mixture combined with a PLS analysis leads to a good agreement between expected and predicted concentrations of each component. From this result it is concluded there is no competition or interference between the tested PAH.

According to the results we have obtained, and if a suitable experimental procedure is followed, the proposed method, besides to be simple to operate, seems to have good reliability and accuracy for rapid PAH-contamination control of drinking waters.

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References

1. Means JC, Wood SG, Hasset JJ, Banwart WL (1980) Environ Sci Technol 14:1524–1528
2. Edwards NT (1983) J Environ Qual 12:427–441
3. Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fate and biological effects. Applied Science, London
4. Vo-Dinh T (1990) Chemical analysis of polycyclic aromatic compounds. Wiley, New York
5. Manoli E, Samara C (1999) Trends Anal Chem 18:417–428
6. Kiss Z, Varga-Puchony J, Hlavay J (1996) J Chromatogr A 725:261–272
7. Williamson KS, Petty JD, Huckins JN, Lebo JA, Kaiser EM (2002) Chemosphere 49:717–729
8. Santos FJ, Galceran MT (2002) Trends Anal Chem 21:672–685
9. Havenga WJ, Rohwer E (2000) Int J Environ Anal Chem 78:205–221
10. Bernal JL, Nozal MJ, Toribio L, Serna ML, Borrull F, Marce RM, Pocurull E (1997) J Chromatogr A 778:321–328
11. Martinez D, Borrull F, Calull M (1999) Trends Anal Chem 18:282–291
12. Thurman EM, Mills MS (1998) Solid-phase extraction. Principles and practice. Wiley, New York, p 17
13. Simpson N (2000) Solid-phase extraction: principles, strategies and applications. M. Dekker, New York
14. US EPA Office of Solid Waste draft PBT Chemical List (1998)
15. Patra D, Mishra AK (2001) Talanta 55:143–153
16. Miller JS (1999) Anal Chim Acta 388:27–34
17. Giamarchy P, Stephan L, Salomon S, Le Bihan A (2000) J Fluoresc 10:393–402
18. Karlitschek P, Lewitzka F, Bünting U (1998) Fresenius J Anal Chem B 67:497–504
19. Burel L, Giamarchi P, Stephan L, Lijour Y, Le Bihan A (2003) Talanta 60:295–302
20. Whitcomb JL, Bystol AJ, Campiglia AD (2002) Anal Chim Acta 464:261–272
21. Hagestuen ED, Campiglia AD (1998) Appl Spectrosc 52:1096–1102
22. Vo-Dinh T (1984) Room temperature phosphorimetry for chemical analysis. In: Elving PJ, Winefordner JD (eds) V68 in: chemical analysis. Kolthoff Editor Emeritus. Wiley, New York
23. Yu JC, Jiang ZT, Liu HY, Yu J, Zhang L (2003) Anal Chim Acta 477:93–101
24. Urbe I, Ruana J (1997) J Chromatogr A 778:337–345
25. Algarra M, Hernandez M (1998) Analyst 123:2217–2221
26. Vo-Dinh T, Gammage RB (1978) Anal Chem 50:2054–2058
27. Poziomek EJ, Eastwoood D, Lidberg RL, Gibson G (1991) Anal Lett 24:1913–1921
28. Eastwood D, Dominguez ME, Lidberg RL, Poziomek EJ (1994) Analysis 22:305–310
29. Carr JW, Harris JM (1988) Anal Chem 60:698–702
30. Vilchez JL, del Olmo M, Avidad R, Capitan-Vallvey LF (1994) Analyst 119:1211–124
31. Dmitrienko SG, Gurariy E Ya, Nosov RE, Zolotov Yu A (2001) Anal Lett 34:425–438
32. Whitcomb JL, Campiglia AD (2001) Talanta 55:509–518
33. Arruda AF, Campiglia AD (1999) Anal Chim Acta 386:271–280
34. Fernández-Sánchez JF, Carretero AS, Cruces-Blanco C, Fernández-Gutiérrez A (2003) Talanta 60:287–293
35. Algarra M, Radin C, Fornier de Violet P, Lamotte M, Garrigues P, Hardy M, Gillard R (2000) J Fluoresc 10:355–359
36. Algarra M, Lamotte M, Fornier de Violet P, Hernandez M, Garrigues P (2000) Polycyclic Aromatic Compounds 19:241–251
37. Wittkampt BL, Tilotta DC (1995) Anal Chem 67:600–605
38. Wittkampt BL, Hawthorne SB, Tilotta DC (1997) Anal Chem 69:1197–1203
39. Lamotte M, Fornier de Violet Ph, Garrigues Ph (2000) Spectra Analysis 222:27–31

40. Radin C, Algarra M, Fornier de Violet Ph, Lamotte M, Garrigues Ph (2000) Luminescence 15:67–68
41. Lamotte M, Belfatmi R, Fornier Ph, Garigues Ph, Lafontaine M, Dumas C (2003) Anal Bioanal Chem 376:816–821
42. Li N, Lee HK (2001) J Chromatogr A 921:255–263
43. Schaller KH, Angerer J, Hausmann N (1991) In: Garrigues P, Lamotte M (eds) Polycyclic aromatic compounds. Proceedings of the 13th international symposium on PAH, Bordeaux. Gordon and Breach, pp1023–1030
44. Wan-Ying S, Kuo-Ching M (2000) J Phys Chem Ref Data 29:41–130
45. Pearlman RS, Yalkowsky SH, Banerjee S (1988) In: Karcher W (ed) Spectral atlas of polycyclic aromatic compounds, vol 2. Kluwer Academic Publisher, Dordrech, p 22
46. European Community Conceal Directive 80/778/CEE (15/07/1980)
47. McCarthy JF, Jimenez BD (1985) Environ Sci Technol 19:1072–1076
48. Kumke MU, Löhmannsröben, Roch Th (1994) Analyst 119:997–1001
49. Li N, Lee HK (2001) J Chromatogr A 921:255–263
50. Kopinke FD, Georgi A, Mackenzie K (2001) Environ Sci Technol 35:2536–2542
51. Kile DE, Chiou CT, Brinton TI (1994) In: Averett RC, Leenheer JA, McKnight DM, Thorn KA (eds) Humic substances in the suwannee river, Georgia: interactions, properties and proposed structures. U.S. Geological Survey Water Supply, Paper 2373, pp21–32
52. Gaulthier TD, Shane EC, Guerin WF, Seitz WR, Grant CL (1986) Environ Sci Technol 20:1162–1166
53. Herbert BE, Bertsch PM, Novak JM (1993) Environ Sci Technol 27:398–403
54. Algarra M (2000) PhD Thesis, University of Málaga
55. Schlautman MA, Morgan JJ (1993) Environ Sci Technol 27:961–969
56. Schulten HR (1998) J Anal Appl Pyrol 49:385–415
57. Plackett RL, Burman JP (1946) Biometrika 33:305–325
58. Bonifazi P, Pierini E, Bruner F (1997) Chromatographia 44:595–600