

Simultaneous spectrophotometric determination of trace amount of polycyclic aromatic hydrocarbons in water samples after magnetic solid-phase extraction by using projection pursuit regression

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Abstract Magnetic solid-phase extraction based on coated nano-magnets Fe_3O_4 was applied for the pre-concentration of four polycyclic aromatic hydrocarbons (PAHs; anthracene, phenanthrene, fluorine, and pyrene) in environmental water samples prior to simultaneous spectrophotometric determination using multivariate calibration method. Magnetic nanoparticles, carrying target metals, were easily separated from the aqueous solution by applying an external magnetic field so, no filtration or centrifugation was necessary. After elution of the adsorbed PAHs, the concentration of PAHs was determined spectrophotometrically with the aid of a new and efficient multivariate spectral analysis base on principal component analysis-projection pursuit regression, without separation of analytes. The obtained results revealed that using projection pursuit regression as a flexible modeling approach improves the predictive quality of the developed models compared with partial least squares and least squares support vector machine methods. The method was used to determine four PAHs in environmental water samples.

Keywords Polycyclic aromatic hydrocarbons · Magnetic solid-phase extraction · Projection pursuit regression

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent an important class of hazardous organic chemicals consisting of two or more fused benzene rings in linear, angular, or cluster arrangements (Bjorseth 1983). They are ubiquitous pollutants present in all compartments of the environment (atmosphere, soil and water) and produced in a variety of industrial processes and are usually associated with incomplete combustion of fossil fuels. Some of PAHs exhibit carcinogenic and mutagenic properties and the wide distribution of them in the environment pose serious health risks to all living organisms (Neff 1979; Cavalieri and Rogan 1998). Moreover, PAHs have attracted increasingly attention as biochemical, immunologic, genetic, and reproductive effects have been widely observed in fish and other animals from marine and freshwater environments upon exposure to PAHs (Pagnout et al. 2006; Geffard et al. 2003). Therefore, reliable analytical methods for the continuous monitoring of these compounds are of great interest. Owing to the complexity of environmental sample matrices and the relative low concentration of PAHs in these samples, separation and preconcentration procedure were necessary in the analysis of PAHs in the environmental samples to improve the sensitivity of method (Pena et al. 2009; Shariati-Feizabadi et al. 2003; Lim et al. 2007; Li et al. 2008b; Oliferova et al. 2005; Saleh et al. 2009).

Solid-phase extraction (SPE) is a routine extraction method for trace levels of contaminants in environmental samples. Recently, use of nanoparticles (NPs) for sample extraction in SPE is gaining research interest (Lin et al. 2007; Zhao et al. 2008; Huang and Hu 2008a, b; Suleiman et al. 2009; Zargar et al. 2009). Compared with traditional SPE sorbents, NPs offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, rapid extraction dynamics, and high extraction efficiencies (Hu et al. 2007; Yao et al. 2008; Huang and Hu 2008b). Among different kinds of NPs, magnetic NPs, mainly including Fe₃O₄ NPs, appears as an interesting advanced composite material. It has received increasing attention in the past decades due to its unique physical and chemical properties and high potential applications in various fields such as cell separation, magnetically assisted drug delivery, enzyme immobilization, and protein separation (Nandigala et al. 1997; Li et al. 2008a, b, c; Li et al. 2007; Whiteaker et al. 2007; Horak et al. 2001). The magnetic NPs with adsorbed sample can be easily collected by using an external magnetic field placed outside of the extraction container without additional centrifugation or filtration of the sample, which makes sampling and collection easier and faster. Moreover, the magnetic NPs may be reused or recycled. These NPs can be coated with surfactants and as a result prevent their aggregation in liquids and improve their chemical stability. The repulsive interactions between particles can be created by coating a surfactant layer on particle surfaces (Li, et al. 2008a, b, c; Sun et al. 2009).

Recently, method development for simultaneous determination of solutes without prior separation has been markedly increased. This was attributed to the availability of powerful instrumentation and robust numerical analytical methods. Multivariate calibration methods such as multiple linear regression (Haaland and Thomas 1988), principal component regression (Al-Degs et al. 2008), and partial least squares regression (Ghasemi and Niazi 2005) are widely used for simultaneous determination with multivariate data, such as those provided by ultraviolet (UV)/visible (vis) absorption (Ghasemi and Zolfonoun 2010), infrared (Kansiz et al. 2000), or fluorescence spectrometry (Madrakian et al. 2009). However, these methods are not suitable when nonlinearity is observed in the system. Artificial neural networks and support vector machines are nonlinear modeling techniques that have attracted increasing interest in recent years. These methods make it possible to

eliminate or reduce the effects of the analyte–analyte interaction, the synergistic effect, the multistep process and any other unknown nonlinearity, and often produce superior models compared with models developed by the linear approaches (Hasani et al. 2007).

Projection pursuit regression (PPR) is a nonlinear multivariate regression procedure, which was proposed by Friedman and Stuetzle (1981). It seeks the “interesting” projections of data from high- to lower-dimensional space and tries to find the intrinsic structural information hidden in the high-dimensional data (Huber 1985). With the obtained interesting projections direction, it can be used for further study of visual pattern recognition and regression (Du et al. 2008a; Ren et al. 2007). At present, it has been applied successfully to tackle some chemical problems (Liu et al. 2007; Du et al. 2008b).

In this paper, a SPE method based on sodium dodecyl sulfate (SDS)-coated magnetic nanoparticles is developed for extraction and preconcentration of PAHs from environmental water samples, prior to their simultaneous spectrophotometric determination using principal component analysis-projection pursuit regression (PC-PPR) algorithm. For comparison, partial least squares (PLS), and least squares support vector machine (LS-SVM) methods are also employed for determination of PAHs.

Theory

Projection pursuit regression

The PPR method is based on an iterative two-stage process of projection (reduction of parameter space) and smoothing (establishing nonlinear relation). The reduction of the parameter space is essential for the application of smoothing; smoothing in high-dimensional spaces quickly becomes impossible because of data sparsity (Huber 1985). In principle, PPR consists of linear combinations of nonlinear transformations of linear combinations of explanatory variables. The basic model takes the form:

$$y = \bar{y} + \sum_{i=1}^M f_i(\alpha_i^T X) + \varepsilon$$

where, \bar{y} is the average output variable, M is the number of incorporated smooths, f is the smooth function (ridge function), α is the parameter of projection direction, and

ε is the residual error after fitting M smooths. The vector $\alpha_i^T X$ is the projection of X onto the unit vector α_i , where the directions α_i are chosen to optimize model fit. The functions f_i are unspecified by the model and estimated using a flexible smoothing method. This allows the PPR to be very general as it fits nonlinear functions f_i of any class of linear combinations in X . Then it can produce a nonlinear regression model by the summation of a number of ridge functions. The PPR algorithm estimates α_i by maximum of an index and f_i by a low dimensional nonparametric regression estimate based on the projected data, iteratively. The procedure is repeated forward until the residual sum of squares (RSS) is less than a predetermined value.

$$RSS = \sum_{i=1}^n \left[y_i - \sum_{i=1}^M f_i(\alpha_i^T x_i) \right]^2$$

Experimental

Reagents

All reagents used were of analytical grade and were used as supplied. SDS, methanol, ammonia solution, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, were purchased from Merck (Germany). Standard stock solutions ($1,000 \mu\text{g mL}^{-1}$) of anthracene, phenanthrene, fluorine, and pyrene were prepared by dissolving the pure solid (Merck) in methanol and stored in dark at 4°C . These Standard stock solutions were diluted with methanol and working solutions were prepared daily by adequate dilution with pure water.

Preparation of magnetic Fe_3O_4 NPs

The Fe_3O_4 NPs were prepared by chemical coprecipitation method (Li et al. 2008a, b, c). Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11.68 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.30 g) were dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring at 85°C . Then, 20 mL of 30 % aqueous ammonia was added to the solution. The color of bulk solution changed from orange to black immediately. After the reaction, the obtained Fe_3O_4 NPs precipitate was separated from the reaction medium by magnetic field, and washed with 200 mL deionized water four times.

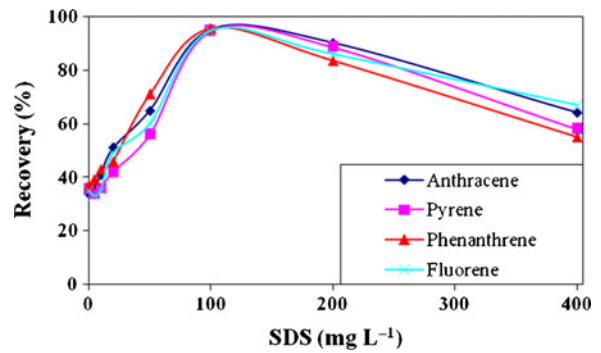


Fig. 1 Effect of SDS concentration on the extraction efficiency of PAHs. Conditions—sample volume, 100 mL; Fe_3O_4 NPs amount, 0.1 g; concentration of analytes, 20 ng mL^{-1} ; and volume of eluent, 1 mL methanol

Instrumentation and software

A Perkin Elmer (Lambda 25) spectrophotometer with 10 mm quartz cells was used for UV–vis spectra acquisition. The data were processed on a Toshiba computer with Pentium IV as central processing unit (4 Gb RAM) using MATLAB software, version 7.7. The PPR optimization and model results were obtained using the statistical pattern recognition toolbox version 2.11. LS-SVM regression was performed using the LS-SVM lab toolbox version 1.5 (MATLAB toolbox for least-squares support vector machines). PLS and other calculations were carried out using PLS-Toolbox, version 5.8 (Eigenvectors Company).

Magnetic SPE procedure

A 100-mL sample or standard solution containing SDS ($100 \mu\text{g mL}^{-1}$) was transferred in a glassware beaker. Then 50 mg Fe_3O_4 NPs was added into the sample solution. The mixture was stirred for 15 min.

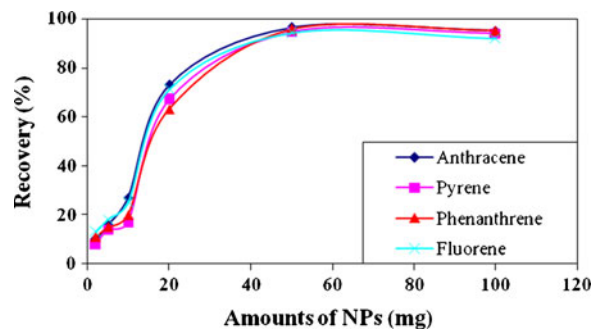


Fig. 2 Effect of the Fe_3O_4 NPs amount on the extraction efficiency of PAHs. Conditions—sample volume, 100 mL; SDS concentration, 100 mg L^{-1} ; concentration of analytes, 20 ng mL^{-1} ; and volume of eluent, 1 mL methanol

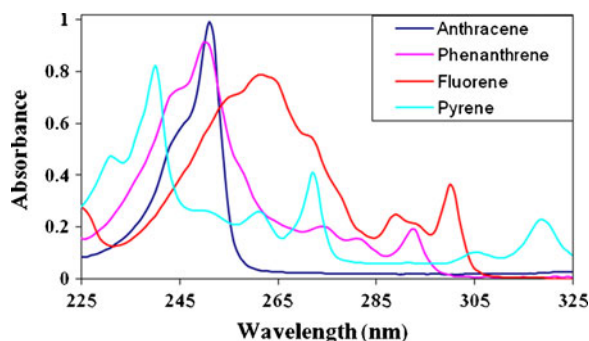


Fig. 3 Absorption spectra of four PAHs after magnetic SPE

Subsequently, the Fe_3O_4 NPs were isolated by placing a strong magnet and the supernatant was poured away. Finally, the preconcentrated target analyte adsorbed on SDS-coated Fe_3O_4 NPs was eluted with 1.0 mL of methanol and transferred to a quartz cell. The absorption spectra were recorded between 325 and 225 nm.

Analysis of the real samples

Tap water, well water, river water and mineral water samples were filtered through 0.45 μm membrane filter and maintained in glass containers, then stored at a temperature of 4 °C. Suitable aliquots were taken and subjected to preconcentration and determination by the procedure described above.

Results and discussion

Optimization of extraction conditions

Influence of SDS concentration on the adsorption of PAHs

The effect of the surfactant amount on the adsolubilization of target compounds was studied in batch mode. As can be seen from Fig. 1, in the absence

of surfactant, the proportion of target compounds that were adsorbed was relatively low. The adsorption amount of PAHs increased remarkably with the increasing amount of SDS. Maximum adsorption was obtained at a concentration of 100 mg L^{-1} of SDS. When SDS concentration was above 100 mg L^{-1} , the adsorption of the analyte decreased gradually, which may be attributed that the SDS molecules began to form micelles in the bulk aqueous solution and the micelles caused the PAHs to redistribute into the solution again. Given these findings, 100 mg L^{-1} was selected as the final addition amount of SDS in the next studies.

Effect of the sorbent amount

In comparison with traditional sorbents (microsized sorbents), NPs offer a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of NPs. In order to study the effect of the sorbent, 2 to 100 mg of Fe_3O_4 NPs was added to 100 mL of the sample solution (Fig. 2). The obtained results showed that by increasing the sorbent amounts from 2 up to 50 mg due to increasing accessible sites, extraction recovery increased and after that remained constant. A 50 mg of the Fe_3O_4 NPs was selected for subsequent experiments.

Effect of eluent type

According to the reported results (Li et al. 2008a, b, c; Sun et al. 2009), adsorbed analytes on the surface of mineral oxides in the presence of a surfactant can be quantitatively eluted using organic solvents. Therefore, to find the best eluent, different organic solvents were tested. Obtained results showed that among the tested organic solvents, methanol was found to be the superior solvent in comparison with other solvents for

Table 1 Analytical parameters of the proposed method

Analyte	λ_{max} (nm)	Linear range (ng mL^{-1})	Calibration equation	R^2	LOD (ng mL^{-1})	RSD% ($n=6$)
Anthracene	251	0.8–20	$y=0.0894x+0.0416$	0.9977	0.21	4.1
Pyrene	240	2–40	$y=0.0363x+0.0015$	0.9984	0.45	3.9
Phenanthrene	250	3–40	$y=0.0296x+0.0234$	0.9982	0.65	4.2
Fluorene	260	5–120	$y=0.0113x+0.0015$	0.9970	1.66	4.5

Table 2 Concentration data of the different mixtures used in the calibration set for the determination of PAHs

Solution number	Concentration (ng mL ⁻¹)			
	Anthracene	Pyrene	Phenanthrene	Fluorene
1	20	0	0	0
2	0	40	0	0
3	0	0	40	0
4	0	0	0	120
5	10	20	0	0
6	10	0	20	0
7	10	0	0	60
8	0	20	20	0
9	0	20	0	60
10	0	0	20	60
11	5	30	0	0
12	5	0	30	0
13	5	0	0	90
14	0	10	30	0
15	0	10	0	90
16	0	0	10	90
17	15	10	0	0
18	15	0	10	0
19	15	0	0	30
20	0	30	10	0
21	0	30	0	30
22	0	0	30	30
23	10	10	10	0
24	10	10	0	30
25	10	0	10	30
26	0	20	10	30
27	5	20	10	0
28	5	20	0	30
29	5	0	20	30
30	5	10	20	0
31	0	10	20	30
32	5	10	0	60
33	5	0	10	60
34	0	10	10	60
35	5	10	10	30

desorption of analytes from surface of the SDS-coated-Fe₃O₄ NPs. To achieve the highest recovery of the adsorbed PAHs, the effect of the volume of the eluent was also tested. The minimum volume of methanol required for quantitative elution of the retained analytes was 1.0 mL.

Effect of solution volume

The effect of solution volume was examined by pre-concentrating different volumes (50–800 mL) of aqueous solutions spiked with a constant mass of 1.0 µg of each analytes. The obtained results showed that when aqueous solution volume was up to 500 mL, recoveries above 95 % were obtained for the four analytes. Thus, 500 mL was considered to be the maximal enrichment volume for water samples.

Absorption spectra

Figure 3 shows the absorption spectra for individual analytes after magnetic SPE. As can be seen in Fig. 3, an important degree of spectral overlap occurs between the PAHs which may limit the application of conventional calibration methods for analysis of the current PAHs. So PC-PPR, PLS, and LS-SVM were used to obtain quantitative information from the spectra. Spectra of mixtures of PAHs solutions between 325 and 225 nm wavelengths by 1-nm intervals were recorded, and then the data were digitized and stored for late treatment.

Univariate calibration

Under the optimum conditions calibration curves were constructed for four PAHs by enriching 100 mL aqueous solutions and measuring the absorbances at λ_{max} of each analyte. With the overall SPE procedure and spectrophotometric analysis method mentioned above, quantitative parameters such as linear range, correlation coefficient, detection limit

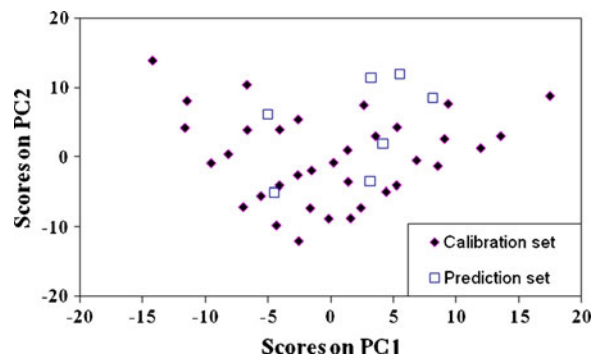


Fig. 4 Score plots for absorption data matrices of the calibration and prediction sets

and relative standard deviation were evaluated and the results are shown in Table 1. It can be seen that the present method has high sensitivity and good precision. The limits of detection were calculated by using signal-to-noise ratio of 3.

Multivariate calibration

The first step in the simultaneous determination of the four analytes by multivariate calibration methods involves constructing the calibration and prediction sets. An experimental design was used to maximize statistically the information content in the spectra. A training set of 35 samples was taken (Table 2). To ensure that the predictions are in the subspace of training set, the score plot of first principal component versus second was sketched and all the samples are spanned with the training set scores (Fig. 4).

Table 4 Statistical parameters obtained by applying the PC-PPR, PLS, and LS-SVM methods to the synthetic mixtures

Method	Analyte	NPC ^a	RMSEP	REP(%)
PC-PPR	Anthracene	5	0.85	12.13
PLS		4	1.16	15.05
LS-SVM		–	1.84	23.88
PC-PPR	Pyrene	2	1.33	9.34
PLS		2	1.92	13.45
LS-SVM		–	2.18	15.23
PC-PPR	Phenanthrene	5	3.13	16.87
PLS		5	5.34	28.77
LS-SVM		–	3.30	17.78
PC-PPR	Fluorene	6	3.39	7.77
PLS		4	3.98	9.13
LS-SVM		–	2.95	6.78

^aNumber of principal component

Table 3 Added and found results of synthetic mixtures of PAHs (in nanograms per milliliter)

Method	Anthracene			Pyrene			Phenanthrene			Fluorene		
	Added	Found	Recovery (%)	Added	Found	Recovery (%)	Added	Found	Recovery (%)	Added	Found	Recovery (%)
PC-PPR	7.0	6.62	94.5	10.0	9.84	98.4	25.0	23.10	92.4	45.0	41.99	93.3
PLS		6.12	87.4		7.78	77.8		18.37	73.5		40.92	90.9
LS-SVM		6.37	91.0		10.70	107.0		21.83	87.3		40.79	90.6
PC-PPR		4.99	99.8		14.07	93.8		21.30	85.2		62.29	95.8
PLS	5.0	3.05	61.0	15.0	11.31	75.4	25.0	22.27	89.1	65.0	62.52	96.2
LS-SVM		5.67	113.4		14.98	99.9		22.92	91.7		63.65	97.9
PC-PPR		13.75	114.6		23.85	95.4		8.61	86.1		23.10	92.4
PLS	12.0	12.42	103.5	25.0	22.62	90.5	10.0	15.46	154.6	25.0	22.73	90.9
LS-SVM		9.26	77.2		21.67	86.7		9.71	97.1		27.29	109.2
PC-PPR		–	–		22.47	112.4		24.48	81.6		48.27	87.8
PLS	0	–	–	20.0	20.06	100.3	30.0	20.13	67.1	55.0	47.51	86.4
LS-SVM		–	–		23.84	119.2		22.45	74.8		53.06	96.5
PC-PPR		8.76	87.6		–	–		16.56	82.8		27.07	90.2
PLS	10.0	9.01	90.1	0	–	–	20.0	16.83	84.2	30.0	26.44	88.13
LS-SVM		8.66	86.6		–	–		18.59	93.0		24.47	81.6
PC-PPR		4.61	92.1		21.99	110.0		–	–		82.45	97.0
PLS	5.0	4.41	88.2	20.0	19.34	96.7	0	–	–	85.0	81.25	95.6
LS-SVM		4.54	90.8		18.80	94.0		–	–		83.61	98.4
PC-PPR		13.90	92.7		9.62	96.2		17.30	86.5		–	–
PLS	15.0	13.17	87.8	10.0	8.91	89.1	20.0	16.65	83.3	0	–	–
LS-SVM		11.34	75.6		12.32	123.2		21.69	108.5		–	–

Table 5 Determination of PAHs in spiked water samples ($N=3$; actual concentrations of anthracene, pyrene, phenanthrene, and fluorene is 5, 10, 10, and 20 ng mL⁻¹, respectively)

Sample	Anthracene		Pyrene		Phenanthrene		Fluorene	
	Found (ng mL ⁻¹)	Recovery (%)	Found (ng mL ⁻¹)	Recovery (%)	Found (ng mL ⁻¹)	Recovery (%)	Found (ng mL ⁻¹)	Recovery (%)
Tap water	4.56 (0.26) ^a	91.2	11.48 (0.43)	114.8	9.39 (0.43)	93.9	18.30 (0.44)	91.5
Mineral water	5.03 (0.09)	100.6	9.46 (0.25)	94.6	8.86 (0.48)	88.6	17.53 (0.63)	87.7
River water	4.83 (0.12)	96.6	9.23 (0.45)	92.3	9.58 (0.40)	95.8	19.36 (0.55)	96.8

^a Standard deviation

In this work, principle component analysis (PCA) was applied as a data pretreatment of the calibration data matrix of the analyte mixtures, and the PC scores were then used as the input of the PPR. When the PCA data reduction procedure is applied prior to the construction of the PPR model, its dimensional effect is to increase the numerical stability of the model construction process and reduce the amount of co-linearity between variables. In addition, PCA allows one to eliminate the irrelevant information such as noise or redundancies present in the data matrix. In this study, spectrophotometric data were employed in PPR to predict the concentrations of the corresponding analytes. The spectrophotometric data, before building the PPR models, were subjected to the principal component analysis and decomposed to PC scores. The PC-PPR models including one to ten PC scores were trained. The lowest RMSECV values were obtained with five, two, five, and six input factors for anthracene, pyrene, phenanthrene, and fluorene, respectively. The chemometrics calibrations were computed with the PC-PPR, PLS, and LS-SVM algorithms, using the correlation for the training set concentration and its current data.

For the evaluation of the predictive ability of multivariate calibration models, the root mean square error

of prediction (RMSEP) and relative error of prediction (REP) can be used: (Table 4)

$$RMSEP = \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5}$$

$$REP\% = \frac{100}{\bar{y}} \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5}$$

where \hat{y} is the predicted concentration in the sample i , y the observed value of the concentration in the sample i , and n is the number of samples in the prediction set.

Determination of PAHs in synthetic mixtures

The predictive ability and validation of the calibration models was assessed using seven synthetic mixtures of four PAHs. The results obtained from simultaneous determination of anthracene, pyrene, phenanthrene, and fluorene by PC-PPR and PLS methods are listed in Table 3. Table 4 shows RMSEP and REP for synthetic series of PAHs mixtures. It can be seen from this table that for anthracene, phenanthrene, and pyrene the

Table 6 Determination of PAHs in the well water samples ($N=3$)

Sample	Anthracene found (ng mL ⁻¹)		Pyrene found (ng mL ⁻¹)		Phenanthrene found (ng mL ⁻¹)		Fluorene found (ng mL ⁻¹)	
	Proposed method	HPLC	Proposed method	HPLC	Proposed method	HPLC	Proposed method	HPLC
1	1.24 (0.27) ^a	1.36	2.68 (0.33)	2.83	BDL	BDL	BDL	BDL
2	4.78 (0.12)	5.23	2.36 (0.44)	2.03	9.58 (0.40)	10.26	BDL	BDL

BDL below the detection limit

^a Standard deviation

statistical parameters of PC-PPR models are superior to that of LS-SVM. In the case of fluorene, LS-SVM results are slightly better than those of PC-PPR. This may be explained by the fact that the PPR method performs a flexible regression in a low-dimensional variable space, contrarily to the SVM regression which uses a fixed transfer function (radial basis function). The PC-PPR models were consistently better than PLS, as shown by the resulting figures of merit for these models (Table 4). Since the PPR analysis takes into account both linearity and nonlinearity in the model construction, therefore it yielded more predictive models than PLS analysis.

Analysis of real water samples

The proposed methodology was applied for the determination of anthracene, phenanthrene, fluorine, and pyrene in different water samples including, tap water, mineral water and river water. The obtained results are given in Table 5. The relative recoveries for the spiked samples were in the range of 87–114 %. Also this method was applied to the determination of PAHs in two well water samples. In addition, the prediction results using PC-PPR were compared with HPLC method. Comparisons of the prediction capability of the proposed method and the HPLC method for determination of PAHs are presented in Table 6. The results demonstrated that the proposed method was suitable for the determination of PAHs in real water samples.

Conclusions

A novel SPE method based on SDS-coated Fe₃O₄ NPs was developed for the preconcentration of four PAHs in environmental water samples without the need for chromatographic separation. The use of NPs endowed the SPE method with high extraction capacity and preconcentration factors. The magnetic separation greatly improved the separation rate while avoided the time-consuming column passing or filtration operation. PC-PPR calibration method was found effective for simultaneous determination of PAHs in water samples. Multivariate calibration methods offer a simple and a reasonable substitute for expensive liquid chromatography for PAHs quantification in water samples. The

results show the strong potential of PC-PPR, as a multivariate calibration method, to be applied to spectral data for multicomponent determinations.

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