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Talanta 49 (1999) 889–897

Talanta

Parafac decomposition of three-way kinetic-spectrophotometric spectral matrices corresponding to mixtures of heavy metal ions

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Received 23 June 1998; received in revised form 14 December 1998; accepted 1 March 1999

Abstract

Binary and ternary mixtures of some of the following heavy metal ions Zn(II), Ni(II), Pb(II), Co(II) and Cd(II) were analyzed by a ligand substitution kinetic method. Three-way data matrices were generated by acquisition of UV–Vis spectra (332–580 nm) as a function of the time of a substitution reaction observed between the complex of the heavy metal ions with the non selective metallochromic indicator 4-(2-pyridylazo) resorcinol (PAR) and EDTA, and of different relative concentration of the metal ions (1–6 mM). The PARAFAC trilinear model, without restrictions, was used in the data analysis. A full decomposition of the data matrices was obtained (spectra, concentration and time profiles). It was shown that ligand substitution kinetic methods coupled to three-way chemometric analytical methods can be used for the development of robust sensors for the analysis of binary [Zn(II) + Ni(II), Pb(II) + Cd(II), Zn(II) + Pb(II)] or ternary [Zn(II) + Pb(II) + Co(II)] mixtures of metal ions in the micromolar concentration range. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic-spectrophotometric data; Mixtures of heavy metal ions; PARAFAC

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1. Introduction

The simultaneous determination of metal ions at trace amounts in complex samples usually requires relatively expensive analysis, involving atomic absorption or emission spectrophotometric equipment. Kinetic methods of analysis constitutes a much simpler alternative to the analysis of mixtures of metal ions [1–13]. Indeed, with a standard UV–Vis spectrophotometer, analytical methodologies can be developed based on metal ion complex formation reactions and, for example, on the different rates of ligand substitution reactions.

If a UV–Vis spectrophotometer equipped with a diode array detector is used in the acquisition of spectra as function of the time of a reaction, each sample generates a two-way data matrix (spectra versus time), i.e. a second-order analytical device is obtained [7–13]. Kinetic methods based on this

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PII: S0039-9140(99)00083-1

type of instruments have one great advantage over traditional kinetic-spectrophotometric methods which is the unnecessary to formulate a kinetic model. Indeed, multivariate calibration techniques allow the development of empirical calibration models to predict the concentrations of analytes in unknown samples. Chemometric calibration techniques of principal components regression, partial least squares and artificial neural networks [14,15] have been used to model kinetic-spectrophotometric data [7–13]. However, these calibration techniques take advantage of only a fraction of all the information available in the data generated by the second-order instrument, i.e. the possibility of analyte quantification in the presence of unknown interferences and complex backgrounds is not possible.

A three-way data matrix is created when a set of two-way data matrices having different relative proportions of the metal ions under analysis are put together. From the simultaneous analysis of these three-way data matrices robust analytical methods for the simultaneous quantitative analysis of metal ions can be developed based on the so-called 'second-order advantage', i.e. robust estimation of the analytes concentration in mixtures that contains unknown interferences [16–18]. The second order advantage achieved from the analysis of three-way data is an application of the 'unique decomposition property' which was first investigated in the field of psychometrics [19–22]. The unique decomposition of kinetic-spectrophotometric matrices should allow the calculation without any a priori information of the three basic properties of the constituents of the mixture under analysis (spectra, concentrations time profiles), which are related to the respective kinetic properties.

The analysis of three-way data matrices in analytical chemistry studies began with a liquid chromatography work [23] and the number of applications is increasing [24–39]. Nevertheless, the number of studies using experimental data is still very limited. One method that is being used to check if a three-way chemical structure is candidate to a unique decomposition is PARAFAC (parallel factor analysis) [22] because of two facts: (1) from a theoretical point of view this method allows a unique decomposition; and (2) this method has a basic trilinear model which is compatible with analytical data structures involving spectrophotometric measurements.

This paper presents a method for the experimental generation of three-way kinetic-spectrophotometric matrices that can be uniquely decomposed by PARAFAC. Data matrices correspond to binary and ternary mixtures of the following heavy metal ions: Zn(II); Ni(II); Pb(II); Co(II); Cd(II). Three-way matrices were generated by the acquisition of spectra of standards, with different relative concentration of the metal ions, during the ligand substitution reaction that is observed when EDTA is added to mixtures of the metal ions and the non-selective metallochromic indicator 4-(2-pyridylazo) resorcinol (PAR).

The objective of this work was to evaluate the performance of the PARAFAC model in the decomposition of three-way kinetic-spectrophotometric data matrices. The results obtained in this work may constitute the basis for the development of analytical methodologies for the detection of heavy metal ions in the micromolar concentration range, that take advantages of the second-order advantage.

2. Theory

A three-way data structure corresponding to a kinetic-spectrophotometric experiment can be expressed by the following equation:

$$a_{ijk} = \sum_{s=1}^{nf} t_{is} w_{js} c_{ks} + e_{ijk}$$

$$i = 1,\ldots,nt \quad j = 1,\ldots,nw \quad k = 1,\ldots,ns \qquad (1)$$

where a_{ijk} are the elements of the experimental matrix of absorbances **A**, w_{js} are the elements of the matrix **S** containing the spectra (each one with nw wavelengths) of the spectroscopically active species (ns species), t_{is} are the elements of the matrix **T** containing the time profiles (each one with nt time points) of the ns species, c_{ks} are the elements of the matrix **C** which contain the relative concentration of the *ns* species, *nf* is the number of factors of the model, e_{ijk} are the elements of the matrix of the spectroscopic error.

Eq. (1) also represents the basic three-way PARAFAC model [22]. After selecting *nf*, the three basic unknown matrices **T**, **S** and **C** are calculated by an iterative alternating least squares method without any restrictions, taking as a first approximation for the three matrices a random generated set; several independent runs are performed to check for a unique decomposition. The number of factors of the model is the intrinsic dimensionally of the data matrix and correspond to the observed no correlated spectral variations. If the absorbance readings are always directly proportional to the concentration of the *ns* species, i.e. the Lambert–Beer law is obeyed in the concentration, wavelength and time ranges used in the experiments, the generated three-way data structure is trilinear. Under this condition, *nf* is equal to *ns*. The number of spectroscopicaly active species in the kinetic-spectroscopic experiments is equal to the number of metal ions plus one corresponding to the metallochromic indicator.

The quality of the fit of experimental data to the tested model is assessed by the value of the loss function after convergence is achieved, which is defined by:

$$\sum_{i=1}^{nt}\sum_{j=1}^{nw}\sum_{k=1}^{ns} e_{ijk}^2 = \sum_{i=1}^{nt}\sum_{j=1}^{nw}\sum_{k=1}^{ns} (a_{ijk} - a'_{ijk})^2 \qquad (2)$$

where a'_{ijk} are the predicted elements of the experimental matrix. In this work, a quite low value for this function (1.0×10^{-8}) was always used as criteria to stop the alternating least squares process.

The elements of the concentration matrix are of particular importance in this work because of the heavy metal ion quantification objective and were subjected to a quality of prediction analysis. This test consisted in the plot of the predicted versus real concentrations and calculation of the following regression parameters: intercept and corresponding confidence interval at 95%; correlation coefficient.

3. Experimental

3.1. Reagents

All reagents were of analytical grade and used without purification. About 1.0 mM aqueous solutions of the metal ions were prepared by weighting the following salts: $CoCl_2{\cdot}6H_2O$; $Zn(NO_3)_2{\cdot}4H_2O$; $Cd(NO_3)_2{\cdot}4H_2O$; $Pb(NO_3)_2$; $NiCl_2{\cdot}6H_2O$. Borax buffer (pH 9.50) was prepared by mixing 4.77 g of borax, 75 ml of 0.10 M NaOH and the necessary volume of 0.10 M KNO_3 until a total volume of 500 ml. PAR [4-(2-pyridylazo) resorcinol] solution (1.0 mM) was prepared in the borax buffer. Standard 0.100 M EDTA solution was prepared from a concentrated solution (Titrisol Merck).

Solutions to be analyzed were prepared by mixing the metal ions to the final concentration in the micromolar range, PAR (20–40 μM) and borax buffer. The design of metal ion solutions followed a full factorial experimental design with four levels for binary mixtures and three levels for ternary mixtures. EDTA solution to be used in the analysis (1.00–6.00 mM) were prepared by diluting the concentrated 0.100 M solution with borax buffer.

3.2. Instruments

A Hewlett-Packard 8452A diode-array spectrophotometer controlled by a Hewlett-Packard computer and equipped with a 1-cm pathlength quartz cell with a cell stirring module (Hewlett-Packard 89054A and 89055A) was used for UV–Vis spectra acquisition. Spectra were acquired between 332 and 580 nm (2 nm resolution), with 0.2 s integration time and 0.5 s cycle time during a 30-s time window (one experiment generated 60 spectra). These integration and cycle times allow the acquisition of relatively low noise spectra at a relatively fast rate.

3.3. Experimental procedures

The mixture of metal ions, PAR and borax buffer (3.00 ml) was placed in the quartz cell together with a magnetic bar (Hewlett-Packard 9301-1161) to promote mixing. Spectra acquisition began with the injection of the diluted EDTA solution (30 μl). The mixtures of heavy metals analyzed in this work, as well as the total concentration of the three constituents involved in the ligand substitution reactions, i.e. metal ion, PAR and EDTA, are shown in Table 1.

3.4. Data analysis

Spectra were translated to ASCII format using homemade software developed in Turbo Pascal (Borland, USA). Each spectrum was composed of 125 points and, to reduce the dimension of the three-way data matrices, each experiment was composed of the first 49 spectra (the last 11 spectra were not considered) because no marked spectral variation was observed in the last spectra. The program TRILIN, obtained from P.M. Kroonenberg (Department of Education, Leiden University), was used for the PARAFAC decomposition.

4. Results and discussion

4.1. Preliminary analysis of spectral data

Fig. 1 shows typical two-way data matrices corresponding to single and mixtures of heavy metal ions. A preliminary analysis of this figure shows a common feature, i.e. a decrease of intensity of a band located at about 500 nm and the increase of the intensity of the band at 414 nm. The decreasing band correspond to the complex formed between PAR and the metal ions and the decreasing trend is due to the substitution reaction of PAR by EDTA, resulting in a spectroscopically inactive species in the visible wavelength range. The band that appears at 414 nm is due to the uncomplexed PAR which free concentration increases with time. In the case of the mixtures (Fig. 1d–f) no marked differences are detected when compared with the single heavy metal ion spectral data (Fig. 1a–c) revealing similar spectral properties. Indeed, the maximum of the band of the complexes observed between PAR and the heavy metal ions fall in a narrow wavelength range of 16 nm. The maximum of the bands of the complexes are (the width at 50% high is about 80 nm): PAR + Zn(II), 490 nm plus a shoulder at 520 nm; PAR + Ni(II), 495 nm plus a shoulder at 526 nm; PAR + Pb(II), 516 nm; PAR + Co(II), 500 nm; PAR + Cd(II), 490 nm plus a shoulder at 522 nm. The broad band characteristic of the

Table 1
Experimental concentrations used to generate three-way data matrices from the mixtures of heavy metal ions

Mixture	Metal ion	Concentration[a]		
		Metal ion	PAR	EDTA
Binary mixtures				
Zn(II) + Ni(II)	Zn(II)	0.0; 1.0; 2.0; 4.0	20.0	13.3
	Ni(II)	0.0; 1.0; 2.0; 4.0		
Pb(II) + Cd(II)	Pb(II)	0.0; 1.0; 3.0; 6.0	20.0	13.3
	Cd(II)	0.0; 1.0; 2.0; 3.0		
Zn(II) + Pb(II)	Zn(II)	0.0; 1.0; 2.0; 3.0	20.0	13.3
	Pb(II)	0.0; 1.0; 3.0; 6.0		
Ternary mixture				
Zn(II) + Pb(II) + Co(II)	Zn(II)	1.0; 3,0; 6.0	40.0	60.0
	Pb(II)	1.0; 3,0; 6.0		
	Co(II)	1.0; 2,0; 3.0		

[a] The concentrations of the metal ions and PAR are expressed in μM and the concentrations of EDTA are expressed in mM.

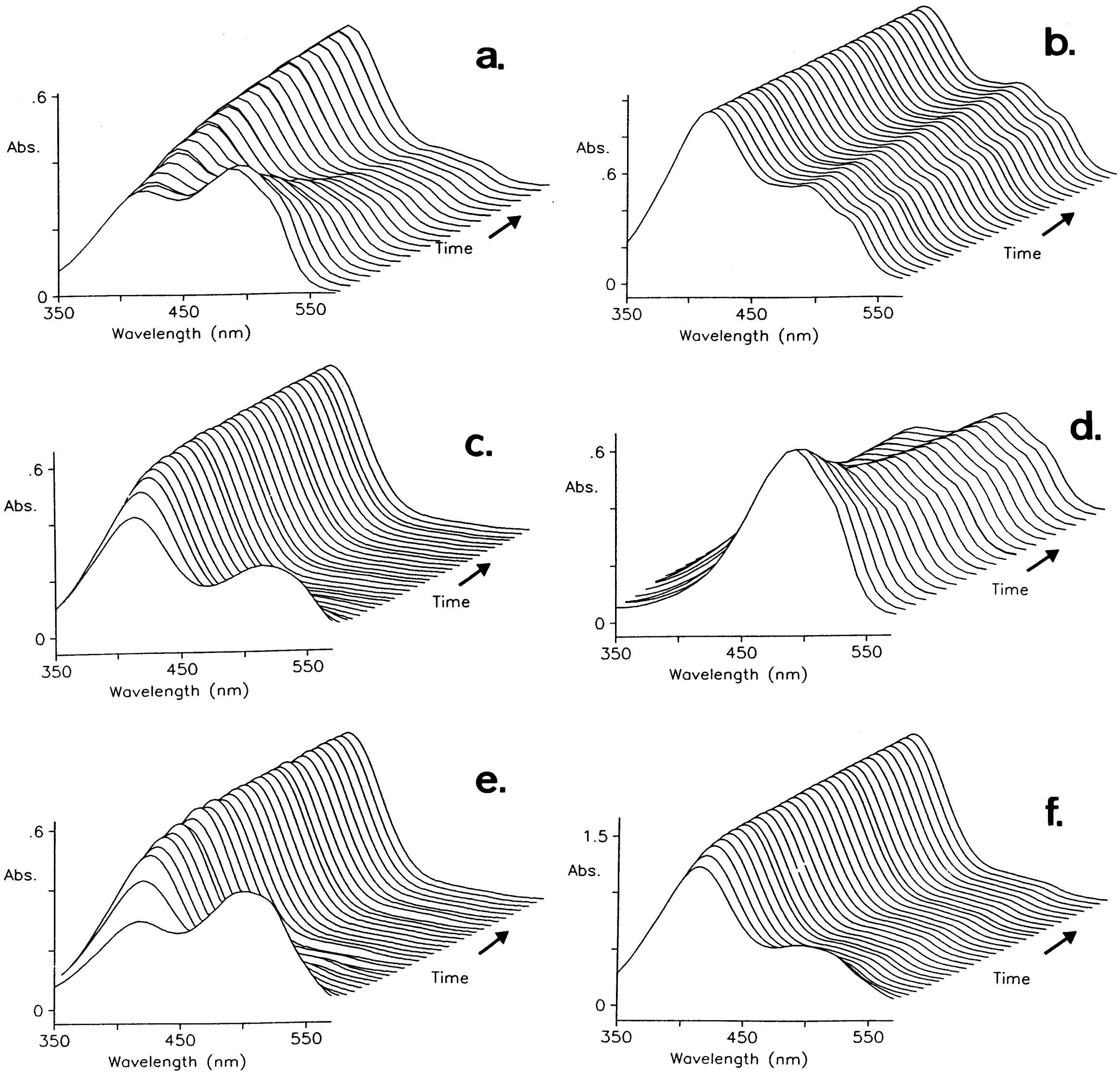

Fig. 1. Three-way spectral data matrices corresponding to the following metal ions or mixtures: (a) Zn(II) (4.0 μM); (b) Ni(II) (6.0 μM); (c) Pb(II) (6.0 μM); (d) Zn(II) + Ni(II) (4.0 μM both ions); (e) Pb(II) + Cd(II) (6.0 and 3.0 μM, respectively); (f) Zn(II) + Pb(II) + Co(II) (6.0, 3.0 and 1.0 μM, respectively).

spectra of the PAR complexes is also responsible for the relatively high spectral overlap.

The direct analysis of the decreasing band at 520 nm for the data sets corresponding to single ions (Fig. 2) allowed to obtain a relative sorting of the ligand substitution reaction rates (decreasing order): Pb(II) > Cd(II) > Zn(II) > Ni(II) ≈ Co(II).

4.2. Single ion three-way data matrices

PARAFAC decomposition of three-way spectral matrices corresponding to single ions was performed using two factors to check for the trilinearity of the single ion data structures. Fig. 3 shows a typical decomposition result [Ni(II) experiments] and Table 2 presents some linear re-

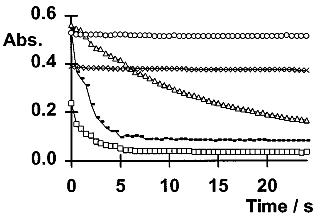

Fig. 2. Absorbance decreasing curves of the spectral band corresponding to the complex formed between the metal ions and PAR with time: (△) Zn(II); (○) Ni(II); ([]) Pb(II); (×) Co(II); (–) Cd(II).

gression parameters observed between the predicted and experimental concentrations.

The analysis of the calculated spectra of the two factors (Fig. 3a) shows that one (the first) has only positive values and the other (the second) has a negative and a positive section. The first one corresponds to the constant spectra (no variation is observed with time) and is constituted by the PAR band at about 414 nm and by the band of the fraction of the unreacted complex, if at the end of the monitoring time (about 30 s) the metal ion complex is not fully exchanged by EDTA. The negative part of the other calculated spectrum corresponds to the band of the complex formed between the metal ion and PAR which concentration decreases with time. The positive section of this spectrum is due to the increasing band of the free PAR. These two sections of the second spectra are a consequence of the opposite but correlated spectral variations of the two chemical species involved: when the concentration of the metal ion PAR complex decreases the concentration of free PAR increases.

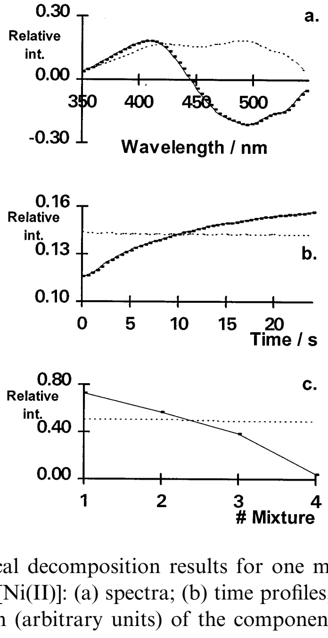

Fig. 3. Typical decomposition results for one metal ion spectral data set [Ni(II)]: (a) spectra; (b) time profiles; (c) estimated concentration (arbitrary units) of the components in the mixtures.

The calculated time profiles have a similar shape, but with different intensity, to that shown in Fig. 3b. The profile corresponding to the constant spectra is, as expected, a horizontal line, showing no time dependence. The other profile is a curve, with an increasing or decreasing trend, corresponding to the observed spectral variation as the substitution reaction is occurring. From the point of view of the metal ion PAR complex a time profile with a decreasing trend is expected because the concentration of the complex is decreasing. On the contrary, and from the point of view of the free PAR, an opposite trend is expected for the free PAR. Because the time variation of the metal ion PAR complex and free PAR are negatively correlated, one profile can be obtained from the other.

For quantitative analysis the most important information is the concentrations of the heavy metal ions that constitute the mixture. In order to assess the estimated values (arbitrary units), plots representing the estimated values as function of the experimental concentration (molar concentration) were obtained. The correlation coefficients and confidence intervals about the intercept are calculated to check for linearity and are shown in Table 2. As shown in Table 2 relatively high correlation coefficients and confidence intervals including the zero support the existence of linearity. However, these statistical parameters were obtained when the zero concentration was not included in the calculations; if this value was included, deviations from linearity were observed.

4.3. Mixtures of metal ions

PARAFAC decomposition of three-way spectral matrices corresponding to mixtures of ions was performed using a number of factors equal to

Table 2
Typical linear regression parameters observed between the predicted (arbitrary units) and experimental (μM) concentrations of heavy metal ions

Mixture	Metal ion	R[a]	Intercept	Confidence interval (95%)
Single ions[b]				
Zn(II)	Zn(II)	0.9932	-1.0×10^{-7}	$[-4.2\times10^{-6}; 4.0\times10^{-6}]$
Ni(II)	Ni(II)	0.9747	-2.6×10^{-7}	$[-1.7\times10^{-5}; 1.2\times10^{-5}]$
Pb(II)	Pb(II)	0.9955	-8.2×10^{-7}	$[-6.4\times10^{-6}; 4.8\times10^{-6}]$
Co(II)	Co(II)	0.9927	3.6×10^{-6}	$[8.4\times10^{-7}; 6.3\times10^{-6}]$
Cd(II)	Cd(II)	0.9989	-2.2×10^{-7}	$[-1.6\times10^{-6}; 1.2\times10^{-6}]$
Binary mixtures				
Zn(II) + Ni(II)	Zn(II)	0.9794	-2.7×10^{-7}	$[-5.8\times10^{-7}; 4.2\times10^{-8}]$
	Ni(II)	0.9981	3.7×10^{-6}	$[3.6\times10^{-6}; 3.8\times10^{-6}]$
Pb(II) + Cd(II)	Pb(II)	0.9527	8.3×10^{-7}	$[7.3\times10^{-8}; 1.6\times10^{-6}]$
	Cd(II)	0.7252	-1.0×10^{-6}	$[-2.6\times10^{-6}; 5.7\times10^{-7}]$
Zn(II) + Pb(II)	Zn(II)	0.9820	-3.3×10^{-8}	$[-2.6\times10^{-7}; 1.9\times10^{-7}]$
	Pb(II)	0.9545	1.2×10^{-7}	$[-5.1\times10^{-5}; 7.1\times10^{-7}]$
Ternary mixture				
Zn(II) + Pb(II) + Co(II)	Zn(II)	0.9970	1.2×10^{-7}	$[-3.4\times10^{-7}; 9.7\times10^{-8}]$
	Pb(II)	0.9603	4.6×10^{-7}	$[-3.2\times10^{-7}; 1.2\times10^{-6}]$
	Co(II)	0.9959	8.0×10^{-6}	$[7.6\times10^{-6}; 8.5\times10^{-6}]$

[a] Correlation coefficient.

[b] Single ion sets constituted by three two-way data matrices correspond to subsets of binary mixtures where the other ion has zero concentration.

the number of metal ions present plus one, to account for the existence of the constant PAR spectra and other constant spectral sections. Several binary and ternary mixtures of the five metal ions were tested but only some were uniquely decomposed with success by PARAFAC (shown in Table 2). It was observed that the most important factor to take into consideration in the design of mixtures candidate to a unique decomposition is the time profile. The greater the differences are in the kinetic properties of the ligand substitution reaction for the metal ions constituents of the mixtures the better the decomposition is achieved.

Fig. 4 [binary mixture of Zn(II) + Pb(II)] and Fig. 5 [ternary mixture of Zn(II) + Pb(II) + Co(II)] show typical decomposition results and Table 2 presents some linear regression parameters observed between the calculated (arbitrary units) and experimental concentrations.

The calculated spectra of the PAR complexes (Fig. 4a and Fig. 5a) have a similar shape to that obtained in the single ions study. The calculated spectra of the PAR complexes exactly matches those observed experimentally. The analysis of Fig. 4a and Fig. 5a also shows that besides the high overlap of the bands, i.e. a relatively low resolution in the wavelength order, the PARAFAC decomposition was able to reconstruct the individual spectral bands without restrictions.

The calculated time profiles (Fig. 4b and Fig. 5b) for the individual constituents of the mixtures followed the expected trend presented above.

The calculated concentrations, shown as examples in Fig. 4c and Fig. 5c, are good estimation of the experimental values, i.e. they are directly proportional, with a prediction quality similar to that obtained for the single ions (Table 2). Worst correlation was obtained for the estimation of Cd(II) in the binary mixture of Pb(II) + Cd(II) which is due to the somewhat similar time profiles of these two cations.

5. Limitations of the unique decomposition process

The general rule to obtain a unique decomposition of the kinetic-spectrophotometric data matrices corresponding to binary or ternary mixtures of the five heavy metal ions analyzed in this work is that the metal ions in the mixture must have different spectra and time profiles. For example, because the species PAR + Zn(II) and PAR + Cd(II) have similar spectra (maximum of the band at 490 nm plus a shoulder at about 520 nm) these two ions do not generate kinetic-spectrophotometric data matrices candidates to a unique decomposition. The same is observed for mixtures of Co(II) and Ni(II), because they have similar time profiles (Fig. 2).

Nevertheless, in the case of mixtures containing ions with similar spectral or kinetic properties the modification of the experimental system, for example the pH or the metallochromic indicator, can give origin to more selective information. Alternatively, other decomposition processes with specific design restrictions could be used [40,41].

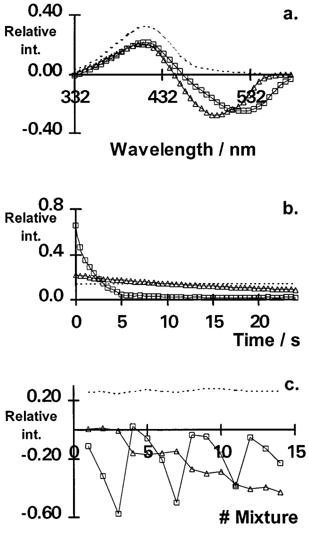

Fig. 4. Typical decomposition results for the mixtures of two metal ions [Zn(II) + Pb(II)]: (a) spectra; (b) time profiles; (c) estimated concentration (arbitrary units) of the components in the mixtures. The symbols correspond to the following metal ions: (△) Zn(II); ([]) Pb(II).

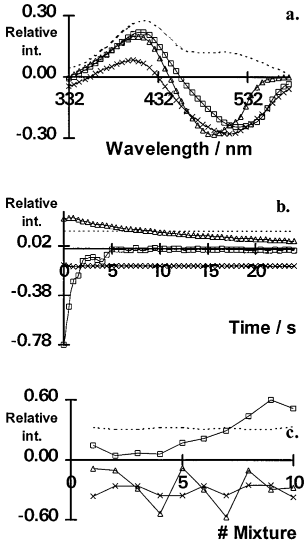

Fig. 5. Typical decomposition results for the mixtures of three metal ions [Zn(II) + Pb(II) + Co(II)]: (a) spectra; (b) time profiles; (c) estimated concentration (arbitrary units) of the components in the mixtures. The symbols correspond to the following metal ions: (△) Zn(II); ([]) Pb(II); (×) Co(II).

6. Conclusion

It was shown that simple kinetic-spectrophotometric experimental procedures are able to generate trilinear data structures from mixtures of heavy metal ions candidates to a unique decomposition process. As consequence, there is the potential for the development of analytical methodologies for the simultaneous and robust quantitative analysis of heavy metal mixtures at the micromolar concentration range.

The PARAFAC model successfully interpreted analytical chemistry data presented in this work. This result supports the usefulness of PARAFAC based chemometric techniques to solve some complex analytical chemistry problems.

Acknowledgements

A PBIC/QUI/C/2177/95 project grant is acknowledged to F.C.T. (Lisbon). A PhD grant (BD/9187/96) to C.J.S. Oliveira is acknowledged to PRAXIS XXI (Lisbon).

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