Chemometrics-assisted excitation–emission fluorescence spectroscopy on nylon-attached rotating disks. Simultaneous determination of polycyclic aromatic hydrocarbons in the presence of interferences

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Abstract

This work presents a green and very simple approach which enables the accurate and simultaneous determination of benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene, benz[*a*]anthracene, and chrysene, concerned and potentially carcinogenic heavy-polycyclic aromatic hydrocarbons (PAHs) in interfering samples. The compounds are extracted from water samples onto a device composed of a small rotating Teflon disk, with a nylon membrane attached to one of its surfaces. After extraction, the nylon membrane containing the concentrated analytes is separated from the Teflon disk, and fluorescence excitation-emission matrices are directly measured on the nylon surface, and processed by applying parallel factor analysis (PARAFAC), without the necessity of a desorption step. Under optimum conditions and for a sample volume of 25 mL, the PAHs extraction was carried out in 20 min. Detection limits based on the IUPAC recommended criterion and relative errors of prediction were in the ranges 20-100 ng L^{-1} and 5-7 %, respectively. Thanks to the combination of the ability of nylon to strongly retain PAHs, the easy rotating disk extraction approach, and the selectivity of second-order calibration, which greatly simplifies sample treatment avoiding the use of toxic solvents, the developed method follows most green analytical chemistry principles.

Keywords: Rotating disk extraction; Nylon membrane; Excitation-emission fluorescence matrices; Second-order calibration; Polycyclic aromatic hydrocarbons

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of bioaccumulative and toxic organic molecules that consist of two or more fused benzene rings. Humans are exposed to PAHs through different sources (wild fires, coal tar, grilled food, industrial processes, transportation, energy production, tobacco smoke, etc.). Because many PAHs have been identified as carcinogenic, mutagenic or teratogenic, the health risk involved may be very serious [1]. In this context, it is not surprising that continuous efforts are devoted to developing methods for PAH quantification, within the framework of green chemistry principles [2,3]. In fact, there is an increasing consciousness of the need to reduce the negative impact of certain analytical methodologies on the environment, and it is notable that one of the most important current trends in analytical chemistry is the development of new eco-friendly and sustainable methods, with no compromise of their good performances.

Most methods for the determination of PAHs in environmental samples are based on chromatographic techniques: high-performance liquid chromatography (HPLC) with either fluorescence or mass spectrometry (MS) detection, and gas chromatography (GC) with MS detection [4]. Chromatographic methods for determination of PAHs in water do not significantly differ from those applied to either soil or air [4]. However, since the levels of PAHs to quantify are very low, analyte enrichment is a prerequisite for the analysis of water samples. Several pre-concentration techniques have been developed for this purpose, including liquid-liquid extraction, solid-phase extraction (SPE), solid-phase microextraction, stir-bar sorptive extraction, and membrane extraction systems. In 2009,

Richter *et al.* introduced an alternative and very useful extraction method called rotating disk sorptive extraction (RDSE) [5]. The typical RDSE technique consists of the extraction of selected analytes onto a rotating Teflon disk coated with a sorbent phase (e.g. polydimethylsiloxane film, octadecyl membrane) in one of its sides, with several advantages over traditional extraction procedures already discussed [5–8]. In addition to be a very simple, rapid and inexpensive approach, other advantages of the RDSE method can be mentioned: (1) the architecture of the device enables a convenient surface-area-to-volume ratio, (2) extractions are carried out from small amounts of aqueous samples, (3) the recirculating regime prevents the collapse of the filter in complex samples, allowing the continuous contact between solid and liquid phases, (4) the fact that the extraction phase is only in contact with the liquid sample permits one to stir at high speeds, and (5) the adsorptive phase is easily replaceable, allowing the use of either commercial or laboratory-synthesized sorbents.

In the present report, a new strategy is proposed which involves, for the first time, a nylon membrane attached to an RDSE device, aimed at the determination of selected heavy PAHs, namely benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DBA), benz[*a*]anthracene (BaA) and chrysene (CHRY). According to the International Agency for Research on Cancer (IARC), BaP and DBA are classified as belonging to group 1 (carcinogenic to humans) and to group 2A (probably carcinogenic to humans) respectively, being the most serious PAH pollutants. The remaining studied compounds, BaA and CHRY, are included in the 2B group, indicating that they are possibly carcinogenic to humans.

Taking advantage of the known ability of the nylon membrane to retain and concentrate PAHs in its surface [9,10], the indicated analytes were simultaneously extracted from the sample with a nylon-based RDSE device, and then determined by

excitation-emission fluorescence matrices (EEFMs), directly recorded on the surface of the solid substrate. Neither organic solvents nor auxiliary reagents are involved in the experiments, and the required equipment can be found in laboratories of low complexity. Subsequently, the chemometric algorithm parallel factor analysis (PARAFAC) [11], which achieves the second-order advantage [12], was applied to the solid-phase EEFMs, in order to develop a fast and reliable procedure for the determination of the four investigated PAHs. The selectivity of the method was evaluated with solutions containing the four analytes and four additional PAHs which have solid-surface fluorescence spectra significantly overlapped with those of the studied analytes.

2. Experimental

2.1. Reagents and solutions

BaP, DBA, BaA, CHRY, benzo[*b*]fluoranthene (BbF), benzo[*g,h,i*]perylene (BghiP), indeno[1,2,3-*d*]pyrene (IcdP), and pyrene (PYR) were purchased from Aldrich (Milwaukee, WI). Methanol was obtained from Merck (Darmstadt, Germany). All reagents were of high-purity grade and used as received. Stock solutions of all PAHs of about 100 μg mL^{-1} were prepared in methanol. From these solutions, more diluted methanol solutions (ranging from 50 to 250 ng mL^{-1}) were obtained. Working aqueous solutions were prepared immediately before their use by taking appropriate aliquots of methanol solutions, evaporating the methanol by use of nitrogen and diluting with water to the desired

concentrations. The PAHs were handled with extreme caution, using gloves and protective clothing.

2.2. Apparatus

Fluorescence measurements were carried out on a PerkinElmer (Waltham MA, USA) LS 55 luminescence spectrometer equipped with a xenon discharge lamp, using excitation and emission slit widths of 5 nm. The photomultiplier tube voltage (PMT) was set at 650 V. The data matrices were collected varying the excitation wavelength between 250 and 367 nm each 3 nm, and registering the emission spectra from 370 to 480 nm each 0.5 nm. A magnetic stirrer HI 190M Hanna (Woonsocket, RI, USA) with speed control was used for the PAHs extraction.

2.3. Rotating disk nylon extraction

The preparation of the rotating disks and the general procedure was similar to that previously described [9,10]. Briefly, a 0.2 μm pore size nylon membrane (Varian, Seattle, WA, USA) was attached with a double-coated sticking tape to one side of a Teflon disk (1.5 cm diameter) containing a magnetic stirring bar (Teflon-coated Micro Stir bar from VWR International, Inc., Radnor, PA, USA). The rotating disk with the attached nylon phase was placed inside a beaker containing 25 mL of aqueous PAHs samples, and the disk was rotated at 1250 rpm for 20 min at room-temperature. After extraction, the nylon membrane was removed from the disk, and placed in a laboratory-made membrane holder.

The latter was then introduced into the spectrofluorimeter, in such a way that the angle formed between the excitation and emission beams was 90°, with an incident angle of 45°.

2.4. Chemometric analysis over the nylon surface

Previous to the second-order calibration experiment, the linear relation of the fluorescence signals for BaP, DBA, BaA and CHRY with concentrations was investigated under the employed experimental conditions. The results indicated that linearity is maintained at least up to 600 ng L^{-1} for the four investigated PAHs, and no attempts were made to establish the upper concentration of the linear range. A calibration set of 10 samples containing the four analytes in the ranges 50-300 ng L^{-1} (for BaP and BaA) and 50-600 ng L^{-1} (for DBA and CHRY) was prepared from the corresponding working solutions (Table 1). Eight samples of the set corresponded to the concentrations provided by a two-level half-factorial design (i.e., 2^{4-1} samples). One of the remaining samples corresponded to a blank solution ($C_{BaP} = C_{DBA} = C_{BAA} = C_{CHRY} = 0$), and the remaining sample contained the studied analytes at intermediate concentrations ($C_{BaP} = C_{BaA} = 150$ ng L^{-1}; $C_{DBA} = C_{CHRY} = 300$ ng L^{-1}). Each sample was subjected to the RDSE procedure and the EEFM measurement described above, and the obtained EEFMs were then analyzed with second-order multivariate calibration. The spectral ranges 250-320 nm (excitation) and 380-480 nm (emission) for the four analytes were chosen after a suitable consideration of the spectral regions corresponding to their maximum signals, while avoiding useless background responses, which may be possibly due to intrinsic impurities of the nylon membrane or to physical dispersion effects.

Table 1
Composition of the samples used in the calibration set[a].

Sample	BaP	CHRY	DBA	BaA
1	0	0	0	0
2	50	100	600	300
3	300	100	600	50
4	50	600	100	300
5	300	100	100	300
6	300	600	600	300
7	50	600	600	50
8	300	600	100	50
9	50	100	100	50
10	150	300	300	150

[a] All concentrations are given in ng L^{-1}.

161

162 A set of 13 validation samples, different from the calibration ones, was prepared and
163 processed in a similar way as the calibration solutions. The concentrations of the analytes in
164 the validation set were selected at random from the corresponding calibration ranges.

165 As will be demonstrated below, different PAHs, namely BbF, BghiP, IcdP, and
166 PYR have fluorescence signals that significantly overlapped with those of the studied
167 compounds. Hence, with the purpose of evaluating the method in the presence of these
168 additional interfering PAHs, a 10-sample test set was prepared containing random
169 concentrations of BaP, DBA, BaA and CHRY in the above evaluated ranges, as well as
170 concentrations of each interferent agent, ranging between 600 and 1000 ng L^{-1}.

171

172 *2.5. Software*

173

174 The PARAFAC theory is well documented [11] and it is not described here. The
175 routines employed for PARAFAC are written in MATLAB 7.6 [13]. PARAFAC was

implemented using the graphical interface of the MVC2 toolbox, which is available on the Internet [14].

3. Results and discussion

3.1. Preliminary studies

As already stated, a nylon membrane is able to retain PAHs and other organic compounds on its surface, and proved to be an appropriate support for their spectrofluorimetric determination [9,10]. Nylon membranes are made from nylon 6,6 (a polymer of adipic acid and hexamethylene diamine) with a chemical structure consisting of amide groups separated by methylene sequences. The amide group is essentially planar due to the partial double-bond character of the C–N bond. The chains are oriented in such a way as to maximize hydrogen bonding between the amino and carbonyl groups. Nonpolar interactions are expected between hydrophobic PAHs and the methylene chains of nylon. The mass transfer towards the membrane is favored by the fact that PAHs are dissolved in an aqueous phase.

Different approaches, such as direct deposit or solid-phase extraction through a syringe procedure, can be performed in order to retain the analyte in the nylon surface. In the present work, a new strategy is proposed which consists in introducing a rotating disk attached with a nylon membrane in an aqueous PAHs solution, allowing the adsorption of the analytes onto the disk. The ability of the nylon membrane to retain PAHs dissolved in water through the rotating disk procedure can be appreciated in Fig. 1, which shows a

199 photograph of two nylon-attached rotating disks irradiated with a UV lamp (365 nm), after
200 the corresponding RDSE approach using pure water (blank) and a solution of the four
201 studied PAHs.
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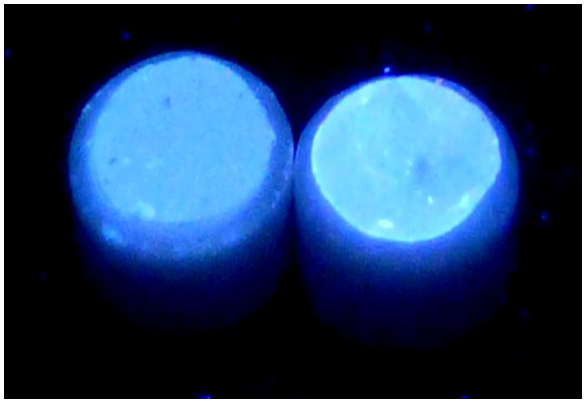

203

204 **Fig. 1.** Photograph of nylon-attached rotating disks irradiated with a UV lamp, after the
205 RDSE treatment of 25 mL of water (left) and 25 mL of a solution containing BaP, DBA,
206 BaA and CHRY (right), all at concentrations of 600 ng L^{-1}.
207

208 Exploratory experiments confirmed that fixing the extraction volume to 25 mL,
209 optimal conditions to obtain higher signals are observed when 10 mm diameter nylon disks
210 of 0.2 μm pore size are stirred at least 20 min at 1250 rpm and room-temperature, and these
211 were the experimental conditions maintained in the subsequent experiments.

212 Fig. 2A shows the fluorescence excitation and emission spectra for BaP, DBA,
213 CHRY, and BaA simultaneously adsorbed on the extraction nylon surface. Although these
214 fluorescence signals, directly related to analyte concentrations, are welcome for the
215 development of a solid-surface fluorescence (SSF) method for the determination of the
216 studied compounds, it is apparent in this figure that the overlapping among the excitation
217 and the emission spectra hinders their quantitation through a direct univariate or zeroth-
218 order calibration. Moreover, the situation becomes critical if other PAHs are also present in

samples (Fig. 2B). Therefore, in order to overcome the spectral overlapping problem, advanced chemometric modeling was applied.

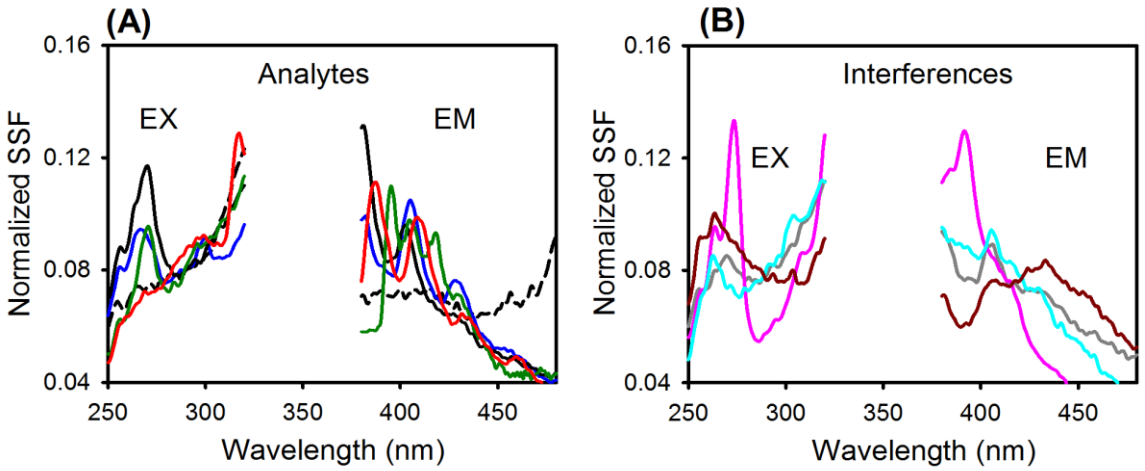

Fig. 2 (A) Normalized solid-surface fluorescence (SSF) excitation (EX) and emission (EM) spectra for BaP (blue), DBA (green), BaA (red), and CHRY (black), and (B) for BbF (brown), BghiP (cyan), IcdP (gray), and PYR (pink) immobilized onto nylon after the rotating disk procedure. The dashed-black lines in (A) correspond to the background signals.

3.2. Quantitative second-order analysis

After the rotating disk procedure under optimal conditions was carried out, the EEFMs were recorded on the nylon surface for calibration and validation samples (Fig. 3A), and were then subjected to chemometric analysis. It is known that a set of EEFMs can be arranged as a three-way array, which usually complies with the trilinearity conditions [15] and, thus, the chemometric analysis was performed using PARAFAC [16], a popular and easy to implement algorithm which achieves the second-order advantage [12]. Second-order advantage refers to the capacity of selected algorithms to predict the concentrations of the analytes in the presence of any number of unsuspected constituents which can be

present in real samples. This useful property avoids the requirement of either interference removal, as in zeroth-order calibration, or the construction of a large and diverse calibration set, as in first-order calibration.

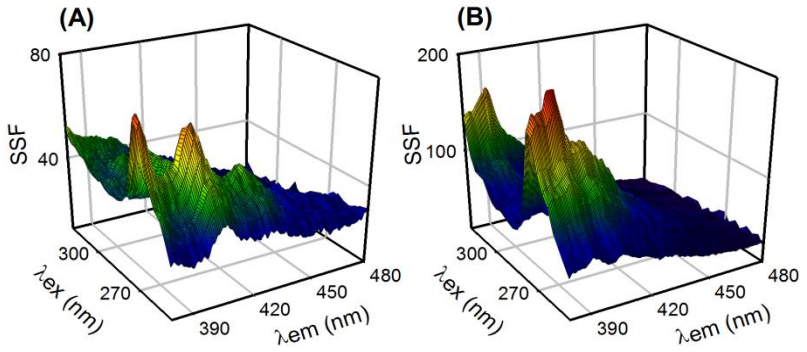

Fig. 3 Three-dimensional plots for solid-surface excitation-emission fluorescence matrices corresponding to nylon membranes treated with (A) a typical validation sample containing 100 ng L^{-1} BaP, 400 ng L^{-1} DBA, 100 ng L^{-1} BaA, and 200 ng L^{-1} CHRY, and (B) a test sample containing 140 ng L^{-1} BaP, 140 ng L^{-1} DBA, 200 ng L^{-1} BaA, 280 ng L^{-1} CHRY, 600 ng L^{-1} BbF, 800 ng L^{-1} BghiP, 700 ng L^{-1} IcdP, and 800 ng L^{-1} PYR.

PARAFAC was applied to three-way data arrays built by joining the calibration data matrices with those for each of the validation samples in turn. The algorithm was initialized with the loadings giving the best fit after a small number of trial runs, selected from the comparison of the results provided by a method known as generalized rank annihilation (GRAM) and several random loadings [11]. The number of PARAFAC components was selected by the so-called core consistency analysis [17], and also through visual inspection of the spectral profiles produced by the addition of new components. The estimated number of components using the above technique was six, which can be justified taking into account the presence of analytes and background signals. No restrictions were applied during the PARAFAC least-squares fit. An advantage of the PARAFAC model is that it retrieves physically interpretable profiles. Identification of the chemical constituents of a

sample is easily done with the aid of the estimated profiles, comparing them with those for a standard solution of each analyte of interest. Fig. 4 displays the spectral profiles retrieved by PARAFAC for a typical sample containing the analytes, where the corresponding signals are clearly distinguished.

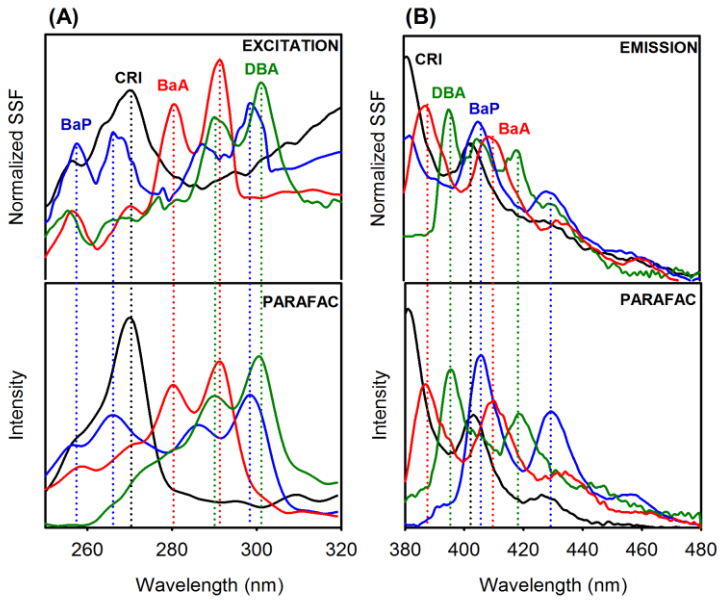

Fig. 4 Normalized solid-surface fluorescence (SSF) excitation (A) and emission (B) spectra for BaP (blue), CRI (black), BaA (red), and DBA (green), and the corresponding PARAFAC fluorescence excitation (A) and emission (B) loadings when processing a typical validation sample with the calibration set of samples. Loadings have been normalized to unit amplitude. Dotted vertical lines serve as guide for the eye. For clarity background signals have been avoided.

Fig. 5A shows the prediction results after the application of PARAFAC to the complete set of validation samples. The elliptical joint confidence region (EJCR) [18] test for the slope and intercept of the predicted vs. nominal concentrations plot shows that the ideal point (1,0) lies inside the EJCR surface, suggesting that PARAFAC successfully resolves the studied system. The corresponding statistical results shown in Table 2 are also indicative of high-quality predictions.

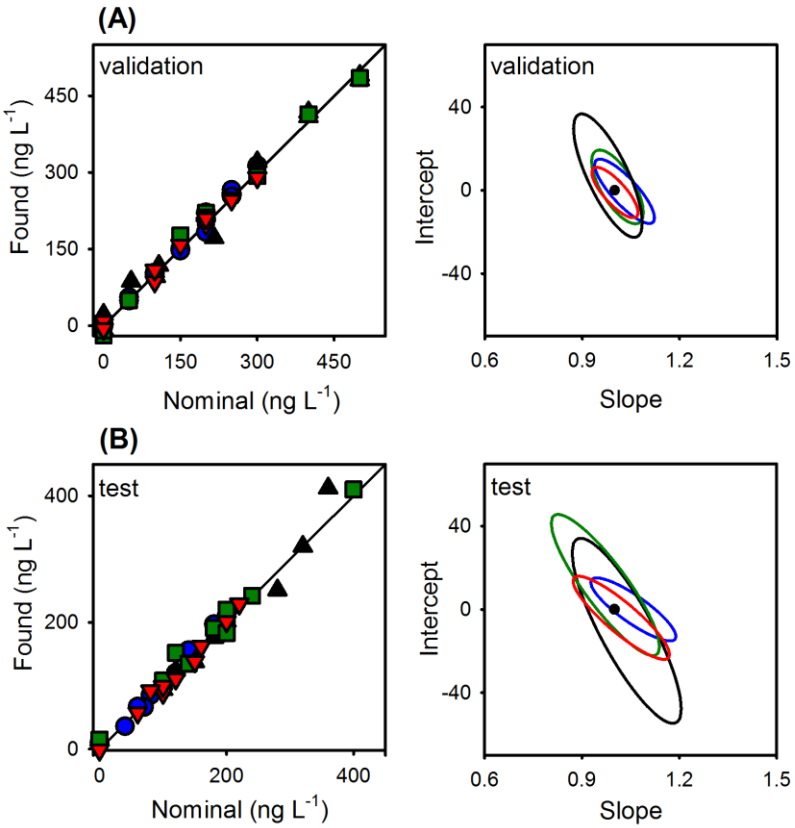

Fig. 5 Plots for the BaP (blue circle), DBA (green square), BaA (red down triangle), and CHRY (black up triangle) predicted concentrations as a function of the nominal values (the solid lines are the perfect fits), and elliptical joint regions (at 95% confidence level) for slope and intercept of the regression of the corresponding data. Black points mark the theoretical (intercept = 0, slope = 1) point. (A) Validation samples and (B) test samples.

In relation to the limits of detection (LODs), it is important to consider the low concentration levels of PAHs admitted by governmental agencies in environmental samples, especially water. The United State Environmental Protection Agency (US-EPA) reports a value of 200 ng L^{-1} as a maximum concentration level for PAHs in safe drinking water [19]. As can be appreciated in Table 2, the low LODs attained are very favorable, especially for BaP (ranked first in the carcinogenic list) and BaA, taking into account the complexity of the evaluated system and the simplicity of the experimental determination. It

is necessary to point out that these limits have been calculated using the expression recommended by the International Union of Pure and Applied Chemistry (IUPAC):

$$\mathrm{LOD} = 3.3\ \sqrt{h s_C^2 + h s_X^2 / \mathrm{SEN}^2 + s_X^2 / \mathrm{SEN}^2} \qquad (1)$$

where h is the sample leverage at zero analyte concentration, s_C^2 is the variance in calibration concentrations, s_X^2 is the variance in the instrumental signal, SEN is the component sensitivity, and the factor 3.3 is the sum of *t*-coefficients accounting for Type I and II errors (false detects and false non-detects, respectively) at 95 % confidence level. Equation (1) takes into account the error propagation from both the slope and the intercept of the pseudo-univariate PARAFAC calibration curve [20].

A method is valuable when satisfactory predictions are obtained in complex systems where other constituents are also present, and may interfere the analysis. Thus, additional PAHs which demonstrated to interfere the analyte signals (Fig. 2B) were added to the samples, and they were evaluated applying the proposed strategy. Figure 3B shows the three-dimensional plot for a solid-surface excitation-emission fluorescence matrix corresponding to a nylon membrane treated with a test sample containing analytes and interferences. Notice in this figure the scale of the intensity axis and compare it with that of Fig. 3A. The number of responsive components in these samples, selected by following a similar procedure to that indicated above for the validation samples, was in the range 7-9. It seems that in some samples, PARAFAC is not able to discern between the profiles of each individual foreign compound, grouping them into overall interfering components. However, this fact does not preclude the obtainment of good analytical results (Fig. 5B), demonstrating the high level of selectivity achieved by this method.

Table 2

PARAFAC statistical results for BaP, DBA, BaA, and CHRY in samples without interferences (validation set) and with BbF, BghiP, IcdP, and PYR as interferences (test set)[a].

	BaP	DBA	BaA	CHRY
Validation set				
RMSEP	10	14	8	21
REP	7	5	5	7
LOD	30	70	20	100
Test set				
RMSEP	10	16	8	21
REP	7	5	5	7
LOD	30	100	30	100

[a] RMSEP (ng L^{-1}), root-mean-square error of prediction; REP (%), relative error of prediction; LOD (ng L^{-1}), limit of detection calculated according to eq (1).

317

318 The statistical results shown in Table 2 for test samples are similar to those obtained
319 for the validation ones, indicating that neither the accuracy and precision, measured through
320 the root mean square error of prediction (RMSEP) and relative error of prediction (REP),
321 nor the sensitivity (LODs remain at the part-per-trillion levels) are significantly affected by
322 the addition of these new PAHs.

323 Several advantages of the proposed methodology in comparison with the
324 chromatographic ones currently employed for PAHs analysis (see Introduction) can be
325 concluded, such as lower experimentally required time, no use of organic solvents, reduced
326 human participation, and considerable more simplicity. In addition, the coupling to
327 multivariate calibration significantly improves the sensitivity and selectivity of the method.

328 When the proposed approach is compared with that carried out in nylon but
329 following a solid-phase extraction via a syringe procedure [8], we can conclude that
330 although the latter one provides lower detection limits (the amide groups of nylon would

enhance the water motion through the sorbent during the extraction, improving the mass transfer) [8] the main advantage of the present strategy is that the recirculating regime prevents collapse of the filter in turbid samples. Regarding the time involved in each experiment, if the extraction is simultaneously performed on several samples, the experimental time can be drastically reduced.

4. Conclusions

The extraction ability of a rotating disk attached with a nylon membrane towards PAHs from water samples has been demonstrated. After extraction, excitation-emission fluorescence matrices were directly measured in the solid-surface, and the analytes were quantified with the aid of PARAFAC algorithm at part-per-trillion levels in a very interfering medium. Beyond the outstanding sensitivity and selectivity achieved using the proposed approach, additional advantages should be mentioned. The coupling with an appropriate chemometric tool makes it unnecessary the use of clean up steps for the removal of interfering compounds, avoiding environmentally unsafe organic solvents, and saving experimental time and operator efforts. The excellent quality of the obtained results suggests that the developed method favorably competes with more sophisticated ones, representing a good choice for the rapid quantitation of PAHs in water samples, and offering routine laboratories the opportunity to work under green chemistry principles.

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