Spectrophotometric simultaneous determination of nickel, cobalt and copper by orthogonal signal correction–partial least squares

Masoud Rohani Moghadam [1,2], Ali Mohammad Haji Shabani [1], Shayessteh Dadfarnia [1,*], Jahanbakhsh Ghasemi[3]

[1] *Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran*
[2] *Present address: Department of Chemistry, Faculty of Science, Vali-e-Asr University, Rafsanjan, Iran*
[3] *Department of Chemistry, Faculty of Science, K. N. Toosi University of Technology, Tehran, Iran*
[*] *E-mail: sdadfarnia@yazduni.ac.ir*

A method for the simultaneous spectrophotometric determination of nickel, cobalt and copper based on the formation of their complexes with 2-(2-Thiazolylazo)-*p*-Cresol (TAC) in micellar media of Triton X-100 is proposed. The absorbance spectra were recorded in the range of 500 to 800 nm. The linear concentration range for nickel, cobalt and copper in solution calibration sets were 0.05–1.80, 0.10–6.41 and 0.10–6.54 µg/ml, respectively. The effects of experimental parameters such as pH, time, concentration of ligand and surfactant on the sensitivity of method were investigated. The data obtained from the experiments were processed by the partial least squares (PLS), orthogonal signal correction-partial least squares (OSC-PLS) and principle component-back propagation artificial neural network (PC-BPANN). A set of synthetic mixtures of nickel, cobalt and copper was evaluated and the results obtained by each chemometric approaches were compared with different testing methods. The OSC-PLS method was selected because afforded better results than the others. The method was satisfactorily applied for determination of nickel, cobalt and copper in alloy samples. The accuracy was determined using comparing the results to the reference values and also independent analysis by flame atomic absorption spectrometry.

Keywords: Multi element determination; Metal ions; 2-(2-Thiazolylazo)-*p*-Cresol; Chemometric method; Spectrophotometry

1. INTRODUCTION

Nickel, cobalt and copper are metals that appear together in many real samples. Several techniques such as X-ray fluorescence [1], near-infrared spectroscopy [2], high performance liquid chromatography [3] and atomic absorbtion spectrometry [4] have been proposed for the simultaneous determination of these metal ions in different media. However, simultaneous determination of these metals by UV-Vis spectrophotometry using conventional metallochromic reagents is difficult because, usually their absorbance spectra overlaps in a manner that the superimposed curves are not suitable for quantitative evaluation. In the past two decays it had been attempted to solve this problem by employing chemometrics methods for the multicomponent analysis of mixture. Several works have been reported for simultaneous spectrophotometric determination of Co^{2+}, Ni^{2+} and Cu^{2+} using various chemometric methods [5-13].

The known chemometric techniques of partial least squares (PLS) and artificial neural networks (ANNs) have the ability to relate the input and output variables without the need for having any pre-knowledge on the system [14]. PLS modeling is one of the powerful multivariate techniques in

which the building of regression models is based on the latent variable decomposition that takes into account the information of responses and concentrations simultaneously [15]. Its basic concept was originally described by Wold et al.[16].

In addition, pre-processing methods can be applied for the enhancement of the relevant information and simpler and easier interpretation of the resulting model. Wold et al. introduced orthogonal signal correction (OSC) as a useful pre-processing step that improves the calibration model by filtering strong structured (i.e. systematic) variation in the **X** values that is not correlated to the **Y** values [16]. Several groups [18-22] have published various OSC algorithms in order to reduce the model complexity by removing orthogonal components from the signal.

Artificial neural networks (ANNs) are based on artificial intelligence and are powerful non-parametric non-linear modeling techniques. The back propagation neural networks (BPNNs) as common ANNs are most often used in analytical applications. This technique receives a set of inputs which is multiplied by each weight and then a non-linear transfer function is applied. The goal of network training is to change the weights between the layers in order to minimize the output errors. The changes in the values of the weights can be obtained using the weight update function, which shows how weights are changed during the learning process. One of the weight update function used in basic back propagation algorithm (BP) is Levenberge Marquardt (LeM) algorithm in which the update function is calculated by the Jacobian matrix containing first derivatives of the network errors with respect to the weights [23].

2-(2-Thiazolylazo)-p-Cresol (TAC) is a chromogentic reagent, belongs to the thiazole azo families. TAC is a water insoluble heterocyclic azo dye which was introduced in 1959 by Kanenina and coworkers [24]. TAC has been used for spectrophotometric determination of some metal ions including vanadium [25], titanium [26], nickel [27], lead [28], indium [29] and uranium [24]. However insoluble ligands and their complexes can be solubilized in the micellar media which eliminate the extraction step and the need for use of toxic organic solvent [30].

In this study the simultaneous spectrophotometric determination of Ni^{2+}, Co^{2+} and Cu^{2+} based on the formation of their complexes with TAC in micellar media of Triton X-100, with the aid of chemometric approaches of PLS, OSC-PLS and PC-FFANN is described. The performance of these calibration models are examined using prediction sets constructed from synthetic solution mixtures. The method was finally applied to determination of Ni^{2+}, Co^{2+} and Cu^{2+} in real samples.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals used were analytical reagent grade (Merck, Darmstadt, Germany) and doubly distilled deionized water was used throughout the work. Stock solutions of Ni^{2+}, Co^{2+} and Cu^{2+} (1000 µg/ml) were prepared by dissolving appropriate amount of their commercial salts (nitrate or sulphate) in 100 ml volumetric flask and diluting to the mark with distilled water. Working standards were made by appropriate dilution daily as required. A 3×10^{-3} mol/l TAC solution was prepared by dissolving 0.1356 g of 2-(2-Thiazolylazo)-p-Cresol powder (97%) in 200 ml of ethanol. A 5% (v/v) Triton X-100 solution was prepared by dissolving 5 ml of this surfactant in 100 ml distilled water. A phosphate buffer solution of pH 7.0 was prepared by mixing KH_2PO_4 (0.04 mol/l) and Na_2HPO_4 (0.04 mol/l) in an appropriate ratio and adjusting the pH to 7.0 by addition of dilute HCl or NaOH solution.

2.2. Apparatus and software

Visible absorbance spectra were recorded on a JENWAY 6505 UV–Vis spectrometer using 5-cm quartz cell. Measurements of pH were made with a JENWAY 3510 pH-meter using a combined glass electrode. The data manipulation have done using MATLAB software, version 7.0 (The

Mathworks). OSC and PLS calculus were carried out using "PLS-Toolbox" (Eigenvector Company, Version 2.1). The artificial neural networks calculations were performed using net–Toolbox of MATLAB 7.0.

2.3. Procedures

Appropriate volumes of Ni^{2+}, Co^{2+} and Cu^{2+} solutions, 1 ml of Triton X-100 (5%(v/v)), 1 ml of buffer solution (pH=7.0) and 1 ml of TAC solution (0.003 mol/l) were added to 10 ml volumetric flask. The flask was made up to the mark with distilled water and allowed to stand for 5 min. A portion of the solution was transferred into a 5 cm quartz cell, and the absorption spectra were recorded on spectrophotometer against a blank solution in the wavelength range of 500–800 nm with 1 nm intervals. The concentration of nickel, cobalt and copper ions in the solutions must be between 0 - 1.80, 0 - 6.41 and 0 - 6.59 µg/ml, respectively.

3. RESULTS AND DISCUSSION

In the preliminary experiments it was observed that in alkaline conditions nickel, cobalt and copper ions form colored complexes with TAC that their absorbance spectra strongly overlap to each others. However, this problem may be solved by chemometric methods. But, in order to obtain optimum conditions, initially the parameters affecting the formation of each complexes were optimized. Then at optimum conditions, different chemometric methods were tested and finally, selected method was applied for simultaneous determination of nickel, cobalt and copper ions in alloy samples.

3.1. Optimization of experimental factors

The pH of the solution, the concentration of TAC, the concentration of surfactant and the time of the reactions are the major factors that must be investigated in order to improve the sensitivity of method. So, the effect of these parameters on development of the colored complexes were carefully studied and optimized, individually. Spectrum pattern of each component was varied in different pH values. For the other parameters, spectrum pattern was not changed and only variation in absorbance signal was observed at different values of these parameters. So for optimization of these variables, intensity of absorbance signal at λ_{max} of each complex were investigated.

3.2. Effect of pH

The complex formation of metal ions with TAC and their spectrum pattern strongly depends on pH of the solution. Spectrums of TAC, Ni-TAC, Co-TAC and Cu-TAC complexes were studied at various pH values in the range of 1.5-8.5. Figure1 shows these spectrums in some of investigated pH values. As it is demonstrated, in acidic conditions Ni-TAC and Co-TAC complexes probably wasn't constructed. In alkalic conditions, although each of metal ions complexed with TAC and shown different spectrum pattern, but the absorbance signal of TAC increased in the wavelengths range of 500-800 nm. In pH values near to 7, TAC did not have significant absorbance in the interested wavelengths range. Thus in order to have maximum sensitivity, the optimum pH value of 7.0 was selected for further studies.

3.3. Effect of reagent concentration

The effect of TAC concentration over the range of 3×10^{-5} to 6×10^{-4} mol/l on the determination of Ni^{2+}, Co^{2+} and Cu^{2+} ions at pH of 7.0 was studied individually. It was found, that the absorbance of the complexes were increased with an increase in TAC concentration up to 3×10^{-4} mol/l and kept

constant with further increase in TAC concentration. Hence, the concentration of 3×10^{-4} mol/l of TAC was chosen for further investigations.
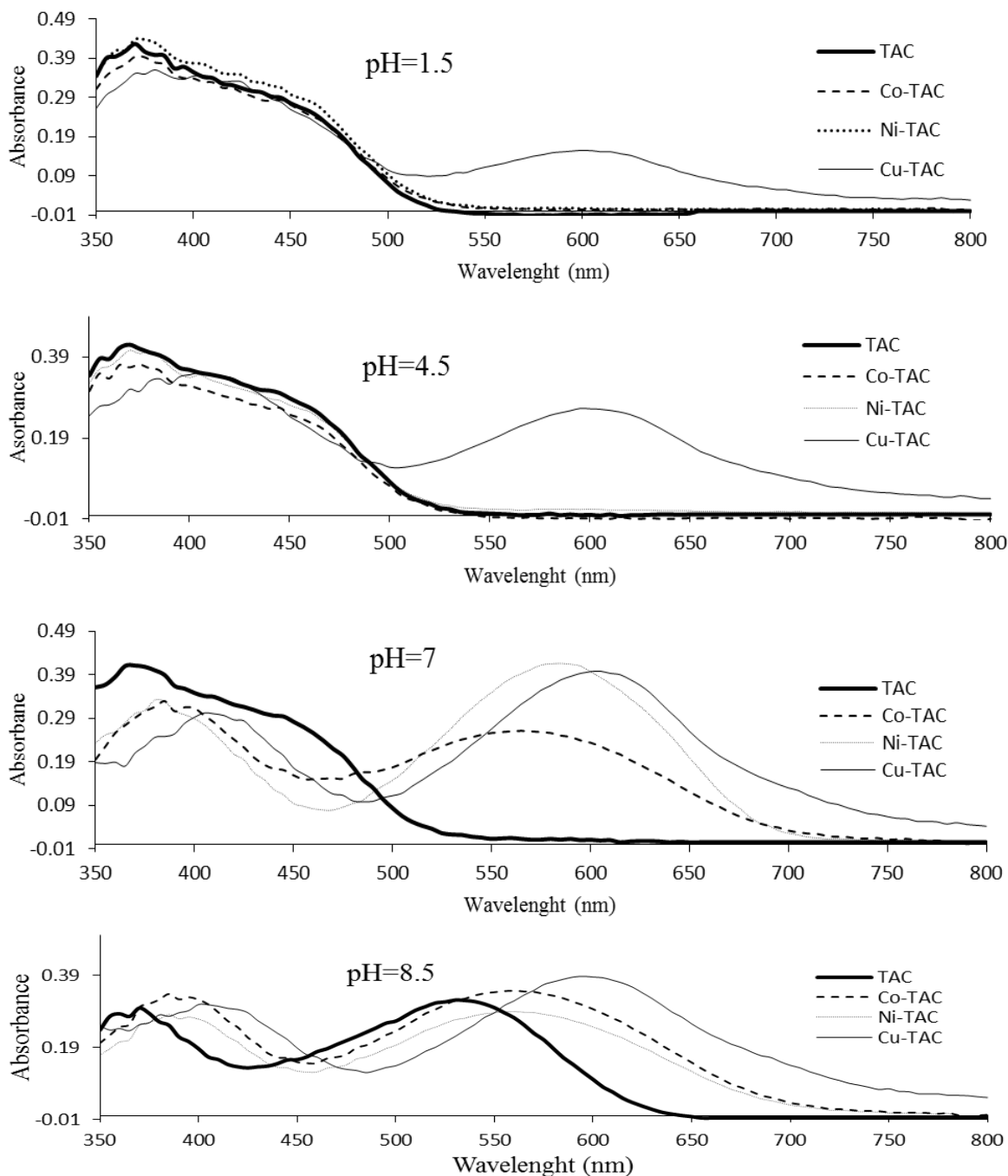

Fig. 1. Effect of pH on the absorbtion of complexes of cobalt, copper and nickel with TAC. The concentration of Triton X-100, TAC, Ni^{2+}, Co^{2+} and Cu^{2+} are 2%(v/v), 0.063 µg/ml, 0.45, 1.08 and 1.60 µg/ml respectively.

3.4. Effect of surfactant concentration

Micellar media play an important role for dissolving insoluble TAC complexes. The effect of Triton X-100 as micellizing agent was investigated in the concentration range of 0.05-5% (v/v).

According to obtained results the absorbance increased up to 0.1% of Triton X-100, leveled off between 0.2 and 3%, and then slightly decreased with further increase in Triton X-100 concentration. Therefore, a concentration of 0.5% (v/v) of Triton X-100 was selected as optimum for subsequent studies.

3.5. Time effect

In order to have a good sensitivity, it is necessary to select a time that guarantees complex formation between the TAC and metal ions. The effect of time on absorbtion of complex was investigated at different time intervals. The results indicated that the complexes of Co^{2+} and Cu^{2+} were immediately completed, but for Ni^{2+} ion, complex formation was completed after 5 min. Therefore, measuring of absorbance was performed at 5 min after mixing of the reagents. Moreover absorbance of the formed complexes was constant for several hours.

3.6. Chemometric methods

3.6.1. Determination of dynamic ranges

In order to construct a set of calibration samples for multivariate chemometric methods, it is necessary to indicate the linear range of each component. So a set of sample solutions with different metal ions concentrations were prepared and measurements were carried out under the optimum conditions and at λ_{max} of each complex. The linear dynamic ranges were 0.05–1.80 µg/ml, 0.1–6.41 µg/ml, and 0.1–6.54 µg/ml for Ni^{2+}, Co^{2+} and Cu^{2+}, respectively. The limits of detection (LOD) defined as the ratios of the three times of the standard deviations of the blank signals over the slope of the calibration curves. The characteristics of calibration graphs are summarized in Table 1.

Table1. Characteristics of calibration graph for the determination of nickel, cobalt and copper.

Parameter	Ni^{2+}	Co^{2+}	Cu^{2+}
Linear Range (µg/ml)	0.05-1.80	0.10-6.41	0.10-6.54
Slope (µg/ml)$^{-1}$	0.875	0.238	0.244
Intercept	0.012	0.0034	0.011
r	0.9998	0.9990	0.9997
LOD(µg/ml)	0.006	0.011	0.009

3.6.2. Multivariate calibration

In order to extract maximum quantitative information from the minimum experimental trials, the mixture design for three component mixtures was applied for the construction of the set of calibration samples. For construction of the model, according to mixture design, 22 calibration samples were designed in 6 levels. The concentration levels for the analytes were as follow: nickel(0, 0.05, 0.60, 1.00, 1.40, 1.80 µg/ml); cobalt(0.0, 0.10, 1.92, 3.20, 5.13, 6.41 µg/ml); and copper(0.0, 0.1, 1.98, 3.30, 5.26, 6.54 µg/ml).

3.6.3. Selection of the best chemometric method

Using the 22 calibration samples, different chemometric methods include PLS, OSC-PLS and PC-FFANN (containing 4, 4 and 14 trials for validation, test and training sets, respectively) were

constructed using in order to obtain a suitable calibration model. The optimum values for characteristics of these models are presented in Table 2. Seven synthetic mixtures of the three analyte compounds were analyzed by chemometric methods to validate and compare the different chemometric models. Square of correlation coefficient (R^2), percent of relative prediction error (%RPE$_S$) for individual compounds (according to Eqs.1) and (%RPE$_T$) for all compounds (according to Eqs.2) as important parameters were determined to evaluate the prediction performance of various chemometric methods.

$$\%RPE_S = 100 \times \left[\frac{\sum_{i=1}^{n}\left(C_{i(estimated)}-C_{i(added)}\right)^2}{\sum_{i=1}^{n}\left(C_{i(added)}\right)^2} \right]^{1/2} \quad (1)$$

$$\%RPE_T = 100 \times \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{m}\left(C_{ij(estimated)}-C_{ij(added)}\right)^2}{\sum_{i=1}^{n}\sum_{j=1}^{m}\left(C_{ij(added)}\right)^2} \right]^{1/2} \quad (2)$$

In these equations $C_{ij(added)}$ indicates the actual concentration of j_{th} component in i_{th} mixtures in the verification data set, $C_{ij(estimated)}$ is its estimation by the calibration models, and n is the number of samples. The calculated parameters are given in Table 3. As it is demonstrated the OSC-PLS with better values of investigated parameters gives the best results comparing to the others.

For further validation a randomization t-test [31] for testing the equality of performance of the prediction methods was used on the synthetic mixtures. So initially the mean squared error of prediction (MSEP) were determined according to Eq. 3.

$$MSEP = (1/n) \sum_{i=1}^{n}\left(C_{i(estimated)} - C_{i(added)}\right)^2 \quad (3)$$

After calculation of MSEP, the randomization t-test applied between models. If at given confidence limit the difference between two models was significant, it will be confirmed that the chosen model is really better than the other and the difference isn't by chance. According to Table 4, the MSEP values of OSC-PLS were lower than the other two chemometric models. Furthermore, the results of randomization test at 95% confidence limit (p=0.05) shown that the difference between OSC-PLS/PCFFANN for all three ions, and OSC-PLS/PLS for Ni^{2+} and Co^{2+} was significant. In the case of Cu^{2+} although the MSEP values of OSC-PLS is better than PLS but randomization test shown that this was by chance. However overall the results it could be confirmed that OSC-PLS is the best chemometric model.

Table 2. Characteristics of different chemometric methods.

Model	Parameter	Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$
PLS	Number of latent variables	6	4	2
OSC-PLS	Number of components for OSC	2	1	3
	Number of latent variables for PLS	3	1	2
PC-FFANN	Number of layers	3	3	3
	Input nodes (number of PCs)	5	4	4
	Hidden nodes	1	1	2
	Output nodes	1	1	1
	Update weight function algorithm	LeM[a]	LeM[a]	LeM[a]
	Hidden layer transfer function	Logsig	Logsig	Tansig
	Output layer transfer function	purelin	purelin	Purelin
	Number of epochs	15	52	20

[a.] Levenberge Marquard

Table 3. Comparison of Correlation coefficient (R^2) and percent of relative prediction error (%RPE) values for different chemometric models.

Method	Nickel		Cobalt		Copper		Total RSE$_T$%
	RPE$_S$%	R^2 Recovery	RPE$_S$%	R^2 Recovery	RPE$_S$%	R^2 Recovery	
PLS	16.00	0.9643	12.73	0.9648	3.48	0.9994	10.65
OSC-PLS	3.31	0.9987	2.67	0.9987	1.13	0.9999	2.29
PC-FFANN	13.34	0.9848	14.99	0.9731	12.64	0.9804	14.11

Table 4. Randomization t-test for comparison of different chemometric models.

Ions	MSEP			Significance values for comparison of models		
	PLS	OSC-PLS	PC-FFANN	OSC-PLS/PC-FFANN	OSC-PLS/PLS	PLS/PC-FFANN
Ni^{2+}	0.0167	0.0007	0.0116	0.010	0.010	0.145
Co^{2+}	0.1200	0.0053	0.1664	0.045	0.045	0.070
Cu^{2+}	0.0054	0.0006	0.0713	0.005	0.115	0.570

All tests were two-sided. Randomization t-test: 199 trials.

3.7. Interferences

The effects of foreign ions on the simultaneous determination of investigated ions were studied by measuring the absorbance of the solutions containing 1.0, 2.0 and 2.0 µg/ml of Ni^{2+}, Co^{2+} and Cu^{2+}, respectively and in presence of various amounts of interferences. The tolerance limit was taken as the amount of added foreign ion causing a relative error of less than ±5% in the determination of Ni^{2+}, Co^{2+} and Cu^{2+}. Table 5 summarizes the maximum tolerances of the investigated cations and anions.

Table 5. Effect of foreign ions on the simultaneous determination of nickel, cobalt and copper. The concentration of Ni^{2+}, Co^{2+} and Cu^{2+} are 1.00, 2.00 and 2.00 µg/ml respectively.

Foreign ion	Tolerance limit (µg/ml)
Na^+, K^+, Ca^{2+}, Mg^{2+}	1000[a]
PO_4^{3-}, SO_4^{2-}, Cl^-, NO_3^-, SiO_3^-	1000[a]
Cr^{6+}, Sn^{2+}	800
Fe^{2+}, Mn^{2+}	600
Cr^{3+}	400
Zn^{2+}	30

[a.] Maximum concentration limit tested

3.8. Comparison with other mtehods

A comparison of the proposed method and some of the published methods for simoultaneous determination of Ni^{2+}, Co^{2+} and Cu^{2+} are summarized in Table 6. It clearly shows that the proposed method has good dynamic ranges and LODs. Also, the duration time of this method is shorter than those reported by other methods [7-13].

Table 6. Comparison of the proposed method with the reported chemometric methods for simultaneous determination of nickel, cobalt and copper.

Method	Dynamic range (µg/ml)			Time	LOD (µg/ml)			Ref.
	Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$	(min)	Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$	
ANNs	0.5-8	1-10	1-10	60	0.123	0.098	0.108	[11]
PLS	0.5-5.5	0.4-2.6	0.6-3.4	-	-	-	-	[8]
PLS	Up to 4.6	Up to 3.0	Up to 2.6	-	-	-	-	[12]
PLS	Up to 3.5	Up to 3.0	Up to 1.5	8	0.021	0.072	0.063	[7]
OSC-PLS	0.05-0.5	0.05-10.0	0.05-4.0	30	0.03	0.04	0.04	[9]
PLS	0.35-5.87	0.35-5.89	0.38-6.35	-	-	-	-	[13]
OCS-PLS	0.05-0.80	0.05-1.05	0.05-1.30	-	-	-	-	[10]
OSC-PLS	0.05-1.80	0.10-6.41	0.10-6.54	5	0.006	0.011	0.009	This work

3.8. Applications

This method was applied to some alloy samples. About 0.1 g of each of alloy was taken in a beaker and 10–15 ml of conc. HCl and 5ml of conc. HNO_3 were added to it. The contents were heated on a hotplate to dissolution, and the final volume was reduced to about 5ml. The solution was filtered through a Millipore 0.45 μm pore-size membrane and the total volume of solution was made up to 500 ml by adding distilled water. An appropriate aliquot of the solution was analyzed. Results are shown in Table 7.

As it is demonstrated, at 95% confidence limit there was no significant difference between the results of developed method and FAAS. The results also shown that the amount of the metal ions in reference alloys obtained by the proposed method are in good agreement with the accepted values. Thus, the results proved that the proposed method is suitable for the simultaneous determination of Ni^{2+}, Co^{2+} and Cu^{2+} in matrix types examined.

Table 7. Simultaneous determination of Ni^{2+}, Co^{2+} and Cu^{2+} in alloy samples.

Alloy sample	Composition	Present(µg/ml)			Found(µg/ml), Mean± SD [a]			FAAS(µg/ml), Mean± SD [a]		
		Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$	Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$	Ni $^{2+}$	Co $^{2+}$	Cu $^{2+}$
Haynes 25	Co=50% Ni =10% Mn=2% Fe=3% Cr=20% W=15%	0.60	3.00	-	0.62 ± 0.02	3.18± 0.02	-	0.61 ± 0.01	3.21± 0.01	-
Monel400	Ni=65% Cu=30% Si=0.3% Fe=2.5% S=0.1% C=0.1% Mn=2%	1.30	-	0.60	1.29± 0.01	-	0.62± 0.02	1.27± 0.01	-	0.61± 0.01
Lemaiguand	Ni=7% Co=8% Cu=39% Sn=9% Zn=7% Fe=30%	0.70	0.80	3.90	0.72± 0.02	0.79± 0.02	3.79± 0.02	0.70± 0.01	0.78± 0.01	3.95± 0.01

[a]. Mean values ± standard deviation (n=4)

4. CONCLUSION

Simultaneous chemometrics determination of Ni^{2+}, Co^{2+} and Cu^{2+} was directly performed by spectrophotometric measurements using 2-(2-Thiazolylazo)-p-Cresol (TAC), as a chromogenic reagent, in micellar media. Different calibration models were constructed using PLS, OSC-PLS and PC-BPANN. It was shown that OSC-PLS is the best performing chemometrics method for this purpose. The results also confirmed that the selected model can be directly applied to simultaneous determination of nickel, cobalt and copper in alloys samples. Furthermore, the method offer simple and fast procedures with good accuracy and precision without any separation step or sophisticated instrument.

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