



Net analyte signal standard addition method for the simultaneous determination of cadmium and nickel

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Abstract: A novel net analyte signal standard addition method (NASSAM) is presented for the simultaneous determination of Cd²⁺ and Ni²⁺ in their mixture by differential pulse polarography. The method combines the advantages of the standard addition method with the net analyte signal concept, which enables the extraction of information concerning a certain analyte from voltammograms of multi-component mixtures. This method has some advantages, such as: the use of a full voltammogram, realization in a single step, therefore it does not require calibration and prediction steps and only a few measurements are required for the determination. The simultaneous determination of Cd²⁺ and Ni²⁺ was performed in Britton–Robinson buffer (pH 2.87) and 0.40 M potassium thiocyanate solution.

Keywords: differential pulse polarography; simultaneous determination; net analyte signal; standard addition method.

INTRODUCTION

Electrochemical techniques such as differential pulse polarography (DPP) and stripping voltammetry are highly sensitive techniques and are widely used in many area of analytical chemistry. However, their applicability to the determination of mixtures of several components is rather limited when they display strongly or partially overlapping polarograms. In this case, one may try to optimize the conditions for maximum separation in order to find a single variable. This, however, is time and cost consuming, and may be the source of errors. Chemometric techniques allow these problems to be overcome and the probability of finding a global optimum is increased.

The use of chemometrics in electrochemistry and the analysis of voltammetric data was reviewed recently.^{1–3} Chemometrics can be applied to different steps of an electro-analytical process or with different objectives. Among the dif-

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ferent steps, the following can be mentioned: *i*) experimental design and optimization of relevant experimental and instrumental parameters, *ii*) preparation and transformation of data for further data treatment, *iii*) data exploration and sample classification and *iv*) concentration determination, calibration, and model identification.²

Several linear and non-linear multivariate calibration methods have been reported for simultaneous determination by electro-analytical techniques.^{4–8} Also, the H-point standard addition method (HPSAM) was established for resolving strongly overlapping spectra of two analytes.^{9,10} This method is based on dual wavelength spectrophotometry and the standard addition method. Shams *et al.*¹¹ used this method for the simultaneous determination of lead and tin by the striping voltammetry method. The HPSAM uses only two data points when the portion of the analytical signal due to the interferent is constant and that due to the analyte is as different as possible.

In this work, a novel standard addition method based on the net analyte signal concept, which does not have the constraints of the HPSAM, is introduced. The net analyte signal was defined by Lorber, based on spectroscopic methods, as the part of the spectrum of a mixture that is unique for the analyte of interest (Fig. 1), *i.e.*, it is orthogonal to the spectra of the interferences.¹² There are some net analyte signal based methods reported for calculation of the NAS.^{13–16} In this work, an attempt was made to calculate NAS vectors and attribute them to the analyte concentration using the polarographic technique.

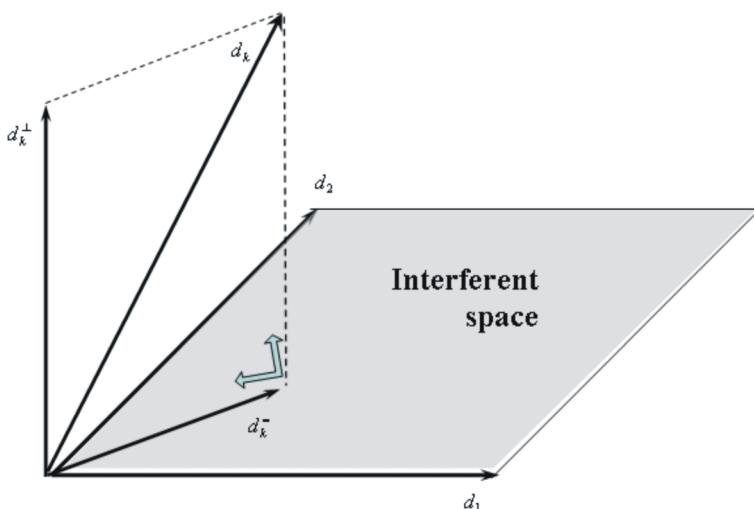


Fig. 1. Representation in J^{th} dimensional vector space analyte (\mathbf{d}_k) and vector of interfering agents (\mathbf{d}_1 and \mathbf{d}_2) and the NAS vector \mathbf{d}_k^{\perp} will be different from \mathbf{d}_k in direction and length.

The vector \mathbf{d}_k^- is the part of \mathbf{d}_k that is in the interference space.

Theory

The conventional notation has been used throughout the following discussion. Thus, a boldface capital letter is used for a matrix, a boldface lower case for a column vector and a lightface lower case italic for a scalar. The superscript T designates the operation of the vector or matrix transposition and the superscript + denotes the pseudo-inverse of a non-square matrix. The digitized polarogram is referred to as a polarogram vector or simply as a vector, while a voltammogram vector of a pure component is called a component vector.

In principal component regression, the concentration prediction of the k^{th} component in an unknown sample can be performed by the following equation:

$$c_{\text{un}} = d_{\text{un}}^T \mathbf{D}^+ c \quad (1)$$

where d_{un} is the vector of the responses of the unknown sample, the matrix \mathbf{D}^+ is the pseudo inverse of the calibration matrix \mathbf{D} ($J \times I$), and is the vector of concentrations of the k^{th} component in the calibration set.

In voltammetric techniques, the currents measured at J potentials are collected in a ($J \times 1$) column vector (d). The matrix \mathbf{D} ($J \times I$) contains the voltammogram of I samples in its columns. Suppose that the analyte of interest (k) is a compound in a mixture of other electro-active compounds that are called interfering agents. By definition, it is always possible to split up the voltammogram (d_k) of the analyte of interest into two distinct parts:

$$d_k = d_k^{\parallel} + d_k^{\perp} \quad (2)$$

where d_k^{\parallel} is the part of the voltammogram that could have been generated by a linear combination of the voltammograms of the interfering agents. The superscript “ \parallel ” indicates that d_k^{\parallel} is in the space spanned by the voltammograms of the interfering agent (Fig. 1). Consequently, d_k^{\parallel} cannot be unique for the analyte of interest because a mixture of interfering agents could have produced it. The other part, d_k^{\perp} , is orthogonal to the voltammograms of the interferences reflecting the part of the voltammogram only depending on the analyte k present in the mixture. This part, called the net analyte signal vector (\mathbf{d}_{NAS}), can therefore be used for quantification of the analyte k .^{12,17,18} The shape of d_k^{\perp} only depends on the presence of the interferences in the mixture, not on their specific concentrations. Only addition or deletion of electro-active components can change d_k^{\perp} . In the following, it is assumed that the spectra and/or voltammograms of samples without the analyte are available and during the determination they do not change. The net analyte signal of the k^{th} component, \mathbf{d}_{NAS} , can be found by the following orthogonal projection:

$$\mathbf{d}_{\text{NAS}} = (\mathbf{I} - \mathbf{R}^+ \mathbf{R}) \mathbf{d}_k \quad (3)$$

where \mathbf{d}_k is the component vector of the k^{th} component with unity concentration and \mathbf{R} is a matrix containing sensitivities to all components except to the k^{th} component.

The NAS of the k^{th} component may be used for concentration prediction of unknown samples using the previously derived equation:

$$c_{\text{un}} = \mathbf{d}_{\text{un}}^T \mathbf{d}_{\text{NAS}} / (\mathbf{d}_{\text{NAS}}^T \mathbf{d}_{\text{NAS}}) \quad (4)$$

By comparing Eqs. (1) and (4), the relation between the regression vector and the net analyte signal of the component of interest can easily be seen:

$$\mathbf{b}_k = \mathbf{d}_{\text{NAS}} / (\mathbf{d}_{\text{NAS}}^T \mathbf{d}_{\text{NAS}}) \quad (5)$$

Clearly, the regression vector \mathbf{b}_k is a part of the component vector (pure spectrum or voltammogram of the k^{th} component with unity concentration), which is orthogonal to the subspace spanned by the pure spectra of all other components, multiplied by a scaling coefficient $(\mathbf{d}_{\text{NAS}}^T \mathbf{d}_{\text{NAS}})^{-1}$.

In binary and/or ternary mixtures when the interferences are known, the \mathbf{d}_{NAS} can be calculated for analyte. The norm of this vector is proportional to the concentration of analyte, therefore this parameter was calculated before and after the addition of standard solutions of analyte and by using standard addition equations, the concentration of the analyte can be obtained. In other words, the norm of the NAS vector (\mathbf{d}_{NAS}) can be used to construct a univariate calibration model, where this parameter is plotted against the analyte concentration and a linear relationship is observed.

In this study, the standard addition method was used in order to eliminate calibration and prediction steps and the determination was realized in a single step. In addition, the other advantage of this method as compared with multivariate calibrations, such as principal component regression (PCR) and partial least squares (PLS), is the elimination of the necessity of choosing an optimum factor number during calibration.

Modeling

To demonstrate the analytical applicability of the proposed method for the analysis of binary mixtures, two voltammograms were created. The curves are two polarograms covering the potential range -200 to -700 mV *versus* the SCE reference electrode (Fig. 2A) and five percent random noise was added to the data. The polarograms after addition of standards from component X are shown in Fig. 2B. Also, the NAS curve for component X and Y are demonstrated in Fig. 2C and Fig. 2D, respectively. The norm NAS for component X versus the standard concentration is shown in Fig. 2E, from which the concentration of the unknown sample can be calculated from the intercept. In this case, the concentration of the unknown sample was 0.50 μM and the calculated amount was 0.52 μM .

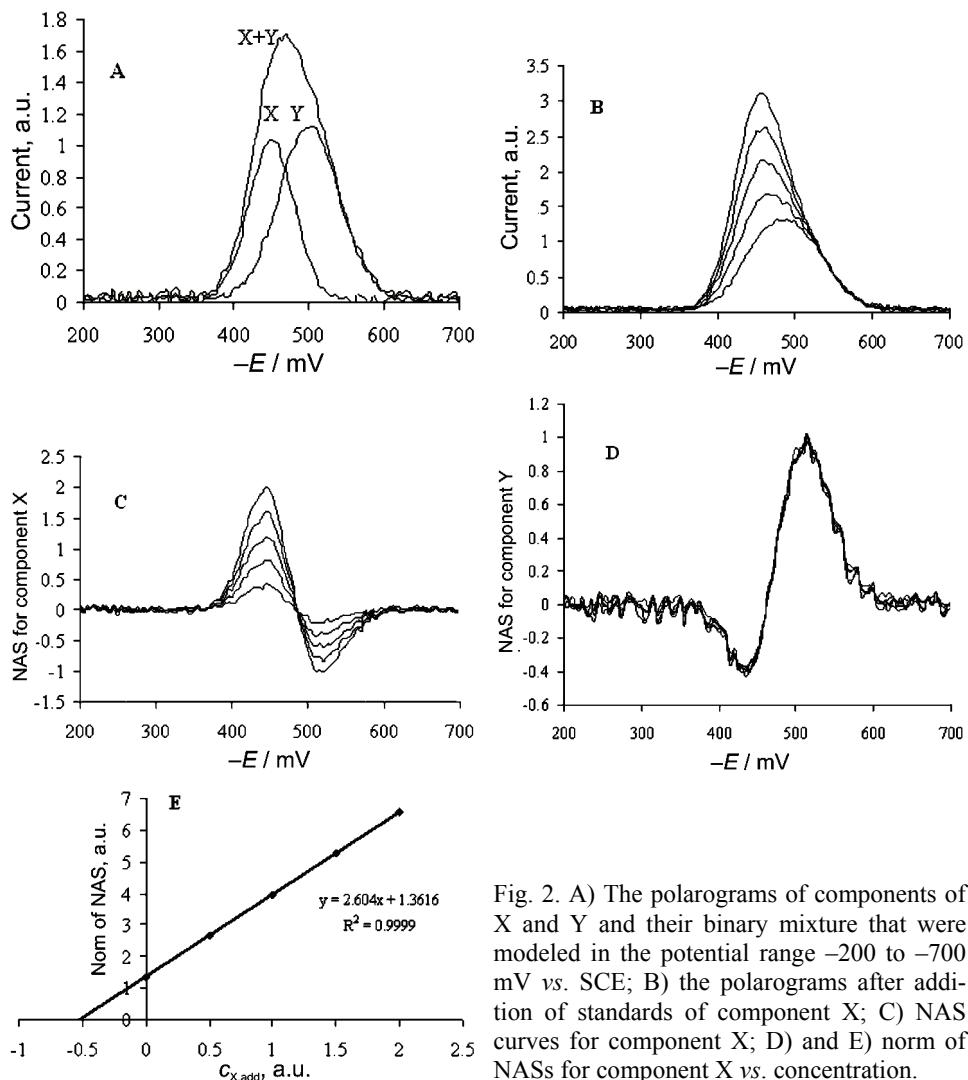


Fig. 2. A) The polarograms of components of X and Y and their binary mixture that were modeled in the potential range -200 to -700 mV vs. SCE; B) the polarograms after addition of standards of component X; C) NAS curves for component X; D) and E) norm of NASs for component X vs. concentration.

EXPERIMENTAL

Apparatus and software

The polarograms were obtained with a Metrohm 747 VA processor. A Metrohm 694 VA stand was used in the dropping mercury electrode (DME) mode. The three electrodes system was completed by means of a platinum wire as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode (both obtained from Azar Electrode Co., Urmia, Iran). All potentials in the text refer to the SCE. The pH measurements were performed by means of a Metrohm pH-Meter 691. Data of polarograms were firstly converted to an EXCEL file, in the next step they were converted to MATLAB format. All calculations were realized in MATLAB medium.¹⁹

Reagents

All reagents were of analytical/reagent grade and were used without further purification. A stock solution of Ni^{2+} (1.0×10^{-2} M) was prepared by dissolving 0.2910 g of the nitrate salt of Ni^{2+} in water and diluting to the mark in a 100 ml volumetric flask. A stock solution of Cd^{2+} (1.0×10^{-2} M) was prepared by dissolving 0.3080 g of the nitrate salt of Cd^{2+} in water and diluting to the mark in a 100 ml volumetric flask. Britton–Robinson buffer (pH 2.87) solution was prepared from phosphoric acid, acetic acid, boric acid and sodium hydroxide. Potassium thiocyanate solution (1.0 M) was prepared by dissolving 9.7200 g of crystals in water and diluting to the mark in a 100 ml volumetric flask. Doubly distilled water was used throughout. All experiments were performed at room temperature ($\approx 25^\circ\text{C}$).

Procedure

The analysis was performed by pipetting a suitable amount of a mixture of cadmium and nickel, together with 2.0 ml of Britton–Robinson buffer (pH 2.87) and 4.0 ml of potassium thiocyanate solution (1.0 M). Standard addition 1, 2, 3 and 4 ml of Cd^{2+} and Ni^{2+} (1.0×10^{-4} M) were individually carried out to the above solution (Figs. 3 and 4). The initial solution was purged with nitrogen gas for 330 s. The optimum values for the pulse amplitude potential, the drop time interval and the scan rate were -50 mV, 2 s and 2.0 mV s $^{-1}$, respectively. A computer sampled 150 data points in the range of -500 to -800 mV.

RESULTS AND DISCUSSION

Influence of effective variables

The effect of potassium thiocyanate concentration on the peak potential and peak current was investigated. The peak currents of both Ni^{2+} and Cd^{2+} reached their maximum with a potassium thiocyanate concentration of 0.40 M, but the potassium thiocyanate concentration in range 0.010 to 1.2 M had no significant effect on the peak potentials of Ni^{2+} and Cd^{2+} . Additionally, it was found that the best peak separation can be obtained with a potassium thiocyanate concentration of 0.40 M.

The effect of pH on the peak currents of Ni^{2+} and Cd^{2+} was investigated, whereby the maximum peak currents for both ions were obtained in pH 2.87, while the peak potentials did not change with increasing pH. Thus, a potassium thiocyanate concentration of 0.40 M and pH 2.87 were selected as a suitable medium.

Under the optimum conditions, the peak currents of the differential pulse polarograms linearly depended on the Cd^{2+} and Ni^{2+} concentrations. The differential pulse polarograms at different concentrations of Cd^{2+} and Ni^{2+} are shown in Figs. 3 and 4, respectively.

Plots of the peak current values as a function of the concentration were drawn. The plots were linear in the concentration range of 2.06×10^{-6} to 9.26×10^{-4} and 2.83×10^{-6} to 1.15×10^{-3} mol dm $^{-3}$ for Cd^{2+} and Ni^{2+} , respectively. Also, the norm of individual polarograms were plotted *versus* concentration and linearity was obtained (see Figs. 3 and 4, Insets B). The lack of bilinearity and additivity

of data are some of difficulties encountered in the application of multivariate calibra-

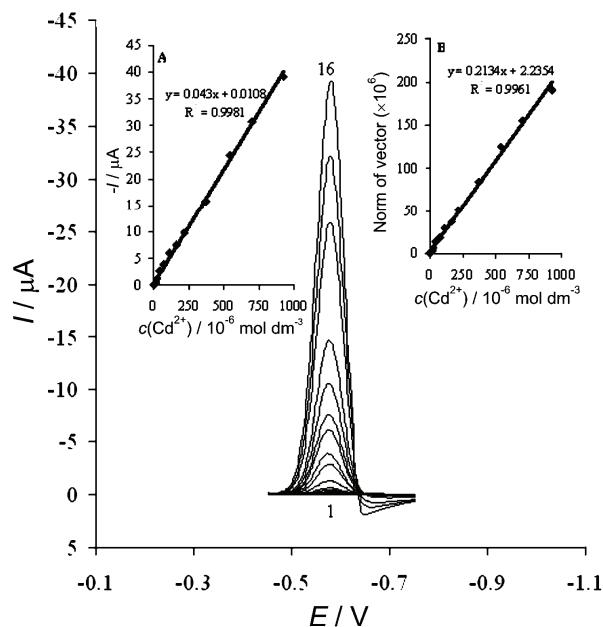


Fig. 3. DPPs for increasing concentrations of Cd^{2+} from 1) 2.60×10^{-6} to 16) 9.26×10^{-4} M in Britton–Robinson buffer (pH 2.87) and potassium thiocyanate (0.40 M) solution. Scan rate: 2 mV/s and modulation amplitude –50 mV. Insets: A) variation of the peak current vs. concentration of Cd^{2+} ; B) variation of the norm NAS for Cd^{2+} vs. concentration of Cd^{2+} .

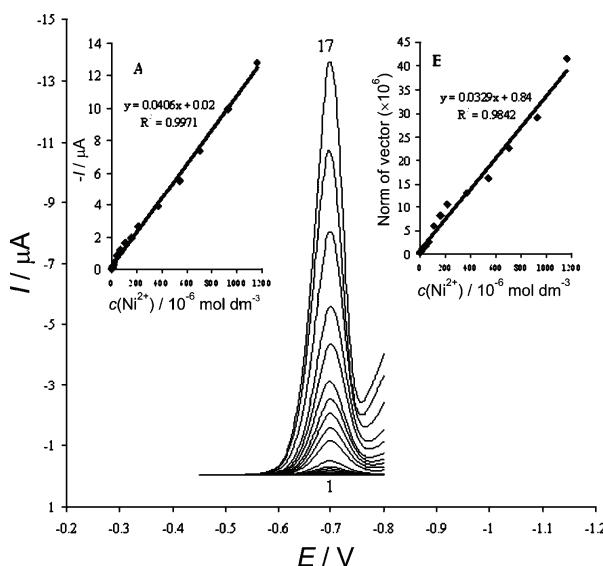


Fig. 4. DPPs for increasing concentrations of Ni^{2+} from 1) 2.83×10^{-6} to 17) 1.16×10^{-3} M in Britton–Robinson buffer (pH 2.87) and potassium thiocyanate (0.40 M) solution. Scan rate: 2 mV/s and modulation amplitude –50 mV. Insets: A) variation of the peak current vs. concentration of Cd^{2+} ; B) variation of norm NAS for Ni^{2+} vs. concentration of Ni^{2+} .

tion methods in voltammetric data analysis. Therefore, the linearity and additivity of the voltammetric responses was checked. In the absence of an intermetallic

effect, the measured current of the binary sample at each potential will be equal to sum of the individual samples. Therefore, to check the additivity of the currents, a polarogram of a mixture (Fig. 5) was compared with the sum of the voltammetric signals of Cd^{2+} and Ni^{2+} . It can be seen from Fig. 5 that is no difference in the two curves. This means that there is no analyte-analyte interaction and/or intermetallic effect during the reduction. Therefore, the position of the peaks and/or shape of the polarograms do not change with these effects.

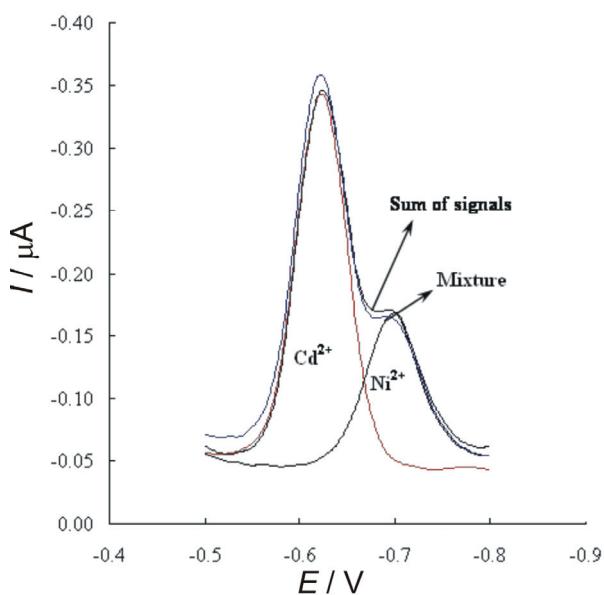


Fig. 5. DPP Ni^{2+} (10 μM) and Cd^{2+} (10 μM) and their mixture under theoretical (sum of the individual signals) and experimental (mixture) condition. Other conditions are as in Figs. 3 and 4.

NASSAM for determination of Ni^{2+} and Cd^{2+} in synthetic samples

The differential pulse polarograms of 10 μM Ni^{2+} and Cd^{2+} in Britton-Robinson buffer (pH 2.87) and potassium thiocyanate solution (0.40 M) in the range of -500 to -800 mV are shown in Fig. 6A, curve a, and after addition of known amounts of Ni^{2+} solutions in Fig. 6A, curves b to e. In this step, Ni^{2+} was considered as the analyte and Cd^{2+} as the interference. The part of the mixture polarograms that is orthogonal to the space of Cd^{2+} (*i.e.*, the NASs for Ni^{2+}) was calculated (see Eq. (3)) and their norms *versus* concentration are shown in the inset of Fig. 6A. The norm of the NAS vectors was attributed to the analyte concentration and only this changes with changes in the analyte concentration. Fig. 6B shows the same plots for the standard addition of Ni^{2+} . From these plots (Insets of Fig. 6A and B) and based on the equations of the univariate standard addition method, the concentrations of Ni^{2+} and Cd^{2+} in the solutions can be calculated.

Under optimum conditions, NASSAM was used for the determination of Cd^{2+} and Ni^{2+} in synthetic samples (the concentrations of the analytes were 10

μM). For three replicated experiments, the mean concentrations of Cd^{2+} and Ni^{2+} were found to be 10.4 and 10.3 μM , respectively.

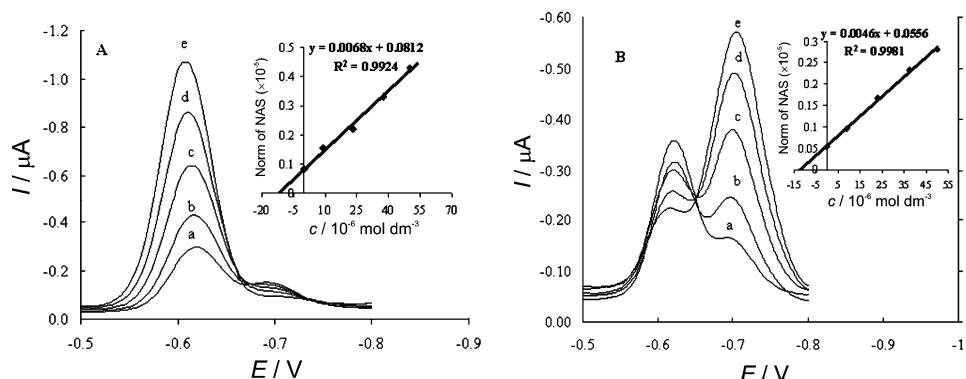


Fig. 6. A) DPP of unknown solution (curve a) and after addition of standard solutions (curves b–e) for the determination of Cd^{2+} . Inset: plot of norm NAS for Cd^{2+} vs. added standard concentration; B) same curves for Ni^{2+} . Conditions were as in Fig. 3 and 4.

Recovery of added metals

To determine the recovery of Cd^{2+} and Ni^{2+} , appropriate volumes of the standard solutions were added to the investigated samples. The results showed mean percentage recoveries of 103.4 and 104.0 % for Cd^{2+} and Ni^{2+} , respectively.

Interferences

By the present method, the concentration of species can be determined in the presence of recognized interferences. Under the experimental conditions, the polarogram of vanadate overlaps with those of nickel and cadmium. Therefore, nickel and cadmium were assayed in the presence of vanadate as an interfering agent (concentrations of the analytes and interferent were 10 μM). In the determination of nickel, the interferent space was constructed with cadmium and vanadate and for the determination of cadmium this space was constructed with nickel and vanadate. The obtained results showed that the presence of vanadate as an interfering agent had negligible effect on the accuracy of the simultaneous determination of nickel and cadmium and their recoveries were 96.8 and 106.4 %, respectively.

CONCLUSIONS

Quantification of Cd^{2+} and Ni^{2+} was accomplished from differential pulse polarography data by a novel method based on the net analyte signal and standard addition method. When the interferents are known, the part of the overlapping voltammograms orthogonal to the interferents space can be calculated as the

net analyte signal and this is attributed to the analyte concentration. Two popular multivariate calibration methods, *i.e.*, PCR and PLS, require that the optimum number of factors or principal components are selected. This selection may lead to overfitting and/or underfitting. In this study, a factor analysis method that does not require factor selection was developed. The proposed method is useful for the determination of analytes in mixtures by DPP without the need for a prior separation or special conditions to resolve the analytes waves. The proposed method is simple, inexpensive, precise and affordable; it also requires no complex pre-treatment. Hence, it is suggested for use in routine analysis of mixtures of analytes giving overlapped polarographic waves.

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ИЗВОД

“NET ANALYTE SIGNAL STANDARD ADDITION” МЕТОДА ЗА ИСТОВРЕМЕНО ОДРЕЂИВАЊЕ КАДМИЈУМА И НИКЛА

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У раду је описана нова “net analyte signal standard addition” метода стандардног додатка за истовремено одређивање Cd^{2+} и Ni^{2+} у смеши, применом диференцијалне пулсне поларографије. Метода обједињује предности методе стандардног додатка са концептом (нето сигнал анализа) што омогућује екстраховање информације која се односи на одређени анализ из волтамограма мултикомпонентних смеша. Метода има предности јер користи целе волтамограме, добијене у једном кораку, па стога не изискује калибрацију и предвиђање. За одређивање је потребно само неколико мерења. Истовремено одређивање Cd^{2+} и Ni^{2+} у смеши изводи се у присуству Britton-Robinson-овог пуфера (рН 2,87), 0,40 М раствора калијум-тиоцијаната.

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