ELSEVIER

Journal of Chromatography A, 802 (1998) 263–275

JOURNAL OF CHROMATOGRAPHY A

Parallel factor analysis of partially resolved chromatographic data Determination of polycyclic aromatic hydrocarbons in water samples

J.L. Beltrán, J. Guiteras*, R. Ferrer

Departament de Química Analítica, Universitat de Barcelona, Avgda. Diagonal 647, E-08028 Barcelona, Spain

Received 10 June 1997; received in revised form 11 November 1997; accepted 14 November 1997

Abstract

A procedure, based on parallel factor analysis (PARAFAC), has been used for the analysis of polycyclic aromatic hydrocarbons in water samples. The chromatographic system has been set to obtain short-time chromatograms containing several unresolved peaks. The detection system consisted of a fast-scanning fluorescence spectra detector, which allowed three-dimensional data – where retention time, emission wavelengths and fluorescence intensity were represented – to be obtained. The procedure has been applied to spiked tap water samples with good results. © 1998 Elsevier Science B.V.

Keywords: Factor analysis; Water analysis; Fluorescence detection; Detection, LC; Polynuclear aromatic hydrocarbons

1. Introduction

The detectors most commonly used in high-performance liquid chromatography are based upon UV–Vis absorption or fluorescent emission. Only a profile of the compounds eluting from the chromatographic system is obtained, however, and in order to achieve good quantitative results, a good resolution between the different compounds is required. Consequently, several chromatographic parameters must be previously optimized (flow-rate, composition of the mobile phase, composition of the stationary phase, etc.), with the corresponding waste of time.

The development of multichannel detectors, such as UV–Vis diode-array (UV–DAD) [1–4], diode-array fluorescence [5–10], charge-coupled devices (CCDs) [10–12], or fast-scanning fluorescence spectrometry (FSFS) [13] detectors, has made it possible to record the full spectra of the eluting compounds, which can therefore be identified not only from their retention time but also from their spectral characteristics. However, to obtain the full advantages offered by multichannel detectors, they should be used in combination with multivariate calibration methodologies. In this way, more information can be obtained from the experimental data, and it is possible to determine compounds whose chromatographic peaks show partial overlapping.

Among the different multivariate methods available, some, such as iterative target transformation factor analysis (ITTFA) [14–16], evolving factor analysis (EFA) [17–19] or window factor analysis (WFA) [20,21], do not provide direct quantitative information, because they only use one data matrix (one sample). The most useful are those which, like

*Corresponding author

0021-9673/98/$19.00
PII S0021-9673(97)01160-6

multiple linear regression (MLR) [22], factor analysis (FA) [23], the adaptive Kalman filter [24,25], or generalized rank annihilation matrix (GRAM) [26–31], can deal with several samples simultaneously and which, therefore, can provide quantitative information; some of them have been used for the calibration of chromatographic systems [14,18,19,21,25,28].

Polycyclic aromatic hydrocarbons (PAHs) are of natural and anthropogenic origin and, therefore, they are likely to be found in many kinds of environmental samples. Moreover, they are extremely hazardous, which has led to 16 of them being included by the Environmental Protection Agency (EPA) in the list of priority pollutants. Most PAHs show strong intrinsic fluorescence, and they are usually determined by HPLC with fluorescence detectors. There is, however, a constant need to improve the sensitivity and selectivity of existing methods and to reduce the time required for an analysis [32–34].

PARAFAC (*n*-factor parallel factor analysis) is a decomposition procedure [35] which has been applied to fluorescence excitation–emission matrices (EEMs) [36,37], or for the prediction of capacity factors in HPLC [38].

This paper describes the application of PARAFAC [39] to the analysis of multicomponent mixtures from the three-dimensional chromatograms obtained by HPLC–FSFS (which is more sensitive than HPLC–DAD and similar to intensified-DAD or laser-induced fluorescence-DAD (LIF-DAD)) [13]. The use of PARAFAC has considerably shortened the time required for a complete analysis, because it is possible to obtain quantitative results for all compounds in a mixture, even if their peaks are partially overlapped and, therefore, a total chromatographic separation is not necessary. Consequently, a simplified, shorter, chromatographic procedure can be used.

This procedure has been applied to the determination of polycyclic aromatic hydrocarbons in spiked tap water samples with good results.

2. Experimental

2.1. Reagents

Stock standard solutions (about 200 μg ml^{-1}) of acenaphthene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, chrysene, dibenzo[*a*,*h*]anthracene, phenanthrene, fluoranthene, fluorene, naphthalene and pyrene were prepared by dissolving the pure solid (Supelco, Bellefonte, PA, USA) in either methanol or acetonitrile, depending on its solubility. Solutions of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene and indene[1,2,3-*cd*]pyrene in either acetonitrile or methylene chloride (all at about 200 μg ml^{-1}), as well as a standard solution containing the 16 PAH classified as primary pollutants by the EPA, were purchased from Supelco. Working standards were prepared by dilution of the stock solutions with acetonitrile.

Acetonitrile was of HPLC quality (J.T. Baker, Deventer, The Netherlands). Cyclohexane and acetone were of residue analysis quality (SDS, Peypin, France).

Doubly distilled water (Milli-Q+, Millipore, Bedford, MA, USA) was used in the mobile phase. The mobile phase consisted of acetonitrile–water (90:10) and, before use, it was filtered through a 0.22-μm membrane filter and degassed with a stream of helium.

Solid-phase extraction cartridges were silica-based C_{18} (Varian, CA, USA).

2.2. Apparatus

The chromatographic system consisted of a twin-piston Gynkotek 480 HPLC pump (Munich, Germany), a Gynkotek MSV6 automatic injector, with a 25-μl injection loop, and a 12.5 cm×4.6 mm Spherisorb S5-PAH column (Phase Separations, UK) with a 5-μm particle size.

An Aminco Bowman Series 2 spectrofluorimeter (SLM-Aminco, Rochester, NY, USA), equipped with a 25-μl flow cell (Hellma 176.752, Baden, Germany) was used for fast-scanning fluorescence spectra detection [13].

2.3. Sample extraction

Polycyclic aromatic hydrocarbons were extracted from the water sample (spiked tap water) by a solid-phase extraction (SPE) procedure. The C_{18} cartridges were conditioned with 2.5 ml of methanol and 5 ml of an acetonitrile–water (5:95) mixture. The sample

(100 ml of water, containing 5% v/v of acetonitrile, to avoid adsorption of PAHs in the container) was introduced in the column at a flow-rate of 2 ml min^{-1}, followed by 5 ml of the acetonitrile–water (5:95) mixture to remove any possible interferences. The cartridges were dried with a nitrogen stream, and the PAHs were eluted with three consecutive portions of 500 μl of acetone. This solution was evaporated to dryness with a nitrogen stream, and the PAHs were dissolved with 500 μl of acetonitrile.

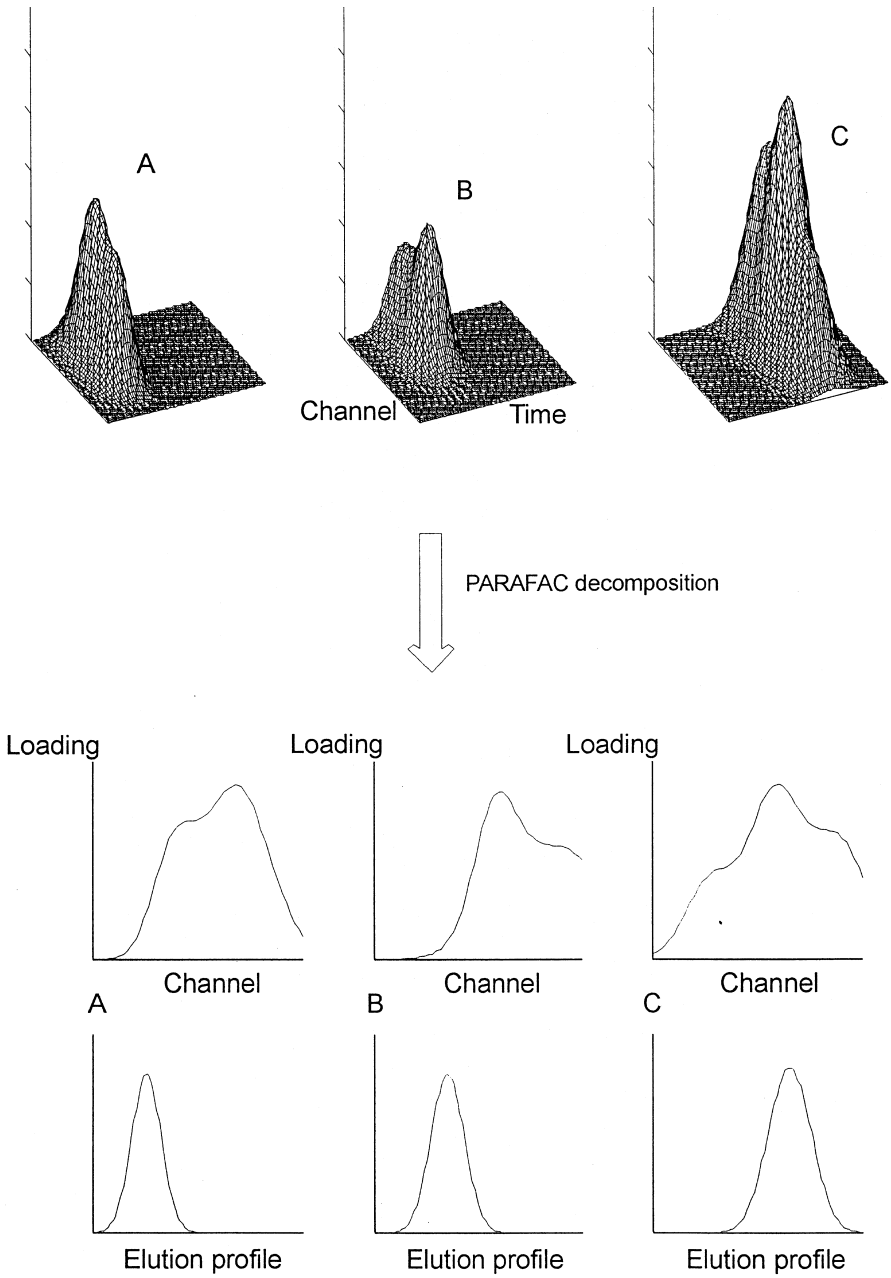

Fig. 1. Simulated three-dimensional chromatograms for three different single compounds and their PARAFAC decomposition.

2.4. PARAFAC

The PARAFAC method allows the decomposition of bilinear data structures taking advantage of their uniqueness properties [39]. In this work, bilinear data are obtained as fluorescence emission spectra at different retention times. These data can be expressed as the product of two column vectors, x and y, where x corresponds to the emission spectra, and y is the elution profile (chromatogram). For a single compound, its three-dimensional chromatogram (R) can be expressed as

$$\boldsymbol{R} = \hat{x}\hat{y}' + \boldsymbol{E}$$

where the prime denotes the transpose of the vector (or matrix), and E indicates the random errors associated with the measurements. The circumflex symbol indicates the estimation of a true vector (or matrix). Fig. 1 shows the simulated three-dimensional chromatogram for a single compound and its PARAFAC decomposition in two vectors, one of which corresponds to the emission spectrum, and the other to the elution profile.

For a sample containing several compounds, R can be assumed to be the linear addition of n pure three-dimensional chromatograms (Fig. 2)

$$\boldsymbol{R} = \sum_{i=1}^{n} \hat{\boldsymbol{x}}_i \hat{\boldsymbol{y}}'_i + \boldsymbol{E} = \hat{\boldsymbol{X}}\hat{\boldsymbol{Y}}' + \boldsymbol{E}$$

The simultaneous treatment of m samples allows to obtain three matrices related with the fluorescence spectra ($\boldsymbol{X}$), elution profiles ($\boldsymbol{Y}$) and concentration of the compounds ($\boldsymbol{Z}$). For a sample (k), containing n compounds at different concentrations, the model R_k can be expressed as

$$R_k = \sum_{i=1}^{n} \hat{\boldsymbol{X}}_i \hat{\boldsymbol{Y}}'_i \hat{\boldsymbol{Z}}_{k,i} + \boldsymbol{E}_k$$

$\hat{\boldsymbol{Z}}$ is a $m \times n$ matrix containing numeric factors related with the concentration of each compound in each sample. The decomposition for all the m samples is done simultaneously, to obtain data related with the emission spectrum and the elution profile of each compound, and also with its relative concentration in each sample. In Fig. 3, three simulated three-dimensional chromatograms and their PARAFAC decompositions are shown. In this case, a new graph showing the relative concentrations for each compound is also represented.

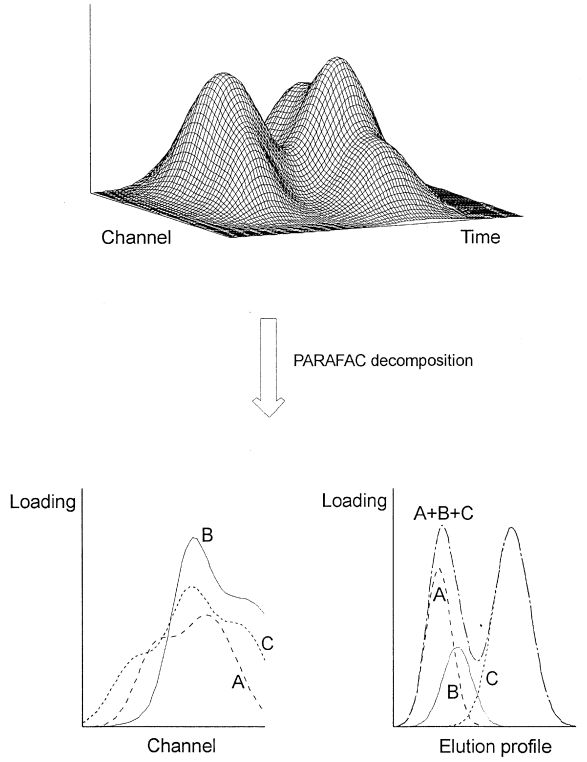

Fig. 2. Simulated three-dimensional chromatograms for a mixture of three compounds and their PARAFAC decomposition.

Two different approaches have been tested with PARAFAC decomposition. One of them had no constraints, meaning that the model found was a purely mathematical solution (that is, the coefficient matrices – or loadings – found for each factor could not be directly related with the chemical characteristics of the compounds, such as emission spectra or chromatographic peaks). The second model was obtained with non-negative constraints, which means that the loadings found must be positive and that, theoretically, they should be directly related with chemical characteristics of the compounds and could be used to represent them, although in practice this is not usually the case, at least for complex mixtures.

The solutions in PARAFAC models have been found by alternating least squares (ALS). From the original data ($\boldsymbol{R}$), initial estimates of $\boldsymbol{X}$ ($\boldsymbol{X}_0$) and $\boldsymbol{Y}$ ($\boldsymbol{Y}_0$) could be obtained, and the $\boldsymbol{Z}$ matrix was

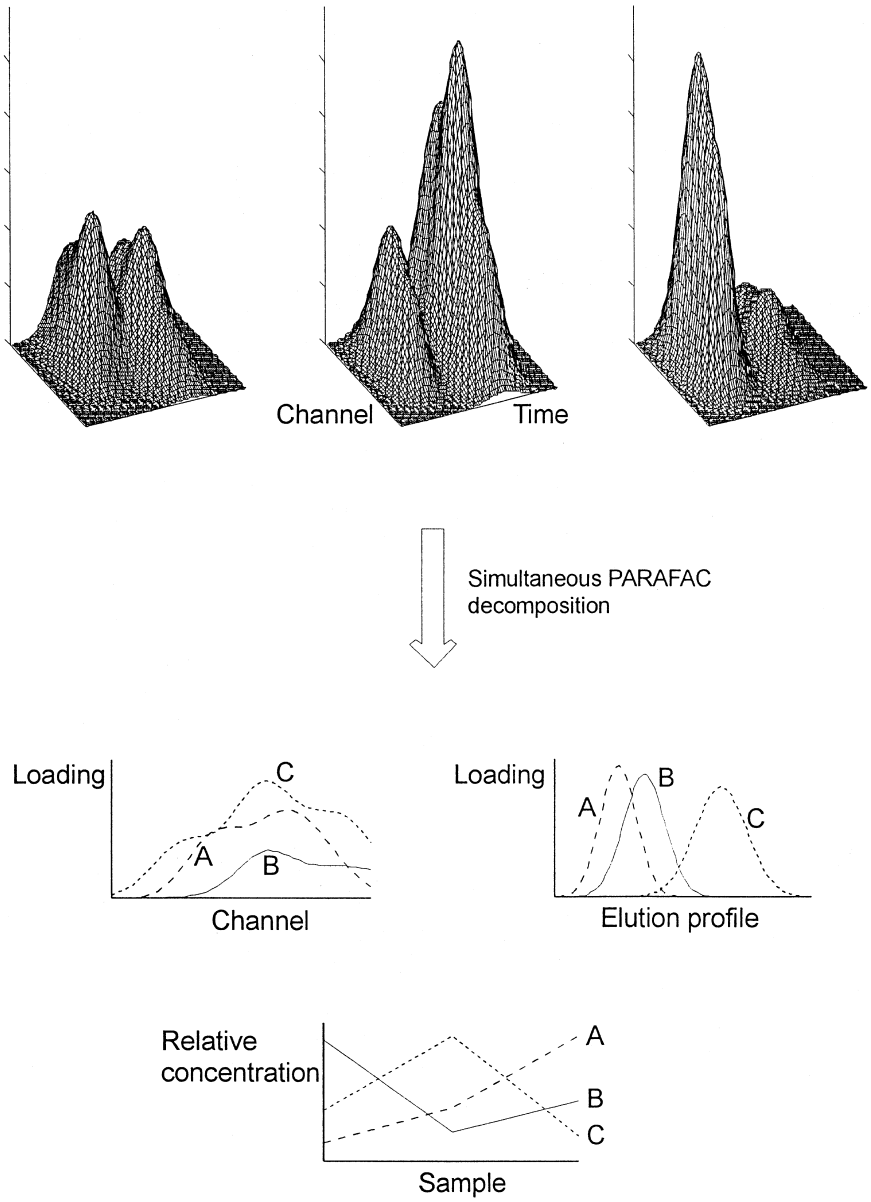

Fig. 3. Simultaneous PARAFAC decomposition of three chromatograms, containing three compounds at different concentrations.

calculated from $\boldsymbol{R}$, $\boldsymbol{X}_0$ and $\boldsymbol{Y}_0$ by a least squares solution ($\boldsymbol{Z}_1$). New values of $\boldsymbol{Y}$ ($\boldsymbol{Y}_1$) were then obtained from $\boldsymbol{X}_0$ and $\boldsymbol{Z}_1$ and, finally, $\boldsymbol{X}_1$ was calculated from $\boldsymbol{Y}_1$ and $\boldsymbol{Z}_1$. This iterative procedure was repeated until the difference of errors between two consecutive iterations was less than a predetermined value (10^{-6} in our case).

2.5. Chromatographic data simulation

One of the most important advantages of PARAFAC lies in its ability to resolve partially overlapped chromatographic peaks, thus making a total chromatographic separation unnecessary and considerably reducing the time required to record a

full chromatogram. There is, however, a limit to the reduction in time, not only because the overlapping of the peaks must be partial, but also because of the characteristics of the detection system. In the working conditions used, the FSFS detector requires 2.7 s to record a single fluorescence spectrum and, as a minimum number of spectra is needed to hold the resolution of the three-dimensional chromatograms, too short a time would mean a considerable loss of resolution and an unacceptable increase in the error of the multivariate calibration.

In order to optimize the chromatographic conditions, the influence of flow-rate, composition of the mobile phase, number of peaks, position of the peaks and degree of overlapping, was tested.

Chromatographic data were generated from an original chromatogram, which had been recorded with the chromatographic system described in the Section 2.2, but at a constant flow-rate of 2 ml min^{-1}. In an isocratic chromatographic system the retention volume of a compound does not depend on flow-rate and, therefore, a MATLAB program was written to simulate chromatograms at different flow gradients. Ten different chromatograms, each with different concentrations of PAHs, were calculated for each gradient flow tested, and the PARAFAC procedure was used for quantification.

Results indicated that the optimum gradient flow should start at 1.5 ml min^{-1}, be constant for the first 4.5 min, rise to 4.0 ml min^{-1} from minute 4.5 to minute 7.2, and remain constant at 4.0 ml min^{-1} from minute 7.2 until the end of the chromatogram. In these conditions, the time required to obtain a full chromatogram was reduced to only 10 min (instead of the 20 min required by the conditions described in a previous paper [40]) but the number of spectra recorded was still high enough to obtain good results by the multivariate calibration procedure.

The change in chromatographic conditions led to a change in fluorimetric conditions, as the time windows used to record the FSFS spectra were shortened to fit the new situation. The new system conditions are described in Table 1.

In Figs. 4 and 5 a well-resolved three-dimensional chromatogram and a three-dimensional chromatogram recorded in the above-mentioned conditions are represented. For comparison purposes, their bidimensional projections are also shown.

3. Results and discussion

For the experimental study of the PARAFAC calibration procedure, 10 standards were used, and they were analyzed in four different ways: both constrained and unconstrained PARAFAC models were applied to the raw chromatograms and to smoothed chromatograms obtained by a factor analysis procedure, as described in the literature [41–43].

The differences between the two PARAFAC models are represented in Fig. 6. When no constraints were used, a purely mathematical solution was obtained, where the calculated coefficient matrices had no direct relationship with spectra or chromatographic peaks. When non-negative constraints were used, a so-called chemical solution was found, where, at least theoretically, the calculated loadings had a direct relationship with spectra or chromatographic peaks and might be used to repre-

Table 1
Characteristics of the method

Isocratic elution with flow gradient[a]		Spectrofluorimeter program	
Time (min)	Flow (ml min^{-1})	Time (min)	Detector wavelengths
0.0	1.5	0.00–2.70	λ_{ex}: 255 nm; λ_{em}: 335–435 nm
4.2	1.5	2.71–5.62	λ_{ex}: 280 nm; λ_{em}: 335–435 nm
7.5	4.0	5.63–8.47	λ_{ex}: 300 nm; λ_{em}: 335–435 nm
		8.48–10.60	λ_{ex}: 360 nm; λ_{em}: 400–500 nm

Working conditions for the chromatographic system: column, 15.0 cm×4.6 mm Spherisorb S5 PAH; mobile phase, acetonitrile–water (90:10, v/v).
[a]Detector conditions: scan speed, 50 nm s^{-1}; slit, 16–16 nm.

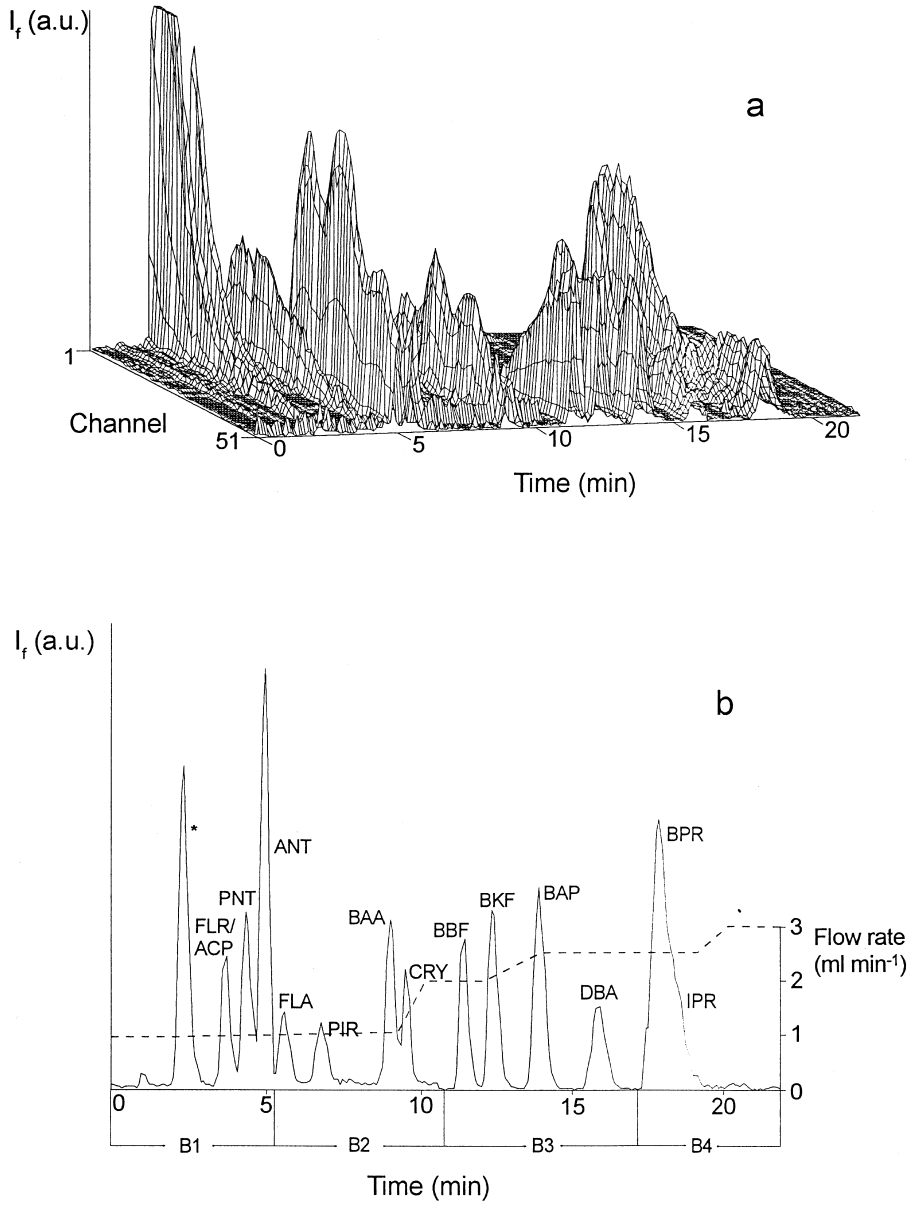

Fig. 4. Conventional FSFS chromatogram of a mixture of 14 PAHs (a) and its bidimensional projection (b). *, Toluene; FLR, fluorene; ACP, acenaphthene; PNT, phenanthrene; ANT, anthracene; FLA, fluoranthene; PYR, pyrene; BAA, benz[*a*]anthracene; CHR, chrysene; BBF, benzo[*b*]fluoranthene; BKF, benzo[*k*]fluoranthene; BAP, benzo[*a*]pyrene; DBA, dibenz[*a*,*h*]anthracene; BPR, benzo[*ghi*]perylene; IPR, indene[1,2,3-*cd*]pyrene.

sent them, although in practice this is usually true only for solutions containing a single compound. As an example, Fig. 6a shows the elution profiles for a mixture of fluoranthene, pyrene, benz[*a*]anthracene and chrysene, and Fig. 6b and Fig. 6c correspond to the decomposition by the unconstrained and constrained PARAFAC models respectively.

The efficiency of the models was tested by comparing the relative root-mean-squared error of fit (RRMSEF) [36],

$$\mathrm{RRMSEF} = \left(\sum_{k=1}^{m} \sum_{j=1}^{J} \sum_{i=1}^{I} (\boldsymbol{R}_{k,j,i} - \hat{\boldsymbol{R}}_{k,j,i})^2 \right)^{1/2} \Big/ \left(\sum_{k=1}^{m} \sum_{j=1}^{J} \sum_{i=1}^{I} (\boldsymbol{R}_{k,j,i})^2 \right)^{1/2}$$

where $\boldsymbol{R}$ is the tensor of real data and $\hat{\boldsymbol{R}}$ is the tensor predicted by the PARAFAC model, for $k=1$ to m chromatograms of standards, $j=1$ to J emission wavelengths, $i=1$ to I retention times.

In Table 2 the percentage of fit of the model for each block (mean of the fit of the 10 standards to the model) is shown, with the optimal number of factors needed to build the model. The differences in the percentage of fit can be mainly attributed to the different fluorescence intensities of the compounds studied. The compounds eluted in the last block (block 4) have fluorescence intensities that are lower than those of the compounds eluted in the first three blocks and, as a consequence, they are more affected by background noise. As the instrumental noise cannot be properly modeled by PARAFAC, results obtained for the last block are usually worse than the results of blocks 1–3. Moreover, the number of factors required to fit the model is, in most cases, higher than the number of compounds to be determined. This can be attributed to the presence of interferences which are not determined, because both the standards and the real samples are simultaneously processed in the data treatment. More factors are usually required to fit block 4 than to fit the other blocks, because it is more affected by background noise. The best fit was obtained, for all blocks, when smoothed data and no constraints were used, and, therefore, all further calculations were carried out using this model.

An additional study was done in order to test the ability of PARAFAC to predict the concentrations of the different compounds in a sample. The 10 standards were divided into two groups: seven were used as calibration set (with concentrations between 3 and 60 ng ml^{-1}) and three as validation set. A PARAFAC model was built for each detection block using the calibration set, and they were used to predict the concentration of each compound in the validation set. In Table 3, the real and the predicted values are shown. For each block the concentrations were calculated for all compounds simultaneously, using data from the whole block. In the case of compounds whose peaks appeared partially overlapped (fluorene–acenaphthene, fluoranthene–pyrene, benz[*a*]anthracene–chrysene), concentrations were also calculated using only data from the time range of the detection block where their peaks

Table 2
Percentage of fit of the PARAFAC model (calculated as 100×(1−RRMSEF))

Number of block	Compounds	Raw data		Smoothed data	
		No constraints	Non-negative constraints	No contraints	Non-negative contraints
1	Fluorene/acenaphthene/phenanthrene/anthracene	91.8[c]	84.5[a]	93.5[c]	85.5[a]
2	Fluoranthene/pyrene/benz[*a*]anthracene/chrysene	90.0[c]	81.7[b]	87.8[c]	84.7[b]
3	Benzo[*b*]fluoranthene/benzo[*k*]fluoranthene/benzo[*a*]pyrene/dibenz[*a*,*h*]anthracene	88.4[c]	84.8[b]	91.3[c]	86.6[b]
4	Benzo[*ghi*]perylene/indene[1,2,3-*cd*]pyrene	62.7[b]	53.9[a]	72.8[b]	59.6[a]

[a]Four factors used to build the model.
[b]Five factors used to build the model.
[c]Six factors used to build the model.

Table 3
Real and predicted values (μg l^{-1}) for the validation set

Compound	Sample 1		Sample 2		Sample 3	
	Pred.	Real	Pred.	Real	Pred.	Real
Fluorene[a]	17.6 (20.1)	20.8	22.1 (22.5)	22.9	23.6 (25.9)	26.0
Acenaphthene[a]	21.2 (22.0)	22.9	28.2 (28.2)	27.1	32.7 (24.4)	33.7
Phenanthrene[a]	14.2	14.6	39.4	39.8	46.7	44.0
Anthracene[a]	14.3	14.7	19.3	18.5	24.6	24.6
Fluoranthene[a]	14.3 (12.8)	13.4	17.7 (14.7)	16.8	25.8 (23.9)	23.8
Pyrene[a]	4.4 (8.4)	10.5	9.5 (28.5)	27.5	8.0 (32.2)	30.9
Benz[*a*]anthracene[a]	11.8 (11.6)	10.9	18.8 (18.6)	17.9	33.1 (32.6)	33.0
Chrysene[a]	9.6 (13.3)	10.7	25.8 (24.2)	25.3	22.6 (24.0)	29.1
Benzo[*b*]fluoranthene[a]	8.5	8.7	12.0	11.6	20.1	20.0
Benzo[*k*]fluoranthene[a]	6.0	7.4	13.8	15.3	3.9	3.1
Benzo[*a*]pyrene[a]	34.4	36.7	17.9	18.7	31.2	32.5
Dibenz[*a,h*]anthracene[a]	8.5	10.8	12.0	14.0	26.5	25.3
Benzo[*ghi*]perylene[b]	10.5	9.7	27.9	25.8	15.9	16.1
Indene[1,2,3-*cd*]pyrene[b]	29.8	31.5	23.2	23.3	11.3	14.6

All values calculated simultaneously. Results in parentheses were calculated for pairs of overlapped compounds.
[a]Six factors used to build the model.
[b]Five factors used to build the model.

appeared, and results obtained in this way are given in parentheses. In the case of indene[1,2,3-*cd*]pyrene, the predicted values disagreed with the real values, but this could be explained by the high background noise and, especially, the low fluorescence intensity of this compound.

After testing the method with standards, the PARAFAC procedure was used for the detection and quantification of polycyclic aromatic hydrocarbons in spiked tap water samples.

The water samples were spiked at 0.10–0.20 μg l^{-1} levels, preconcentrated as described in Section 2

Table 4
Spiked tap water samples

Compound	Sample 1 (μg l^{-1})			Sample 2 (μg l^{-1})	
	Added	Found[a], FSFS[b]	Found[a], WP[c]	Added	Found[a], FSFS
Fluorene	0.10	0.10±0.005	0.08±0.005	0.21	0.21±0.01
Acenaphthene	0.10	0.11±0.01	0.14±0.01	0.21	0.19±0.02
Phenanthrene	0.10	0.09±0.005	0.11±0.01	0.20	0.20±0.01
Anthracene	0.10	0.09±0.005	0.06±0.005	0.20	0.22±0.01
Fluoranthene	0.09	0.08±0.005	0.10±0.005	0.18	0.19±0.015
Pyrene	0.09	0.11±0.01	0.07±0.005	0.19	0.16±0.02
Benz[*a*]anthracene	0.10	0.09±0.01	0.09±0.01	0.19	0.21±0.015
Chrysene	0.10	0.09±0.005	0.09±0.005	0.20	0.21±0.01
Benzo[*b*]fluoranthene	0.10	0.10±0.005	0.12±0.005	0.21	0.21±0.021
Benzo[*k*]fluoranthene	0.10	0.10±0.005	0.10±0.005	0.21	0.21±0.01
Benzo[*a*]pyrene	0.10	0.09±0.01	0.10±0.01	0.20	0.22±0.02
Dibenz[*a,h*]anthracene	0.09	0.09±0.005	0.11±0.005	0.19	0.19±0.01
Benzo[*ghi*]perylene	0.10	0.09±0.01	0.11±0.01	0.20	0.22±0.02
Indene[1,2,3-*cd*]pyrene	0.10	0.11±0.01	0.12±0.01	0.21	0.18±0.02

[a]Mean of three independent samples.
[b]Fast-scanning fluorescence spectra detector.
[c]Wavelength programming fluorescence detector.

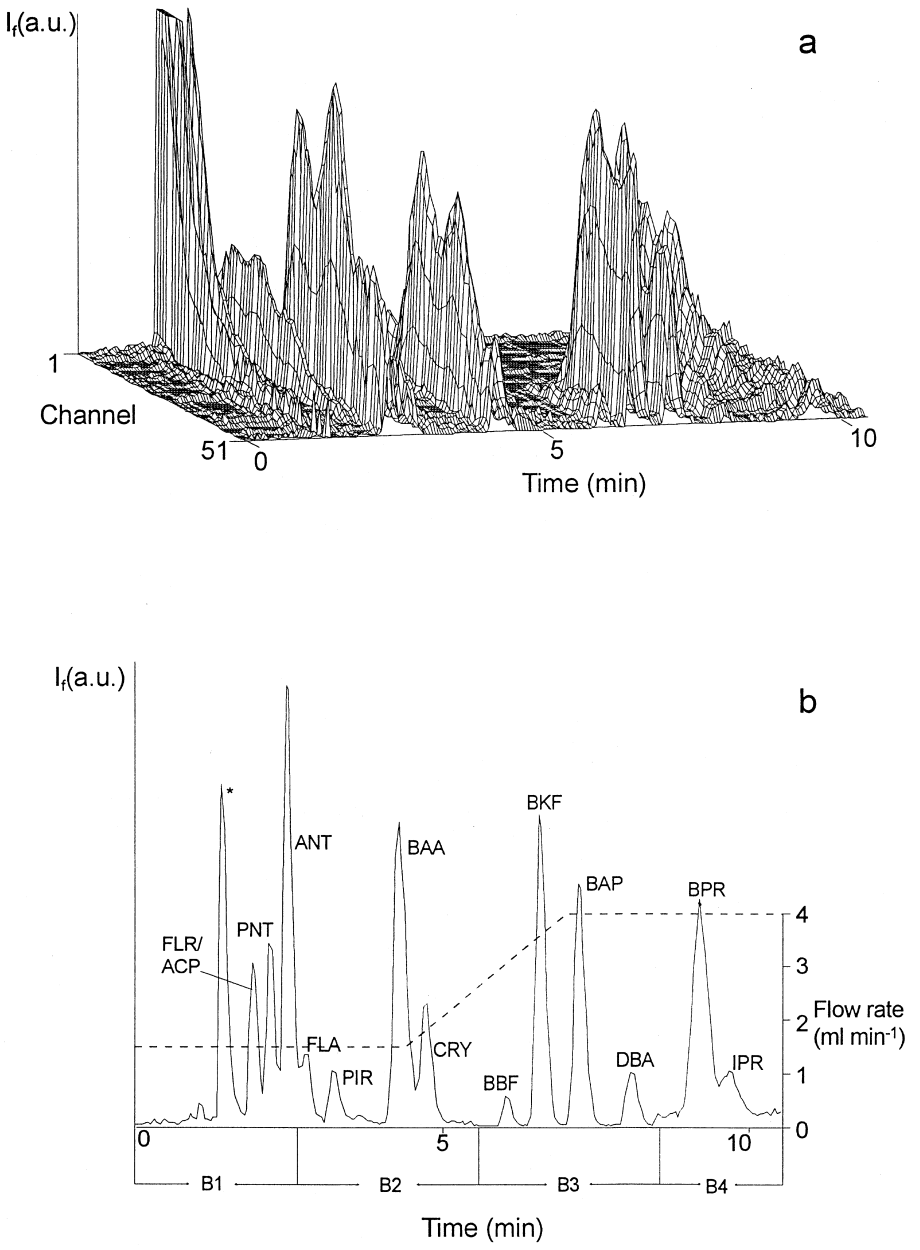

Fig. 5. Shortened HPLC–FSFS chromatogram obtained at the conditions given in Table 1 (a) and its bidimensional projection (b). Symbols as in Fig. 4.

and analyzed by the PARAFAC procedure. The results obtained, corrected with respect to recoveries, are shown in Table 4. In addition, the more diluted sample was also analyzed by a conventional HPLC procedure with a wavelength-programmed fluorescence detector [40], and the results are also given in

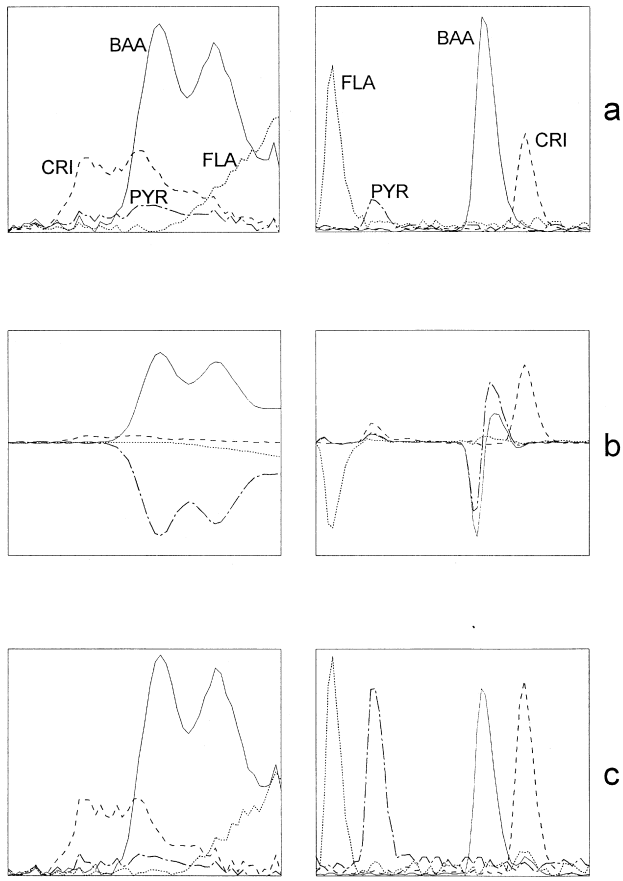

Fig. 6. (a) Real individual emission spectra and elution profiles for the different compounds present in a mixture. (b) Loadings obtained by unconstrained PARAFAC decomposition. (c) Loadings obtained by PARAFAC decomposition with non-negative constraints.

Table 4, for comparison purposes. A chromatogram of the sample spiked at 0.1 μg l^{-1} is shown in Fig. 7.

4. Conclusions

The PARAFAC decomposition of HPLC–FSFS data, obtained by an alternating least-squares procedure, is a valid alternative to conventional chromatographic methods for the determination of polycyclic aromatic hydrocarbons. Results are similar, but the chromatographic system can be simplified and the time required to record a chromatogram is considerably shortened, as a total separation of the different compounds is not necessary.

This proposed procedure could also be applied to other bilinear data, such as those obtained by the diode array detectors used in HPLC or capillary electrophoresis.

Acknowledgements

The authors thank Dr. Rasmus Bro (KVL, Denmark) for kindly supplying the PARAFAC program.

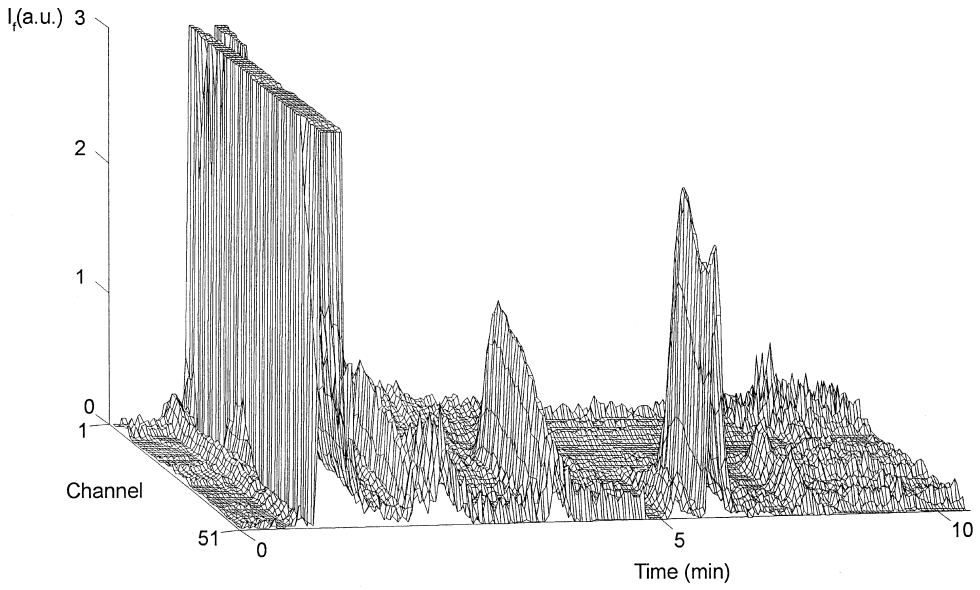

Fig. 7. Chromatogram of a water sample spiked at a 0.10 μg l^{-1} level.

References

[1] E.R. Brouwer, A.N.J. Hermans, H. Lingeman, U.A.Th. Brinkman, J. Chromatogr. A 669 (1994) 45.
[2] J.C. Fetzer, W.R. Biggs, J. Chromatogr. 642 (1993) 319.
[3] J.G. Dorsey, W.T. Cooper, J.F. Wheeler, H.G. Barth, F.P. Foley, Anal. Chem. 66 (1994) R500.
[4] O. Bruggemann, R. Freitag, J. Chromatogr. A 717 (1995) 309.
[5] T.L. Cecil, S.C. Rutan, J. Chromatogr. 556 (1991) 495.
[6] J. Wegrzyn, G. Patonay, M. Ford, I. Warner, Anal. Chem. 62 (1990) 1754.
[7] R.B. Poe, S.C. Rutan, Anal. Chim. Acta 283 (1993) 845.
[8] J.C. Gluckmann, D.C. Shelly, M.V. Novotny, Anal. Chem. 57 (1985) 1546.
[9] R.J.v.d. Nesse, C. Gooijer, G.Ph. Hoornweg, U.A.Th. Brinkman, N.H. Velhorst, Anal. Lett. 23 (1990) 1235.
[10] S.J. Kok, R. Posthumus, I. Bakker, C. Gooijer, U.A.Th. Brikman, N.H. Velhorst, Anal. Chim. Acta 303 (1995) 3.
[11] G.A.M. Dalhoeven, N.V. Joshi, N. Rodriguez, R. Hernandez, J. Liq. Chromatogr. 18 (1995) 3729.
[12] J. Johanson, D.T. Witte, M. Larsson, S. Nilson, Anal. Chem. 68 (1996) 2766.
[13] R. Ferrer, J. Guiteras, J.L. Beltrán, J. Chromatogr. A 779 (1997) 123.
[14] B.G.M. Vandeginste, W. Darks, G. Kateman, Anal. Chim. Acta 173 (1985) 253.
[15] X.H. Liang, J.E. Andrews, J.A. Dehaselh, Anal. Chem. 68 (1996) 378.
[16] Y.N. Ni, S. Kokot, M. Selby, M. Hodkinson, Anal. Chim. Acta 316 (1995) 233.
[17] H. Gammp, M. Maeder, Ch. Meyer, A.D. Zuberbühler, Talanta 32 (1985) 1133.
[18] M. Elomma, C.H. Lochmuller, M. Kaljurand, M. Koel, Chem. Intell. Lab. Sys. 30 (1995) 129.
[19] F.C. Sanchez, J. Toft, O.M. Kvalheim, D.L. Massart, Anal. Chim. Acta 314 (1995) 131.
[20] E.R. Malinowski, J. Chemometr. 6 (1992) 29.
[21] R.G. Brereton, S.P. Gorden, J.A. Groves, Chem. Intell. Lab. Sys. 27 (1995) 73.
[22] K.R. Beebe, B.R. Kowalski, Anal. Chem. 59 (1987) 1007A.
[23] E.R. Malinowski, Factor Analysis in Chemistry, 2nd ed., Wiley, New York, 1991.
[24] S.C. Rutan, Anal. Chem. 63 (1991) 1103A.
[25] P.D. Wentzell, S.H. Hughes, S.J. Vanslyke, Anal. Chim. Acta 307 (1995) 459.
[26] E. Sanchez, B.R. Kowalski, Anal. Chem. 58 (1986) 496.
[27] B.E. Wilson, E. Sanchez, B.R. Kowalski, J. Chemometr. 3 (1989) 493.
[28] S. Li, J.C. Hamilton, J. Gemperline, Anal. Chem. 64 (1992) 599.
[29] N.M. Faber, M.J. Meinders, P. Geladi, M. Sjostrom, L.M.C. Buydens, G. Kateman, Anal. Chim. Acta 304 (1995) 273.
[30] Y.L. Xie, J.J. Baeza-Baeza, G. Ramis-Ramos, Chem. Intell. Lab. Sys. 32 (1996) 215.
[31] B. Antalek, W. Windag, J. Am. Chem. Soc. 118 (1996) 10331.
[32] T. Vo-Dinh (Ed.), Chemical Analysis of Polycyclic Aromatic Compounds, Wiley, New York, 1989.

[33] A. Bjorseth, Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, New York, 1983.
[34] C.A. Menzie, B.B. Potocki, J. Santodonato, Environ. Sci. Technol. 26 (1992) 1278.
[35] P. Kroonenberg, J. deLeeuw, Psychometrika 45 (1980) 69–97.
[36] A.R. Muroski, K.S. Booksh, M.L. Myrick, Anal. Chem. 68 (1996) 3534.
[37] K.S. Booksh, A.R. Muroski, M.L. Myrick, Anal. Chem. 68 (1996) 3539.
[38] A.K. Smilde, D.A. Doorbos, J. Chemometr. 5 (1991) 345.
[39] R. Bro, Chemometr. Intel. Lab. (in press).
[40] R. Ferrer, J. Guiteras, J.L. Beltrán, Anal. Lett. 29 (1996) 2201.
[41] M. Meloun, J. Havel, E. Högfeldt, Computation of Solution Equilibria: A Guide to Methods in Potentiometry, Extraction and Spectrophotometry, Horwood, Chichester, 1988.
[42] E.R. Malinowski, D.G. Howery, Factor Analysis in Chemistry, Wiley, New York, 1980.
[43] J.J. Kankare, Anal. Chem. 42 (1970) 1322.