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Application of the spectral correction method and “neural networks” for simultaneous determination of V(V) and Al(III)

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Abstract

Simultaneous determination of V(V) and Al(III) was performed by application of neural networks when the calibration matrix was performed using β-correction spectra. Two reactions between V(V) and Al(III) and Alizarin Red S (ARS) as a ligand have been investigated and applied for the simultaneous spectrophotometric determination of these metal ions. The parameters controlling behavior of the system were investigated and optimum conditions selected. Feed-forward neural networks have been trained to quantify considered metal ions in mixtures under optimum conditions. Sigmoidal functions were used in the hidden and output layers. Determinations were made over the concentration range 0.10–7.80 $\mu g\,ml^{-1}$ of V(V) and 0.11–4.20 $\mu g\,ml^{-1}$ of Al(III). Applying this method satisfactorily to simultaneous determination of these metal ions in several synthetic solutions with total relative standard error less than 4.02% validated the proposed method.

Keywords: V(V); Al(III); β-Correction; Artificial neural networks; Alizarin Red S

1. Introduction

Aluminum and vanadium species play important role in many industrial and environmental processes. They are used as structural material in the construction, automotive and production of metal alloys. On the other hand, both vanadium and aluminum may find their way in to the natural environment, in particular, surface water as toxic pollutants and they are responsible for industrial and environmental pollutions therefore, their determination is always an important subject in analytical chemistry. The toxicity of vanadium compounds on its physico–chemical state, particularly on its valance and solubility, pentavalent vanadium is generally considered to be the most toxic form of vanadium, regardless of whether it functions as an anion or cation [1–4]. The chemical properties of V(V) and Al(III) make them essential in different processes. Moreover, V(V) and Al(III) are metal ions, which appear together in a wide variety of samples (environmental, industrial, and geometrical). This point testifies the interest in simultaneous determination of these metal ions. Different methods such as, HPLC, ICP-MS, ICP-AES, AAS, spectrophotometry, [5–9] are most frequently used for the individual determination of these ions.

In spite of the importance of simultaneous determination of Al(III) and V(V), only few works have been reported for simultaneous determination of these ions [10]. Some of these methods are unsuitable for the analysis of samples involving complex matrix or for the analysis of a large number of samples [11,12]. Current efforts towards the development of new methods are focused primarily on increasing sensitivity and selectivity of the detection methods and simplifying the procedure by eliminating treating and sampling steps. Simultaneous determination of several analytes is possible using multivariate calibration. These techniques present the advantages over other methods as they are faster, sample treatment is usually reduced and the removal of interference is not strictly required in many cases.

Nowadays, artificial neural networks (ANNs) modeling method has been found extensive application in the field of simultaneous determination of several species in a given sample. Several researchers have reported the application of these methods to spectrophotometric analysis for resolution of multi component samples [13,14]. This method makes it possible to eliminate or reduce the effect of the analyte–analyte interaction, the multi-step process and any

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other unknown non-linearity in systems. The feed-forward neural networks trained by back-propagation of the errors have one obvious advantage; there is no need to know the exact form of the analytical function on which the model should be built. That is neither, the functional type (linear, polynomial, exponential, etc.) nor are the number and position of parameters required. Basic theory and application to chemical problems of ANN with back-propagation algorithm is well-discussed in [15–17].

In spectrophotometric analysis, linear dynamic range is obtained by plotting the absorbance versus sample concentration at the wavelength of maximum absorption. Deviation from Beer–Lambert law at very low and high concentrations limits the observed dynamic range, especially at simultaneous determination. We have therefore attempted to develop and validate of a new method to solve this problem. It seems, in the case of simultaneous determination, this limitation can be mostly overcome by use a combination of β-correction spectrophotometery with a non-linear modeling technique such as artificial neural network, In this work a back-propagation artificial neural network (BP-ANN) algorithm was used to handle such non-linear spectral data for increasing range of determination and obtain wider determination ranges in simultaneous determination of V(V) and Al(III).

β-Correction spectrophotometery, elaborated by Gao et al. [18–25] is applicable where both reagent and its complex with metal ion exhibit chromophoric properties. This method is a dual-wavelength technique for determination of trace metal, which is different from ordinary spectrophotometry because it may eliminate the interference of excess of chromomeric reagent from its metal-colored solution to give the real absorbance of the chelate formed. Then the sensitivity, precision and accuracy by the dual-wavelength β-correction method are all higher than those for the ordinary one. The reaction between V(V) and Al(III) with ARS was sensitive at pH 4.8, over this condition absorption peak of the V(V)–ARS complex was located at 483 nm and that of Al(III)–ARS complex at 495 nm (against reagent blank reference), but that of ARS at 424 nm. It is difficult by conventional method to obtain an accurate measurement of each of the mixed complexes.

2. β-Correction theory

Although basic theory and application of β-correction method was discussed in detail by Gao et al., in several papers here, a brief discussion of the general principle is required. In order to consider the general principle of β-correction spectrophotometry, the reaction of metal (M) with a colorant (L) can be expressed as follow:

$$\mathrm{M} + \gamma\mathrm{L} \rightarrow \mathrm{ML}_{\gamma} + \mathrm{L}(\text{excess})$$

where γ represents the complexation ratio of M with L. The following expression was developed for determination of real absorbance A_c of metal (M) complex, ML_{γ} produced with a ligand (L):

$$A_{\mathrm{c}} = \frac{A_{\beta}}{1 - \alpha\beta} \tag{1}$$

$$A_{\beta} = \Delta A - \beta \Delta A' \tag{2}$$

here, the term A_{β} was named β-correction absorbance, which was proportional to metal concentration. ΔA and $\Delta A'$ are the absorbances of the reacted solution between M and L at wavelengths λ_1 and λ_2 against the reagent blank, respectively. The coefficients α and β are named correction factors and they can be obtained as follows:

$$\alpha = \frac{\varepsilon_{\mathrm{ML}_{\gamma}}^{\lambda_1}}{\varepsilon_{\mathrm{ML}_{\gamma}}^{\lambda_2}} \tag{3}$$

and

$$\beta = \frac{\varepsilon_{\mathrm{L}}^{\lambda_2}}{\varepsilon_{\mathrm{L}}^{\lambda_1}} \tag{4}$$

The terms $\varepsilon_{\mathrm{ML}_{\gamma}}^{\lambda_1}$, $\varepsilon_{\mathrm{ML}_{\gamma}}^{\lambda_2}$, $\varepsilon_{\mathrm{L}}^{\lambda_1}$ and $\varepsilon_{\mathrm{L}}^{\lambda_2}$ are the molar absorbtivities of $\mathrm{ML}\gamma$ and L at wavelengths λ_1 and λ_2, respectively. λ_1 is absorption peak of reagent and λ_2 that of complex ($\lambda_{\max}$). In fact, with the help of β-correction technique true absorbance of chelate produced can be calculated because the quantity of absorbance, which has related to the fraction of reagent that reacted with metal ion, and has been subtracted when reagent applied as reference by this correction has compensated. β-correction method can also applied to spectra of mixtures [24]. In a mixture, each of the metal will form a color complex with ligand and the fractional absorbance of each color compound can be calculated by the following correction equation:

$$A_{\beta} = \sum_{j1}^{n} a_{ij} x_j = \Delta A_i - \beta_i \Delta A' \quad (i = 1, 2, \ldots, n) \tag{5}$$

3. Experimental

3.1. Chemicals and reagents

All chemicals were of analytical-reagent grade and were used directly without further purification (all from Merck). Triply distilled water was used to prepare buffer and reagent solutions. Stock solutions of V(V) and Al(III)) both of them ($200\,\mu\mathrm{g\,ml}^{-1}$) were prepared by dissolving 0.0459 g of $\mathrm{NH_4VO_3}$ and 0.2780 g of $\mathrm{Al(NO_3)_3{\cdot}9H_2O}$, respectively in distilled water and diluting to 100 ml, ($\mathrm{NH_4VO_3}$ dissolved by heat in slowly). Alizarin Red S solution (0.01 M) was prepared by dissolving appropriate amount of the powder in distilled water and diluting with water to 100 ml. An acetate buffer (pH 4.8, 0.1 M of acetic acid) was also prepared.

3.2. Apparatus and software

UV-Vis absorption spectra were recorded on a spectrophotometer model Citra 5, which equipped with a 1.00 cm path length quartz cells. The spectra of mixtures were recorded between 350 and 800 nm, digitized absorbance was sampled at 1 nm intervals. Measurements of pH were made with a metrohm 654 pH meter (Metrohm Ltd., CH-9100-Hesau Switzerland) using a combined glass electrode. The back-propagation neural network algorithm having three layers was used in MATLAB (version 6, Math Work Inc.) using NNet toolbox. All program were run on a Pentium (III), 633 MHz, personal computer, with windows 98 operating system.

3.3. Procedure

To a series of 10 ml volumetric flasks, 5 ml of Alizarin Red S (0.01 M) was added, to obtain a final concentration of 5×10^{-3} M. A 3 ml buffer solution (pH 4.8) and was also added. Finally, an appropriate amount of each metal ion containing 1–78 μg of V(V) and 1–42 μg of Al(III) were added and the solutions were made up to the mark with distilled water. Excess concentration of reagent has been applied to ensure quantitative formation of the complexes in the whole range of determination. The concentration ranges were chosen so that the absorbances obtained for all standard solutions were not greater than 1.8. The spectral correction data obtained by proposed method at 483 and 495 nm were processed by ANN which was trained with the back-propagation of errors learning algorithm for simultaneous determination of V(V) and Al(III) ions.

4. Results and discussion

4.1. Optimization of experimental conditions

Assay conditions such as pH and mole ratios were investigated for optimization. The influence of pH on the spectrum of each complex was studied from pH 1–6. The spectrum of each complex at a constant concentration of metal ion as a function of pH was studied separately. For the V(V) complex, absorbance at 483 nm increased up to pH 5 and complex shows maximum absorbance at about pH 4.5–5.0, beyond this region no significant change was observed in the spectrum of V(V) complex. Maximum sensitivity for Al(III) complex was occurred at about pH values larger than 4.8 (Fig. 1). Since at pH values larger than 6, Alizarin Red S has a high molar absorptivity, the pH value selected as an optimum pH for simultaneous determination of V(V), Al(III) was pH 4.8 at which the absorbances for both of the complexes were high, while the absorbance of ARS was low. This pH was achieved via an addition of 3 ml buffer solution (pH 4.8) per 10 ml final solution.

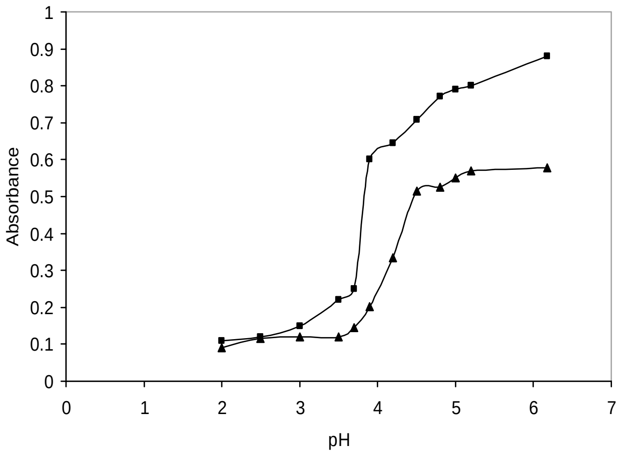

Fig. 1. Effect of pH on change in absorbance, V(V)–ARS (▲) and Al(III)–ARS (■), at 3×10^{-4} M of Alizarin Red S, 2 μg ml^{-1} of V(V) and 1.2 μg ml^{-1} of Al(III) complexes.

To study the stoichiometry of the reactions, mole ratio (mole of metal ion/mole of ligand) method was applied for each complex at a constant concentration of the ligand (Alizarin Red S 3×10^{-4} M) and varying concentration of each metal ion. The results revealed that V(V) and Al(III) react with Alizarin Red S in, (1:2) and (1:2) mole ratio, respectively; Fig. 2 shows these experiments. An excess concentration of Alizarin Red S has been chosen to ensure quantitative formation of the complexes in 1:2 mole ratio.

4.2. Absorption spectra

Fig. 3 shows the absorption spectra of ARS, V(V)–ARS and Al(III)–ARS solutions. The reaction between V(V) and Al(III) with ARS was sensitive at pH 4.8, over this condition absorption peak of the V(V)–ARS complex was located at 483 nm and that of Al(III)–ARS complex at 495 nm (against reagent blank reference), but that of ARS at 424 nm. These three wavelengths, such that the positive and negative

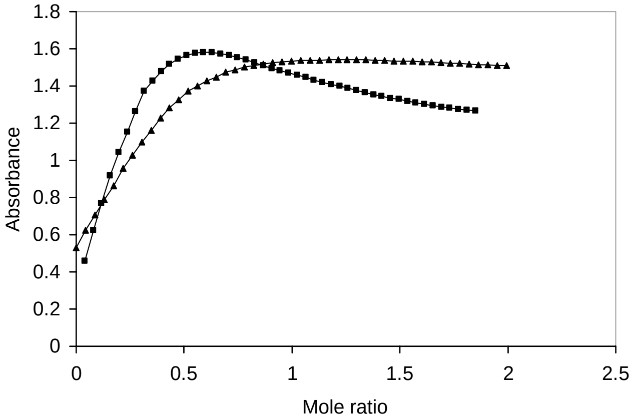

Fig. 2. Stoichiometry of V(V)–ARS (▲) and Al(III)–ARS (■) reaction, mole ratio (mole of metal ion/mole of ligand) at 3×10^{-4} M of Alizarin Red S, and pH 4.8.

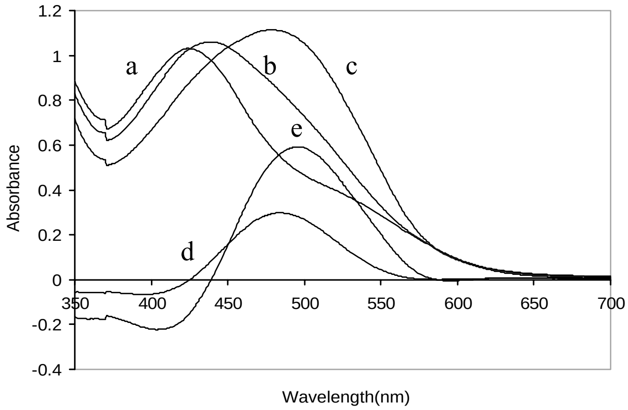

Fig. 3. Absorption spectra of ARS,V(V)–ARS and Al(III)–ARS, curve (a) reagent blank (reference, water), (b) V(V)–ARS (reference, water), (c) Al(III)–ARS (reference, water), (d) V(V)–ARS (reagent, reference), and (e) Al(III)–ARS (reagent reference), curves for $4\,\mu g\,ml^{-1}$ of V(V) and $1.35\,\mu g\,ml^{-1}$ of Al(III) complexes and 5×10^{-4} M of Alizarin Red S.

absorbances approach the maximum, were selected for correction coefficients. From curve a, the correction coefficient was calculated to be $\beta = 0.501$ at 483 nm and $\beta = 0.435$ at 495 nm. From curves (b) and (c), the correction coefficients were calculated to be $\alpha_{483} = 1.105$ and $\alpha_{495} = 0.549$ for V(V) and Al(III), respectively. β-Corrected absorbances were calculated using these coefficients and Eqs. (1) and (2).

4.3. Individual determination

To find the linear dynamic range of each component calibration graph were obtained. The absorption spectra were recorded over 350–700 against a reagent blank. Under optimum conditions β-correction was applied on absorbance values. Linear range for each metal ion was determined by plotting the absorbances at its λ_{max} versus sample concentration. Conventional calibration curves were linear between $0.9–6.80\,\mu g\,ml^{-1}$ of V(V) and $0.1–2.5\,\mu g\,ml^{-1}$ of Al(III). In β-corrected calibration curves, sensitivity were increased. Linear equations are $A_\beta = 0.2292C_i + 0.1326$ and $A = 0.1017C_i + 0.0577$ for V(V) and $A_\beta = 0.4801C_i + 0.0808$ and $A = 0.3652C_i + 0.0614$, for Al(III), (where C_i is in $\mu g\,ml^{-1}$), regression coefficients were higher than 0.9989 in both V(V) and Al(III).

4.4. Simultaneous determination

Fig. 3 shows that the spectral overlapping of V(V)–ARS and Al(III)–ARS complexes. It can be seen that significance overlapping prevents resolution of the mixtures by conventional method to obtain an accurate measurement of each the mixed complexes. Moreover, in the binary mixture of these metal ions, linearity for each metal in mixture is very limited in the presence of another and deviation from Beer–Lambert law is more extensive. (an excess concentration of Alizarin Red S has been chosen to ensure quantitative formation of the complexes in 1:2 mole ratio). Because of this non-linearity, the linear chemometrics methods are unsuitable for simultaneous analysis of mixtures. Thus, in order to reduce effect of analyte–analyte interaction and this non-linearity, ANN is proposed as a powerful non-linear technique for solving the problem. The spectral correction data obtained from application of β-correction method on conventional spectra were processed by AAN in order to increasing dynamic range of determination and to obtain wider dynamic ranges in simultaneous determination of V(V) and Al(III).

4.5. Multivariate calibration

4.5.1. Mixture design

The first step in simultaneous determination of different species by multivariate methods involves constructing the calibration set for binary mixtures of them. In this work, we performed the calibration with the β-correction data. The multivariate calibration requires a careful experimental design of the standard composition of calibration set to provide the best predictions. In order to select the mixtures that provide more information using a few experimental trials, from calibration set, their compositions were randomly designed. Twenty-five binary mixtures were selected as the calibration set. Training set of V(V) and Al(III) ions in calibration set were between $0.10–7.80\,\mu g\,ml^{-1}$ of V(V) and $0.11–4.20\,\mu g\,ml^{-1}$ of Al(III). In order to construct ANN model, a prediction set was prepared involve 20 synthetic test samples. The prediction set was also randomly designed. In order to evaluate the quality of the model, we prepared an independent validation set consisted of 17 binary mixtures of V(V) and Al(III) which analyzed with the optimized model. The compositions of the prediction and validation sets are given in Tables 1 and 2.

4.5.2. Data processing and model building

ANN method, which was trained with the back-propagation of errors learning algorithm was run on the calibration data constructed with the β-correction technique. Three layer back-propagation networks, an input, a hidden, and an output layer, were used. The input nodes transferred the weighed input signals to the nodes in the hidden layer, and the same as the hidden nodes for the output layers. A connection between the nodes of different layers was represented by a weight, $w_{ij,}$ and during the training process, the connection of weight was performed according to delta rule. Assuming that:

$$C = f(A) + E \tag{6}$$

where $A_{n\times p}$ represents the measurement spectral matrix, in which each row denotes one of the n mixture spectra obtained at p different wavelengths, $C_{n\times m}$ denotes the corresponding concentration matrix with each row expressing the concentration vector for one known mixture sample containing m distinct components in the training set. The task for the BP-ANN technique is to find a non-linear mapping,

Table 1
Composition of prediction set, their results obtained by suggested method and relative standard errors for simultaneous determination of analytes

Prediction set							
Actual (μg ml^{-1})		Found (μg ml^{-1})		Actual (μg ml^{-1})		Found (μg ml^{-1})	
V(V)	Al(III)	V(V)	Al(III)	V(V)	Al(III)	V(V)	Al(III)
0.11	0.12	0.13	0.12	3.87	2.17	3.92	2.18
0.62	0.33	0.59	0.36	4.18	2.65	4.21	2.64
0.95	0.46	0.92	0.47	4.80	2.51	4.83	2.67
2.29	0.95	2.29	0.95	7.82	4.22	7.83	4.20
1.30	0.63	1.28	0.62	0.45	0.25	0.45	0.24
2.60	0.97	2.58	0.96	0.75	0.20	0.74	0.29
3.25	1.52	3.06	1.52	6.38	1.85	6.47	1.84
1.64	0.66	1.64	0.64	5.78	1.32	5.78	1.34
2.94	1.19	2.96	1.18	1.70	0.35	1.74	0.44
3.56	2.17	3.50	2.18	2.70	3.27	2.72	3.33
R.S.E. (%)		2.50	1.87				

denoted by f in Eq. (6), which specifies the mathematical relationship between matrix C and A. This procedure is known as supervised training in BP-ANN in which the network is trained to generate correct outputs from inputs. After this mathematical relationship f has been determined, one can easily find the concentration matrix of an unknown sample, $C_{\text{unknown},k\times m}$, from the corresponding measurement spectral matrix, $A_{\text{unknown},k\times p}$, according to the following equation:

$$C_{\text{unknown},k\times m} = f(A_{\text{unknown},k\times p}) \tag{7}$$

This procedure, defined by Eq. (7), is known as the prediction step in BP-ANN. The training procedure, defined by Eq. (6), is achieved by supervised learning, which corrects weights after one sample spectrum (a multivariate signal) passes through the network. The correction of weights is based on the error (difference) between the desired target and the actual output. The iteration would be finished when the error of prediction reached a minimum.

In our experiment, the digitized absorbance of calibration mixtures were gathered in a 25 × 2 data matrix and absorbances of prediction matrixes were collected in a 20 × 2 data matrix. To further investigate the prediction ability of method neural networked models for individual component were also made with respect to output layer considered as a single node corresponding to the analyte. In order to evaluate the performance of the models, the neural network model was also tested on an additional validation set which, its samples belonging to neither the calibration nor the prediction. In our system sigmoidal transfer function was applied between the input and output of a node in hidden layer and purelin output layer function was found to be optimum for calculations. The variables of network consist of the number of nodes in the hidden layer and the number of epochs, learning rate were optimized for each element separately.

As learning rates were being investigated, momentum values were also varied in the hopes of finding a ratio for the relative combination of the two parameters that would give the most rapid optimization of network. The optimum of

Table 2
Composition of validation set, their results obtained by suggested method, relative standard errors and root mean squares errors, for simultaneous determination of analytes

Validation set							
Actual (μg ml^{-1})		Found (μg ml^{-1})		Actual (μg ml^{-1})		Found (μg ml^{-1})	
V(V)	Al(III)	V(V)	Al(III)	V(V)	Al(III)	V(V)	Al(III)
2.26	3.27	2.40	3.27	4.54	0.85	4.34	0.81
3.21	3.85	2.72	3.33	5.42	1.32	5.22	1.30
0.98	0.45	0.94	0.45	5.78	1.35	5.78	1.34
1.05	0.66	1.19	0.66	6.38	1.85	6.43	1.84
1.44	0.65	1.29	0.65	7.00	2.63	6.98	2.67
1.22	1.19	1.21	0.96	7.59	2.63	7.60	2.63
2.30	3.81	2.24	3.81	0.15	0.99	0.17	0.95
3.30	0.40	2.99	0.40	1.64	1.12	1.65	1.10
0.00	0.52	−0.41	0.52				
R.S.E. (%)						4.02	3.51
RMSE						0.14	0.20

Table 3
Optimized parameters used for construction of ANN models

Parameter	Compound	
	V(V)	Al(III)
Input nodes	2	2
Hidden nodes	4	3
Output nodes	1	1
Learning rate	0.47	0.68
Momentum	0.73	0.75
Number of iteration	3000	1000

learning rate and momentum were evaluated by obtaining those, which yielded a minimum in the relative error of prediction. The proper number of nodes in the hidden layer was determined by training ANN with different number of nodes in hidden layer and computing relative standard error of prediction, a minimum in RSEP occurred when four and three nodes were used in the hidden layers of V(V) and Al(III), respectively. The optimum number of epochs for each metal ion was also obtained, continued training beyond 3000 iterations for V(V) and 1000 iteration for Al(III) frequently resulted in a slight increase in root mean square of prediction as the number of epochs increased while root mean square of calibration decreased slightly. The optimized parameters for ANN models used are given in Table 3. The detection limits [26] obtained for V(V) and Al(III) were 0.1 and 0.05 μg ml^{-1}, respectively.

4.5.3. Statistical parameters

The root-mean-square error (RMSE) of prediction is defined as follows [27]:

$$\mathrm{RMSE} = \left[\frac{\sum_{s=1}^{r}\sum_{i=1}^{n}((t_{s_i} - y_{si})/t_{si})^2}{rn}\right]^{1/2} \tag{8}$$

both summation in the above equation run overall r input objects of the test set and overall n output variables. The RMSE value measures how good output y_s values are in comparison with the target values t_s. The aim of any training is to reach as smallest RMSE values as possible in the shortest possible time. Also the prediction error of a single component in the mixture was calculated as the relative standard error (R.S.E.) of the prediction concentration [27],

$$\mathrm{R.S.E.}\ (\%) = 100 \times \left(\frac{\sum_{j=1}^{N}(\hat{C}_j - C_j)^2}{\sum_{j=1}^{N}(C_j)^2}\right)^{1/2} \tag{9}$$

where N is the number of samples, C_j is the concentration of the component in the jth mixture and $\hat{C}_j$ is the estimated concentration. The low RMSE and R.S.E. were obtained indicate that the networks used, can process β-correction spectral data and model the complex relationship between the concentration of ions and corrected absorbance in the wider ranges. The reasonable relative standard errors for each analyte in both set indicate the accuracy of the proposed method.

Table 4
Estimated and actual concentration of V(V) and Al(III) in synthetic and real mixtures

Sample synthetic solution	V(V) (μg ml^{-1})		Al(III) (μg ml^{-1})	
	Added	Found	Added	Found
1	3.20	3.26	0.20	0.18
2	4.25	4.31	1.50	1.51
3	0.35	0.37	2.40	2.35
4	6.50	6.50	4.00	3.85
5	2.00	1.98	3.50	3.58
Synthetic alloy				
V–Al alloy	5.00	5.00	1.62	1.52
V–Al alloy[a]	7.00	6.92	2.90	3.12
Tap water				
1	3.50	3.56	1.00	1.01
2	7.00	7.03	0.50	0.58
3	2.25	2.32	3.00	3.00

[a] This alloy is also composed of 0.5% Si, 0.4% Fe, 0.2% C (proposed method can be applied after the removal of interferences).

4.6. Interference study

The influence of various species on the absorbance of a solution mixture containing 2 μg ml^{-1} of V(V) and 2 μg ml^{-1} of Al(III) was investigated. An ion was considered as interference when its presence produced a variation in the absorbance of the sample greater than 5%. This increment of absorbance was evaluated at two wavelengths, 483 and 495 (corresponding to the maximum absorption of V(V) and Al(III) complexes, respectively), in order to establish the different effects of the interfering ions on each analyte. Among the interfering ions tested; V^{4+}, Mo^{6+}, Ag^{+}, Hg_2^{2+}, Zn^{2+}, Tl^{3+}, $\mathrm{Cr}\ ^{3+}$, SO_4^{2-}, Na^{+}, Co^{2+}, K^{+}, $\mathrm{CH_3COO}^{-}$, NO_3^{-}, IO^{3-}, and Br^{-} did not interfere at concentrations 1000 times higher than those of the analytes and Cu^{2+}, $\mathrm{C_2O}_4^{2-}$, Tl^{+}, Ni^{2+} did not interfere at concentrations 100 times higher than those of the analytes. Fe(III) showed interference in determination of Al(III) at concentrations five times higher than that of analyte. Fe(III) ion could easily be masked by sodium dithionite.

4.7. Application

The proposed method (at optimum conditions) was also applied to simultaneous determination of V(V) and Al(III) in tap water and synthetic mixture alloys, the results of prediction are summarized in Table 4. The good agreement between these results and known values indicates the successful applicability of proposed method for simultaneous determination of V(V) and Al(III) in real samples.

5. Conclusion

Based on the results obtained in this work, application of ANN method, which was trained with the back-propagation of errors learning algorithm on the calibration data constructed with the β-correction technique for simultaneous determination of V(V) and Al(III) is an effective and accurate way. ANN modeling using a calibration matrix constructed with β-correction absorption has been successfully applied to simultaneous analysis of these metal ions in synthetic mixtures of some alloys. Non-linear effects resulting from analyte–analyte interaction in this system can be modeled by artificial neural network. There is no need to know the exact form of the analytical function on which the model should be built also it requires no complex pretreatment or chromatographic separations of the samples containing analytes. This technique is simple, fast and affordable. This modeling shows a combination of β-correction spectrophotometery with back-propagation artificial neural network (BP-ANN) algorithm is a powerful technique to handle non-linear spectral data for increasing sensitivity, precision and accuracy and to obtain wider dynamic ranges in simultaneous determination of V(V) and Al(III).

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