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Orthogonal Signal Correction – Partial Least Squares Method for Simultaneous Spectrophotometric Determination of Nickel, Cobalt, and Zinc

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The simultaneous determination of nickel, cobalt, and zinc mixtures by spectrophotometric method is a difficult problem in analytical chemistry, due to spectral interferences. By multivariate calibration methods, such as partial least squares (PLS) regression, it is possible to obtain a model adjusted to the concentration values of the mixtures used in the calibration range. Orthogonal signal correction (OSC) is a preprocessing technique used for removing the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for partial least squares calibration of mixtures without loss of prediction capacity using spectrophotometric method. In this study, the calibration model is based on absorption spectra in the 450-600 nm range for 21 different mixtures of nickel, cobalt, and zinc. Calibration matrices were formed from samples containing 0.025-0.55, 0.025-0.50, and 0.025-0.50 $\mu\text{g mL}^{-1}$ for nickel, cobalt, and zinc, respectively. The RMSEP for nickel, cobalt, and zinc with OSC and without OSC were 0.0127, 0.0101, and 0.0145, and 0.0045, 0.0049, and 0.0058 $\mu\text{g mL}^{-1}$, respectively. This procedure allows the simultaneous determination of nickel, cobalt, and zinc in synthetic and real samples and good reliability of the determination was proved.

Key Words: Nickel, cobalt, zinc, determination, spectrophotometric, PLS, OSC .

Introduction

Several techniques have been proposed and evaluated for the simultaneous quantification of nickel, cobalt, and zinc in different media. Some of these methods comprise high performance liquid chromatography, voltammetry, atomic absorption spectrometry, and neutron activation analysis.¹⁻⁶ The simultaneous determination of these ions by use of the UV-vis spectrophotometry techniques and conventional metallochromic indicators in aqueous solution is difficult because, generally, the absorption spectra overlap in this region

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and the superimposed curves are not suitable for quantitative evaluation. Nowadays the combination of chemometric methods with the computer controlled instruments to monitor the molecular absorption spectra creates a powerful method in multicomponent analysis avoiding a preliminary separation step.

Partial least squares (PLS) is the widely used regression method in chemometrics.^{7,8} 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 regression analysis is the most widely used method for this purpose, and it is based on the latent variable decomposition relating 2 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:

$$X = TP^T + E = \sum t_f p'_f + E \quad (1)$$

$$Y = UQ^T + F = \sum u_f q'_f + F \quad (2)$$

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; and E and F are the residual matrices. The 2 matrices are correlated by the scores T and U , for each latent variable, as follows:

$$u_f = b_f t_f \quad (3)$$

in which b_f is the regression coefficient for the f latent variable. The matrix Y can be calculated from u_f , as in Eq. (4), and the concentration of the new samples can be estimated from the new scores T^* , which are substituted in Eq. (4), leading to Eq. (5):

$$Y = TBQ^T + F \quad (4)$$

$$Y_{new} = T^*BQ^T \quad (5)$$

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. The basic concept of PLS regression was originally developed by Wold⁹ and the application of PLS in multicomponent determination and quantitative structure activity relationship (QSAR) have been discussed in several studies.^{10–17}

Orthogonal signal correction (OSC) was introduced by Wold et al.¹⁸ to remove systematic variation from the response matrix (absorption) that is unrelated, or orthogonal, to the property matrix (concentration). Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups^{19–21} have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal compounds from the signal. Recently, application of orthogonal signal correction in spectrophotometry for simultaneous determination by PLS has been reported.^{22–24} These requirements fit the description of structured noise in X . Thus the OSC filter can be used as a preprocessing step prior to latent variable regression modeling, e.g., PLS, to remove the structured noise in X . The general, the single-component OSC model of X can be expressed by:

$$X = t_{osc} p_{osc}^T + X' \quad (6)$$

where $t_{osc} = Xw_{osc}$ and $Y^T t_{osc} = 0$. Here, t_{osc} , p_{osc} , and w_{osc} represented the single OSC component. X' is the OSC-filtered matrix subsequently used in the latent variable regression model. More than one OSC

component can be identified and removed from X . For additional OSC components the filter is applied to the X' matrix. The OSC component is similar to the standard PLS component, as it has 2 sets of loading vectors, but with the difference that the score vector t_{osc} is orthogonal to Y . Comparisons between the results of different OSC filters are often made with regard to the number of OSC components removed. However, comparisons are difficult to make, because one OSC component can be derived from different multicomponent prediction models.

This study describes an analytical methodology for simultaneous determination of nickel, cobalt, and zinc by spectrophotometric method and multivariate calibration technique (PLS-2) with preprocessing by OSC. The aim of this work was to propose an orthogonal signal correction - partial least squares (OSC-PLS) method to resolve ternary mixtures of nickel, cobalt, and zinc in synthetic and real water samples without prior separation. The method is based on the reaction between the analyte and 4-(2-pyridylazo) resorcinol (PAR) at pH 7.5.

Experimental

Reagents and standard solutions

All the chemicals used were of analytical reagent grade; sub-boiling, distilled water was used throughout. Stock solutions of nickel, cobalt, and zinc were prepared from their commercial salts (nitrate or sulfate). The stock PAR solution (1×10^{-3} mol L⁻¹) was prepared by dissolving reagent in water. A buffer solution (pH 7.5) was prepared using universal buffer solution. Universal buffer solutions were prepared by mixing phosphoric, acetic, and boric acid.²⁵

Instrumentation and software

A Hewlett-Packard 8453 diode array spectrophotometer controlled by a Hewlett-Packard computer and equipped with a 1-cm pathlength quartz cell was used for UV-Visible spectra acquisition. Data acquisition between 450 and 600 nm was performed with a UV-Visible ChemStation program (Agilent Technologies), running under Windows XP. A Metrohm 692 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least 2 buffer solutions at pH 3 and 9.

Data acquisition was accomplished with a Pentium IV (CPU 3.0 GHz and RAM 1 Gb) microcomputer using MATLAB software, version 6.5 (The MathWorks). OSC and PLS calculus were carried out in the PLS Toolbox, version 2.0 (Eigenvector Technologies).

Procedure

Standard calibration set

A mixture design was used to maximize statistically the information content in the spectra.²⁶ A training set of 21 samples was taken (Table 1). The concentrations of nickel, cobalt, and zinc were 0.025-0.55, 0.025-0.50, and 0.025-0.50 $\mu\text{g mL}^{-1}$, respectively. The mixed standard solutions were placed in a 10 mL volumetric flask and completed to the final volume with deionized water (final pH 7.5). The absorption spectra were recorded between 450 and 600 nm against a blank of universal buffer. The spectral region between 450 and 600 nm, which implies working with 151 experimental points per spectrum (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. All absorption data were preprocessed by mean-centering.

Table 1. Concentration data of the different mixtures used in the calibration set for the determination of nickel, cobalt, and zinc ($\mu\text{g mL}^{-1}$).

mixture	Nickel	Cobalt	Zinc
M1	0.025	0.025	0.50
M2	0.13	0.025	0.41
M3	0.24	0.025	0.31
M4	0.34	0.025	0.22
M5	0.45	0.025	0.12
M6	0.55	0.025	0.025
M7	0.45	0.12	0.025
M8	0.34	0.22	0.025
M9	0.24	0.31	0.025
M10	0.13	0.41	0.025
M11	0.025	0.50	0.025
M12	0.025	0.41	0.12
M13	0.025	0.31	0.22
M14	0.025	0.22	0.31
M15	0.025	0.12	0.41
M16	0.13	0.12	0.31
M17	0.24	0.12	0.22
M18	0.34	0.12	0.12
M19	0.13	0.22	0.22
M20	0.24	0.22	0.12
M21	0.13	0.31	0.12

Prediction set and analysis of real samples

For the prediction set, 8 mixtures prepared that were not included in the previous set were employed as an independent test (Table 2). The real samples in this study were collected from tap water from Arak city. The ranges of concentrations added were 0.025-0.55, 0.025-0.50, and 0.025-0.50 $\mu\text{g mL}^{-1}$ for nickel, cobalt, and zinc, respectively.

Results and Discussion

Selection of the optimum chemical conditions

Nickel, cobalt, and zinc react sensitively with PAR to form colored complexes in the aqueous media. Their absorption spectra (Figure 1) show that the spectra of these complexes overlapped completely with the spectrum of PAR and with each other. Spectra of mixture of nickel, cobalt, and zinc solutions between 450

Table 2. Composition of synthetic mixtures and predicted values for nickel, cobalt, and zinc ($\mu\text{g mL}^{-1}$).

Added			Found (PLS)			Error (%)			Found (OSC-PLS)			Error (%)		
Nickel	Cobalt	Zinc	Nickel	Cobalt	Zinc	Nickel	Cobalt	Zinc	Nickel	Cobalt	Zinc	Nickel	Cobalt	Zinc
0.03	0.10	0.30	0.02	0.09	0.31	-8.00	-7.00	4.00	0.03	0.10	0.30	0.00	-2.00	0.33
0.40	0.40	0.20	0.41	0.39	0.21	2.50	-2.75	5.50	0.40	0.39	0.20	0.25	-1.75	1.50
0.35	0.30	0.35	0.37	0.31	0.34	5.43	2.00	-3.43	0.35	0.30	0.34	0.86	0.67	-2.29
0.11	0.25	0.18	0.11	0.24	0.19	1.82	-4.80	6.11	0.11	0.24	0.19	-0.91	-3.60	3.33
0.03	0.16	0.40	0.02	0.17	0.37	-8.00	7.50	-7.25	0.03	0.16	0.39	0.00	-2.50	-2.75
0.30	0.20	0.10	0.28	0.21	0.09	-8.00	6.00	-8.00	0.29	0.20	0.10	-3.67	1.00	-1.00
0.25	0.25	0.25	0.24	0.26	0.26	-3.60	3.60	2.40	0.25	0.25	0.25	-1.20	1.20	-0.80
0.03	0.10	0.30	0.02	0.09	0.31	-8.00	-7.00	4.00	0.03	0.10	0.30	0.00	-2.00	0.33
NF ^a			5	5	6				3	3	3			
PRESS			0.0149	0.0056	0.0162				0.0012	0.0006	0.0014			
RMSEP ($\mu\text{g mL}^{-1}$)			0.0127	0.0101	0.0145				0.0045	0.0049	0.0058			
RSEP (%)			5.0203	3.9946	5.3320				1.7734	1.9251	2.1357			
γ ($\mu\text{g}^{-1} \text{mL}^{-1}$) ^b			121	113	124				86	81	92			
LOD ($\mu\text{g mL}^{-1}$) ^b			0.015	0.016	0.013				0.009	0.011	0.010			

^aNumber of factors

^b γ (analytical sensitivity) = $\text{SEN}/[\text{V}(\text{R})]^{1/2}$ where SEN is the sensitivity (estimated as the net analyte signal) and $\text{V}(\text{R})$ is the variance of the instrumental signal and LOD (limit of detection) = $3.3s(0)$ where $s(0)$ is the S.D. in the predicted concentration of nickel, cobalt, and zinc in a blank sample²⁸

and 600 nm wavelengths by 1-nm intervals were recorded, and then the data digitized and stored for all treatments. The formation of the Ni-PAR, Co-PAR, and Zn-PAR complexes in aqueous solutions is a fast process. The colored solutions were highly stable for at least 24 h.

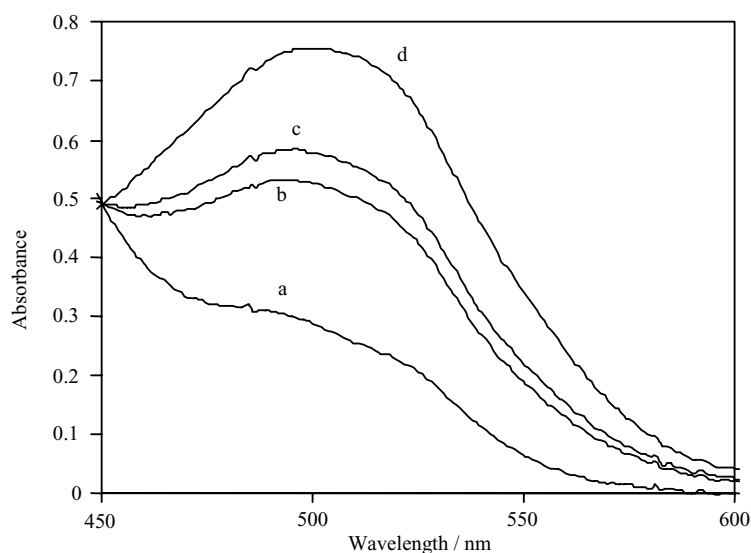


Figure 1. Absorption spectra of: (a) PAR, (b) Ni-PAR complex, (c) Co-PAR complex, and (d) Zn-PAR complex at pH 7.5: $C_{Ni} = 0.20 \mu\text{g mL}^{-1}$, $C_{Co} = 0.25 \mu\text{g mL}^{-1}$, and $C_{Zn} = 0.30 \mu\text{g mL}^{-1}$ in aqueous media.

The effect of pH on the absorption spectra of each metal complex was studied over the range 2.0-12.0. These results are shown in Figure 2. The maximum sensitivity for nickel, cobalt, and zinc occurred at approximately pH 7.5. Therefore, 2.0 mL of the universal buffer solution of pH 7.5 was used to adjust the pH. In an attempt to control the variables of this chemical system more efficiently, all experiments were planned to be run with a larger excess amount of PAR than usual. This would restrict wider variations in [PAR]:[M] concentration ratios, reducing the changes in composition of the various equilibria involved during the analysis. In this particular case, the PAR used was more than 2.5 times (mol/mol) excess over the amount needed to form 1:1 complexes with 0.55, 0.50, and 0.50 $\mu\text{g mL}^{-1}$ of Ni^{2+} , Co^{2+} , and Zn^{2+} , respectively, which corresponds to the highest concentrations of the analytes in the complete experimental design.

Individual calibration curves were constructed with several points at absorbance versus nickel, cobalt, and zinc concentration. For constructing the individual calibration lines the absorbances were measured at 494, 497, and 501 nm against a blank for Ni-PAR, Co-PAR, and Zn-PAR, respectively. The linear regression equation for the calibration graph for nickel for the concentration range 0.025-0.55 $\mu\text{g mL}^{-1}$ was $A = 0.2575 + 1.2641C_{Ni}$ ($r^2 = 0.9979$, $n = 10$), for cobalt for the concentration range 0.025-0.50 $\mu\text{g mL}^{-1}$ was $A = 0.2736 + 1.1253C_{Co}$ ($r^2 = 0.9962$, $n = 11$), and for zinc for the concentration range of 0.025-0.50 $\mu\text{g mL}^{-1}$ was $A = 0.5003 + 0.7910C_{Zn}$ ($r^2 = 0.9967$, $n = 11$). The limits of detection were 0.012, 0.014, and 0.012 $\mu\text{g mL}^{-1}$ for nickel, cobalt, and zinc, respectively, and were calculated according to calibration line characteristics.

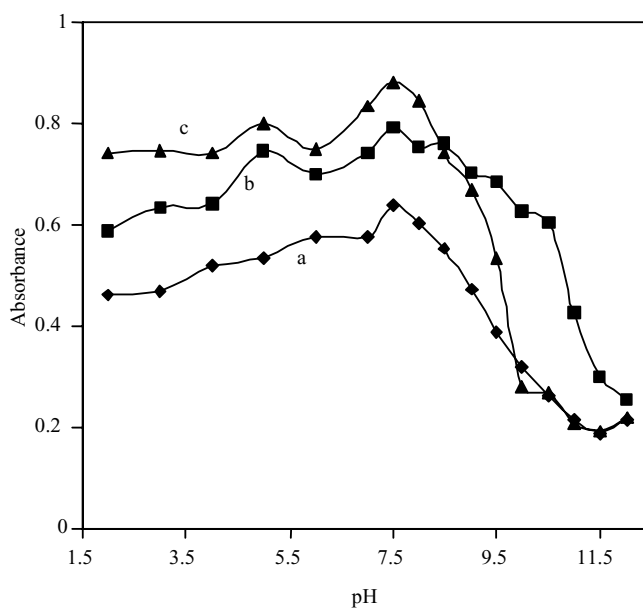


Figure 2. The effect of pH on the absorbance of: (a) Ni-PAR ($\lambda_{max} = 494$ nm), (b) Co-PAR ($\lambda_{max} = 497$ nm), and (c) Zn-PAR ($\lambda_{max} = 501$ nm) complexes in aqueous media.

Multivariate calibration

The determination of the nickel, cobalt, and zinc in mixtures by spectrophotometry using multivariate calibration involves constructing calibration and prediction sets. An experimental design was used to maximize statistically the information content in the spectra. A training set of 21 samples was taken (Table 1). The concentrations of nickel, cobalt, and zinc were 0.025-0.55, 0.025-0.50, and 0.025-0.50 $\mu\text{g mL}^{-1}$, respectively. For the prediction set, 8 mixtures were prepared (see Table 2). To ensure that the predictions were in the subspace of the training set, the score plot of first principal component versus second was sketched and all the samples were spanned with the training set scores. Spectra of each standard, prediction, and real samples were prepared as described in the Procedure section. The chemometrics calibrations were computed with the PLS and OSC-PLS algorithms, using the correlation for the training set concentration and its current data.

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

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

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

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 prediction set.

Orthogonal signal correction - partial least squares (OSC-PLS)

Orthogonal signal correction (OSC) is a preprocessing technique used to remove the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for PLS calibration of mixtures without loss of prediction capacity using a spectrophotometric method. For the calibration set 3 OSC components were used for filtering. Evaluation of the prediction errors of the validation set reveals that the OSC treated data give substantially lower root mean squares error of prediction values than the original data. Moreover, the OSC-filtered data give much simpler calibration models with fewer components than the ones based on the original data (Table 2). The results imply that the OSC method indeed removes information from spectrophotometric data not necessary for fitting of the Y-variables. In some cases the OSC method also removes non-linear relationships between X and Y. Figure 3 shows the score plot for when the PLS and OSC-PLS are used. The score plots are shown for comparison of the results obtained from PLS and OSC-PLS. The results show that score plots have better results when OSC-PLS is used. Score plots reveal the geometrical placement of the solutions in principal components space. The experimental noise can destroy this relation but removing the noise using OSC filtering depicts the OSC-PLS score plot (Figure 3) in a clearer way.

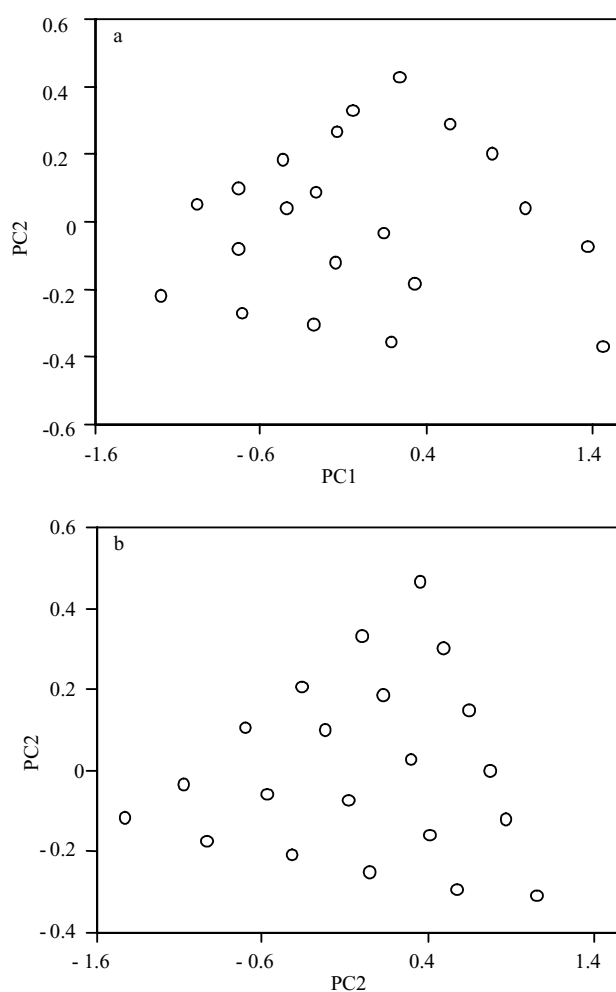


Figure 3. Plots of first principal component against second principal component for nickel, cobalt, and zinc determination: (a) by PLS and (b) OSC-PLS models.

Determining how many factors are to be used in the calibration is a key step in factor based methods. Only those factors that contain analytical information must be kept. The discarded factors should contain only noise. The cross-validation procedure leaving out one (CV-LOO) sample at a time is used for this purpose and the predicted residual error sum-of-squares (PRESS) is calculated.

$$PRESS = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (9)$$

where y_i is the reference concentration for the i^{th} sample, \hat{y}_i represents the estimated concentration, and n is the total number of samples. The optimum number of factors was determined rather than the selection of the model, which yields a minimum in prediction error variance or PRESS; the model selected is the one with the fewest number of factors such that PRESS for that model is not significantly greater than the minimum PRESS. In our case, 11 factors (half the standards + 1) were used as the maximum number of initial factors. One reasonable choice for the optimum number of factors would be the number that yielded the minimum PRESS. Since there are a finite number of samples in the training set, in many cases the minimum PRESS value causes overfitting for unknown samples that were not included in the model. A solution to this problem has been suggested by Haaland et al.⁷ in which the PRESS values for all previous factors are compared to the PRESS values at the minimum. The F-test can be used to determine the significance of PRESS values greater than the minimum. Table 2 shows the optimum number of factor for nickel, cobalt, and zinc. In Figure 4, the PRESS obtained by optimizing the calibration matrix of the spectrophotometric data with PLS and OSC-PLS models is shown.

Determination of nickel, cobalt, and zinc in synthetic mixtures

The proposed method was successfully applied for determination of nickel, cobalt, and zinc in several synthetic samples (their compositions are given in Table 2). The results obtained from simultaneous determination of nickel, cobalt, and zinc by PLS and OSC-PLS methods are listed in Table 2. Table 2 also shows RMSEP, RSEP, and the percentage error for synthetic series of nickel, cobalt, and zinc mixtures. As can be seen, the percentage error was also quite acceptable. Good results were achieved in the OSC-PLS model with percentage error ranges of -3.67% to 0.86%, -2.60% to 1.20%, and -2.75% to 3.33% for nickel, cobalt, and zinc, respectively. Figures of merit are regularly employed for method comparison. They are best understood by resorting to the useful concept of net analyte signal (NAS), first developed by Lorber et al.²⁷ The results for the determination of these 3 cations and their reported figure of merits are reported in Table 2.

Assay of nickel, cobalt, and zinc in water samples

The proposed procedure was successfully applied for the assay of nickel, cobalt, and zinc simultaneously in real samples (Table 3). To evaluate the validity of the proposed method for the determination of nickel, cobalt, and zinc, a recovery study was carried out on samples to which definite amounts of nickel, cobalt, and zinc standard were added. The result showed that the obtained relative standard deviation (RSD) was acceptable (RSD values are given in Table 3). Therefore, the OSC-PLS model is able to predict the concentrations of nickel, cobalt, and zinc in real matrix samples.

Table 3. OSC-PLS results applied on the real matrix samples ($\mu\text{g mL}^{-1}$).

Samples ^a	Nickel			Cobalt			Zinc					
	Added	Found ^b	RSD ^c	Recovery (%)	Added	Found ^b	RSD ^c	Recovery (%)	Added	Found ^b	RSD ^c	Recovery (%)
Tap water 1	-	n.d. ^d	-	-	-	n.d.	-	-	-	0.032	0.006	-
	0.15	0.158	0.011	-	0.20	0.209	0.013	-	0.30	0.336	0.011	101.3
Tap water 2	-	0.042	0.014	-	-	0.028	0.009	-	-	0.086	0.012	-
	0.20	0.243	0.023	100.5	0.20	0.231	0.032	101.5	0.20	0.281	0.028	97.5
Tap water 3	-	n.d.	-	-	-	0.031	0.010	-	-	0.125	0.075	-
	0.30	0.305	0.045	-	0.25	0.279	0.054	99.2	0.15	0.280	0.027	103.3

^aTap water samples were collected in tap water from Arak city

^bAverage of 3 separate determinations

^cStandard deviation for n = 3

^dNot detected

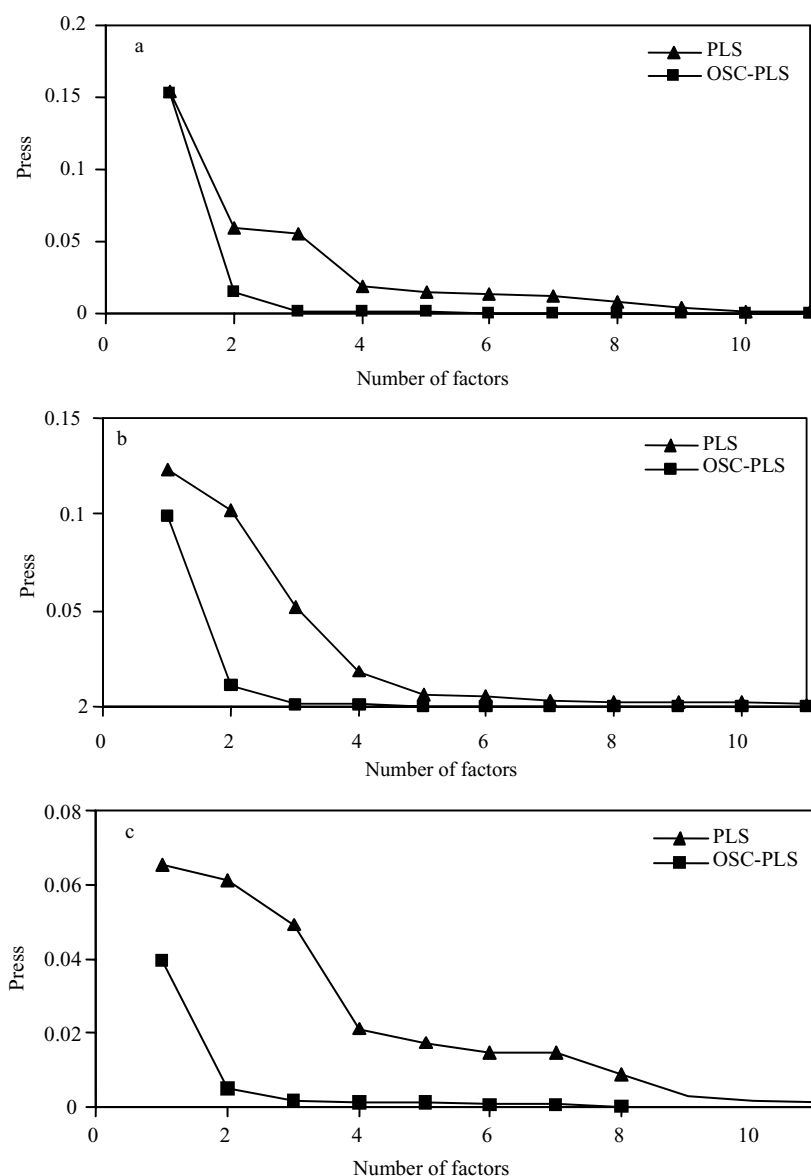


Figure 4. Plots of PRESS versus number of factors by PLS and OSC-PLS (a) nickel, (b) cobalt, and (c) zinc.

Conclusion

A method for the simultaneous determination of nickel, cobalt, and zinc using spectrophotometric and orthogonal signal correction - partial least squares (OSC-PLS) method is proposed. A simple, sensitive, inexpensive, and non-polluting scheme for the simultaneous determination of nickel, cobalt, and zinc was developed and optimized. The nickel, cobalt, and zinc complexes with PAR are an extremely difficult complex system due to the high spectrophotometric overlapping observed between the spectrophotometric data of their components. To overcome the drawback of spectrophotometric interferences OSC-PLS multivariate calibration approaches are applied. The method gives good RSD values. The results of this study clearly show the potential and versatility of this method, which could be applied to simultaneous determination of nickel, cobalt, and zinc in synthetic and real samples.

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