

اندازه گیری همزمان اسپکتروفتومتری هیدروکربن های آروماتیک چند حلقه ای با استفاده از روش تصحیح عمودی سیگنال و تبدیل موجک و کمترین مربعات جزئی بعد از پیش تغلیظ استخراج مایع-مایع کمک شده با نمک زنی

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Simultaneous Spectrophotometric Determination of Some Polycyclic Aromatic Hydrocarbons Using Chemometrics Methods after Their Preconcentration by Salting-Out Assisted Liquid-Liquid Extraction

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چکیده

یک روش پیش پردازش سیگنال سریع، قدرتمند، رضایت بخش و اصلاح شده که ترکیبی از تبدیلی موجک با اصلاح سیگنال عمودی (OSC) است برای پیش پردازش داده های اسپکتروفتومتری نفتالن، آنتراسن و پیرن به عنوان آنالیت ها پس از پیش تغلیظ آنها توسط روش استخراج مایع-مایع کمک شده با اثر نمک زنی (SALLE) مورد استفاده قرار گرفته است. حلال استخراج مخلوط در آب (۱،۰ میلی لیتر استونیتریل) و مقدار مناسب نمک (۱،۰ گرم از $(\text{NH}_4)_2\text{SO}_4$) به محلول آبی (۴،۰ میلی لیتر) اضافه می شود و با استفاده از یک ورتکس که موجب جداسازی فاز می شود، حل می شود. آنالیت های هدف موجود در نمونه به حلال استخراج کننده وارد می شوند. بعد از استخراج جذب مخلوط آنالیت ها در ناحیه ۴۰۰-۲۰۰ نانومتر اندازه گیری می شود. پارامترهای مؤثر بر این روش استخراجی مورد مطالعه و بهینه سازی قرار گرفت. روش پیش پردازش تبدیلی موجک و تصحیح عمودی سیگنال برای برداشتن نویز داده های اسپکتروفتومتری و کوپل با روش مدل سازی کمترین مربعات جزئی برای اندازه گیری همزمان آنالیت های مطالعه شده بعد از فرآیند استخراج مایع-مایع کمک شده با اثر نمک زنی استفاده شده است. ارقام شایستگی روش مطالعه شده با استفاده از روش سیگنال خالص آنالیت تعیین گردید. مدل ارائه شده در این کار دارای توانایی پیشگویی خوب با ریشه میانگین مربعات خطا پیشگویی (RMSEP) به ترتیب برای نفتالن، آنتراسن و پیرن 0.03 ، 0.024 و 0.013 است. روش ساده PLS-WOSC با موفقیت برای اندازه گیری همزمان سه آنالیت در نمونه های پساب آبی استفاده شد.

واژه های کلیدی

اندازه گیری همزمان؛ موجک-تبدیلی عمودی سیگنال؛ استخراج مایع-مایع کمک شده با نمک زنی.

Abstract

A rapid, powerful, satisfactory and modified signal-pre-processing method that is a hybrid of the wavelet transform with orthogonal signal correction (OSC) is used for pre-processing of spectrophotometric data of naphthalene, anthracene and pyrene as analytes after their preconcentration by salting-out assisted liquid-liquid extraction (SALLE) method. Water-miscible extraction solvent (1.0 mL of acetonitrile) and a suitable amount of salt (1.0 g of $(\text{NH}_4)_2\text{SO}_4$) are added into the aqueous solution (4.0 mL) and dissolved using a vortex leading to the occurrence of phase separation. The target analytes in the sample was extracted into the water-miscible extraction solvent. After extraction, the absorbance of the analytes mixture was measured in the wavelength range of 200-400 nm. The wavelet orthogonal signal correction (WOSC) was established for denoising and reduction of spectrophotometric data and hybrid with partial least squares (PLS) regression method for simultaneous determination of the studied analytes after the SALLE procedure. The influence of various parameters, such as extraction solvent and volume, type and amount of salt, vortex time and sample pH were studied and

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optimized. The net analyte signal (NAS) method was used for calculating figures of merit. Linear range (LR) of calibration graphs for naphthalene, anthracene and pyrene were between 0.20 - 2.00, 0.10 - 1.50 and 0.07 -1.00 $\mu\text{g mL}^{-1}$, respectively. The obtained model showed good prediction capability with root mean square error of prediction (RMSEP) of 0.030, 0.024 and 0.013 $\mu\text{g mL}^{-1}$ for naphthalene, anthracene and pyrene, respectively. The simple WOSC-PLS method has been successfully applied for the simultaneous determination of these analytes in the spiked wastewater samples.

Keywords

Simultaneous Determination; Wavelet Orthogonal Signal Correction; Salting-Out Assisted Liquid-Liquid Extraction.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic pollutants known for their teratogenic, carcinogenic and mutagenic potential; hence, their monitoring is of importance to the process [1, 2]. The simultaneous spectrophotometric determination of several active components in a mixture can be a major drawback, specifically for components that have become excessively overlapped as a result of similar analytical characteristics. Also, it is not easy to determine these PAHs with conventional methods [3]. Nowadays, rapid-scanning technique spectrophotometers are used in combination with chemometric methods to solve the overlapping spectrum. However, the obtained data have complex structures, which are contaminated by noise and redundancy and can potentially cause nonlinearities [4, 5]. To improve the predictive capability of multivariate calibration models, the first data are often pre-processed for removal of unnecessary information.

A review of several literatures showed that a variety of techniques such as gas chromatography- mass- spectrometry [6] high performance liquid chromatography [7, 8] liquid chromatography [9] and excitation-emission fluorescence spectroscopy [10] have been reported for the determination of PAHs. These methods have some serious shortcomings, such as being a time-consuming and complicated procedure, use of hazardous organic solvents, as well as produce waste with a high percentage of organic solvents. Spectrophotometric methods are the most popularly used methods due to common availability of instrumentation, wide application range, experimental speed, precision and accuracy of the technique [1, 2, 11].

Pre-processing of OSC [12-14] is aimed at eliminating undesired information in the response matrix, to make it mathematically orthogonal to the concentration matrix. The wavelet transform is an excellent mathematical technique, created purposely for the denoising of raw spectral data [15]. In PLS [16-19] regression, errors in both the concentrations and analytical signals were considered in the calculation to improve predictive ability. The SALLE is based on liquid-liquid extraction, in which a suitable amount of salt was added to a mixture of water sample and

water-miscible solvent. The mixture solution was then shaken until the salt was dissolved, resulting in a separation of the solvent from the mixture and thus, the formation of a two-phase system and simultaneously, the target analytes were separated into the organic phase [7, 20-24]. This research investigated the possibility of having SALLE and WOSC-PLS hybrids for the simultaneous preconcentration and spectrophotometric determination of some PAHs. The WOSC [16, 25-27] as a pre-processing technique prior to modelling, can improve the predictive ability. Generally, it can be observed that the outcome of the newly proposed WOSC-PLS method was better than that of the OSC-PLS and PLS model. The WOSC-PLS method was designed for simultaneous spectrophotometric determination of PAHs of interest in the wastewater samples.

2. EXPERIMENTAL

2.1. Chemicals and materials

Acetonitrile, tetrahydrofuran (THF), ethanol, acetone, isopropanol, ammonium sulfate, sodium chloride, sodium carbonate, were purchased from Merck Chemical (Darmstadt, Germany). All solutions were prepared with deionized water (Milli-Q system, Millipore, USA). Naphthalene, anthracene and pyrene were obtained from Sigma-Aldrich (USA). The universal buffer solution was prepared by Ref [28].

2.2. Instrumentation and software

A Perkin Elmer Lambda 25 spectrophotometer (1 nm resolution, 1-mm path length, Integration Time 0.08 s) equipped with a 350 μL quartz microcell was employed for all experimental. All evaluations for this work were carried out in MATLAB (Version 7.8.0 (R2009), Mathwork Inc.) on a personal computer. PLS, OSC, and WOSC estimates were obtained using the PLS-Toolbox version 4.0 from Eigenvector Research Inc.

2.3. Sample preparation

Standard stock solutions of naphthalene, anthracene and pyrene were prepared by dissolving each analyte in methanol with concentration of 100 $\mu\text{g mL}^{-1}$. Working standard solutions at different concentrations were freshly

prepared by mixing the appropriate volumes of the stock solutions and diluting such with deionized water. Wastewater samples were collected from Shazand Petrochemical Corporation. Samples were filtered using a 0.45 μm membrane filters and adjusted to pH 7.0 prior to extraction.

2.4. SALLE procedure

In this study, 4.0 ml of aqueous sample containing PAHs was transferred into a test tube with conical bottom. 1.0 ml of acetonitrile as extraction solvent and 1.0 g of $(\text{NH}_4)_2\text{SO}_4$ were added, and the mixture was vortexed using a vortex mixer at 3000 rpm for 3.0 min. The cloudy mixture was centrifuged for 2.0 min at 4000 rpm. Finally, 300 μl of the organic phase was withdrawn and transferred into a 350 μl spectrophotometric cell. Absorbance data were taken in the range of 200–400 nm against acetonitrile as blank. The spectra were analyzed by the WOSC-PLS method for simultaneous determination of PAHs of interest.

3. RESULT AND DISCUSSION

In this study, the effect of various parameters on the extraction efficiency of the SALLE procedure of analytes were studied and optimized. The absorption spectra of naphthalene, anthracene, pyrene, and their mixture are shown in Fig. 1. The figure shows, clear overlapping which could not be easily resolved by conventional methods. To resolve this problem, a useful and satisfactory technique such as the WOSC-PLS regression which presents versatility results is used. Thereafter, at optimal experimental conditions, WOSC-PLS was used as a useful chemometric method in the analysis of overlapping spectra and simultaneous spectrophotometric determination of PAHs of interest in the prepared mixtures.

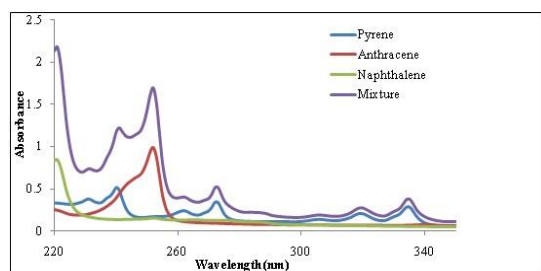


Fig. 1. The absorption spectrum of 0.2 $\mu\text{g mL}^{-1}$ of pyrene, 0.2 $\mu\text{g mL}^{-1}$ of Anthracene, 0.2 $\mu\text{g mL}^{-1}$ naphthalene and 0.21 $\mu\text{g mL}^{-1}$ of pyrene, 0.3 $\mu\text{g mL}^{-1}$ of Anthracene and 0.48 $\mu\text{g mL}^{-1}$ naphthalene in a mixture after SALLE procedure.

3.1. Optimization of extraction conditions

3.1.1. Selection of the organic solvent

In most sample preparation methods, the selection of a suitable extracting solvent is a key step. The

organic solvent must be very polar, miscible in aqueous phase and induce phase separation upon addition of suitable inorganic salts [29] this inference is wrong and applies only to the Salting-out assisted liquid–liquid extraction procedure. Various water-miscible organic solvents, such as acetonitrile, tetrahydrofuran (THF), isopropanol, ethanol, acetone, and binary mixture, were tested as the extracting solvent, except for acetone and ethanol, in which the two phase system was not observed (Fig. 2). Under similar conditions, the results showed that acetonitrile exhibited the highest extraction recoveries when compared with the other solvents. Thus, acetonitrile was chosen throughout the study.

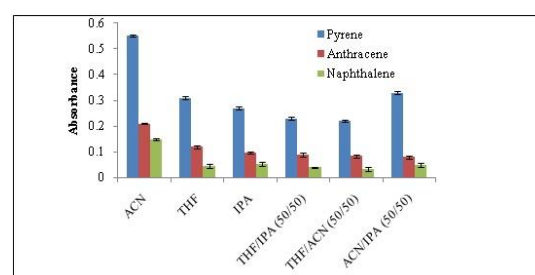


Fig. 2. Effect of a water-miscible organic solvent on the extraction of PAHs of interest. Extraction conditions: extraction solvent volume, 1.0 mL; salt concentration, 1.0 g; vortex time, 3 min; IPA, isopropanol; ACN, acetonitrile; and THF, tetrahydrofuran.

3.1.2. Study of acetonitrile volume

The effect of acetonitrile volume on extraction was considered in the range of 0.8–2.0 mL (Figure 3). As can be seen, the highest extraction efficiency was obtained in a 1.0 mL volume of acetonitrile.

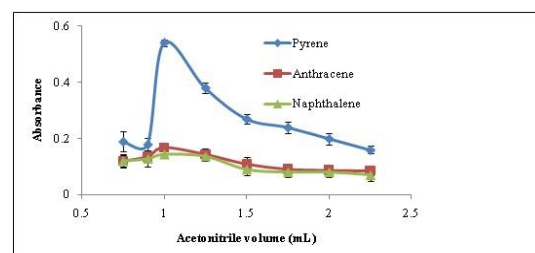


Fig. 3. Effect of acetonitrile volume on the extraction of PAHs of interest. Extraction conditions: extraction solvent, acetonitrile; salt amount, 1.0 g and vortex time, 3 min.

3.1.3. Effects of salt type and amount

In SALLE, the solubility of hydrophilic compounds and organic solvent in the aqueous phase decreased on addition of salt and consequently, increased the transfer of analytes into the organic phase. In order to obtain phase separation and highest extraction recoveries, different salts, including sodium chloride,

ammonium sulfate, and sodium carbonate were evaluated. The results showed that the extraction recovery with ammonium sulfate was higher than that with other salts. Afterwards, the effect of ammonium sulfate concentration on extraction recoveries was tested by adding various amounts in the range 0.75-2.00 g in the aqueous sample solution. Fig. 4 shows that the extraction efficiency of the three analytes were improved as the amount of salt increased from 0.75-1.00 g and remained constant upon addition of higher amounts of salt. Thus, 1.00 g of ammonium sulfate was selected as the optimal concentration throughout the study.

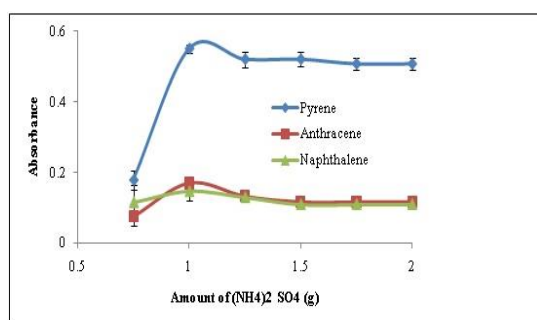


Fig. 4. Effect of amount salt on the extraction of PAHs of interest. Extraction conditions: extraction solvent; acetonitrile; extraction solvent volume, 1.0 mL; vortex time, 3 min.

3.1.4. Effect of sample pH

The effect of sample pH on extraction recoveries was evaluated in the range 2.0-11.0. The results obtained clearly show that the quantity of analytes extracted was constant in the studied pH range. The reason of this behavior can be attributed to the studied analytes (Non-polar compounds), which do not participate in acid-base equilibriums. Consequently, the pH of sample solution was not adjusted for subsequent studies. Therefore, no pH adjustment was performed throughout the study.

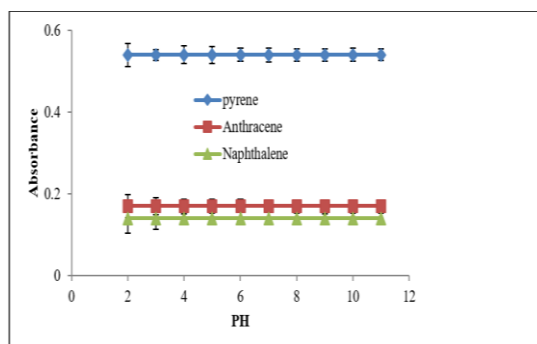


Fig. 5. Effect of PH on the extraction of PAHs of interest. Extraction conditions: extraction solvent; acetonitrile; extraction solvent volume, 1.0 mL; vortex time, 3 min.

3.1.5. Effect of vortex agitation time

Stimulation of the sample mixture also plays a major role, possibly the kinetics of the extraction. Vortexing increases contact between acetonitrile and analytes and also, dissolve the added salt. Therefore, a vortex time was investigated in the range of 1–5 min, and efficiency extraction recoveries were obtained at a vortex time of 3 min. It is evident from Figure 5, that 3 min was selected as the optimal vortex time in further experiments.

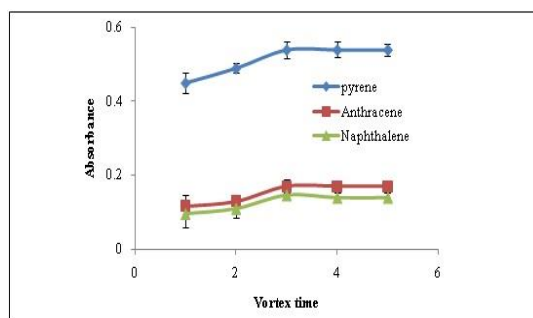


Fig. 6. Effect of vortex time on the extraction of PAHs of interest. Extraction conditions: extraction solvent, acetonitrile; extraction solvent volume, 1.0 mL; salt concentration, 1.0 g.

3.1.6. Effect of centrifugation time

In the proposed method, a centrifuge time of 2.0 min at 4000 rpm was selected as optimum, as complete separation occurred within this time.

3.2. Individual calibration

Individual calibration curves were constructed with several points as absorbance versus naphthalene, anthracene and pyrene concentration. The linear regression equation for naphthalene in the concentration range of 0.2- 2.0 $\mu\text{g mL}^{-1}$, was $A = 0.571C + 0.03$ for anthracene in the concentration range of 0.1-1.5 $\mu\text{g mL}^{-1}$; the equation was $A = 2.26C + 0.09$ and for pyrene, for the concentration range of 0.07-1.0 $\mu\text{g mL}^{-1}$ the equation was $A = 3.12C + 0.025$. The detection of limits were 0.017, 0.016 and 0.014 $\mu\text{g mL}^{-1}$ for naphthalene, anthracene and pyrene, respectively, and were calculated using the NAS method [30-32].

3.3. Multivariate calibration

The present similarity spectra of the three PAHs could be resolved using multivariate calibration WOSC-PLS. To have a satisfactory model, 15 mixtures were designed as the calibration set. The model calibration was verified with six synthetic mixtures containing naphthalene, anthracene and pyrene. Thereafter, chemometric models such as PLS, OSC-PLS, and WOSC-PLS algorithms were estimated, using the correlation for the training set

concentration and its current data. All calibration and validation of synthetic mixtures were constructed in accordance with the SALLE procedure previously mentioned. The spectral zone between 200 and 400 nm with scan rate of 450 nm was measured against acetonitrile as blank. Absorbance data spectral region between 240 and 350 nm was chosen for the modelling, as this is the region with maximum spectral information on the mixed PAHs of interest.

3.4. WOSC-PLS method

To ensure the predictive ability of the calibration model, raw spectral data are often denoised prior to construction of the model. In this study, two pre-processing approaches (OSC and WT), combined for building the chemometric calibration were chosen due to pre-processing of the raw spectral data with WOSC correction being more of the unnecessary spectral data than that filtered with OSC or WT alone. A couple of wavelet with orthogonal signal correction was employed in this study, which is very effective in improving the predictive ability of the PLS model in comparison to other methods used. Also, PLS or OSC-PLS greatly contributed to the success of obtaining a satisfactory result using the WOSC-PLS technique, with several parameters such as wavelet functions, decomposition level (L) and the number of PLS factors tested [16]. There is no theoretical formula about the selection of the number of OSC components, because this parameter depends on the complexity of the problem. The selection of the number of OSC components was empirical; one to three numbers of OSC components were tested in this case. The lowest RSEP value was obtained with 3 OSC

components. In this research, various wavelet functions (Coiflet 1, 2, ..., 5, Daubechies 4, 5, 6, and Symmlet3, 4, 5, ..., 8) as well as decomposition levels (L=1-6) were investigated. To estimate and find the optimum values selection of the mentioned parameters, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be applied. Therefore, optimal value parameters were selected in this method as Symmlet3, L=1 and number of PLS factors=4.

3.5. Selection of optimum number of factors

To help determine significant latent variables in the PLS calibration model, cross validation methods were used. The predicted concentration of the calibration samples were calculated and compared with the actual concentrations, and the predictive residual error sum of squares (PRESS) was computed. A graph of PRESS versus number of factors for each sample reveals a minimum value for optimum number of factors. For estimating the fewest number of factors, F-statistics test was used in determining the significance [5]. The optimum number of factors was achieved as 4 for PAHs interest.

3.6. Determination of naphthalene, anthracene and pyrene in synthetic mixture

The predictive ability and verification of WOSC-PLS method was determined using 6 three-component PAHs mixtures interest. The results obtained from simultaneous determination of naphthalene, anthracene and pyrene after SALLE by WOSC-PLS method are shown in Table 1.

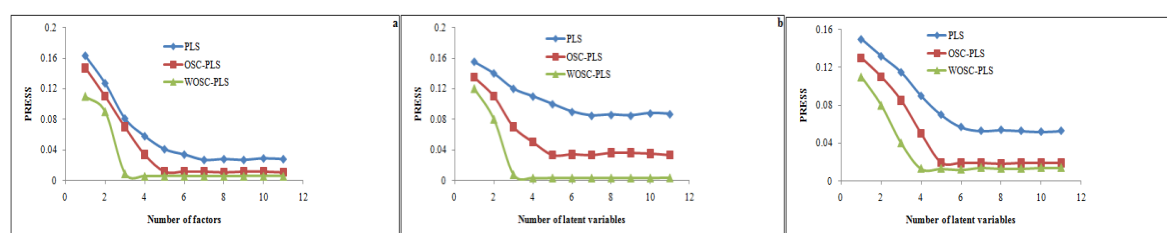


Fig. 7. Plots of PRESS versus number of factors by PLS, OSC-PLS and WOSC-PLS (a) Pyrene, (b) Anthracene, and (c) Naphthalene.

Table 1. Added and found results of synthetic PAHs mixtures interest ($\mu\text{g mL}^{-1}$).

Naphthalene			Anthracene			Pyrene		
Added	Found	Recovery (%)	Added	Found	Recovery (%)	Added	Found	Recovery (%)
0.30	0.33	110.00	0.20	0.21	115.00	0.12	0.14	108.33
0.56	0.57	101.80	0.40	0.38	92.50	0.26	0.27	96.15
0.83	0.82	98.80	0.60	0.56	96.66	0.40	0.40	100.00
1.00	0.97	97.00	0.74	0.70	102.70	0.50	0.51	102.00
1.20	1.25	104.16	0.87	0.92	96.55	0.60	0.65	96.66
2.00	1.94	97.00	1.50	1.48	100.00	1.00	0.95	102.00

Table 2. Statistical parameters obtained by applying the three methods to the synthetic mixtures.

Methods	PLS			OSC-PLS			WOSC-PLS		
	Naphthalene	Anthracene	Pyrene	Naphthalene	Anthracene	Pyrene	Naphthalene	Anthracene	Pyrene
NLVs ^a	7	7	7	5	5	5	4	4	4
RMSEP	0.110	0.119	0.066	0.057	0.075	0.044	0.030	0.024	0.013
RSEP (%)	9.78	14.37	11.86	5.10	9.06	8.05	2.70	2.87	2.38
R ²	.9900	.9813	.9847	.9908	.9825	.9886	.9972	.9967	.9981

^a Number of latent variables.**Table 3.** Analytical figures of merit obtained by the NAS method.

Component	Selectivity	Sensitivity	LOD (µg mL ⁻¹)	LOQ (µg mL ⁻¹)
Naphthalene	0.0773	0.1826	0.017	0.055
Anthracene	0.0387	0.1897	0.016	0.053
Pyrene	0.1582	0.0565	0.014	0.048

Table 4. Accuracy data for naphthalene, anthracene and pyrene spiked in a wastewater sample.

Compound	Add (µg mL ⁻¹)	Found (µg mL ⁻¹)	Recovery (%)	RSD (%) (n=4)
Naphthalene	0.0	N.D	-	-
	0.60	0.60	100.00	2.14
	0.95	0.96	101.05	4.40
	1.32	1.33	100.75	3.15
Anthracene	0.0	N.D	-	-
	0.35	0.34	97.14	3.55
	0.85	0.84	98.82	3.80
	0.93	0.96	103.22	2.60
Pyrene	0.0	N.D	-	-
	0.27	0.27	100.00	2.72
	0.70	0.68	97.14	3.70
	0.82	0.74	90.24	4.17

3.7. Evaluation of the performance of the test methods

To assess the predictive power of WOSC-PLS technique, three methods (PLS, OSC-PLS, and WOSC-PLS) were used with a set of synthetic mixture samples. To verify the predictive ability of these models, the RMSEP and RSEP can be used (Table 5).

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_{pred} - y_{obs})^2}{n}} \quad (1)$$

$$RSEP(\%) = \sqrt{\frac{\sum_{i=1}^n (y_{pred} - y_{obs})^2}{\sum_{i=1}^n (y_{obs})^2}} \quad (2)$$

Where y_{pred} is the predicted concentration, y_{obs} observed value of the sample, and n is the number of samples in the validation set. The values RMSEP were minimized when optimum value of LVs is 7, 5, and 4 for PLS, OSC-PLS, and WOSC-PLS; thus, 4 was chosen as the optimum number of LVs for the training set of the WOSC-PLS method. Table 2 shows the RMSEP and RSEP for the three methods. This method clearly reveals better results with high statistical quality

and minimum prediction error in the newly proposed WOSC-PLS model.

3.8. Analytical characteristics of the method

Quantitative specifications of the developed method were achieved under optimum conditions. Calculation of the NAS, allows the calculation of several figures of merit (selectivity, sensitivity, limit of detection (LOD), limit of quantification (LOQ), useful for method comparison and to describe the quality of the proposed multivariate calibration (Table 3). A linear range (LR) of calibration graphs were determined for naphthalene, anthracene and pyrene, between 0.20 - 2.00, 0.10 - 1.50 and 0.07 - 1.00 µg mL⁻¹, respectively, and also the limits of detection values of 0.017, .016 and 0.014 µg mL⁻¹ were calculated according to the NAS method. The enrichment factors of the chosen PAHs, computed as the ratio of the slope preconcentration samples to those obtained without preconcentration, were 25.70 for naphthalene, 34.80 for anthracene and 38.10 for pyrene. The repeatability of the methods

was investigated using three repeat measurements of a $0.4 \mu\text{g mL}^{-1}$ PAHs were 3.10, 2.90 and 2.60 % for naphthalene, anthracene and pyrene, respectively.

3.9. Applications

This newly proposed method has been applied in the simultaneous preconcentration and determination of naphthalene, anthracene, and pyrene after SALLE procedure, under optimal conditions in the different wastewater samples. The validity of the WOSC-PLS method was determined by analysis of the samples spiked with a known concentration of PAHs interest. The satisfactory results are shown in Table 4. This percentage recovery of the proposed methods shows the ability to predict concentration of PAHs interest in the wastewater samples of matrixes.

3.10. Comparison of the proposed method with other methods

A comparison of the figures of merit of the WOSC-PLS method with some of the previously reported methods of the analytes is shown in Table 5. In addition, the proposed pre-processing approach led to enhancement of the PLS model performance. The proposed method rates best in comparison with other approaches because it is simple, cheap, powerful, produces better results, non-polluting, possesses much simpler calibration models, highly sensitive, and similar repeatability. These results show that the WOSC method is successful at the simultaneous spectrophotometric determination of overlapping peaks.

4. CONCLUSION

In this research, a modified, simple, useful and satisfactory method was applied for pre-processing data spectral raw and simultaneous spectrophotometric determination of these compounds in various environmental water samples. The simultaneous spectrophotometric determination of naphthalene, anthracene, and pyrene is extremely challenging and complex due to spectral interferences observed in the absorption spectra of these components. The results show how satisfactory and reliable the SALLE method could be in simultaneous extraction and preconcentration of the PAHs interest. Generally, it can be observed that the newly proposed "WOSC-PLS" gave better outcome than the OSC-PLS and PLS models. Future research on the WOSC-PLS should focus on improving this approach in relation with variable selection techniques.

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Table 5. Comparison of analytical parameters of the proposed SALLE method with some of the methods reported in literature.

Method	Analyte	Instrument	LOD ($\mu\text{g mL}^{-1}$)	RSD (%)	Recovery (%)	Refs.
UDSA-DLLME ^a	Naphthalene	GC-MS	-	-	-	33
	Anthracene		2.80×10^{-5}	4.3	93-111	
	Pyrene		6.30×10^{-5}	9.1	93-107	
SPME ^b	Naphthalene	GC-MS	3.00×10^{-6}	< 20	-	34
	Anthracene		2.00×10^{-5}	< 20	-	
	Pyrene		1.00×10^{-6}	< 20	-	
USAEME ^c	Naphthalene	GC-FID	2.00×10^{-5}	5.8	59.2	35
	Anthracene		5.00×10^{-5}	5.2	74.8	
	Pyrene		5.00×10^{-5}	7.7	77.6	
SAALLME ^d	Naphthalene	HPLC-UV	8.34×10^{-6}	<6.6	95.0-98.8	7
	Anthracene		2.20×10^{-7}	<7.2	92.0-96.8	
	Pyrene		-	-	-	
SALLME ^e	Naphthalene	UV/Vis	0.20 – 2.00	3.1	100.00 - 101.05	Proposed
	Anthracene		0.10 – 1.50	2.9	97.14 – 103.22	method
	Pyrene		0.07 – 1.00	2.6	90.24 – 100.00	

^a Up-and-down shaker-assisted dispersive liquid-liquid microextraction. ^bSolid-phase microextraction. ^cUltrasound-assisted emulsification microextraction. ^dSalt-and air- assisted liquid-liquid microextraction. ^eSalting-out assisted liquid-liquid extraction.

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