Simultaneous determination of antimony and bismuth by beta-correction spectrophotometry and an artificial neural network algorithm

A. Abbaspour*, L. Baramakeh

Department of Chemistry, College of Science, Shiraz University, Shiraz 71454, Iran

Abstract

Simultaneous determinations of antimony and bismuth were done by β-correction spectrophotometry and a feed forward neural network algorithm with back propagation of error. The sensitivity was improved using β-correction spectrophotometry. The determination of trace amounts of mixtures of Sb and Bi in various matrices (river, tap and industrial wastewater) were investigated by neural network and β-correction spectrophotometry using the complexes formed between pyrogallol red, Sb and Bi. The results showed that measurement is possible in the ranges of 0.05–5.0 and 0.2–3.2 $\mu g\,ml^{-1}$ for Sb(III) and Bi(III), respectively. The results also show very good agreement between true and predicted concentration values and have the ability to use in routine analysis.
© 2004 Elsevier B.V. All rights reserved.

Keywords: β-correction; Neural network; Back propagation of error; Pyrogallol red; Antimony; Bismuth

1. Introduction

Simultaneous determination of trace amounts of metals in environmental samples is still a challenging analytical problem because of the sensitivity and specificity required in environmental monitoring and regulations. Although some of the spectroscopic techniques such as graphite furnace atomic absorption spectroscopy, ICP–AES and ICP–mass can be used for such analysis, the cross-interferences among different metal species often cause problem, which in turn raise the uncertainty level in the analytical results. Further more, those techniques require expensive instrumentation and maintenance, which limit the application of the techniques in many laboratories.

Antimony is in the group of non-essential elements and its toxicity is comparable in behavior to arsenic and bismuth. Although almost neglected before the early 1990s, the area of analytical development for the ultra trace determination and speciation of antimony compounds has undergone exciting progress during the last 8 years. The interest in studies of Sb and its compounds is increased because of the potentially harmful effects of Sb have been recognized by several authorities and thereafter Sb was listed as a priority pollutant by the UEPA (US Environmental Protection Agency) and by the German Research Community [1,2]. There is considerably disagreement amongst researchers about the toxicity of antimony [3,4] but is generally recognized that stibnite (Sb_2S_3) is the most toxic of all antimony compounds. Exposure to 0.3 ppm (in a short term of about 10 min) [5] affects the central nervous system. Water soluble antimony compounds cause nausea, vomiting and diarrhea [3,4]. However, very few cases of antimony poisoning have been reported since the kidneys rapidly exert antimony in the blood stream and therefore increased levels are found in urine.

Toxic effects that have been reported for bismuth compounds in humans are nephropathy, encephalopathy, osteoarthropathy, gingivitis, stomatitis and colitis. People exposed to bismuth usually have a problem in their walking, standing or writing, deterioration of memory, changes in behavior, insomnia and muscle cramps, together with several psychiatric symptoms [6]. Clinical/medical interest in bismuth dates back about 70 years, when the element was first introduced in a pharmaceutical used in the treatment

* Corresponding author. Tel.: +98 9117184524; fax: +98 7112280926.
E-mail address: abbaspour@chem.susc.ac.ir (A. Abbaspour).

of syphilis [7]. Its pharmaceutical uses have expanded to anti-acids, peptic ulcer treatments, and topical dermatological creams. Therefore, there is a necessity for methods to determine bismuth contents in substances [8].

In addition, antimony and bismuth are similar in nature and have the same substances, which are together [9] in nature (e.g. in ultramafic, mafic, intermediate and granite rocks.) therefore it is important to measure them in the presence of each other.

Pyrogallol red (PRD) is one of the first reagents used for the spectrophotometric determination of Sb and Bi [10–11]. The methods used for determination of Sb and Bi suffer from poor sensitivity (due to excess of colorant reagent) and a very limited working range. Present work proposed a solution to these problems. In order to eliminate the effect of colorant reagent, β-correction method was applied to the absorbance values to calculate the real absorbances. And with using a non-linear curve-fitting method (feed forward neural network with back-propagation error), the measuring range can be improved.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade. Triply distilled water was used throughout. Stock Sb and Bi solutions ($1000 \, \mu g \, ml^{-1}$) were prepared from potassium antimony tartarat and bismuth (III) nitrate (Merck), respectively. Pyrogallol red (Merck) stock solution (0.01%) was prepared by dissolving appropriate amount of reagent in methanol [12]. A buffer of pH 2.4 was prepared by using a mixture of (0.04 M) phosphoric, acetic and boric acid, and pH was ad-

justed with sodium hydroxide solution (0.2 N) at appropriate concentrations [13]. One thousand micrograms per milliliter solutions of studied interfering ions were prepared from their appropriate salts.

2.2. Apparatus and software

UV–visible absorbance spectra were recorded on a Cintra 5 spectrometer, which were equipped with a 1 cm path length quartz cell. The spectra were recorded between 300 and 700 nm at 1.0 nm intervals. Measurements of pH were made with Metrohm 780 pH meter using a combined glass electrode.

The back-propagation neural network algorithm having three layers was used in MATLAB (version 5, Math Work Inc.) using NNet toolbox. All program were run on a Pentium (III), personal computer, with Windows 98 operating system.

2.3. Procedure

A volume of 3.2 ml of pyrogallol red (0.01%), 1 ml of buffer solution and appropriate volume of Sb and Bi were added to a 5-ml volumetric flask and made up to the mark with distilled water. The mixed solution was left for 30 min and then absorbances were measured.

3. Results and discussions

3.1. Principle and algorithm

Pyrogallol red formed colored complexes with Sb and Bi. Fig. 1 shows the absorbance spectra of pyrogallol red and of complexes formed with Bi and Sb. As this figure shows,
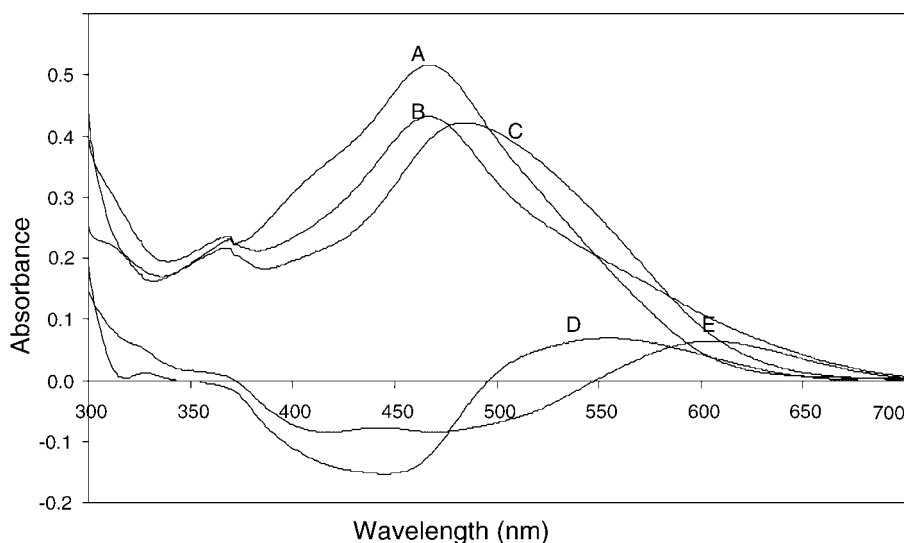

Fig. 1. Absorption spectra of PR Sb and Bi at pH = 2.4. Curve A is reagent blank (PR 6.4×10^{-3}%) (reference, water), curve B is Bi (3.5 ppm) and 6.4×10^{-3}% of PR(reference, water), curve C is Sb (7 ppm) and 6.4×10^{-3}% of PR (reference, water), D and E are Sb and Bi–PR, respectively; their concentrations are as in curves B and C (reference, reagent blank).

there is a clear overlapping of the two spectra. This prevents a simultaneous determination of the two ions by direct UV–vis absorbance measurements. On the other hand in the previously reported works [14], the sensitivity was low because of a colored reagent. However, as mentioned earlier, the effect of colorant was eliminated by applying β-correction method to the absorbance values in order to calculate the real absorbances. And with using a non-linear curve fitting method (feed forward neural network with back-propagation error) the simultaneous measurement were made and the measuring range were improved.

3.1.1. Principles of spectral correction technique

β-Correction method [15–23] is an analytical method, which is different from other dual-wavelength spectrophotometric methods. It can eliminate completely the interference of excess of colorant reagents, thus increasing the sensitivity and decreasing the analytical error. In order to consider the general principle of β-correction spectrophotometry, the reaction of a metal (M) with a colorant (L) can be expressed as follow:

$$M + \gamma L \rightarrow ML\gamma + L \,(excess) \tag{1}$$
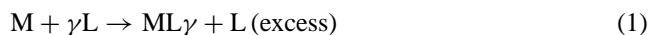
where, term γ represents the complexation ratio. The true absorbance ($A\beta$) of the chelate $ML\gamma$ is expressed by:

$$A\beta = \frac{(\Delta A - \beta \Delta A')}{(1 - \alpha\beta)} \tag{2}$$

where ΔA and $\Delta A'$ are the absorbances of $ML\gamma$ against L reference at λ_0 and λ_i, respectively, which is determined with the reagent blank as reference. α and β are the correction coefficients, and can be calculated from:

$$\alpha = \frac{\varepsilon_{ML\gamma}^{\lambda_i}}{\varepsilon_{ML\gamma}^{\lambda_0}} \tag{3}$$

and

$$\beta = \frac{\varepsilon_{L}^{\lambda_0}}{\varepsilon_{L}^{\lambda_i}} \tag{4}$$

where $\varepsilon_{ML\gamma}^{\lambda_i}$, $\varepsilon_{ML\gamma}^{\lambda_0}$, $\varepsilon_{L}^{\lambda_i}$ and $\varepsilon_{L}^{\lambda_0}$ are the molar absorption of $ML\gamma$ and blank solution at λ_i and λ_0, respectively (when water is considered as the reference). The analytical sensitivity will be at a maximum when λ_i and λ_0 are selected in a manner that positive and negative values were reached maximum. Three wavelengths were selected, which corresponded to the peak absorption of PRD, Sb-PRD and Bi-PRD, respectively 470, 550, 600 nm. From the curve A, in Fig. 1, correction coefficient were calculated to be $\beta = 0.53$ at 550 nm and $\beta = 0.122$ at 600 nm for Sb and Bi, respectively. The other correction coefficient α for Sb and Bi were obtained as $\alpha_{550}^{SbL} = 1.36$, $\alpha_{600}^{SbL} = 1.67$ $\alpha_{550}^{BiL} = 1.48$ and $\alpha_{600}^{BiL} = 3.1$ from curves C and B, respectively.

As this result shows, excess of PRD will considerably affect the any single wavelength spectrophotometric determination of trace Sb or Bi and the correction method enhanced sensitivity of the results strongly. (See Figs. 2 and 3)

3.1.2. Back propagation-ANN (BP-ANN) algorithm and index for model approximation

A powerful non-linear technique is the BP-ANN [24,25] and has been applied in the multivariate non-linear calibration [26]. As discussed before, one of the problems in this case was limiting linear range, therefore a non-linear mapping technique, which requires no assumed mathematical model, was used. A multi-layer feed forward ANN with sigmoidal transformation functions in the nodes and the back-propagation of errors learning algorithm. ANN method was run on the calibration data constructed with the β-correction technique. Three layer back-propagation networks, including an input, a hidden and an output layer, were used. The input nodes
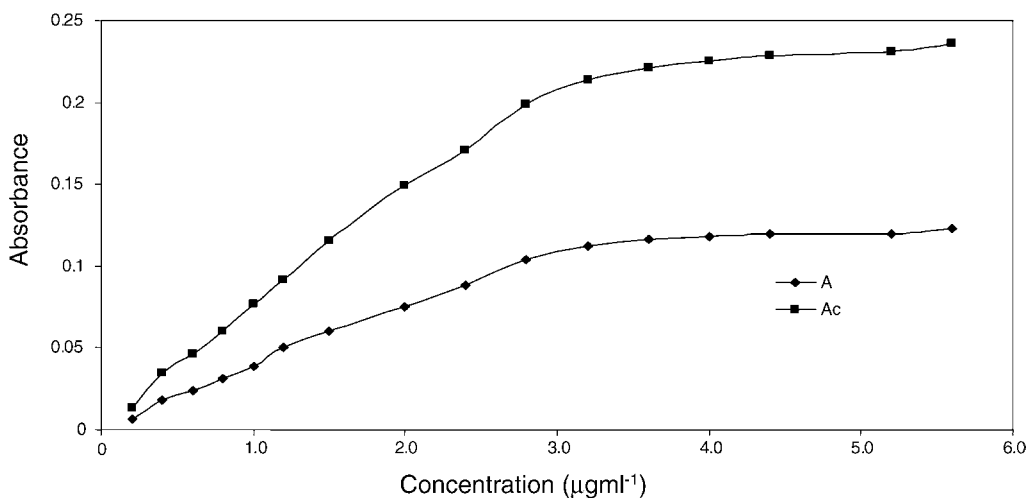

Fig. 2. Standard curves for determination of Bi with (Ac) and without (A) spectral correction in 6.4×10^{-3}% of pyrogallo red and pH = 2.4 at 600 nm.
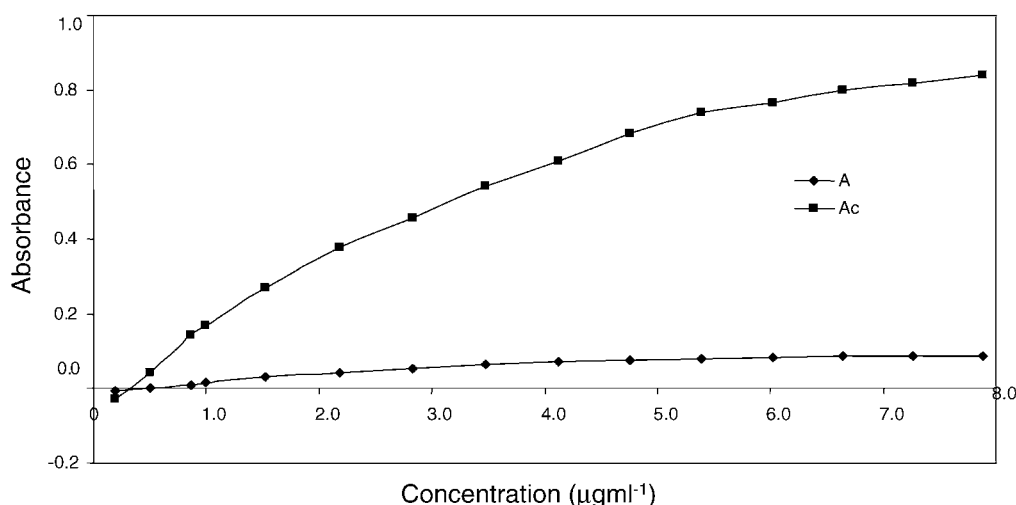
Fig. 3. Standard curves for determination of Sb with (Ac) and without (A) spectral correction in 6.4×10^{-3}% of pyrogallo red and pH = 2.4 at 550 nm.

transferred the weighted 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

$$C = f(A) + E \qquad (5)$$

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, denoted by f in Eq. (5), 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, $C_{unknown, k \times m}$, from the corresponding measurement spectral matrix, $A_{unknown, k \times p}$, according to the following equation:

$$C_{unknown, k \times m} = f(A_{unknown, k \times p}) \qquad (6)$$

This procedure, defined by Eq. (6), is known as the prediction step in BP-ANN. The training procedure, defined by Eq. (5), 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. The digitized absorbance of calibration mixtures were gathered in a 23×2 data matrix and absorbances of prediction matrixes were collected in a 19×2 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 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 rates 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 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 eight nodes were used in the hidden layers of Sb and Bi, respectively. The optimized parameters for ANN models used are given in Table 1. The detection limits obtained as 3 SD of the blank [27] in each model were 0.05 $\mu g \, ml^{-1}$ and 0.2 $\mu g \, ml^{-1}$ for Sb and Bi, respectively.

Table 1
Optimized parameters to achieve the best results

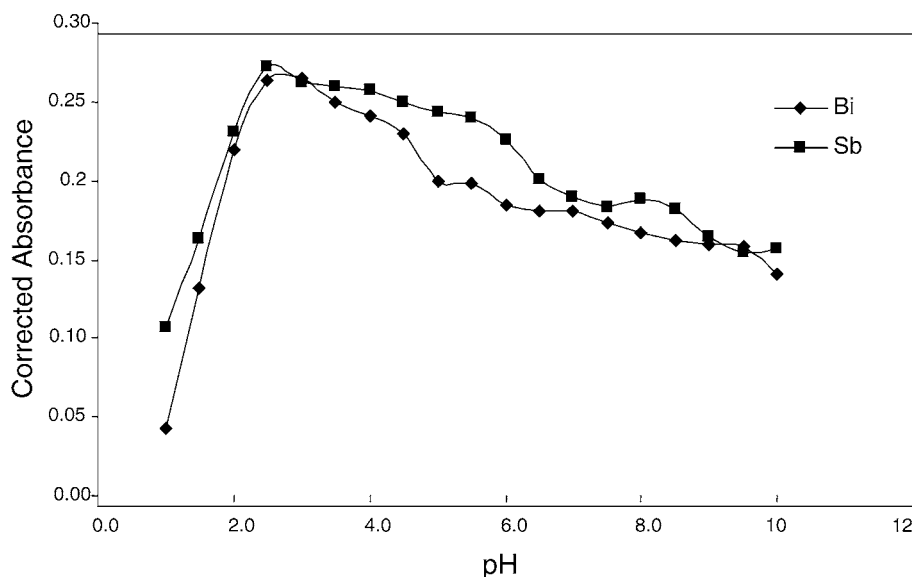| Parameters	Compounds	
	Sb	Bi
Input nodes	2	2
Output nodes	1	1
Number of Iteration	1200	1600
Learning rate	0.01	0.01
Momentum constant	0.9	0.9
Hidden layer nodes	4	8

Fig. 4. Effect of pH on the absorbances of the Bi and Sb complexes (in 6.4×10^{-3}% of pyrogallo red and pH = 2.4 at 550 and 600 nm for Sb and Bi, respectively).

3.1.3. Statistical parameters

The root-mean-square error (RMSE) of prediction is defined as follows [28]:

$$\text{RMSE} = \left[\frac{\sum_{s=1}^{r} \sum_{i=1}^{n} \left((t_{si} - y_{si}) / t_{si} \right)^2}{rn} \right]^{1/2} \tag{7}$$

Both summations in the above equation run over all r input objects (the objects in prediction set) of the test set and over 0, all n output variables (the number of analytes studied). 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

(RSE) of the prediction concentration [28]:

$$\text{RSE}(\%) = 100 \times \left(\frac{\sum_{j=1}^{N} (\hat{C}_j - C_j)^2}{\sum_{j=1}^{N} (C_j)^2} \right)^{1/2} \tag{8}$$

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 RSE 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 sets indicate the accuracy of the proposed method.
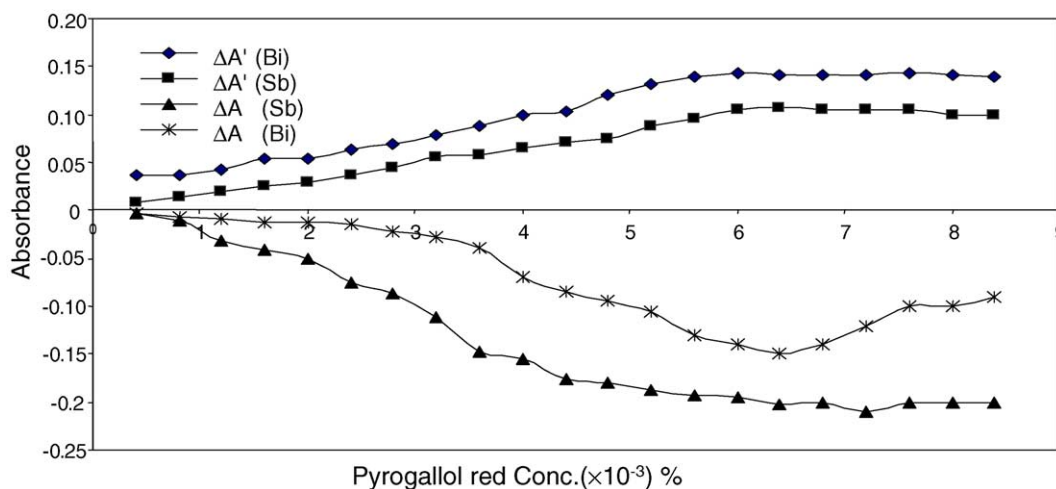

Fig. 5. Effect of addition of PRD solution on absorbance's of Sb ($6.0 \,\mu\text{g ml}^{-1}$) and Bi ($3.5 \,\mu\text{g ml}^{-1}$) at pH = 2.4. ΔA (at 470 nm) and $\Delta A'$ (at 550 and 600 nm for Sb and Bi, respectively) are the absorbances of complexes against the reagent blank as reference.
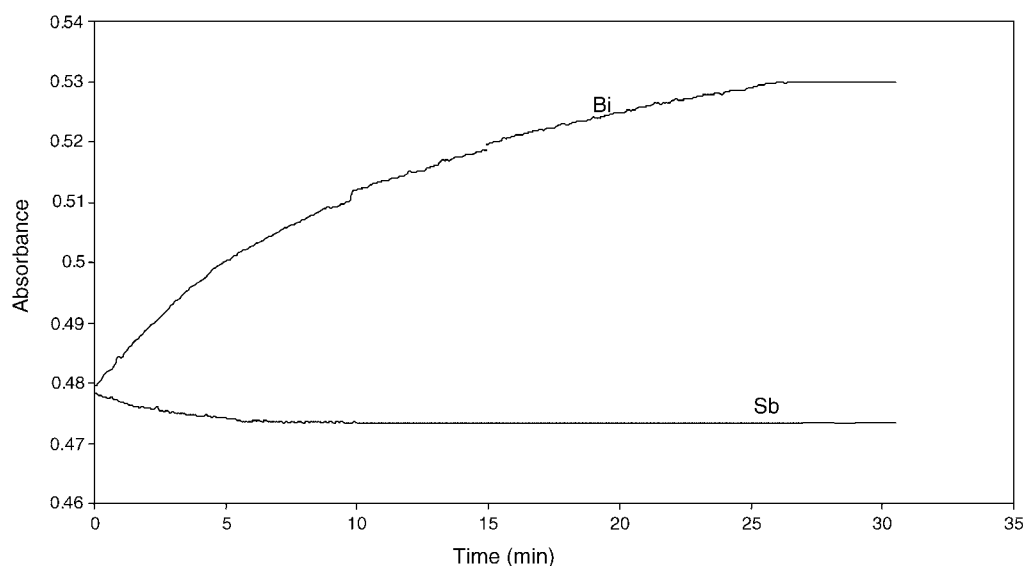
Fig. 6. Stability of formed complex of Sb and Bi (in 6.4×10^{-3}% of pyrogallo red and pH = 2.4 in the presence of 6.5 and 4.0 μg ml^{-1} of Sb and Bi, respectively).

3.2. Optimizations of the system

For finding the optimum condition, the influence of pH values on the spectrum of each complex at a constant concentration was studied. The formed complexes of Sb and Bi were similarly affected with pH (Fig. 4). The pH of 2.4 was chosen as optimum, since both complexes have maximum absorbance at this pH. Effect of the concentration of the pyrogallo red was also investigated (Fig. 5). The absorbance values of the solutions containing a constant concentration of Sb (6.0 μg ml^{-1}) or Bi (3.5 μg ml^{-1}) at pH = 2.4 were obtained at varied concentration of PRD. The results showed that the absorbance reaches to a maximum value almost at 6.4×10^{-3}% pyrogallol red. This value was chosen as the optimum concentration for pyrogallol red.

Stability of the formed complex was examined (Fig. 6) at the optimum condition (pH = 2.4 and 6.4×10^{-3}% of pyrogallol red). Results showed that the complex of Sb is stable after a few minutes while complex of Bi would be stable after 30 min and therefore, they are appropriate for quantitative measurement in this condition.

3.3. Requirements for applying BP-NNT

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, which provide more information using a few experimental trials, from calibration set, their compositions were randomly designed. Twenty-three binary mixtures were selected as the calibration set. Training set of Sb and Bi ions in calibration set were between 0.00–5.00 μg ml^{-1} of Sb and 0.20–3.20 μg ml^{-1} of Bi. In order to construct the ANN model, a prediction set was prepared involving 19 synthetic test samples. In order to evaluate the performance of the model, the neural network model was also tested on an additional validation set with its samples belonging to neither the calibration nor the prediction set. The compositions of the prediction and validation sets are given in Tables 2 and 3.

Table 2

Composition of prediction set, their results obtained by suggested method for simultaneous determination of analytes

Mixture	Added (μg ml^{-1})		Found (μg ml^{-1})		Mixture	Added (μg ml^{-1})		Found (μg ml^{-1})	
	Sb	Bi	Sb	Bi		Sb	Bi	Sb	Bi
1	0.00	0.20	−0.04	0.21	11	3.00	0.60	2.86	0.57
2	0.00	0.60	0.03	0.59	12	3.00	0.80	3.23	0.74
3	0.20	1.60	0.24	1.59	13	3.00	2.40	2.85	2.33
4	0.50	3.20	0.60	3.20	14	4.00	0.60	3.80	0.61
5	1.00	0.60	1.04	0.62	15	4.00	2.40	4.21	2.42
6	1.00	1.60	0.93	1.64	16	4.50	0.20	4.60	0.21
7	2.00	0.60	2.00	0.57	17	4.50	2.40	4.42	2.49
8	2.00	1.20	2.07	1.19	18	5.00	0.20	5.04	0.21
9	2.00	3.20	2.25	3.23	19	5.00	1.60	4.90	1.59
10	3.00	0.20	3.00	0.25					

Table 3
Composition of validation set, their results obtained by suggested method for simultaneous determination of analytes

Mixture	Added (μg ml^{-1})		Found (μg ml^{-1})	
	Sb	Bi	Sb	Bi
1	0.00	0.4	0.06	0.36
2	0.00	0.8	0.01	0.71
3	0.60	2.40	0.60	2.47
4	0.60	0.40	0.71	0.41
5	1.00	1.20	0.97	1.25
6	1.00	3.20	1.07	3.13
7	2.00	0.40	2.17	0.36
8	2.00	0.80	2.10	0.78
9	2.00	2.40	1.92	2.36
10	3.00	0.40	3.18	0.36
11	3.00	1.20	3.12	1.15
12	3.00	3.20	2.96	3.24
13	4.00	0.40	3.94	0.47
14	4.50	0.40	4.65	0.45
15	4.50	1.20	4.54	1.16
16	4.50	3.20	4.41	3.21
17	5.00	1.20	4.95	1.12

Table 5
Actual composition and calculated concentration of Sb(III) and Bi(III) in different matrices

Source	Added (μg ml^{-1})		Found (μg ml^{-1})	
	Sb	Bi	Sb	Bi
River water	5.00	1.0	5.10	1.00
Industrial waste water	3.00	2.00	2.90	1.80
Industrial waste water	1.00	2.50	1.00	2.40
Tap water	2.50	0.50	2.60	0.60
Synthetic sample[a]	2.00	1.00	2.05	1.10
Synthetic sample[b]	3.50	0.50	3.60	0.70

[a] Contents of synthetic samples were: $Sb^{3+} = 2.00 \mu$g ml^{-1}, $Bi^{3+} = 1.00 \mu$g ml^{-1}, $Li^{1+} = 40.00 \mu$g ml^{-1}, $Cr^{3+} = 15.00 \mu$g ml^{-1}, Mn $= 50.00 \mu$g ml^{-1}, $Ni^{2+} = 7.00 \mu$g ml^{-1}, $Co^{2+} = 3.00 \mu$g ml^{-1}, $Zn^{2+} = 50.00 \mu$g ml^{-1}, $As^{3+} = 1.50 \mu$g ml^{-1}, $Ag^{1+} = 0.04 \mu$g ml^{-1}, $Pb^{2+} = 20.00 \mu$g ml^{-1} and $Cu^{2+} = 15.00 \mu$g ml^{-1} (after adding acac).
[b] $Sb^{3+} = 3.50 \mu$g ml^{-1}, $Bi^{3+} = 0.50 \mu$g ml^{-1}, $K^{1+} = 10 \mu$g ml^{-1}, Mo $= 5.00 \mu$g ml^{-1}, $Co^{2+} = 2.00 \mu$g ml^{-1}, $Cr^{3+} = 7.00 \mu$g ml^{-1}, $Ag^{1+} = 1.00 \mu$g ml^{-1}, $Pb^{2+} = 15.00 \mu$g ml^{-1}, $Ni^{2+} = 10.00 \mu$g ml^{-1}, $V^{5+} = 7.00 \mu$g ml^{-1}, $Cu^{2+} = 10.00 \mu$g ml^{-1} (after adding acac and manitol).

All parameters, which influenced the model, were optimized (Table 1). These results show very good agreement between true and predicted concentration values. Mean square errors of 0.16 and 0.03, correlation values of 0.9994 and 0.9999 for calibrations and mean square errors of 0.11 and 0.05, correlation values of 0.9991 and 0.9988 for prediction sets of antimony and bismuth, respectively obtained with a sigmoidal transfer function and optimized parameters in Table 1.

3.4. Interference study

The effect of interfering ions at different concentrations on the absorbance of a solution mixture containing 1.00 μg ml^{-1} Sb and Bi were studied. An ion was considered as interference, the presence of which produced a variation in the absorbance of the sample (at considered wavelengths) greater than 3%. The results indicate that (Table 4) most of the cations did not show significant spectral interferences at concentrations 100 times greater than those of the analyte. Only Al^{3+}, Cu^{2+}, Mo^{5+}, In^{3+} and V^{5+} showed interference. However, interfering of Al^{3+}, Cu^{2+} and In^{3+} with acethylacetonate (acac) and Mo^{5+} and V^{5+} with manitol were completely masked, and their tolerance limits were at least 20 times greater than Sb or Bi.

Table 4
Influence of foreign ions on the determination of a mixture of 1.0 μg ml^{-1} of Sb and Bi solution

Ion	Tolerance ion ratio
Cr^{3+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Mg^{2+}, Co^{2+}, Sn^{2+}, Ca^{2+}, Pb^{2+}, As^{3+}, Li^+, Na^+, K^+, Ce^{3+}, Hg^{2+}, Fe^{2+}, Ag^+	100
Al^{3+}, V^{5+}, In^{3+}	5
Cu^{2+}, Mo^{5+}	3

3.5. Applications of the method

The proposed method was successfully applied to the determination of some mixtures of Sb and Bi. For this purpose, several spiked samples were prepared by adding aliquots (a few microliters) of Sb and Bi solution to river, tap and waste water, and the effect of matrix and interfering ions were investigated. Results show (Table 5) that this method has good results, and it is applicable for routine measurements.

4. 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 Sb and Bi 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 net-work (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 Sb and Bi.

Acknowledgements

References

[1] Deutsche Forschungsgemeinschaft (DFG), Analyses of Hazardous Substances in Biological Materials, VCH, Weinheim, 1994.

[2] M. Krachler, M. Burow, H. Emons, Analyst 124 (1999) 923.

[3] L. Friberg, G.F. Nordberg, V.B. Vouk, Handbook on Toxicology of Metals, Elsevier, Amesterdam, 1979.

[4] E. Browning, Toxicity of Industrial Metals, 2nd ed., Butterworths, London, 1969.

[5] Health and Safety Excutive, Guidance Notes EH 40, Occupational Exposure Limits, HM Stationary Office, London, 1984.

[6] A. Slikkerveer, F.A. de Wolff, Med. Toxicol. Adverse Drug Exp. 4 (5) (1989).

[7] R.L. Bertholf, B.W. Renoe, Anal. Chem. Acta 139 (1982) 287.

[8] D.L. Tsalev, Z.K. Zaprianov, Atomic absorption spectrometry in occupational and environmental health practice, in: Analytical Aspects and Health Significance, vol. 1, CRC Press, Boca Raton, FL, 1983.

[9] J.M. Guibert, C.F. Paric, The Geology of Ore Deposits, W.H. Freeman and company, 1997.

[10] R. Lopez Nunanes, M. Callejon Mochon, A. Guira Um Perez, Anal. Chim. Acta 192 (1987) 119.

[11] A. Majed, M.S. Khan, Anal. Chim. Acta 175 (1985) 345.

[12] A. Safavi, A.A. Ensafi, Anal. Chim. Acta 244 (1991) 231.

[13] J. Lurie, Handbook of Analytical Chemistry (English Translation), Mir, Moscow, 1975.

[14] A. Abbaspour, M. Najafi, Talanta 60 (2003) 1079–1084.

[15] H.W. Gao, Anal. Proc. 32 (1995) 479.

[16] H.W. Gao, Anal. Chem. 52 (1997) 160.

[17] H.W. Gao, N.L. Hu, H.F. Zhou, M.L. Zhang, Anal. Chem. 46 (2001) 75.

[18] N.L. Hu, H.W. Gao, M.L. Zhang, H.F. Zhou, Asian J. Chem. 12 (2000) 792.

[19] H.W. Gao, P.F. Zhang, L. Wang, J. Anal. Chem. 55 (2000) 863.

[20] H.W. Gao, Asian J. Chem. 12 (2000) 1101.

[21] H.W. Gao, Armenian Chem. J. 51 (1998) 21.

[22] H.W. Gao, Q.S. Ye, Bull. Korean Chem. Soc. 22 (2001) 565.

[23] A. Abbaspour, L. Baramakeh, Talanta 57 (2002) 807.

[24] J.R.M. Simits, W.J. Melssen, L.M.C. Buydens, G. Kateman, Chemom. Intell. Lab. Syst. 22 (1994) 165.

[25] J.R.M. Simits, W.J. Melssen, L.M.C. Buydens, G. Kateman, Chemom. Intell. Lab. Syst. 23 (1994) 267.

[26] P. Liu, Y. Liang, S. Wang, X. Seng, R. Yu, Chem. J. Chin. Univ. 16 (1995) 456.

[27] J.C. Miller, J.N. Miller, Statistics and Chemometrics for Analytical Chemistry, 4th ed., Prentice Hall, UK, 2000.

[28] M. Blanco, J. Coello, H.M. Iturriaga, S. Maspoch, M. Redon, Appl. Spectrosc. 48 (1994) 37.