



## Simultaneous spectrophotometric determination of Zinc and Copper with 4-(2-thiazolylazo) resorcinol using parallel factor analysis (PARAFAC), partial least squares (PLS) and orthogonal signal correction- partial least squares (OSC-PLS).

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Received: 01.02.2015; Accepted: 05.05.2015

**Abstract.** An Ultraviolet Spectrophotometry method utilizing 4-(2-thiazolylazo)resorcinol (TAR) was developed to simultaneous determination of Zn(II) and Cu(II) using parallel factor analysis (PARAFAC) and partial least squares (PLS) and orthogonal signal correction- partial least squares (OSC-PLS). TAR was chosen as the visible absorbing chelating ligand because of its ability to form stable complexes with a wide variety of metals. The work was carried out in pH range from 5.0 to 10.0 and wavelength range was from 200 to 500 nm. Multivariate calibration models using PLS, OSC-PLS and PARAFAC at different pH were elaborated for ultraviolet spectra deconvolution and metals quantitation. The calibration set was constructed with standard solutions in a concentration range of 2.0-20.0 ppm. The best model for the system were obtained with PARAFAC at pH=8 and. The capabilities of the method for the analysis of real samples were evaluated by determination of Zn(II) and Cu(II) in waste water. The accuracy of method, evaluated through the root mean square error of prediction (RMSEP), were 0.021 and 0.017 for Zn and Cu, respectively. This procedure allows the simultaneous determination of Cu(II) and Zn(II) with TAR in synthetic and real samples and good reliability of determination was proved.

**Keywords:** TAR, PARAFAC, PLS, OSC-PLS, simultaneous determination.

### 1. INTRODUCTION

The Cu (II) complexes with high numbers of ligands have been used as the basis for the development of spectrophotometric methods. However, Zn is a metallic ion that has not been widely studied; the information on zinc concentration in environmental samples is limited, primarily owing to the difficulties in measuring its levels [1]. Copper and Zinc are metals which appear together in many real samples. Several techniques such as solid phase extraction coupled with chromatography [2], atomic absorption spectrophotometry [3, 4] and inductively coupled plasma mass spectrometry [5, 6], have been used for the simultaneous determination of these ions in different samples and spectrophotometry. One of the main drawbacks of the application of spectrophotometric methods in the simultaneous determination of these cations is the high degree of spectral overlapping of these constituents. Nowadays combination of chemometrics methods with the computer-controlled instruments to monitor the molecular absorption spectra creates a powerful method in multicomponent analysis. Thiazolylazoreagents, like 4-(2-thiazolylazo) resorcinol (TAR) are popular as metal complexing ligands in spectrophotometry, high performance liquid chromatography (HPLC) [7,8] and capillary electrophoresis (CE) [9,10] due to the advantages that they can form highly sensitive metal complexes, and are very easily synthesized and purified. Complexation with 4-(2-thiazolylazo)resorcinol (HL) through the resorcinol OH, azo N and thiazolylazo N produces colored chelates with transition metalions.

In this paper, we report the investigation and development of rapid analytical methodology for the simultaneous prediction of two cations. The method is based on spectrophotometry, and the resulting heavily overlapping responses are processed by chemometrics. The application of

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chemometrics allows the interpretation of multivariate and is vital to the success of the simultaneous determination of the cations. Conversely, the continuing research, development and verification of such novel methods as described here, continue to emphasize the significant potential of chemometrics in practical, modern chemical and multicomponent analysis. The advantage of multicomponent analysis using multivariate calibration is the speed in the determination of components in a mixture, avoiding preliminary separation step.

Parallel factor analysis (PARAFAC), is a multi-way method originating from psychometrics [11]. It is gaining more and more interest in chemometric and associated areas for many reason: simply increased awareness of the method and its possibilities, the increased complexity of the data dealt with in science and industry, and increased computational power. PARAFAC, one of several decomposition methods for N-way data, is a generalization of principal component analysis (PCA) to higher orders. A PARAFAC model of a three-way array is given by three loading matrices, A, B and C, with elements  $a_{if}$ ,  $b_{jf}$  and  $c_{kf}$  (Eq. (1)), respectively ( $f=1-F$  principal components). The tri-linear model is found to minimize the sum of squares of the residues,  $e_{ijk}$  in the model[12], which is represented as follows:

$$X_{ijk} = \sum a_{if} b_{jf} c_{kf} + e_{ijk} \quad (1)$$

where  $a_f$ ,  $b_f$  and  $c_f$  are the  $f$ th columns of the loading matrices A, B and C, respectively. An important difference between the two-way PCA and multi-way PARAFAC is that the PARAFAC model is not nested. This fact means that the parameters of an  $F+1$  component model are not equal to the parameters of an  $F$  component model plus one additional component. The reason for this is that the components are not required to be orthogonal, hence independent. Therefore, every model has to be calculated specifically with all its components. Application of PARAFAC in spectrophotometry has been discussed by several reports[13-18].

The basic principle of the multivariate calibration is the simultaneous utilization of many independent variables,  $x_1, x_2, \dots, x_n$ , to quantify one or more dependent variables of interest,  $y$ . The partial least squares (PLS) regression analysis [19,20] is the most widely used method for this purpose, and it is based on the latent variable decomposition relating two blocks of variables, matrices X and Y, which may contain spectral and concentration data, respectively. These matrices can be simultaneously decomposed into a sum of  $f$  latent variables, as follows:

$$X = TP^T + E = \sum t_f p_f' + E \quad (2)$$

$$Y = UQ^T + F = \sum u_f q_f' + F \quad (3)$$

in which T and U are the score matrices for X and Y, respectively; P and Q are the loadings matrices for X and Y, respectively, E and F are the residual matrices. The two matrices are correlated by the scores T and U, for each latent variable, as follows:

$$u_f = b_f t_f \quad (4)$$

in which  $b_f$  is the regression coefficient for the  $f$  latent variable. The matrix Y can be calculated from  $u_f$ , as Eq. (5), and the concentration of the new samples can be estimated from the new scores, which are substituted in Eq. (5), leading to Eq. (6)

$$Y = TBQ^T + F \quad (5)$$

$$Y_{new} = T^* BQ^T \quad (6)$$

In this procedure, it is necessary to find the best number of latent variables, which normally is performed by using cross-validation, based on determination of minimum prediction error. Application of PLS in spectrophotometry has been reported by several papers [21-26].

Orthogonal signal correction (OSC) was introduced by Wold et al.[27] to remove systematic variation from the response matrix X that is unrelated, or orthogonal, to the property matrix Y. Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups [28-34] have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal components from the signal. Recently, application of orthogonal signal correction in

UV-Vis spectrophotometry for simultaneous determination by partial least squares has been reported [35-36]. In this study 4-(2-thiazolylazo) resorcinol (TAR) was applied to simultaneous determination of Zn(II) and Cu(II) using parallel factor analysis (PARAFAC) and partial least squares (PLS) and orthogonal signal correction- partial least squares (OSC-PLS).

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be used.

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_{pred} - y_{obs})^2}{n}} \quad (7)$$

$$RSEP(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^n (y_{pred} - y_{obs})^2}{\sum_{i=1}^n (y_{obs})^2}} \quad (8)$$

Where  $y_{pred}$  is the predicted concentration in the sample,  $y_{obs}$  is the observed value of the concentration in the sample and  $n$  is the number of samples in the validation set.

## 2. EXPERIMENTAL

### 2.1. Materials and measurements

All chemicals used were of the analytical reagent grade. Metal salts were of Acros and Merck. 4-(2-Thiazolylazo)resorcinol, obtained from Fluka.

A Hewlett-Packard 8453 diode array spectrophotometer controlled by a Hewlett-Packard computer and equipped with a 1-cm path length quartz cell was used for UV-vis spectra acquisition. A Metrohm 692 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 2.0 and 11.0.

The data were treated in an AMD 2000 XP (256 Mb RAM) microcomputer using MATLAB software, version 6.5 (The MathWorks). PARAFAC, OSC and PLS calculations were carried out in the 'PLS Toolbox', version 2.0 (Eigenvector Technologies)

### 2.2.Procedure

Three milliliter of buffer solution, 1 mL of stock TAN solution and appropriate volume of Cu and Zn were added to a 10-mL volumetric flask and made up to the mark with distilled water (final pH 8). The real samples in this study were collected in wastewater and, copper and Zinc were added to these solutions. A mixture design was used to maximize statistically the

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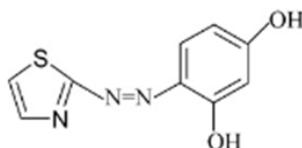
information content in the spectra. The calibration set was constructed with standard solutions in a concentration range of 2.0-20.0 ppm. A training set of 25 samples was taken (Table 1). The concentrations of cobalt, copper and nickel were between 2.0-20.0  $\mu\text{g}/\text{mL}$ . The absorption spectra were recorded between 200 and 700 nm against a blank. The spectral region between 300 and 500 nm, which implies working with 200 experimental points per spectra (as the spectra are digitized each 1.0 nm), was selected for analysis, because this is the zone with the maximum spectral information from the mixture components of interest.

### 3.RESULTS AND DISCUSSION

4-(2-Thiazolylazo)resorcinol, HL (Fig. 1), considered to be a tridentate ligand with the thiazole nitrogen, azo nitrogen and the ortho hydroxyl oxygen as coordination sites, usually forms 1:2, metal: ligand, chelates(Fig.2). All the complexes are colored, in soluble in water.

**Table 1.** Concentration data of the different mixtures used in the calibration set ( $\mu\text{g}/\text{mL}$ ).

Mixture	Cu	Zn
1	0.1	0.1
2	0.1	0.5
3	0.1	1
4	0.1	1.5
5	0.1	2
6	0.5	0.1
7	0.5	0.5
8	0.5	1
9	0.5	1.5
10	0.5	2
11	1	0.1
12	1	0.5
13	1	1
14	1	1.5
15	1	2
16	1.5	0.1
17	1.5	0.5
18	1.5	1
19	1.5	1.5
20	1.5	2
21	2	0.1
22	2	0.5
23	2	1
24	2	1.5
25	2	2



**Figure 1.** 4-(2-Thiaolylazo) resorcinol, HL (TAR)

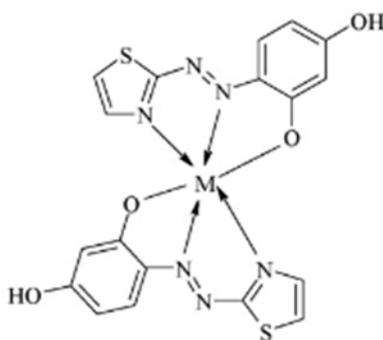


Figure 2. Suggested Structural Formulae Of Metal Complexes.

### 3.1. Spectrophotometric measurements

Fig. 3 shows the absorption spectra for the individual metal complexes at pH 8.0. With the aim of investigation the possibility of determination of copper and Zn in mixtures, the optimum working conditions were studied under the conditions previously established for each metal ion.

A universal buffer solution of pH 8.0 was selected. In order to select the optimum pH value at which the minimum overlap occurs, influences of the pH of the medium on the absorption spectra of metal complexes were studied over the pH range 2.0–10.0.

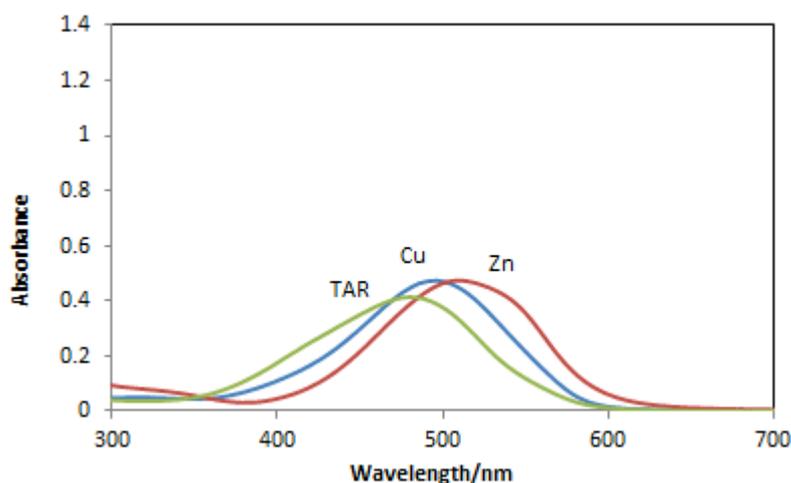


Figure 3. Absorption spectra of 1 µg/ mL of Cu and 1 µg/ mL of Zn with 100 µg/mL of TAR at pH 8.0.

### 3.2. Optimization of experimental condition

For finding the optimum conditions, the influence of pH values on the spectrum of each complex at a constant concentration of each ion was studied. The formed complexes with Cu and Zn were affected differently with pH. In order to select the optimum pH value at which the minimum overlap occurs, influences of the pH of the medium on the absorption spectra of Cu and Zn complexes were studied over the pH range 1.0-10.0 . However pH 8.0 was chosen as the optimum pH for this work because both complexes have maximum absorbance and minimum overlap at this pH.

### 3.3. Calibration and prediction data sets

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The multivariate calibration is a powerful tool for determinations, because it extracts more information from the data and allows building more robust models. According to 25 experimental design (Table 1) solutions were used to construct the models (calibration set) and another 6 solutions to validate them (prediction set) in that these were not included in the calibration set but were employed for independent tests (see Table 2).

**Table 2a.** Added and determined results of synthetic mixtures of copper and zinc using PLS model ( $\mu\text{g/ mL}$ ).

Sample	Added		Found		Error %	
	Cu	Zn	Cu	Zn	Cu	Zn
M1	0.30	0.70	0.27	0.73	-10.00	4.20
M2	0.60	0.40	0.65	0.38	8.30	-5.00
M3	1.20	1.10	1.17	1.16	-2.50	5.40
M4	0.90	1.30	0.94	1.32	4.40	1.50
M5	0.60	1.20	0.58	1.23	-3.30	2.50
M6	1.70	0.80	1.75	0.84	2.90	5.00
NF			6	9		
RMSEC			0.078	0.054		
RMSEP			0.015	0.015		
RSEP(%)			1.555	3.839		

**Table 2b.** Added and determined results of synthetic mixtures of copper and zinc using OSC-PLS model ( $\mu\text{g/ mL}$ ).

Sample	Added		Founded		Error %	
	Cu	Zn	Cu	Zn	Cu	Zn
M1	0.30	0.7	0.29	0.73	-3.30	4.20
M2	0.60	0.4	0.64	0.39	6.60	-2.50
M3	1.20	1.1	1.18	1.13	-1.30	2.70
M4	0.90	1.3	0.93	1.31	3.30	0.76
M5	0.60	1.20	0.59	1.21	-1.60	0.83
M6	1.70	0.80	1.73	0.82	1.70	2.50
NF			4	4		
RMSEC			0.0641	0.0271		
RMSEP			0.025	0.020		
RSEP(%)			2.592	2.107		

**Table 2c.** Added and determined results of synthetic mixtures of cooper and zinc using OSC-PLS model ( $\mu\text{g/ mL}$ ).

Sample	Added		Founded		Error %	
	Cu	Zn	Cu	Zn	Cu	Zn
M1	0.30	0.70	0.29	0.72	-3.30	2.80
M2	0.60	0.40	0.62	0.38	3.30	-5.00
M3	1.20	1.10	1.17	1.14	-2.50	3.60
M4	0.90	1.30	0.91	1.32	1.10	1.50
M5	0.60	1.20	0.59	1.20	-1.60	0
M6	1.70	0.80	1.72	0.81	1.10	1.20
NF			2	2		
RMSEC			0	0		
RMSEP			0.017	0.021		
RSEP(%)			1.833	2.592		

The optimum number of factors (NF) to be included in the calibration model was determined by computing the prediction error sum of squares (PRESS) for cross-validated models using a high number of factors. The optimum number of factors obtained by PLS, OSC-PLS and PARAFAC models and PRESS values are summarized in Table 2.

### 3.4. Determination of uranium and thorium in real matrix samples

In order to test the applicability and matrix interferences of the proposed method to the analysis of real samples, the method was applied in a variety of situations. For this purpose, spiked samples were analyzed. The best model for the system were obtained with PARAFAC at pH=8.

**Table 3.** OSC-PLS and PARAFAC results applied on the real matrix samples ( $\mu\text{g/ mL}$ ).

Added		oundedF			
		SCO -SLP		PARAFAC	
Cu	Zn	Cu	Zn	uC	Zn
0.0	0.0	N. D	D. N	N. D	N. D
0.25	0.25	0.27	0.32	0.27	0.26
0.50	0.50	0.5	0.6	0.52	0.53

## 4. CONCLUSIONS

The cooper and zinc mixture is a complex system due to its high spectral overlapping between the absorption spectra of their individual component. However, a simple, easy and inexpensive methods such as PLS, OSC-PLS and PARAFAC in a very short time was applied to overcome this problem. Finally it can be concluded that the model developed by the PARAFAC method has more prediction ability especially for real samples with respect to PLS or OSC-PLS methods, which clearly reveals that the tolerance limit of three-way calibration methods for matrix effect is higher than of the two-way methods.

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