

1

2 **Chemometrics-assisted excitation–emission fluorescence**
3 **spectroscopy on nylon-attached rotating disks.**

4 **Simultaneous determination of polycyclic aromatic**
5 **hydrocarbons in the presence of interferences**

6

7 **Alejandro Cañas,^a Pablo Richter,^{a,*} Graciela M. Escandar^{b,*}**

8

9 ^a *Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y*
10 *Farmacéuticas, Universidad de Chile, Casilla 653, Santiago, Chile. E-mail:*
11 *prichter@ciq.uchile.cl*

12 ^b *Instituto de Química Rosario (CONICET-UNR), Facultad de Ciencias Bioquímicas y*
13 *Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, 2000 Rosario, Argentina.*
14 *E-mail: escandar@iquir-conicet.gov.ar*

15

16

17

18

19

20

21 * Corresponding authors

22 **Abstract**

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

39

40

41

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

44

45 **1. Introduction**

46

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

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

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

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

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

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

101

102 **2. Experimental**

103

104 *2.1. Reagents and solutions*

105

106 BaP, DBA, BaA, CHRY, benzo[*b*]fluoranthene (BbF), benzo[*g,h,i*]perylene
107 (BghiP), indeno[1,2,3-*d*]pyrene (IcdP), and pyrene (PYR) were purchased from Aldrich
108 (Milwaukee, WI). Methanol was obtained from Merck (Darmstadt, Germany). All reagents
109 were of high-purity grade and used as received. Stock solutions of all PAHs of about 100
110 $\mu\text{g mL}^{-1}$ were prepared in methanol. From these solutions, more diluted methanol solutions
111 (ranging from 50 to 250 ng mL^{-1}) were obtained. Working aqueous solutions were prepared
112 immediately before their use by taking appropriate aliquots of methanol solutions,
113 evaporating the methanol by use of nitrogen and diluting with water to the desired

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

116

117 *2.2. Apparatus*

118

119 Fluorescence measurements were carried out on a PerkinElmer (Waltham
120 MA, USA) LS 55 luminescence spectrometer equipped with a xenon discharge lamp, using
121 excitation and emission slit widths of 5 nm. The photomultiplier tube voltage (PMT) was
122 set at 650 V. The data matrices were collected varying the excitation wavelength between
123 250 and 367 nm each 3 nm, and registering the emission spectra from 370 to 480 nm each
124 0.5 nm. A magnetic stirrer HI 190M Hanna (Woonsocket, RI, USA) with speed control was
125 used for the PAHs extraction.

126

127 *2.3. Rotating disk nylon extraction*

128

129 The preparation of the rotating disks and the general procedure was similar to that
130 previously described [9,10]. Briefly, a 0.2 μm pore size nylon membrane (Varian, Seattle,
131 WA, USA) was attached with a double-coated sticking tape to one side of a Teflon disk
132 (1.5 cm diameter) containing a magnetic stirring bar (Teflon-coated Micro Stir bar from
133 VWR International, Inc., Radnor, PA, USA). The rotating disk with the attached nylon
134 phase was placed inside a beaker containing 25 mL of aqueous PAHs samples, and the disk
135 was rotated at 1250 rpm for 20 min at room-temperature. After extraction, the nylon
136 membrane was removed from the disk, and placed in a laboratory-made membrane holder.

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

139

140 *2.4. Chemometric analysis over the nylon surface*

141

142 Previous to the second-order calibration experiment, the linear relation of the
143 fluorescence signals for BaP, DBA, BaA and CHRY with concentrations was investigated
144 under the employed experimental conditions. The results indicated that linearity is
145 maintained at least up to 600 ng L⁻¹ for the four investigated PAHs, and no attempts were
146 made to establish the upper concentration of the linear range. A calibration set of 10
147 samples containing the four analytes in the ranges 50-300 ng L⁻¹ (for BaP and BaA) and
148 50-600 ng L⁻¹ (for DBA and CHRY) was prepared from the corresponding working
149 solutions (Table 1). Eight samples of the set corresponded to the concentrations provided
150 by a two-level half-factorial design (i.e., 2⁴⁻¹ samples). One of the remaining samples
151 corresponded to a blank solution ($C_{\text{BaP}} = C_{\text{DBA}} = C_{\text{BaA}} = C_{\text{CHRY}} = 0$), and the remaining
152 sample contained the studied analytes at intermediate concentrations ($C_{\text{BaP}} = C_{\text{BaA}} = 150$ ng
153 L⁻¹; $C_{\text{DBA}} = C_{\text{CHRY}} = 300$ ng L⁻¹). Each sample was subjected to the RDSE procedure and
154 the EEFM measurement described above, and the obtained EEFMs were then analyzed
155 with second-order multivariate calibration. The spectral ranges 250-320 nm (excitation) and
156 380-480 nm (emission) for the four analytes were chosen after a suitable consideration of
157 the spectral regions corresponding to their maximum signals, while avoiding useless
158 background responses, which may be possibly due to intrinsic impurities of the nylon
159 membrane or to physical dispersion effects.

160

Table 1Composition 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

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

178

179 **3. Results and discussion**

180

181 *3.1. Preliminary studies*

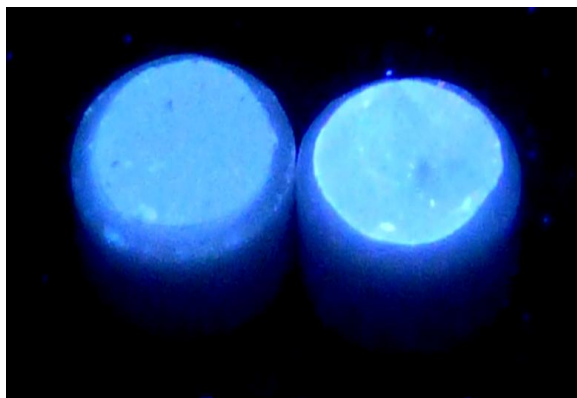
182

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

193 Different approaches, such as direct deposit or solid-phase extraction through a
194 syringe procedure, can be performed in order to retain the analyte in the nylon surface. In
195 the present work, a new strategy is proposed which consists in introducing a rotating disk
196 attached with a nylon membrane in an aqueous PAHs solution, allowing the adsorption of
197 the analytes onto the disk. The ability of the nylon membrane to retain PAHs dissolved in
198 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.

202



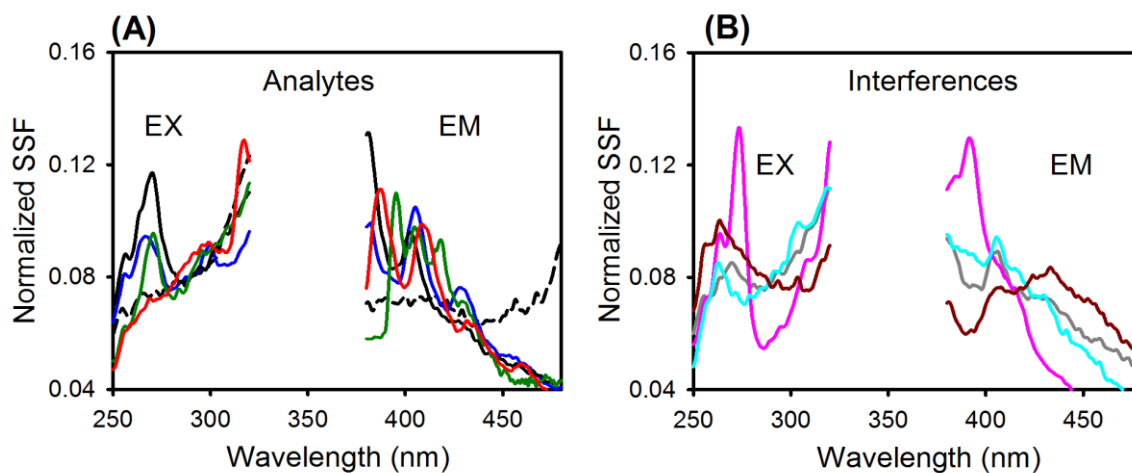
203

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

219 samples (Fig. 2B). Therefore, in order to overcome the spectral overlapping problem,
220 advanced chemometric modeling was applied.
221



222

223 **Fig. 2** (A) Normalized solid-surface fluorescence (SSF) excitation (EX) and emission (EM)
224 spectra for BaP (blue), DBA (green), BaA (red), and CHRY (black), and (B) for BbF
225 (brown), BghiP (cyan), IcdP (gray), and PYR (pink) immobilized onto nylon after the
226 rotating disk procedure. The dashed-black lines in (A) correspond to the background
227 signals.
228

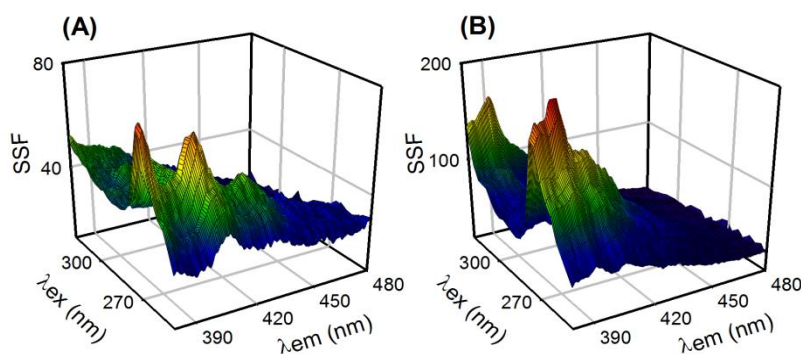
229 3.2. Quantitative second-order analysis

230

231 After the rotating disk procedure under optimal conditions was carried out, the
232 EEFMs were recorded on the nylon surface for calibration and validation samples (Fig.
233 3A), and were then subjected to chemometric analysis. It is known that a set of EEFMs can
234 be arranged as a three-way array, which usually complies with the trilinearity conditions
235 [15] and, thus, the chemometric analysis was performed using PARAFAC [16], a popular
236 and easy to implement algorithm which achieves the second-order advantage [12]. Second-
237 order advantage refers to the capacity of selected algorithms to predict the concentrations of
238 the analytes in the presence of any number of unsuspected constituents which can be

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

242



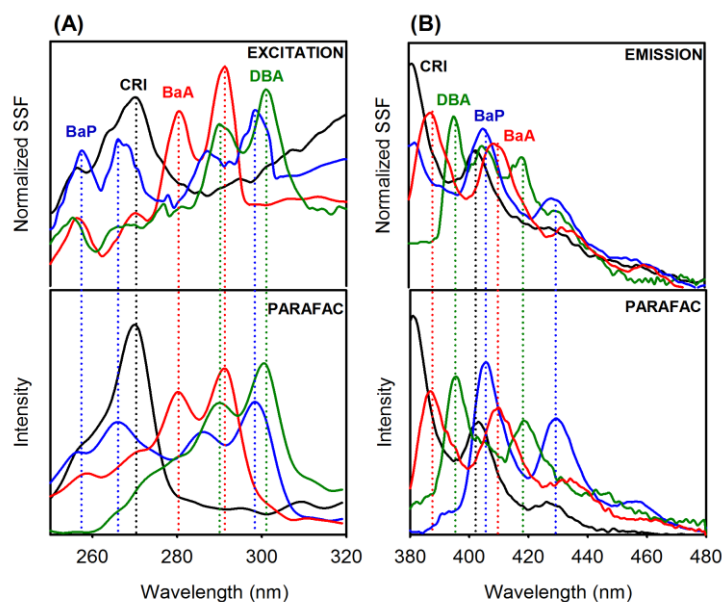
243

244 **Fig. 3** Three-dimensional plots for solid-surface excitation-emission fluorescence matrices
245 corresponding to nylon membranes treated with (A) a typical validation sample containing
246 100 ng L^{-1} BaP, 400 ng L^{-1} DBA, 100 ng L^{-1} BaA, and 200 ng L^{-1} CHRY, and (B) a test
247 sample containing 140 ng L^{-1} BaP, 140 ng L^{-1} DBA, 200 ng L^{-1} BaA, 280 ng L^{-1} CHRY,
248 600 ng L^{-1} BbF, 800 ng L^{-1} BghiP, 700 ng L^{-1} IcdP, and 800 ng L^{-1} PYR.

249

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

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

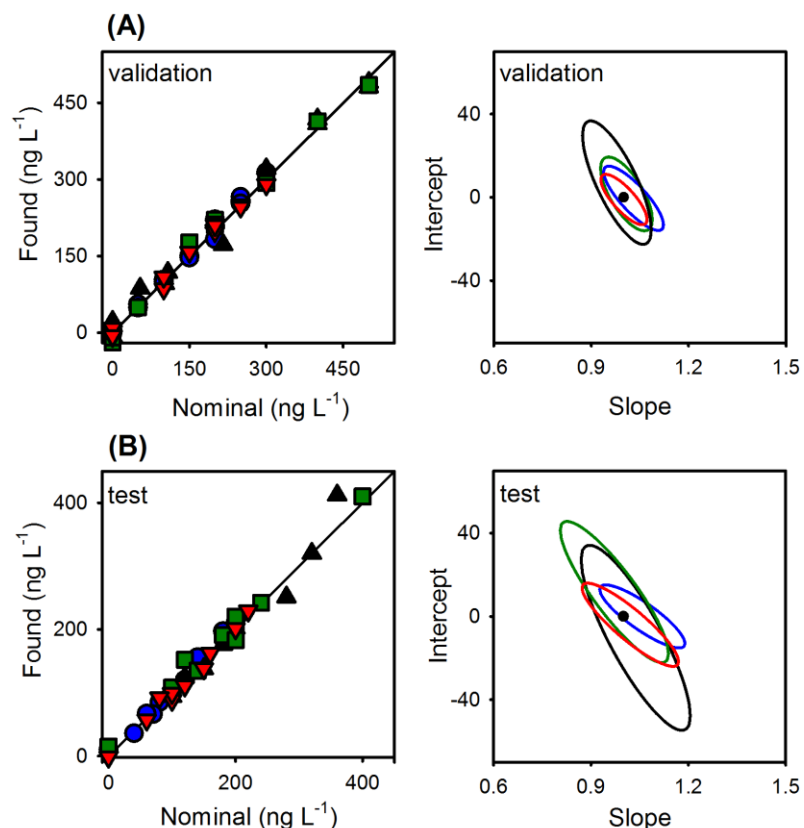


265

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

272

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



279

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

285

286

287

288 In relation to the limits of detection (LODs), it is important to consider the low
 289 concentration levels of PAHs admitted by governmental agencies in environmental
 290 samples, especially water. The United State Environmental Protection Agency (US-EPA)
 291 reports a value of 200 ng L⁻¹ as a maximum concentration level for PAHs in safe drinking
 292 water [19]. As can be appreciated in Table 2, the low LODs attained are very favorable,
 293 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

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

$$296 \quad \text{LOD} = 3.3 \sqrt{hs_C^2 + hs_X^2 / \text{SEN}^2 + s_X^2 / \text{SEN}^2} \quad (1)$$

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

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

316

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

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

336
337
338

4. Conclusions

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

351

Acknowledgements

353

354 Fondecyt, Chile (Project 1140716), Universidad Nacional de Rosario and CONICET
355 (Consejo Nacional de Investigaciones Científicas y Técnicas) are gratefully acknowledged
356 for financial support.

357

358 **References**

- [1] A. Dipple, Q.A. Khan, J.E. Page, I. Pontén I, J. Szeliga, DNA reactions, mutagenic action and stealth properties of polycyclic aromatic hydrocarbon carcinogens (review), *Int. J. Oncol.* 14 (1999) 103–111.
- [2] J.A. Linthorst, An overview: origins and development of green chemistry, *Found Chem.* 12 (2010) 55–68.
- [3] A. Molina Díaz, J.F. García Reyes, B. Gilbert López, Solid-phase spectroscopy from the point of view of green analytical chemistry, *Trends Anal. Chem.* 29 (2010) 654–666.
- [4] T. Wenzl, R. Simon, J. Kleiner, E. Anklam, Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union, *Trends Anal. Chem.* 25 (2006) 716–725.
- [5] P. Richter, C. Leiva, C. Choque, A. Giordano, B. Sepulveda, Rotating-disk sorptive extraction of nonylphenol from water samples, *J. Chromatogr. A* 1216 (2009) 8598–8602.
- [6] P. Richter, A. Cañas, C. Muñoz, C. Leiva, I. Ahumada, Rotating disk sorbent extraction for pre-concentration of chromogenic organic compounds and direct determination by solid phase spectrophotometry, *Anal. Chim. Acta* 695 (2011) 73–76.

- [7] A. Giordano, P. Richter, I. Ahumada, Determination of pesticides in river water using rotating disk sorptive extraction and gas chromatography–mass spectrometry, *Talanta* 85 (2011) 2425–2429.
- [8] V. Manzo, L. Honda, O. Navarro, L. Ascar, P. Richter, Microextraction of non-steroidal anti-inflammatory drugs from waste water samples by rotating-disk sorptive extraction, *Talanta* 128 (2014) 486–492.
- [9] S.A. Bortolato, J.A. Arancibia, G. M. Escandar, A novel application of nylon membranes to the luminescent determination of benzo[*a*]pyrene at ultra trace levels in water samples, *Anal. Chim. Acta* 613 (2008) 218–227.
- [10] S.A. Bortolato, J.A. Arancibia, G.M. Escandar, Chemometrics-assisted excitation-emission fluorescence spectroscopy on nylon membranes. Simultaneous determination of benzo[*a*]pyrene and dibenz[*a,h*]anthracene at parts-per-trillion levels in the presence of the remaining EPA PAH priority pollutants as interferences, *Anal. Chem.* 80 (2008) 8276–8286.
- [11] R. Bro, PARAFAC. Tutorial and applications, *Chemom. Intell. Lab. Syst.* 38 (1997) 149–171.
- [12] K.S Booksh, B.R. Kowalski, Theory of analytical chemistry, *Anal. Chem.* 66 (1994) 782A–791A.
- [13] MATLAB R2011b, The MathWorks Inc, Natick, MA, USA.
- [14] www.iquir-conicet.gov.ar/descargas/mvc2.rar. Accessed September 2014.

- [15] A.C. Olivieri, G.M. Escandar, A. Muñoz de la Peña, Second-order and higher-order multivariate calibration methods applied to non-multilinear data using different algorithms, *Trends Anal. Chem.* 30 (2011) 607–617.
- [16] A.C. Olivieri, G.M. Escandar, *Practical three-way calibration*, Elsevier, Waltham, MA, USA, 2014.
- [17] R. Bro, H.L. Kiers, A new efficient method for determining the number of components in PARAFAC models, *J. Chemom.* 17 (2003) 274–286.
- [18] A.G. González, M.A. Herrador, A.G. Asuero, Intra-laboratory testing of method accuracy from recovery assays, *Talanta*, 48 (1999) 729–736.
- [19] Technical Factsheet on: Polycyclic Aromatic Hydrocarbons (PAHs). <http://www.epa.gov/safewater/pdfs/factsheets/soc/tech/pahs.pdf>. Accessed September 2014.
- [20] A.C. Olivieri, Analytical figures of merit: from univariate to multiway calibration *Chem. Rev.* 114 (2014) 5358–5378.