Application of Model-Based Rank Annihilation Factor Analysis in Complex Formation Systems and Comparison of the Results with Hard and Soft Modeling Methods

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In present work, rank annihilation factor analysis was used to determine the formation constants of complexes between 3,6-*bis*[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulphonic acid disodium salt Arsenazo(III) and 13 lanthanides. The applicability of rank annihilation factor analysis for resolving the three competitive complex formation equilibria with large spectral overlapping of the three complex species was shown by comparison of the results with those obtained with the hard- and soft-modeling methods, which show satisfactory agreement between the results. The results showed that all the 13 lanthanides (M) studied form similar type of complexes and spectral profiles with Arsenazo (III) (L). For each of them, the three formation constants correspond, respectively, to M to L ratios of 1:1, 1:2 and 2:2.

Key Words: Rank annihilation factor analysis, Chemometrics, Hard modeling, Soft modeling, Lanthanides, Arsenazo(III).

INTRODUCTION

Spectrophotometric titrations are important methods for the investigation of solution equilibria. The titration consists of a collection of spectra of a solution measured as a function of reagent added which influences the equilibrium under the investigation[1,2].

Recently, second-order instruments and techniques have gained multiply importance in analytical chemistry laboratories. Second-order techniques depend on two separated analytical methods linked in. A second-order tensor or a data matrix is generated for each single measurement run. The spectra measured from a chemical equilibrium process can form a second-order data matrix, which contains both the equilibrium information and the pure spectrum of each component involved in the chemical process. The proper chemometric algorithms can be used for evaluating the equilibrium information such as the stability constant through analysis of the second-order spectroscopic data. Several soft and hard-modeling algorithms have been developed to analyze bilinear data obtained from chemical systems.

Soft-modeling methods range from general approaches, such as evolving factor analysis (EFA)[3], which is particularly used to estimate the number of species involved in equilibrium studies and the kinetic process by repeated factor analysis of rationally selected subsets of spectra. Factor analysis investigates the rank of the subset of spectra by determining its number of significant eigenvalues[4].

Hard-modeling approaches of fitting multivariate response data are based on mathematical relationships, which describe the measurements quantitatively[5,6]. In chemical equilibria, the analysis is based on the equilibrium model, which quantitatively describes the reaction and all concentrations in the solution under investigation. Within the hard-modeling methods, analysis of spectral data has shown an optimal performance on many occasions[7-9].

Soft-modeling approaches are based on much more general prerequisites, such as positive molar absorbances and concentrations. Multivariate curve resolution-alternating least-squares (MCR-ALS)[10] is an iterative soft-modeling resolution method that has been successfully applied to solve many mixed dynamic processes monitored spectrometrically, such as chromatographic runs[11,12], biomacromolecular reactions[13,14], voltammetric data and environmental data[15-17]. In fact multivariate curve resolution is a self-modeling chemometric discipline that comprises several techniques for establishing an initial model on the data and extracting maximum amount of information from the data. These results are useful to validate

hard-modeling results and investigating the complex chemical systems[18].

Rank annihilation factor analysis (RAFA) is an efficient chemometric technique based on rank analysis for two-way spectrum data and can be employed to analyze the system with unknown background quantitatively. Rank annihilation factor analysis was originally developed by Ho *et al.*[19] as an iterative procedure and modified by Lorber[20,21] to yield a direct solution of a standard eigenvalue problem. Sanchez and Kowalski[22] extended the method to the general case of several components that are not necessarily present in both the calibration and the unknown samples; obtained the solution by solving a generalized eigen problem and called the method generalized rank annihilation method (GRAM). Rank annihilation factor analysis has been used to analyze the two-way chromatographic spectral data[23], for spectrophotometric study of chemical kinetics[24,25] and acidity constants[26-28], the correction of several types of instrumental inconsistencies[29] and for resolving a chemical system, which suffers from one type of rank deficiency problem[30]. The rank annihilation factor analysis algorithm can solve the rank deficiency arising from the full spectral overlapping of some chemical species involved in chemical processes. The rank deficient matrix can be resolved without combining the other matrices with suitable information to reveal the presence of hidden components. Although the method has been used successfully for different applications, the feasible abilities of rank annihilation factor analysis for studying complexation equilibria are limited[30].

In this work the method is suggested for the spectrophotometric study of three competitive complex formations. The applicability of the methodology is serving as an example by the estimation of the complexation constants of lanthanide cations (M) by arsenazo(III) (L). Arsenazo(III) is the common descriptive name of [3,6-*bis*[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphtalenedisulphonic acid disodium salt]; as a disodium salt with the general formula of: $C_{22}H_{16}N_4O_{14}S_2As_2Na_2$. This *bis*-azo derivative of chromotropic acid forms stable complexes with large variety different cations[31]. The chromophore groups in the ligand promote the spectrophotometric study in the visible field. Specifically, this multi purpose complexing ligand is extensively used for spectrophotometric analysis. Interactions of arsenazo(III) with lanthanides were investigated in some detail[32-35]. In particular, Arsenazo(III) was shown to make the similar type of complex with lanthanides and is a very useful remark to minimize the number of models for this series.

Our interest in the behaviour of this ligand is stimulated by at least two reasons. First: formation constant values of the above complexes were reported[36] for 11 lanthanides by Lu, which makes use of the data from the first stages of the complexometric titration and is based on the Taylor expansion of the concentration of the ligand as a function of the titrant concentration. This method is rather complicated and is not user friendly.

The second reason was the fact that arsenazo(III) was shown to build up the similar type of complex with lanthanides. In this context, three different methodologies were proposed to evaluate formation constants. These methodologies are based on rank annihilation factor analysis expression and also

soft and hard modeling, that leads to the evaluation of stoichiometry of the main species and formation constants. Meanwhile, we have presented the spectral and concentration profiles for each species in the titration process.

EXPERIMENTAL

An Agilent photodiode-array spectrophotometer Model 8453 equipped with cm^{-1} path length glass cell was used for recording absorbance spectra. A Pentium four personal computer was used for controlling the spectrophotometer and collecting the data from its interface. All spectral measurements were performed using a blank solution as a reference. Measurements of pH were made with a Metrohm 632 pH-meter using a combined glass electrode. The computations were made with a Pentium four computer. All the programs in the computing process were written in MATLAB 6.5 for Windows.

All reagents were of analytical reagent grade an distilled water was used throughout. All the 13 lanthanides stock solutions (0.01 M) were prepared by dissolving the following weight and kind of salts in 10 mL of distilled water.

La, 43.30 mg Lanthanum nitrate (Merck); Ce, 56.84 mg cerium(III) sulfate (Reacton); Pr, 17.02 mg praseodymium oxide (reacton); Nd, 16.82 mg neodimum oxide (reacton); Sm, 25.67 mg samarium chloride (reacton); Eu, 42.81 mg europium(III) nitrate (reacton); Gd, 18.13 mg gadolinium oxide (reacton); Tb, 18.69 mg terbium oxide (reacton); Dy, 18.65 mg dysprosium oxide (reacton); Ho, 18.89 mg holium oxide (reacton); Er, 19.10 mg erbium oxide (reacton); Yb, 19.70 mg ytterbium(III) oxide (reacton); Lu, 19.89 mg lutetium oxide (reacton).

A stock solution of monochloroacetic acid (BDH) buffer solution (0.1 M) was prepared daily by dissolving 9.44 g of $CH_2ClCOOH$ in water and diluting to 1000 mL after adjusting the pH to 3.2.

A stock solution of arsenazo(III) (0.001 M) was prepared by dissolving 0.0820 g of arsenazo chloride as a disodium salt (Merck) in water and diluting to 100 mL.

A 5.0 mL solution of arsenazo(III) (0.001 M) and 50.0 mL monochloroacetic acid buffer (pH = 3.2) (0.1 M) were added in a 100 mL volumetric flask and diluted to the mark with distilled water after adjusting the pH to 3.2. 3 mL of arsenazo(III) solution (5×10^{-5} M at pH = 3.2) was transferred to a spectrophotometric cell and the titration was started by successive 0.2 µL additions of each standard stock lanthanides solution (0.01 M) to the cell. The absorbance data of this solution were recorded (at 380 to 780 nm) after each addition, against a reagent blank. The titration was followed until the absorbance variations became small and nearly constant.

RESULTS AND DISCUSSION

Determination of the number of efficient factors and species by factor analysis: In order to estimate the number of coexisting absorbing species in the reaction systems (*i.e.* the number of produced complexes) principal component analysis (PCA) were performed on the digitized absorbance mole ratio data matrices, which was obtained from the
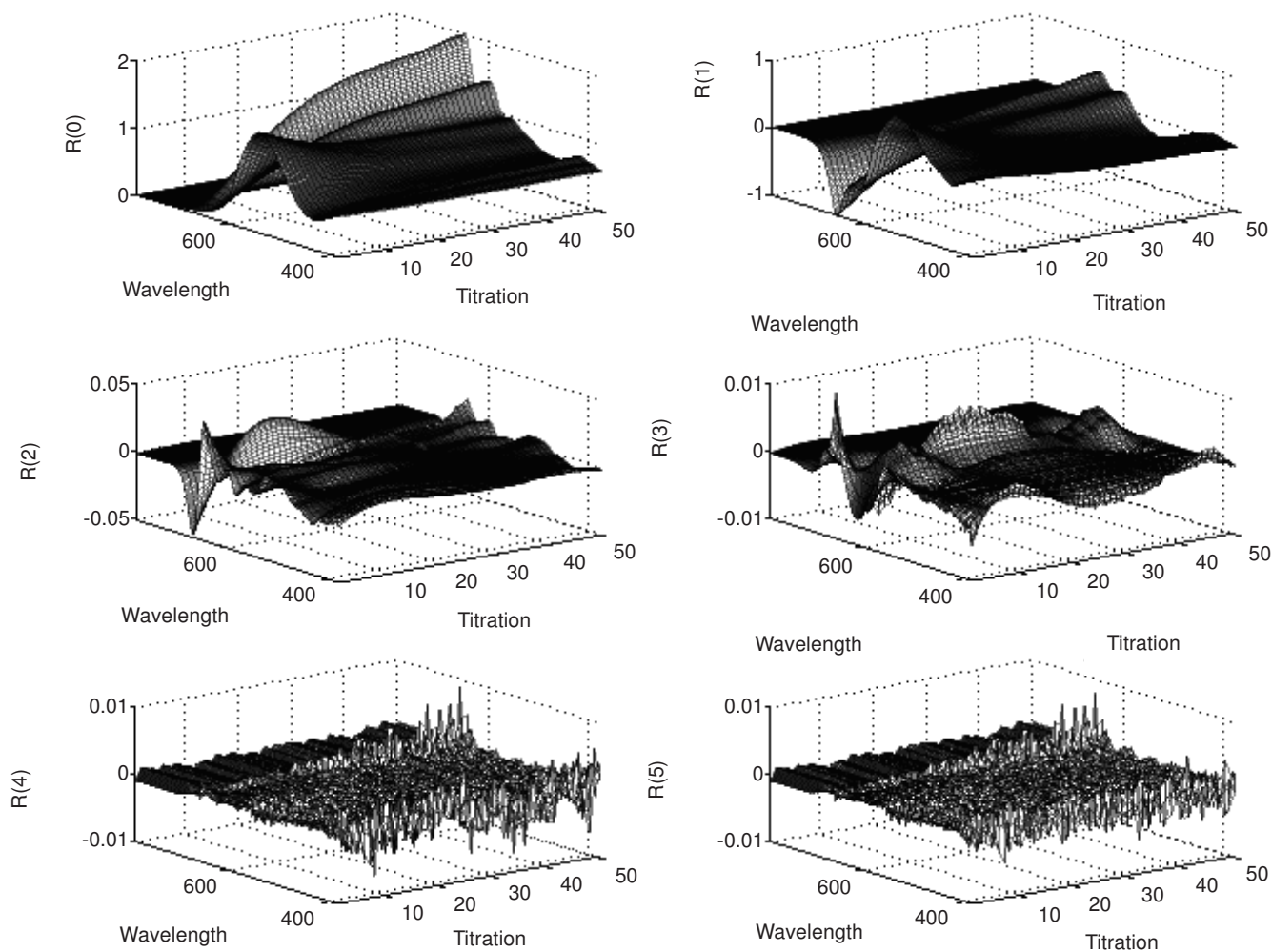
Fig. 1.   Structure of the residuals after the subtraction of the contribution of the first 0, 1, 2, 3, 4 and 5 eigenvectors from main data matrix in euoprium - arsenazo(III) titration process

spectrophotometric titration of arsenazo(III) with each lanthanide cations, separately.

According to Fig. 1, the structure of the residuals shows that only noise is remained after the subtraction of the contributions of first four eigenvectors. Therefore, according to this figure and some other methods based on principal component analysis, there are four absorbing species created in titration process.

Models for the complexation: Studies of multiple equilibria in solutions are essential for the solution of many analytical and speciation problems. There are different analytical procedures in this field[37,38], using least-squares methods, to estimate the number of species present in the reaction system, their stoichiometries and their stability constants. The experimental data needed usually arises from the successive steps of a potentiometric or spectrometric titration. Least-squares methods are hard model and require knowledge about the chemistry of the reaction system, *i.e.*, an initial set of stoichiometric coefficients and stability constants for the postulated species. Moreover, these methods by using a systematic search of the possible models and with the aid of chemical reasoning, can determine the composition of the species and the stability constants, provided that mass-law and mass-balance equations are fulfilled. Therefore, based on the results obtained by factor

analysis methods and multivariate curve resolution-alternating least-squares (MCR-ALS) (Fig. 2), we confined our studies on the systems containing four absorbing species and by using the mass balance equations and equilibria expressions, a hard model was generated for lanthanides-arsenazo(III) systems by using the following simple equilibria (eqns. 1 to 3) and ML, ML_2 and M_2L_2 complexes were tested and defined.

$$M + L \rightleftharpoons ML \qquad K_{11} = [ML]/[M][L] \qquad (1)$$

$$M + 2L \rightleftharpoons ML_2 \qquad K_{12} = [ML_2]/[M][L]^2 \qquad (2)$$

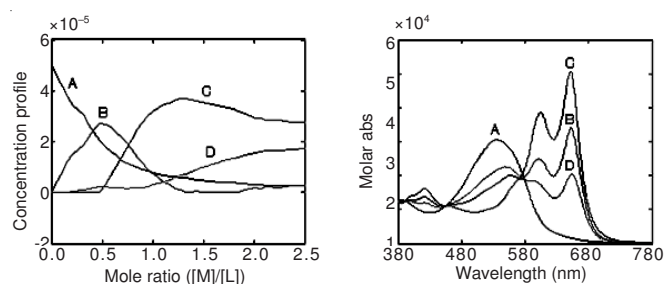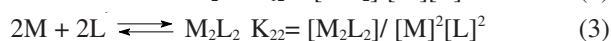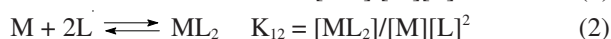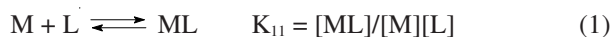$$2M + 2L \rightleftharpoons M_2L_2 \quad K_{22} = [M_2L_2]/[M]^2[L]^2 \qquad (3)$$

Fig. 2.   Results of the data analysis in the absorption region of arsenazo(III) titration with Europium data matrix by MCR-ALS. Left panel: concentration profiles, right panel: pure absorption spectra. A, L; B, ML_2; C, ML; D, M_2L_2

Theoretical background: Suppose that a system contains M, L, ML, ML_2 and M_2L_2 species with three competitive conditional complex formations that defined by three different chemical equilibria (eqns. 1 to 3).

According to Fig. 2, each solution at a particular mole ratio can be considered as a mixture of four components (*i.e.* L, ML, ML_2 and M_2L_2). By using the equilibria and mass balance expressions the following equation is obtained:

$$2 \times (K_{22} \times X^2 + K_{12} \times X) \times L^2 + K_{11} \times X \times L + L - C_L = 0 \quad (4)$$

In which C_L is the initial concentration of ligand and X is defined by eq. 5.

$$X = \frac{-(1 + K_{11} \times L + K_{12} \times L^2) + [(1 + K_{11} \times L + K_{12} \times L^2)^2 + (8 \times CM \times K_{22} L^2)^{0.5}]}{(4 \times K_{22} \times L^2)} \quad (5)$$

Consider D is a data matrix obtained by spectrophotometric titration of arsenazo(III) with each lanthanide, which can be decomposed into two concentration and spectral matrices C and S, respectively.

$$D = CS^T + R \quad (6)$$

Matrix D is the spectral data matrix containing rows of UV-VIS spectra recorded during a titration experiment. The columns of the C matrix are the pure concentration profiles of each absorptive species in modeled components and the rows in the S^T matrix are their related pure spectra and R is the matrix of residuals not explained by the model and includes any other components and noise. Matrix C consists of the concentration values of p components in n_S mol ratios and S consists of the molar absorptivities of p components in λ wavelengths.

On the other hand, assuming that only the ligand and complexes are absorbing, eqn. 6 can be written as the sum of the absorbencies of different species:

$$D = A_L + A_{ML} + A_{ML_2} + A_{M_2L_2} + R \quad (7)$$
or
$$D = e_L[L]^T + e_{ML}[ML]^T + e_{ML_2}[ML_2]^T + e_{M_2L_2}[M_2L_2]^T + R \quad (8)$$

where, A_L, A_{ML}, A_{ML_2} and $A_{M_2L_2}$ are the bilinear measuring matrix of pure ligand, 1:1, 1:2 and 2:2 species, respectively and each one can be decomposed into the corresponding molar absorptivity spectrum ε_L, ε_{ML}, ε_{ML_2} and $\varepsilon_{M_2L_2}$ (column vectors) and the concentration profiles $[L]^T$, $[ML]^T$, $[ML_2]^T$ and $[M_2L_2]^T$ (row vectors, superscript T denotes the transpose of a matrix or vector).

For certain values of K_{11}, K_{12} and K_{22}, the equilibrium concentrations of all species in different mole ratios are calculated by obtaining the roots of eqn. (4) and therefore, a vector of concentration profiles of ligand is determined separately. With the known pure spectrum of ligand (*i.e.* ε_L), the part of absorbance of the mixture due to this species (*i.e.* A_L) is readily calculated and its contribution is annihilated from the original absorbance data matrix according to eqn. (9):

$$F = D - A_L = D - \varepsilon_L[L]^T \quad (9)$$

where, F is the absorbance data matrix of all reacting species except L. The main goal of rank annihilation factor analysis approach is to find a suitable set of K_{11}, K_{12} and K_{22} so that rank of matrix F can be reduced by one from that of matrix D through introduction of the concentration profiles of ligand species obtained from the roots of eqn. (4).

For this purpose, the parameters that should be changed are equilibrium constants (K_{11}, K_{12} and K_{22}) and total concentration of the lanthanides. The calculated concentration profiles based on hard chemical models should be multiplied with the pure spectra and make some absorbance matrix with the similar dimension to the original matrix D. equilibrium constants should be changed simultaneously in a wide range and at each value, the concentration profiles are calculated. Whenever the rank of residual matrix F decreases, the best values for K_{11}, K_{12} and K_{22} can be obtained.

For this purpose, the rank analysis on the residual matrix F was done by singular value decomposition (SVD). Chemical components give rise to larger singular values than noise or instrument contributions. Therefore, the chemical rank can be estimated by the number of singular values larger than singular values associated with noise.

For estimation of the equilibrium constant, an iterative rank annihilation factor analysis was operated. In each iteration, different values of K_{11}, K_{12} and K_{22} were selected and used to estimate the concentration profiles and then the pure spectrum of the ligand. The contribution of the absorbance of ligand was then removed from the original absorbance data (Fig. 3) using eqn. (9). Factor analysis was applied on the resulted matrix (F), which its rank must be equal 3. Therefore, sum of residual factor (SORF) of the F was monitored for optimization of the equilibrium constants. The values of K_{11}, K_{12} and K_{22}, which resulted in minimum sum of residual factor, were considered as the equilibrium constants of the complex formation reactions.
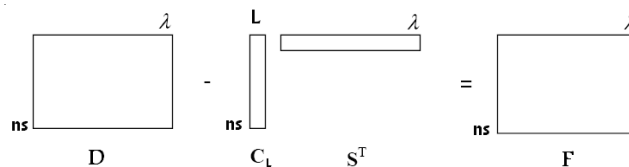

Fig. 3. Contribution removing of the ligand absorbance from the original absorbance data by rank annihilation factor analysis process

For checking the potential of the proposed method, the algorithm was tested by using the simulated data set that created according to mole ratio method and were very similar to the real data set.

For simulating the three different competitive complexation systems, four simulated spectra of species were formed according to the spectral profiles obtained by MCR-ALS (Fig. 2) and summed together in a known proportion in such a way to mimic model of mole ratio method using the equilibrium constants as $K_{11} = 10^5$, $K_{12} = 10^{10}$, $K_{22} = 10^{15}$ and concentration of arsenazo(III), $C_L = 5.0 \times 10^{-5}$ M.

Random error was added to the set of generated artificial data. The error is a set of noise drawn from a normal distribution with mean zero and standard deviation equal to 0.25 % of absorbance value.

The total concentration of ligand was kept constant in the creation of the spectral data and the ligand equilibrium concentration profile could be obtained using eqn. (4). If the values of C_M, C_L, K_{11}, K_{12} and K_{22} are known, it is possible to obtain the free ligand concentration [L] from the roots of the

associated polynomial which can be simply obtained using MATLAB software.

Application of rank annihilation factor analysis method

Simulated data: The simulated data matrix D is processed by rank annihilation factor analysis method and the relationships between sums of residual factors of residual matrix F were investigated as a function of different values of K_{11}, K_{12} and K_{22} in iterative process.

In each iteration, different values of K_{11}, K_{12} and K_{22} were selected and used to estimate the concentration profiles and then the contribution of the absorbance of ligand was removed from the original absorbance data. Factor analysis was applied to the resulted matrix (F), which its rank must decrease one unit. Therefore, sum of residual factor of F was monitored for optimization of equilibrium constants.

The three-dimensional surface plots of sum of residual factor against the log K_{11} and log K_{12} taking log $K_{22} = 15$ are shown in Fig. 4.

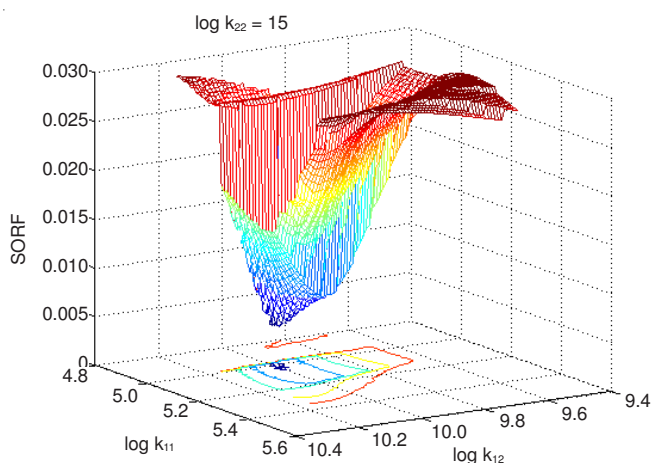Fig. 5.   Relationship between sum of residual factor and log K_{22} value for the simulated data

Fig. 4.   Sum of residual factor surface and contour plot obtained by rank annihilation factor analysis for the simulated data against log K_{11} and log K_{12} in (log $K_{22} = 15$)

The sum of residual factor results obtained by each iteration were collected in three dimensional matrices (tensor) to make a three way data. So the minimum value in this cubic space data, estimates the conditional stability constants for lanthanide-arsenazo(III) complexes.

The values of sum of residual factor, which resulted in minimum, were considered as the equilibrium constants, log K_{11}, log K_{12} and log K_{22}, of the complex formation reactions. Because of our limitation to plot the three way data, the minimum value in each layer that attributed to log K_{11} and log K_{12} were plotted against the number of layers or log K_{22} in Fig. 5.

Experimental data: The three-dimensional absorbance plot (absorbance *vs*. wavelength *vs*. mole ratio) of arsenazo(III) titrated with europium cation in a solution of pH = 3.2 is shown in Fig. 6. This lanthanide is selected as a representative example, because basically similar observations are made with all other 12 investigated lanthanides in this research. The λ_{max} of Arsenazo(III) is 530 nm and a shift with two narrow and distinct isobestic points is observed in its spectrum to longer wavelengths upon addition of metal cations.
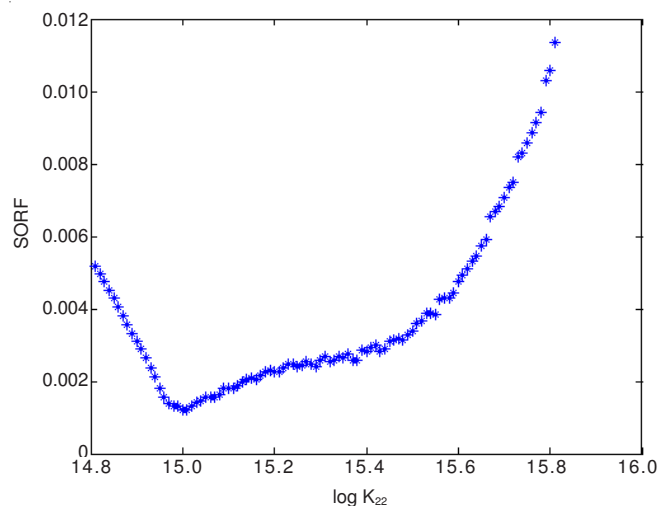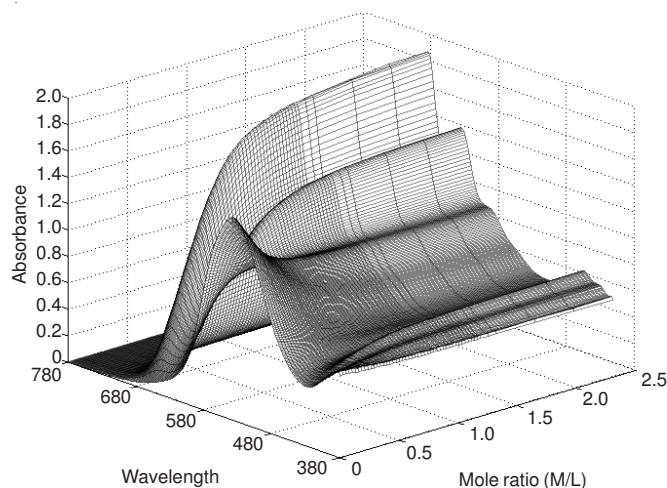

Fig. 6.   Three-dimensional absorbance plot (absorbance *vs*. wavelength *vs*. mole ratio) of europium-arsenazo(III) complex in pH 3.2

After building up the titration data matrices (A) for arsenazo(III) with each of the thirteen lanthanide-arsenazo(III) complex systems; the next step was the estimation of the conditional constants for the complexes formed based on mole ratio data. An iterative rank annihilation factor analysis method; previously described in details; was used.

In each iteration, different values of K_{11}, K_{12} and K_{22} were selected and used to estimate the concentration profiles and then the contribution of the absorbance of ligand was removed from the original absorbance data. Factor analysis was applied to the resulted matrix (F), which its rank must decrease one unit. Therefore, sum of residual factor of F was monitored for optimization of equilibrium constants. As described the sum of residual factor results obtained by each iteration, were collected in three dimensional matrices (tensor) to make a three way data. So the minimum value in this cubic space data, estimates the conditional stability constants for lanthanide-arsenazo(III) complexes.

The values of sum of residual factor, which resulted in minimum, were considered as the equilibrium constants, log K_{11}, log K_{12} and log K_{22}, of the complex formation reactions.

Correspondingly, the minimum value in each layer attributed to log K_{11} and log K_{12} were plotted against the number of layers or log K_{22} (Fig. 7).

From similar plots represented in Fig. 7, the values of the conditional stability constants were estimated and listed in Table-1 for all other lanthanides.

Figs. 8 (a, b and c) illustrates the results obtained by different methods; MCR-ALS, fitting and rank annihilation factor analysis, which were used separately to find the complex formation constants and a comparison with Taylor expansion results reported earlier[36].
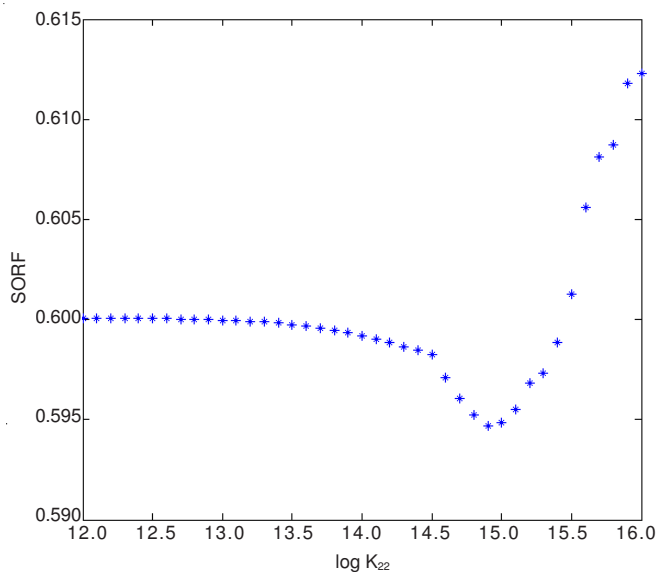

Fig. 7. Relationship between sum of residual factor and log K_{22} value for the europium-arsenazo(III) complex

TABLE-1
FORMATION CONSTANTS OF LANTHANIDE–ARSENAZO(III) COMPLEXES OBTAINED BY RAFA PROCEDURE

No.	Lanthanide	log K_{11}	log K_{12}	log K_{22}
1	La	5.31	10.00	15.14
2	Ce	4.83	10.41	15.39
3	Pr	5.32	10.80	14.58
4	Nd	5.46	10.74	16.08
5	Sm	5.21	10.33	15.78
6	Eu	5.65	9.67	14.96
7	Gd	5.24	9.36	14.05
8	Tb	4.84	9.57	14.31
9	Dy	4.65	9.38	14.39
10	Ho	4.97	9.63	13.86
11	Er	4.18	9.54	12.94
12	Yb	4.75	9.63	14.17
13	Lu	4.91	9.92	14.16

Conclusion

The proposed work is to illustrate that rank annihilation factor analysis is a capable and efficient chemometric algorithm to extract complex formation constants from a system with several chemical equilibria from analysis of the data pertaining by spectrophotometric mole ratio titration method and is comparable with the results obtained by MCR-ALS and curve fitting methods. The rank annihilation factor analysis is based on the principle that the rank of two-way bilinear matrix of pure
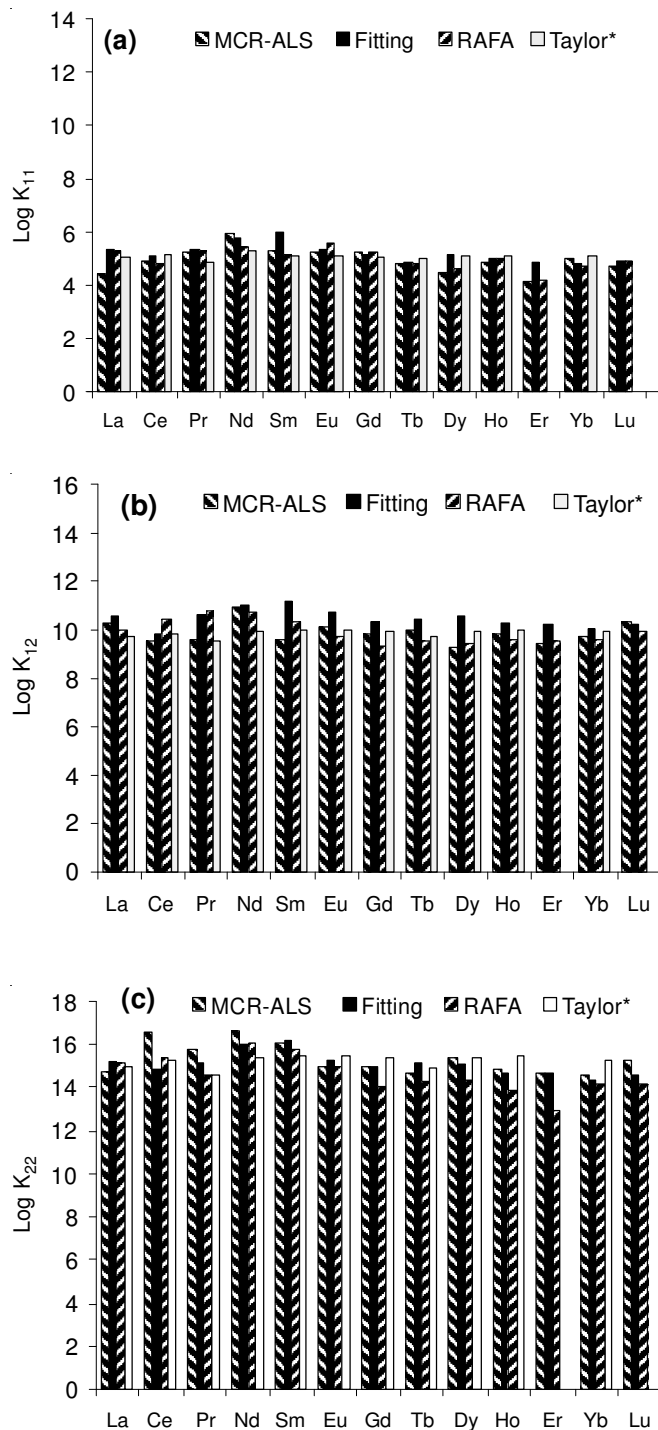

Fig. 8. (a), (b) and (c) comprized the results obtained by four different methods; MCR-ALS, fitting, rank annihilation factor analysis and Taylor expansion 36 for log K_{11}, log K_{12} and log K_{22} respectively

compound is one. The knowledge about the chemical behaviour of the analytes, which obtained by factor analysis and soft and hard modeling methods was used to implement a hard modeling equilibrium constraint in the rank annihilation factor analysis algorithm that ensures the correct complex formation constants. The proposed method makes it possible to obtain the stability equilibrium constants, pure absorption spectra and species concentration profiles in several ligand-metal ion complex formation systems by sever spectral overlapping. In addition rank annihilation factor analysis algorithm

was tested with simulated data sets, which created according to mole ratio method and were very similar to the real data set. The proposed method can be applied for resolving the real three competitive complex formation processes, with full spectral overlapping of two complex species. The results opens up a new way to study this kind of competitive complexation processes based on the following achievements.

(i) MCR-ALS was used for initial estimation of parameters related to the equilibrium concentration and spectra and then they were confirmed by hard model.

(ii) Capability and efficiencies of iterative rank annihilation factor analysis technique was shown for resolving complex systems with three competitive complex formation processes for extracting complex formation constants of species with sever spectral overlapping.

(iii) Complexation constants were measured by three different methods (rank annihilation factor analysis, MCR-ALS and Fitting) with satisfactory results and good agreement with the earlier published work[36].

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