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Simultaneous Spectrophotometric Determination Of Trace Amounts Of Gallium And Nickel By Benzo 15-Crown-5 And PAN Using Orthogonal Signal Correction Partial Least Squares

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ABSTRACT

Orthogonal signal correction partial least squares (OSC-PLS) modeling as a powerful multivariate statistical tool applied to spectrophotometric simultaneous determination of mixtures of gallium and nickel. An ion-selective bulk optode (ISBO) for sensing Ga^{3+} and Ni^{2+} ion based on plasticized poly(vinyl chloride) containing benzo-15-crown-5(B15C5) and kryptofix as ionophores and 1-(2-pyridilazo)-2-naphthol (PAN) as chromoionophore was prepared. The method is based on the formation of the complexes of PAN with gallium and nickel. The ISBO membrane shows enhanced selectivities for Ga^{3+} and Ni^{2+} but their absorption spectra of these two complexes overlap strongly, thus it is difficult to analyze the compounds in their mixtures. In this study, the calibration model is based on absorption spectra in the 400-650 nm range for 25 different mixtures of gallium and nickel. A series of synthetic solutions containing different concentrations of gallium and nickel were used to check the prediction ability of the OSC-PLS model. The RMSEP were 0.3587 and 0.8496 for gallium and nickel, respectively. © 2007

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KEYWORDS

Orthogonal signal correction-partial least squares;
Gallium;
Nickel;
ISBO.

INTRODUCTION

In ion-selective optodes, the use of ion carrier molecules such as macrocyclic ligands allows the determination of ions by measurement of absorbance or fluorescence of membrane. Hence an ion-selective

optical sensor could be constructed based on an ion-pair extraction process using a selective ionophore in conjunction with and an indicator. In addition to chemical selectivity, an optical selectivity can be obtained with suitable wavelength selection for measurements. Several macrocyclic compounds have

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been evaluated as ionophores some of which had been used successfully in ion-selective electrodes for copper (II) and lead (II)^[1,2].

The azo-dye PAN (1-[2-pyridylazo]-2-naphthol) is a well-known metallochromic indicator for the quantitative and qualitative determination of variety of metal ions^[3]. A recently constructed flow-through optical chemical sensor utilizing immobilized PAN in a nafion membrane has shown promising results in the detection of various metal ions^[4]. One of the common methods to measure gallium ion is the use of ion-selective electrodes. Ion-selective electrodes measure the potential against a reference electrode, whereas the optical sensors need not to use a reference electrode^[5]. Additionally, ions such as Cr or Fe interfere with ion-selective electrodes, whereas they do not cause any significant interference with optical electrodes^[6,7]. Another advantage for optical sensors is their ability to measure non-ionized species^[8]. However, the simultaneous determination of gallium and nickel by traditional spectrophotometric techniques is difficult because, generally, the absorption spectra overlap in a bright region and the superimposed curves are not suitable for quantitative evaluation.

Under computer-controlled instrumentation, derivative techniques and multivariate calibration methods play a very important role in the multicomponent analysis of mixtures by ultraviolet (UV)/visible, molecular absorption spectrophotometry^[9-11]. The application of quantitative chemometrics, particularly partial least squares (PLS), to multivariate chemical data is becoming more widespread owing to the availability of digitized spectroscopic data and commercial software for laboratory computers.

The theory and application of PLS in spectrometry have been discussed by several authors^[12-18]. Several multicomponent determination of inorganic substances based on the application of these methods to spectrophotometric data has also been reported^[19-27]. A particularly detailed study of multivariate calibration by PLS was carried out for the spectrophotometric determination of metals^[28]. Orthogonal signal correction (OSC) was introduced by Wold et al.^[29] to remove systematic variation from the response matrix (X) that is unrelated, or orthogonal, to the

properly matrix (Y). Therefore, one can be certain that important information regarding the analyte is retained. Recently, multicomponent determinations based on the application of OSC-PLS method to spectrophotometric and voltammetric data have been published^[26,29,30].

In the present work, the orthogonal signal correction-partial least squares tools were applied to simultaneous determination of gallium and nickel. The method is based on employing PAN as a chromo ionophore because of its ability to form highly colored complexes with gallium and nickel and its solubility in the membrane phase. Thus, the proposed optical sensor for Ga³⁺ and Ni²⁺ ion consist on a plasticized solvent polymeric membrane incorporating lipophilic anionic sites, where PAN is as a chromo ionophore and benzo-15-crown-5 (B15C5) and kryptofix are as ionophores.

EXPERIMENTAL

Reagents and apparatus

1-(2-Pyridylazo)-2-naphthol (PAN), 2-nitrophenyl octyl ether (NPOE), high relative molecular weight PVC, sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), kryptofix and B15C5 were purchased from Fluka chemical company and used as received. All inorganic salts (from Merck) were of analytical reagent grade and solutions were made using doubly distilled water.

A UV-VIS spectrophotometer (LABOMED Inc, spectral bandpass 0.2 nm and scan rate 500 nm/min) controlled by a computer and an equipment of a 1 cm path length quartz cell was used for UV-Vis spectra acquisition. An Elmetron cp-501 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least 3 buffer solutions at pH 3.00, 7.00 and 9.00. Glass plates covered by membranes of similar properties were mounted into the measuring cells. The reference cell contained a glass plate membrane without any chromoionophore. All measurements were made in the absorbance mode. The pHs of the solutions were kept constant by using 0.01M sodium acetate at pH 5.0.

Software's

The data were processed on a Pentium IV (256

Mb RAM) microcomputer using MATLAB software, version 6.5 (The Mathworks). All absorption spectra were digitized and sorted at wavelength range 400-650 nm with 1 nm steps and transferred in ASCII format for subsequent manipulation by OSC-PLS program. PLS and other calculations were carried out using PLS-Toolbox, version 2.0 (Eigenvectors Company).

Membrane preparation

The optimized composition for the preparation of the ion-selective bulk optode (ISBO) consisted of 32 mg of PVC, 66 mg of NPOE, 1.2 mg of PAN, 10.6 mg of B15C5, 10.5 mg kryptofix and 13.6 mg of additive NaTPB completely dissolved in 10 ml of freshly distilled THF. A 100 μ l portion of this solution was poured and uniformly spread out on a dust-free glass plate of 300 mm², in area placed in a saturated THF atmosphere. After about 5 h, the glass plate covering with the PVC membrane was removed and stored in air for further drying. The prepared membranes were put in a buffer solution of pH 5 for 12 h to reach equilibrium. Then the membrane was placed vertically inside the sample cuvette containing 3 ml buffer solution of pH 5, and a blank membrane (without chromoionophore) was put in the reference cuvette containing the buffer solution. The sample cell was finally titrated with standardized metal ion solutions and the absorbance value of system was measured after 90 min, required to reach the equilibrium.

RESULTS AND DISCUSSION

Effect of pH

The complexation reactions of PAN with metal ions are well known to be strongly dependent on the

pH, figure 2. In its neutral form, PAN is nearly insoluble in water, while it is quite soluble in organic solvents. The influence of pH values was studied over the pH range 2-10 at a constant concentration of each ion. The results are shown in figure 3. As can be seen, after pH 4 the pH has a constant effect on the absorbance value thus pH 5 was chosen as the optimum value for the subsequent steps of the analysis.

Effect of membrane composition

It is well known that the sensitivity and selectivity obtained for a given ionophore depend on significantly on the membrane composition and the nature of solvent mediator and additives used^[31]. Thus, the influences of the nature of plasticizer, amount of ionophore and amount of sodium tetraphenylborate as a lipophilic additive (anionic site) on the response behavior and leaching of sensor were investigated.

Solvent polymeric membranes used in ion sensors are usually based on a matrix containing above 33% (w/w) of PVC and 66% of a membrane sol-

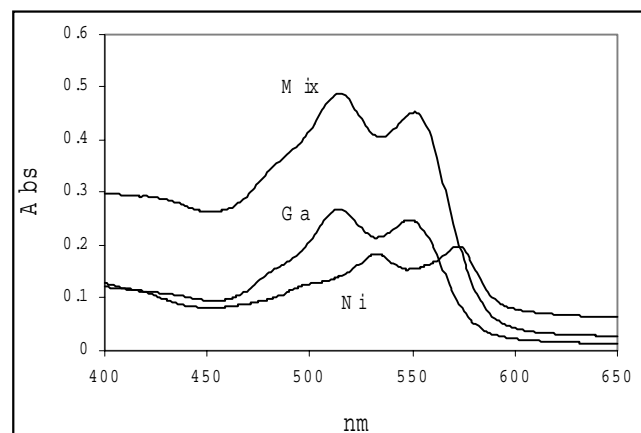


Figure 1: Absorption spectra of gallium and nickel complexes and their mixture in acetate buffer (pH=5), concentration of Ga³⁺ and Ni²⁺ 5 μ g mL⁻¹

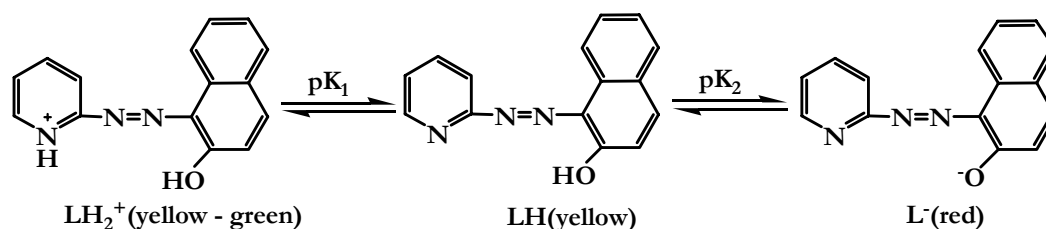
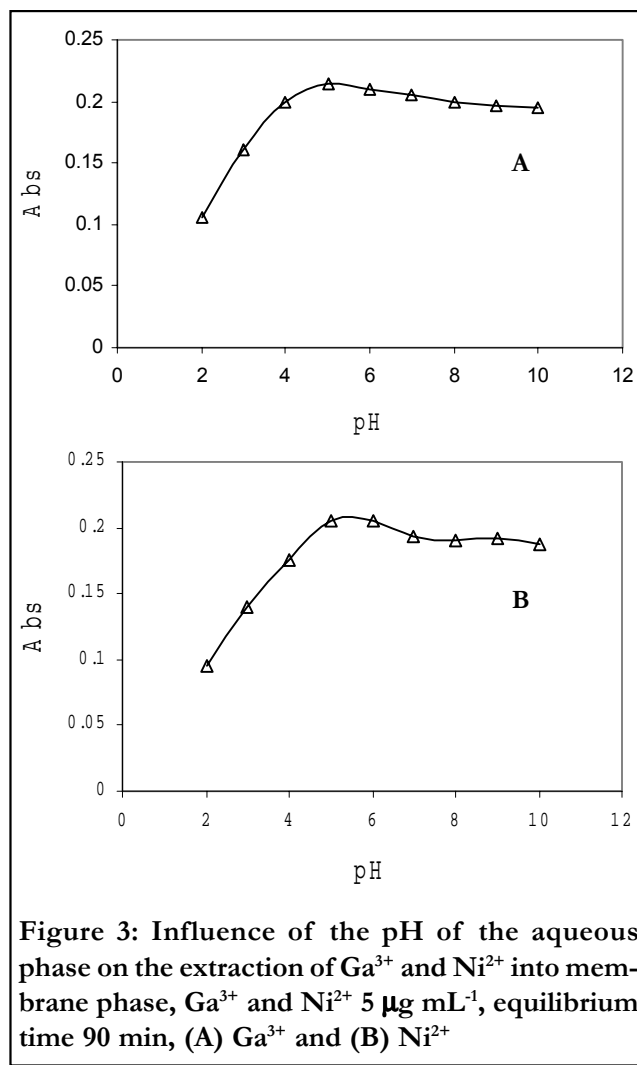
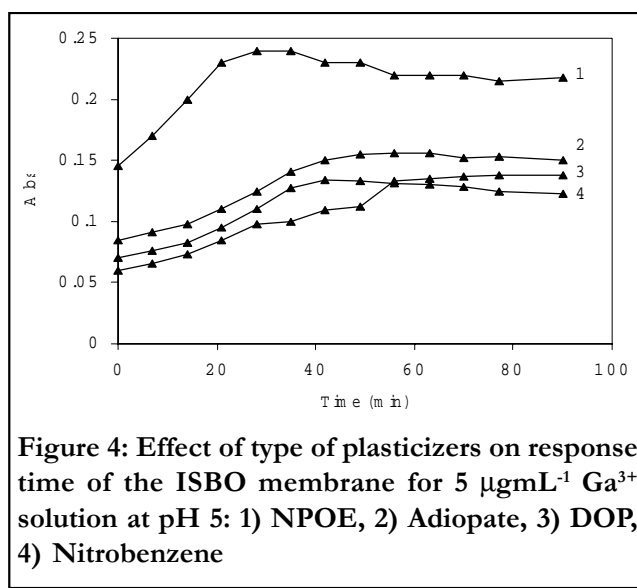


Figure 2: Protolytic reactions and color change of PAN

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vent^[32, 33]. In order to have a homogenous organic phase, the membrane solvent must be physically compatible with the polymer. In this work nitrobenzene, adiopat, DOP and NPOE with different polarities were tested as potential plasticizers. As it is shown in figure 4, among the other three plasticizers used, NPOE resulted in the fastest response time of the resulting membrane sensor; thus, it was selected for further studies. This is most probably due to the increased polarity of NPOE which facilitates the extraction-complexation of the metal ions into the bulk of the PVC-membrane sensor. In addition to the optimization of the type of plasticizer, it is also necessary to optimize the molar ratio of ionophore to chromoionophore in the optical membrane, so an ionophore/chromoionophore molar ratio of 9:1 was selected that shows the widest dynamic concentration range and minimum leaching of the complexes

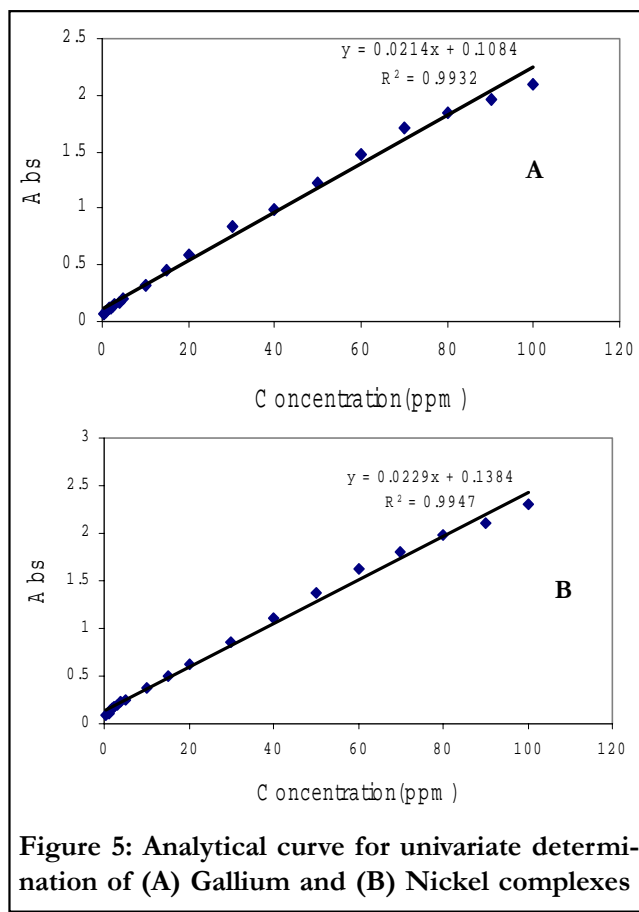


from membrane.

Individual calibration curves were constructed with several data points as absorbance vs. metal ion concentration in the range 0.5-100 μg mL⁻¹ in 517.0 and 574.0 nm for gallium and nickel, respectively, figure 5. The detection limits were 0.15 and 0.35 μg mL⁻¹ for gallium and nickel, respectively. Linear regression results, line equations and R² are shown in figure 5.

Calibration and validation sets

Multivariate calibration methods are suitable for the analysis of large numbers of samples. However, they are not recommended for the determination of large numbers of analytes because the complexity of the calibration matrix. Moreover, the preparation and analysis of the standards belong to the calibration set are the most expensive step in the multivariate calibration procedure. Multivariate calibration methods such as PLS require a suitable experimental design of the standards belonging to the calibration set in order to provide good predictions. The calibration for OSC-PLS model was optimized with the aid of the orthogonal design method^[34]. A set of standard samples was prepared according to a five-level orthogonal array design, denoted by OA₂₅(5⁵). This leads to 25 samples for calibration set that was designed over the concentration ranges 1.0-20.0 μg mL⁻¹ for gallium and nickel. The composition of the calibration set is given in TABLE 1. For prediction or test set 12 samples of binary mixtures of two



analytes were used. The spectral region is between 400 and 650 nm and each spectrum is digitized with 1 nm steps.

Preprocessing by orthogonal signal correction

Generally the OSC operate on the scaled data (mean centered and variance scale of the X and Y), and it removes the uncorrelated variations of X with respect to Y variables. For calibration set the optimum number of OSC components was found one for filtering. Evaluation of the prediction errors for the validation set reveals that the OSC treated data give substantially lower root mean squares error of prediction (RMSEP) values than original data. The results imply that the OSC method indeed removes information from spectral like data that is not necessary for fitting of the Y-variables, as excess reagent in this special case. In some cases the OSC method also removes some orthogonal part of the relationship between X and Y. The effect of the OSC on the calibration model can be also seen from the score plots of the PLS and OSC-PLS. This difference in

TABLE 1: Concentration data of the different mixtures used in the calibration set for the determination of Ga^{3+} and Ni^{2+} .

Solution number	Concentration(ppm)	
	Ga^{3+}	Ni^{2+}
M1	1.00	1.00
M2	1.00	5.00
M3	1.00	10.00
M4	1.00	15.00
M5	1.00	20.00
M6	5.00	1.00
M7	5.00	5.00
M8	5.00	10.00
M9	5.00	15.00
M10	5.00	20.00
M11	10.00	1.00
M12	10.00	5.00
M13	10.00	10.00
M14	10.00	15.00
M15	10.00	20.00
M16	15.00	1.00
M17	15.00	5.00
M18	15.00	10.00
M19	15.00	15.00
M20	15.00	20.00
M21	20.00	1.00
M22	20.00	5.00
M23	20.00	10.00
M24	20.00	15.00
M25	20.00	20.00

the score plots (which is object map in a reduced multidimensional space) reveals that the OSC removed the orthogonal part of the X variation to the Y variables. Now, the geometrical coordinates of the objects in the two-dimensional score plot are similar to the expected values of the concentration of the mixtures solution of calibration samples. The similar trend has been observed previously^[35,29,36].

Selection of optimum number of factors

The optimum number of factors (latent variables) 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 (half the number of total

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standard + 1), which is defined as follows:

$$\text{PRESS} = \sum (y_i - \hat{y}_i)^2 \quad (1)$$

where y_i is the reference concentration for the i th sample and \hat{y}_i represents the estimated concentration. A cross-validation method was employed to eliminate only one sample at a time and then OSC-PLS algorithm models the remaining Y matrix and corresponding X matrix. By using the established calibration model the concentration of the sample, left out was predicted. This process was repeated until each standard had been out once.

One reasonable choice for the optimum number of factors would be that number which 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 and Thomas^[37] in which the PRESS values for all previous factors are compared to the PRESS value at the minimum. The F-statistical test can be used to determine the significance of PRESS values greater than the minimum.

The maximum number of factors used to calculate the optimum PRESS was selected as 12 and the optimum number of factors obtained by the application PLS and OSC-PLS models are summarized in TABLE 3. In all instances, the number of factors for the first PRESS values whose F-ratio probability drops below 0.75 was selected as the optimum. The figure 6 shows the PRESS obtained by optimizing the calibration matrix of the spectrophotometric data with OSC-PLS.

Determination of gallium and nickel in synthetic mixtures

The predictive ability and validation of the calibration model was assessed using twelve two-component of Ga^{3+} and Ni^{2+} mixtures (their compositions are given in TABLE 2). The results obtained by applying OSC-PLS based calibration model to twelve synthetic samples are listed in TABLE 2.

Statistical parameters

For each final optimized model three parameters were selected to assess prediction ability in simulta-

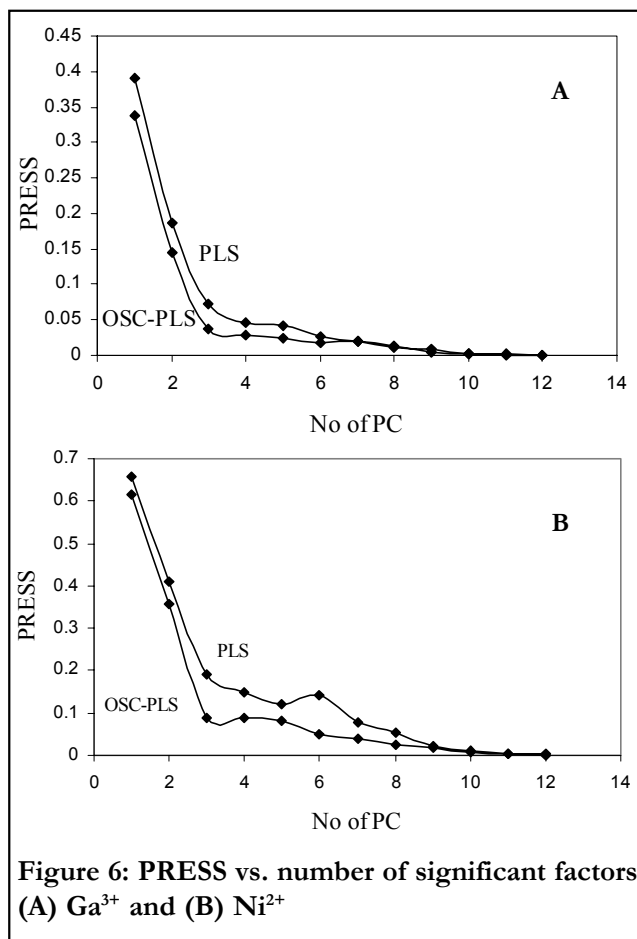


Figure 6: PRESS vs. number of significant factors (A) Ga^{3+} and (B) Ni^{2+}

neous determination of Ga^{3+} and Ni^{2+} . Root mean squares error of prediction (RMSEP), which is an indication of the average error in the analysis, for each component:

$$\text{RMSEP} = \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5} \quad (2)$$

Another useful parameter is the relative error of prediction (REP%) that shows the predictive ability of model for each component, calculated as:

$$\text{REP}\% = \frac{100}{y} \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5} \quad (3)$$

The square of the correlation coefficient (R^2), which indicates the quality of fit of all the data to a straight line is calculated for the checking of each calibration, and is calculated as:

$$R^2 = \frac{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (4)$$

where y_i is the true concentration of the analyte and \hat{y}_i represents the estimated concentration of the analyte and the mean of the true concentration in

TABLE 2: Added and found results of synthetic mixtures of Ga³⁺ and Ni²⁺.

Prediction mixtures	Added		PLS				OSC-PLS			
			Found		Recovery		Found		Recovery	
	Ga ³⁺	Ni ²⁺	Ga ³⁺	Ni ²⁺	Ga ³⁺	Ni ²⁺	Ga ³⁺	Ni ²⁺	Ga ³⁺	Ni ²⁺
P1	1	5	1.1670	5.4211	116.70	108.42	1.1258	5.3944	112.58	107.89
P2	1	10	1.1441	9.6601	114.41	96.60	1.0290	9.8354	102.9	98.35
P3	5	1	5.0138	0.9135	100.28	91.35	5.2205	0.9377	104.41	93.77
P4	5	15	4.3684	14.5912	87.37	97.27	4.6117	14.7556	92.23	98.37
P5	10	10	10.1593	9.2744	101.59	92.74	10.0366	9.2337	100.36	92.33
P6	10	20	10.1429	20.8617	101.43	104.31	10.1420	20.7412	101.42	103.70
P7	10	5	9.5651	6.2801	95.65	125.60	9.7337	5.7613	115.23	115.22
P8	15	1	14.1116	1.2322	94.08	123.22	14.5227	1.1116	96.81	111.16
P9	15	10	15.1226	10.8031	100.81	108.03	15.1217	10.5611	100.81	105.61
P10	20	5	19.7633	4.3326	98.82	86.65	19.6125	4.6706	98.06	93.41
P11	20	15	21.0752	15.6029	105.38	104.02	20.9083	15.3491	104.54	102.32
P12	20	20	20.1912	22.5681	100.96	112.84	20.1360	22.4874	100.68	112.43

TABLE 3: Statistical parameters obtained by applying the PLS and OSC-PLS methods to the synthetic mixtures

Parameters	PLS		OSC-PLS	
	Ga ³⁺	Ni ²⁺	Ga ³⁺	Ni ²⁺
NPC ^a	4	5	3	3
RMSEP	0.4774	0.9736	0.3587	0.8496
REP(%)	4.34	9.98	3.26	8.71
R ²	1.030	1.146	1.017	1.137
R	1.014	1.070	1.008	1.066

^aNumber of Principal Component

the prediction set and n is \bar{y} of the analyte in the sample i , the total number of sample used in the prediction set. The value of RMSEP, REP(%) and R² for Ga³⁺ and Ni²⁺ summarized in TABLE 3. The results of the TABLE 3 clearly show the successful application of the each calibration model. The three statistical parameters of OSC-PLS algorithm are drastically smaller than the corresponding parameters for the PLS algorithm, which is an indication of the successful application of OSC as a filtering process before multivariate calibration.

CONCLUSION

The gallium-nickel mixture is an extremely complex system due to high spectral overlapping of the absorption spectra for the components. The deter-

mination of these two important cations were tackled with a optode based sensor including B15C5 and PAN as an ionophore and chromoionophore, respectively and OSC-PLS multivariate calibration method. The results showed the ability of the OSC-PLS model in the deconvolution of mixture spectra. The proposed method is simple, inexpensive, and precise and does not require any complex pre-treatment.

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