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Application of artificial neural network to simultaneous potentiometric determination of silver(I), mercury(II) and copper(II) ions by an unmodified carbon paste electrode

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Abstract

The response characteristics and selectivity coefficients of an unmodified carbon paste electrode (CPEs) towards Ag^+, Cu^{2+} and Hg^{2+} were evaluated. The electrode was used as an indicator electrode for the simultaneous determination of the three metal ions in their mixtures via potentiometric titration with a standard thiocyanate solution. A three-layered feed-forward artificial neural network (ANN) trained by back-propagation learning algorithm was used to model the complex non-linear relationship between the concentration of silver, copper and mercury in their different mixtures and the potential of solution at different volumes of the added titrant. The network architecture and parameters were optimized to give low prediction errors. The optimized networks were able to precisely predict the concentrations of the three cations in synthetic mixtures.

Keywords: Multicomponent analysis; Ag^+, Cu^{2+} and Hg^{2+}; Potentiometric titration; Carbon paste electrode; Artificial neural network

1. Introduction

The use of both carbon paste electrodes (CPEs) and chemically modified carbon paste electrodes (CMCPEs) may result in very sensitive and promising analytical methods [1–3]. More interesting designs of CPEs are usually reported in association with carbon paste-based flow cells [4], electrochemical detectors, [5] coulometric [6], amperometric [7,8], and potentiometric [9] sensors, or some sensing devices for special in vivo measurements [10,11]. Unmodified CPEs have already been used for the potentiometric determination of traces of silver [12] and copper ions [13].

The simultaneous determination of several analytes in a given sample is now an interesting area in chemometrics [14,15]. In recent years, artificial neural network (ANN) as a powerful non-parametric non-linear modeling technique has attracted increasing interest [16,17]. The strength of modeling with layered, feed-forward ANNs lies in the flexibility of the distributed soft model defined by the weight of the network. The multilayer feed forward neural network trained with back-propagation learning algorithm becomes an increasingly popular technique [18]. The application of ANN to non-linear calibration of ion selective array [19–21] and multi-metal analysis utilizing optical sensors [22–24], quantitative structure-activity relationship [25], optimization of experimental conditions [26] and modeling of kinetic data [27] have already been reported. Recently, we reported the application of ANN to the non-linear calibration by using derivative spectra [28].

The application of multivariate calibration method to the potentiometric titration data was introduced by Lindberg and Kowalski [29]. After that, the PLS calibration method has been applied to different potentiometric titration methods [30,31]. In our previous work, we discussed some limitations of these methods and proposed an ANN model to process the nonlinear relationship between the concentration of acids in a given mixture (as an independent variable) and

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the pH of solution at different volumes of the titrant added (as dependent variables) [32].

In this work, we used a three-layer ANN with back-propagation of error algorithm for modeling the relationship between potential and concentration through a multi-component potentiometric titration of Ag^+, Cu^{2+} and Hg^{2+} with thiocyanate as a titrant using an unmodified carbon paste electrode as the indicator electrode.

2. Experimental

2.1. Apparatus and reagents

The titrations were carried out in a batch system in which an unmodified carbon paste electrode was used as an indicator electrode and a calomel electrode as a reference electrode. The potential was measured by a digital pH-meter (Metrohm, model 654).

All reagents used were of analytical reagent grade. Doubly distilled deionized water was used throughout. A 1.0 M potassium thiocyanate solution of was prepared by dissolving appropriate amount of KSCN in water and diluting to 500 ml. Adjustment of the ionic strength of the sample solutions was made by a potassium nitrate solution. Silver(I), copper(II) and mercury(II) solutions of 0.100 M were prepared by dissolving suitable amounts of their nitrate salts and diluting to 1000 ml.

2.2. Preparation of carbon paste electrode

Pure graphite powder (0.1 g) and liquid paraffin (Nojul, 0.06 g) were placed in a 25 ml beaker and mixed well for 15–20 min to form a uniform paste. Electrode bodies were made from disposable 1 ml polyethylene syringes, the tip of which had been cut off with a razor blade. These bodies were filled with approximately 0.3 ml of carbon paste. Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a smooth solid support. A fresh carbon paste electrode of a shiny appearance was prepared by squeezing out a small amount of the paste, scrapping off the excess against a conventional paper and polishing the electrode on a smooth paper. The electrical connection was made with a copper wire.

2.3. Procedure

In a typical titration, suitable amounts of individual cation or cation mixtures were placed in a 100 ml vessel and 5.0 ml of 1.0 M potassium nitrate was added to the solution and diluted to 50 ml with distilled water. The stirring solution was then titrated with a 0.1 M potassium thiocyanate

Table 1
Concentrations of different cations in the binary and ternary standard solutions

Sample	Mixture								
	Ag^+–Cu^{2+}(mM)		Ag^+–Hg^{2+}(mM)		Cu^{2+}–Hg^{2+}(mM)		Ag^+–Cu^{2+}–Hg^{2+}(mM)		
	Ag^+	Cu^{2+}	Ag^+	Hg^{2+}	Cu^{2+}	Hg^{2+}	Ag^+	Cu^{2+}	Hg^{2+}
1	2.0	4.0	0.4	8.0	2.0	0.8	1.0	12.0	2.0
2	6.0	4.0	0.8	16.0	2.0	1.0	4.0	14.0	1.2
3	8.0	2.0	1.4	6.0	8.0	1.2	8.0	2.0	1.0
4	16.0	10.0	0.8	4.0	10.0	1.6	14.0	2.0	0.6
5	18.0	14.0	0.0	0.0	16.0	2.0	16.0	2.0	1.4
6	20.0	16.0	0.1	0.2	0.8	0.0	6.0	2.0	0.6
7	0.2	0.0	0.1	0.6	1.4	0.0	4.0	0.2	1.2
8	0.4	0.6	0.1	0.8	0.4	0.1	1.0	1.4	1.0
9	0.0	0.8	0.0	1.2	2.0	0.2	16.0	1.0	1.2
10	1.0	1.0	0.3	1.4	1.0	0.1	8.0	0.6	1.6
11	1.4	0.0	0.1	1.8	0.8	0.2	0.6	8.0	0.4
12	1.6	1.8	0.1	2.0	8.0	0.2	2.0	4.0	1.8
13	2.0	1.0	0.8	4.0	1.0	0.4	1.0	2.0	0.0
14	0.2	10.0	0.1	0.4	16.0	0.0	10.0	2.0	0.2
15	4.0	0.8	0.1	6.0	0.8	0.6	10.0	1.0	0.2
16	0.6	6.0	4.0	0.2	6.0	0.2	1.4	0.4	0.6
17	4.0	6.0	2.0	0.1	4.0	0.4	2.0	6.0	0.8
18	–	–	–	–	–	–	1.8	0.8	0.1
19	–	–	–	–	–	–	2.0	1.6	0.2
20	–	–	–	–	–	–	10.0	1.4	0.6
21	–	–	–	–	–	–	12.0	1.0	1.4
22	–	–	–	–	–	–	4.0	4.0	1.0
23	–	–	–	–	–	–	6.0	0.6	0.6
24	–	–	–	–	–	–	2.0	1.4	0.8
25	–	–	–	–	–	–	12.0	1.0	1.6
26	–	–	–	–	–	–	1.0	12.0	2.0

solution, using a digital burette. In the presence of carbon paste electrode, as an indicator electrode, and calomel reference electrode (SCE) the potential was recorded after each 0.1 ml addition of the titrant. For each solution, 50 data points were recorded.

2.4. Standard solutions

Binary mixtures of the three cations (i.e. Ag^+–Hg^{2+}, Ag^+–Cu^{2+}, Hg^{2+}–Cu^{2+}) as well their ternary mixtures Ag^+–Hg^{2+}–Cu^{2+} were analyzed. In Table 1, the concentrations of standard solutions in the binary and ternary mixtures of the cations are presented. In order to evaluate the performance of the ANN model, eight standard solutions were considered in the prediction set. The concentrations of cations in the mixtures were in the *millimolar* range and selected randomly.

2.5. Data processing and ANN modeling

The data matrix used as input for the neural network was the potential of standard solutions in the presence of different volumes of thiocyanate solution at 0.1 ml intervals. Since the large number of nodes in the input layer of the network (i.e. the number of potential readings for each solution) increases the CPU time for ANN modeling, the data matrix was factor analyzed before introducing into the network and PC–ANN model was run [33,34]. Consider that the data matrix $\boldsymbol{D}$ has a dimension of $n \times m$, where n and m are the number of standard solutions and the number of potential readings for each solution, respectively. The score and loading of this matrix were calculated by the singular value decomposition (SVD) [32]. A feed-forward three-layered ANN was used to precede the titration data of cation mixtures for simultaneous determination of silver, copper and mercury ions. The ANN model was the same as that we discussed in our previous paper [32]. Through the ANN modeling, the numbers of input nodes (i.e. the number of principal components f) and the number of nodes in the hidden layer were optimized. The weights of hidden and output layers were adjusted by back-propagation of error algorithm [17] through an iterative procedure until a minimum value for standard error (S.E.) of prediction was obtained. The momentum and learning rate of the network were also optimized for minimum S.E.

3. Results and discussion

3.1. Potentiometric response and selectivity coefficients of the CPE

Fig. 1 shows the potentiometric responses of the carbon paste electrode to silver, copper and mercury ions. The slopes of the linear parts of the resulting curves are 29.1, 64.4, and >200 mV per decade for copper, silver and mercury ion, respectively. The linear ranges of the resulting potential

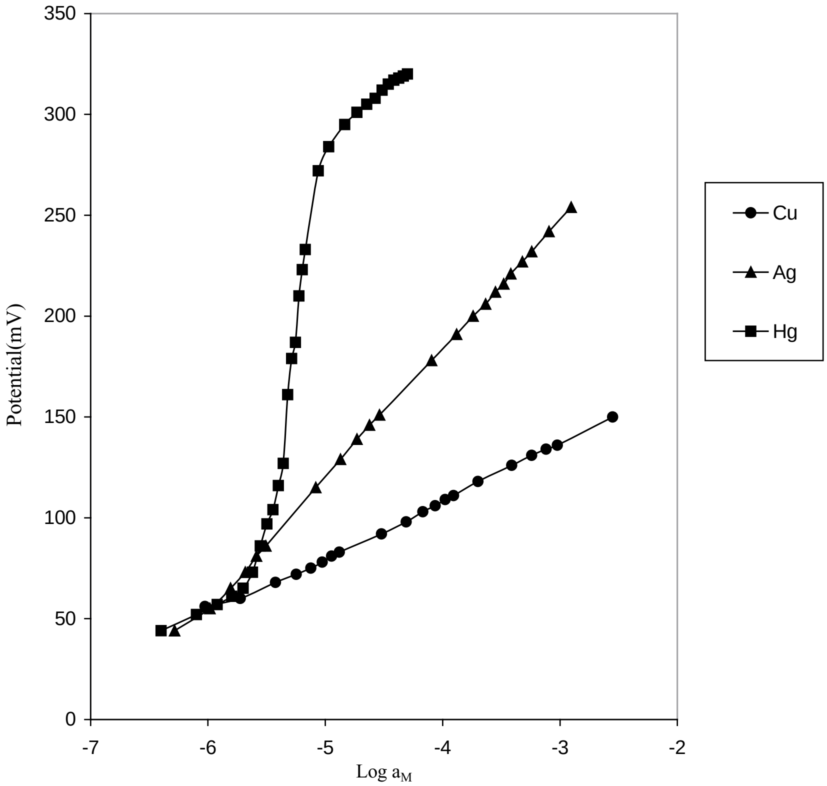

Fig. 1. Calibration curves for silver, copper and mercury ions.

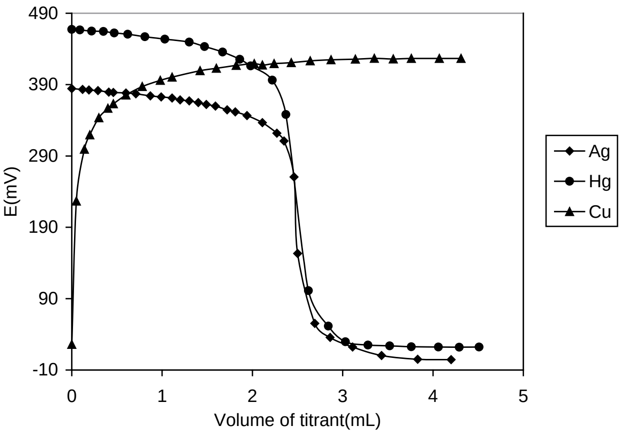

Fig. 2. Potentiometric titration curves for titration of 25 ml of 0.1 M silver, 0.1 M copper and 0.05 M mercury with 0.1 M potassium thiocyanate as titrant, using the CPE as an indicator electrode.

versus pM plots for Cu^{2+} Ag^{+} and Hg^{2+} are 1.0×10^{-6} to 3.2×10^{-3}, 1.0×10^{-6} to 1.0×10^{-3} and 2.0×10^{-6} to 1.0×10^{-5} M, respectively.

The selectivity coefficients of the carbon paste electrode for various cations were determined by to the match potential method (MPM) [35] and the results are summarized in Table 2. From the data given in Table 2, it is obvious that the selectivity coefficients of the CPE toward cations other than Ag^{+}, Cu^{2+} and Hg^{2+} ions are very low. However, the selectivity of electrode toward Ag^{+}, Cu^{2+} and Hg^{2+} cations relative to each other is too high to allow their simultaneous determination in a given sample by simple titration or calibration procedures.

Table 2
Selectivity coefficients of the CPE for different cations

Cation	$\log K_{Cu,M}$	$\log K_{Ag,M}$	$\log K_{Hg,M}$
Na^{+}	−4.0	−4.0	−4.0
Al^{3+}	−2.2	−2.6	−4.4
Cu^{2+}	0.0	−2.9	−2.8
Zn^{2+}	−3.2	−4.0	−4.0
Pb^{2+}	−3.1	−4.0	−4.0
Co^{2+}	−4.0	−4.0	−4.0
Ca^{2+}	−4.0	−4.0	−4.0
Ni^{2+}	−3.0	−4.0	−4.0
Hg^{2+}	2.1	0.3	0.0
Cd^{2+}	−4.0	−4.0	−4.0
Ag^{+}	1.9	0.0	−0.9
$NH_4{}^{+}$	−2.6	−4.0	−4.0
La^{3+}	−4.0	−4.0	−4.0
Ce^{3+}	−4.0	−4.0	−4.0

3.2. *Titration curves*

Fig. 2 shows the potentiometric titration curves of 25.0 ml of individual cations (Ag^{+}, 0.010 M; Cu^{2+}, 0.010 M; and Hg^{2+} 0.005 M) with a 0.100 M potassium thiocyanate solution. As it is seen, in the case of Ag^{+} and Hg^{2+}, the potentials are decreased during titration with increasing amount of the thiocyanate solution, and possess well-defined inflection points at the end-point of titrations due to the precipitation of these cations in the presence of thiocyanate ion. As is obvious, at the end-point of titration, one and two moles of SCN^{-} are consumed per each mole of Ag^{+} and Hg^{2+} ions, respectively. On other hand, the potential of Cu^{2+} solution is increased when titrated with thiocyanate ion and begin to level off at a SCN^{-}/Cu^{2+} molar ratio of about 1 (i.e. 2.5 ml of titrant). This is most probably due to the formation of

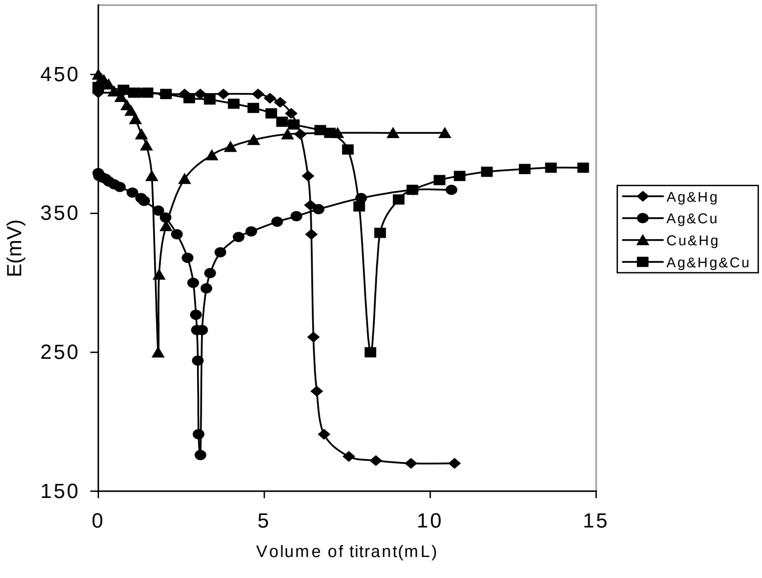

Fig. 3. Potentiometric titration curves for 50 ml of the binary and ternary mixtures of silver, copper and mercury with 0.1 M potassium thiocyanate titrant. Concentrations of the cations in different mixtures used are: (0.01 M Ag^{+} and 0.0016 M Hg^{2+}) (0.006 M Ag^{+} and 0.0006 M Cu^{2+}) (0.01 M Cu^{2+} and 0.0016 M Hg^{2+}) (0.014 M Ag^{+}, 0.001 M Hg^{2+} and 0.018 M Cu^{2+}).

the $CuSCN^+$ complex, the potential response of the CPE to which is expected to be higher than that to the Cu^{2+} ion. Obviously, since the titration curve obtained for Cu^{2+} does not show a distinct inflection point, the exact amount of copper ion cannot be determined quantitatively via titration with SCN^- using the CPE as an indicator electrode.

Fig. 3 shows the potentiometric titration curves of the binary and ternary mixtures of the cations used. As it is obvious, the titration curves of the cations in their mixtures are overlapped seriously. The titration curve obtained for the binary mixture of Ag^+–Hg^{2+} shows a single inflection point, which means that the simultaneous determination of these cations is not feasible. While, in the case of the binary mixtures of Ag^+–Cu^{2+} and Hg^{2+}–Cu^{2+} and the ternary mixture of Ag^+–Cu^{2+}–Hg^{2+}, a sharp minimum is observed in the resulting titration curves due to the end points of the titration of Ag^+, Hg^{2+} and the Ag^+–Hg^{2+} mixture, respectively. However, in all three cases, further addition of the titrant will result in an increased potential of the electrode due to the formation of $CuSCN^+$ species in solution.

Thus, based on the above observations, it is not possible to determine simultaneously the amount each cation in these mixtures. In spite of the fact that the unmodified CPE has many advantages and has already been used as a good indicator electrode for the determination of Ag^+ and Cu^{2+} cations separately [12,13], it cannot be used for the determination of these cations as well as Hg^{2+} in the presence of each other. Since the multivariate calibration methods are good choices for processing the potentiometric titration data [36], here, we tried an artificial neural network model to analyze the potentiometric titration data obtained for the binary and ternary mixtures of Ag^+, Cu^{2+} and Hg^{2+} cations.

3.3. ANN modeling

For each cation mixture used (i.e. Ag^+–Cu^{2+},Ag^+–Hg^{2+}, Cu^{2+}–Hg^{2+} and Ag^+–Cu^{2+}–Hg^{2+}), two sets of standard solutions were prepared. From the potential data of the calibration sets of the above mixtures, whose concentrations were selected randomly, the ANN model was optimized and the data of the prediction sets were used to evaluate the performance of the resulting ANN model. To obtain the best network performance, the optimal network architecture and parameters must be chosen. Studies on the network structure include the selection of the number of layers and the number of nodes in each layer.

We confined our network to three layers, because learning of a network with higher layers is very complex and is more time consuming. Since the high number of nodes in the input layer will increase the learning time, the potential data were subjected to principal component analysis before introducing to the network and, therefore, the input of the ANN model was the extracted principle components of the potential data matrix. Since the number of nodes in the hidden layer is dependent on the number of input nodes, the number of nodes in the input and hidden layers were optimized simultaneously [32]. The eigenvectors were entered step-by-step, and in each step the number of nodes in the hidden layer was varied to reach the maximum value of S.E.

The network parameters that should be optimized include the transfer functions in the layers, the momentum and the learning rate. The most versatile transfer function that can be used to model a variety of non-liner relationships is a sigmoid transfer function. In our network, it was found that the sigmoid transfer function in the hidden layer has a better performance than the other transfer functions (i.e. tangent, Gaussian and linear functions). The characteristics of the optimized networks used to modeling the titration data are summarized in the Table 3.

3.4. Prediction of cation concentrations in synthetic mixtures

In order to complete our investigation about the performance of the optimized model, the proposed ANN model was used to predict the concentration of silver, copper and mercury ions in some other mixtures that were not used in the training and validation sets and the results are given in Table 4. It is immediately obvious that the ANN model possesses a high ability to predict the concentration of the cations with low error levels. The prediction ability of a single component and total components in the mixtures were evaluated in terms of the percent relative error of the predicted concentrations, REP [34], root mean square error

Table 3
Different parameters of the optimized ANN model used

Parameter	Mixture								
	Ag^+–Cu^{2+}		Hg^{2+}–Cu^{2+}		Ag^+–Hg^{2+}		Ag^+–Cu^{2+}–Hg^{2+}		
	Ag^+	Cu^{2+}	Hg^{2+}	Cu^{2+}	Ag^+	Hg^{2+}	Ag^+	Cu^{2+}	Hg^{2+}
Input nodes	3	3	3	3	5	5	10	10	10
Hidden nodes	5	2	2	4	2	3	3	4	5
Output nodes	1	1	1	1	1	1	1	1	1
Learning rate	0.3	0.5	0.4	0.9	0.7	0.4	0.4	0.2	0.7
Momentum	0.4	0.7	0.6	0.89	0.6	0.83	0.66	0.5	0.2
Gain	1	1	1	1	1	1	1	1	1
Number of iteration	1500	7000	2000	500	10000	5000	1600	5000	3000

Table 4
Prediction results for determination of binary mixtures of cations using the optimized neural network models

Sample	Mixtures																												
	Ag^+–Cu^{2+}						Hg^{2+}–Cu^{2+}						Ag^+–Hg^{2+}						Ag^+–Cu^{2+}–Hg^{2+}								
	Ag^+ (mM)			Cu^{2+} (mM)			Hg^{2+} (mM)			Cu^{2+} (mM)			Ag^+ (mM)			Hg^{2+} (mM)			Ag^+ (mM			Cu^{2+} (mM)			Hg^{2+} (mM)		
	Actual	Found	A.E	Actual	Found	A.E	Actual	Found	A.E.	Actual	Found	A.E.	Actual	Found	A.E	Actual	Found	A.E	Actual	Found	A.E	Actual	Found	A.E	Actual	Found	A.E
1	4.0	3.70	−0.30	6.0	6.0	0.00	0.20	0.20	0.00	6.0	6.6	0.60	4.0	4.1	0.10	0.20	0.17	−0.03	12.0	12.1	0.10	1.0	1.0	0.00	1.60	1.50	−0.10
2	1.2	1.20	0.00	8.0	9.0	1.00	0.40	0.43	0.03	4.0	4.0	0.00	2.0	1.7	−0.30	0.08	0.07	−0.01	10.0	9.9	−0.10	2.0	1.8	−0.20	1.20	1.20	0.00
3	14.0	13.4	−0.60	12.0	11.8	−0.20	0.60	0.58	−0.02	1.4	1.5	0.10	6.0	5.8	−0.20	0.10	0.09	−0.01	16.0	15.6	−0.40	2.0	1.8	−0.20	0.60	0.62	0.02
4	0.6	0.56	−0.04	1.4	1.5	0.10	1.80	1.77	−0.03	12.0	11.8	−0.20	4.0	4.3	0.30	0.18	0.17	−0.01	8.0	8.9	0.90	6.0	5.9	−0.10	0.18	0.18	0.00
5	0.6	0.53	−0.07	1.2	1.3	0.10	0.42	0.45	0.03	0.6	0.5	−0.10	1.0	1.0	0.00	1.00	0.93	−0.07	6.0	5.7	−0.30	10.0	10.2	0.20	1.20	1.10	−0.10
6	2.0	1.80	−0.20	4.0	4.0	0.00	0.08	0.08	0.00	1.2	1.0	−0.20	1.6	1.7	0.10	0.60	0.61	0.01	2.0	1.0	−1.00	0.6	0.7	0.10	0.60	0.56	−0.04
7	0.4	0.45	0.05	8.0	7.4	−0.60	0.16	0.16	0.00	1.8	1.8	0.00	0.4	0.4	0.00	0.4	0.42	0.02	0.8	0.9	0.10	1.2	1.1	−0.10	1.20	1.10	−0.10
8	6.0	6.30	0.30	0.6	0.57	−0.03	0.05	0.06	0.01	10.0	9.4	−0.60	0.6	0..59	−0.01	0.06	0.05	−0.01	2.0	2.2	0.20	8.0	9.0	1.00	0.60	0.58	−0.02

(RMSE), and square of correlation coefficient (r^2) of the results. The low values of REP (in the range of 0.1–0.55%) and RMSE (in the range of 0.02–0.54 mM) indicated that the networks used can properly process the titration data and model the complex relationship between the concentration of cations in the mixture and the potential data at different volumes of titrant. The plot of the predicted concentrations of each cation in the binary and ternary mixtures versus their actual concentrations showed a nice fit of data to a straight line (with $r^2 > 0.990$). This confirms the excellent predictive ability of the networks used in this study.

4. Conclusions

A principle component ANN calibration model was proposed for the simultaneous determination of silver, copper and mercury ions, by a potentiometric titration method, using an unmodified CPE as an indicator electrode. This modeling could nicely process the non-linear relationship between the potential at a given volume of the titrant and predict the concentration of cations in unknown sample solutions. For all cations, low prediction errors and high correlation coefficients ($r > 0.990$) were obtained.

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