APPLICATION OF MULTIVARIATE CALIBRATION IN THE SIMULTANEOUS DETERMINATION OF Cd AND In BY ANODIC STRIPPING VOLTAMMETRY

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ABSTRACT

The application of multivariate calibration methods to stripping voltammetry is reported. The ability of Partial Least Square (PLS) regression in the resolution of the overlapped peaks is illustrated in the simultaneous determination of cadmium and indium by differential pulse anodic stripping voltammetry. The results obtained in the analysis of synthetic mixtures were satisfactory.

INTRODUCTION

Stripping voltammetry is a very sensitive technique for measuring multiple electroactive species. However, in the analysis of complex samples the simultaneous determination of several components is at time difficulted by the occurrence of overlapped peaks. Several, chemical [1], instrumental [2] and mathematical [3] methods, have been employed to solve this problem.

Recently, multivariate calibration methods have been used in electroanalytical techniques with purpose to resolve the problem of overlapped peaks [4,5].

In this study, PLS method was applied to the simultaneous determination of In and Cd in synthetic samples from their overlapping voltammetrics signals.

EXPERIMENTAL

Voltammetric measurements were performed with a stand type EGMA (Tacussel). A three electrodes electrochemical cell was used: the hanging mercury drop electrode (HMDE) as working electrode, the Ag/AgCl electrode as reference electrode and a platinum wire as auxiliary electrode.

All experiments were carried out at room temperature.

Separate stock solutions of cadmium and indium were prepared by dissolving the

appropriate amounts of In and Cd metallic, in a minimum of HCl 1:1 and then diluting them with distilled water. All reagents used were of analytical grade.

The standard and artificial samples were prepared by mixing appropriate volumes of Cd and In stock solutions.

RESULTS AND DISCUSSION

Figure 1 shows the differential pulse anodic stripping voltammograms obtained in the analysis of separate solutions containing In or Cd as well as a mixture containing both In and Cd. The closeness between the Ep values for In and Cd give rise a complete overlapping of their peaks in a solution mixture, resulting only one peak. Therefore, the quantitative determination of the ions in a mixture solution by measuring the peak current (ip) is not possible.

In this case the simultaneous determination of In and Cd can be achieved using multivariate calibration methods, among which the PLS method is one of the most commonly used in quantitative analysis.

Fig. 1 – Differential pulse anodic stripping voltammograms of solution containing (a) Cd^{2+} (150 µg/L), (b) In^{3+} (150 µg/L) and (c) both Cd^{2+} and In^{3+} at same concentration (150 µg/L). $E_d = -1000$ mV vs Ag/AgCl; $t_d = 60$ s; Pulse height = 50mV; Scan rate = 5 mV/s; Supporting electrolyte: HCL 0.1M.

PLS

In this work the PLS method was used to develop a calibration model that relates the voltammetric data with ions concentration.

PLS calibration comprises two steps: calibration and prediction. In the calibration step the relationship between the analytical signal and component concentration is established. In the prediction step the results of the calibration are used to estimate the component concentration from the unknown sample.

A set of mixtures is prepared and their composition is represented by matrix Y, with m rows (number of mixtures) and l columns (number of components). The voltammetric signals was described by a matrix X with m rows (each row correspond a voltammogram of a standard) and k columns (each column correspond to the current intensities values of all the standards at a certain potential).

Calibration by the PLS method involves the decomposition of X and Y matrices into product of two smaller matrices [6,7]:
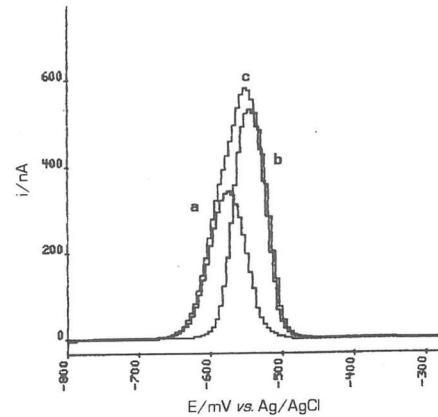
$$X(m,k) = T(m,a)\ P(a,k) + E(m,k) \tag{1}$$

$$Y(m,l) = U(m,a)\ Q(a,l) + F(m,l) \tag{2}$$

where $T(m,a)$ and $U(m,a)$ are the scores matrices, $P(a,k)$ and $Q(a,l)$ are the loadings matrices, while $E(m,k)$ and $F(m,l)$ are corresponding residual matrices; a is the number of principal components or factors.

The aim of this decomp or "data compression" is to select only the useful information – described by the factors – required to obtain optimal predictions.

However, the Equations (1) and (2) are related by the following equation:

$$u_h = b_h\, t_h$$

where b_h are the regression coefficients for each principal component. A prediction equation is obtained by replacing U in Eq. 2 by TB:

$$Y' = TBQ$$

CALIBRATION

In order to establish the calibration model, a training set of nine standards were prepared containing different amounts of In and Cd in the concentration range of 0 to 250 µg/L. The composition of the training set is given in Table 1.

The voltammograms of each standard were recorded and digitized, every 4 mV, in the potential range between -700 and -452 mV, resulting 63 experimental points per voltammogram. This potential region was selected because it contains the useful analytical information.

A vector Y (9x1) and a matrix X (9x63), respectively, were constructed with this experimental data and the calibration was carried out by applying the PLS algorithm, included in the Unscrambler [8].
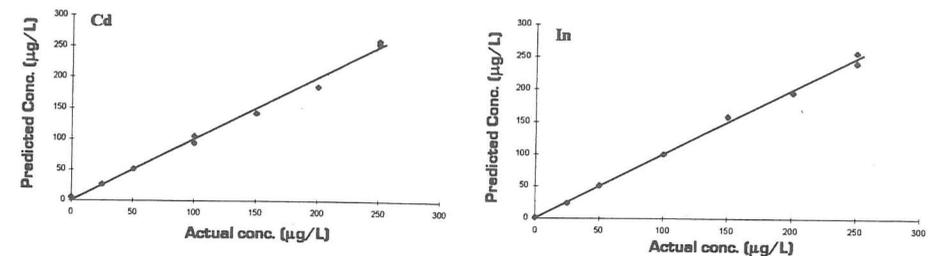
Table 1 – Training set composition

Mixtures	Cd²⁺(µg/L)	In³⁺(µg/L)
1	100.8	200.6
2	25.0	100.5
3	50.1	25.3
4	200.2	250.6
5	100.7	100.2
6	150.7	50.2
7	250.4	150.3
8	150.2	0
9	0	150.2

Fig. 2 – Predicted vs. actual concentration plots for the training set.

The quality of the calibration model obtained, was evaluated by plotting the predicted concentrations against the actual concentrations for each standard (Fig. 2). The correlation coefficients found by PLS model, with 2 factors, are 0.996 and 0.998 for calibration of Cd and In, respectively, indicated a good agreement between the actual and predicted concentrations.

APPLICATIONS

The calibration model was applied to the determination of In and Cd in artificial samples in order to verify its predictive ability. The results obtained are summarized in Table 2.

Table 2 – Simultaneous determination of In and Cd in artificial mixtures.

Artificial Mixtures	Cd²⁺ (µg/L) Actual	Cd²⁺ (µg/L) Predicted	Relative Error (%)	Recovery (%)	In³⁺ (µg/L) Actual	In³⁺ (µg/L) Predicted	Relative Error (%)	Recovery (%)
I	50.0	54.4	8.8	108.8	150.1	146.1	-2.7	97.4
II	100.2	107.9	7.7	107.7	200.2	195.7	-2.2	97.7
III	100.0	95.6	-4.4	95.6	25.0	21.2	-15.2	84.8
IV	247.8	229.2	-7.5	92.5	0	-1.0	—	—
V	150.0	150.1	0.1	100.1	49.9	49.8	-0.2	99.8

The results indicate that the magnitude of the error depends greatly on the relative amount of each component in the mixture: the error is large for the minor component amount.

On the other hand, high relative errors are observed in the determination of Cd. This is probably due to the relatively large differences in sensitivity of the analytical signal. Because the sensitivity of the voltammetric peak of Cd is smaller than that of In (Fig. 1), the contribution of Cd for the overall analytical signal is, in some way, masked by the In.

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EFFECT OF THE TEMPERATURE ON THE RESPONSE OF ALL-SOLID-STATE NONACTIN AMMONIUM ISE's WITH PVC MEMBRANES APPLIED TO GRAPHITE FILLED EPOXY SUPPORTS

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ABSTRACT: Preliminary results of a study of the effect of the temperature on the response of all-solid-state ammonium ISE's prepared by casting PVC membranes with nonactin on supports of graphite/epoxy composites with up to 60% of graphite are presented. The study showed that: (i) the conductive suppport must contain at least 40% of graphite to produce ISE's with adequate response characteristics; and (ii) the variation of the percentage of graphite between 40 and 60% has no influence on the slope and potential temperature coefficients and on the hysteresis curves of the electrodes.

RESUMO: Apresentam-se resultados preliminares do estudo do efeito da temperatura na resposta de eléctrodos selectivos sensíveis a catião amónio construídos por aplicação de membranas de PVC, com sensor de nonactina, sobre suportes condutores constituídos por misturas de grafite com uma resina epoxídica, com percentagens de grafite até 60%. Este estudo mostrou que: (i) o suporte condutor deve conter pelo menos 40% de grafite para se obterem ESI's com características de resposta adequadas; e (ii) a variação da percentagem de grafite no suporte condutor entre 40 e 60%, não influencia os coeficientes térmicos de declive e de potencial nem as curvas de histerese dos eléctrodos.

KEYWORDS: Temperature properties; conductive epoxy electrodes; all-solid-state electrodes; ammonium nonactin PVC electrodes; graphite/epoxy composite.

INTRODUCTION

The differentiation with respect to the temperature of the response equation of an ion selective electrode (ISE) shows that the effect of the temperature on the electrode response is intrinsically complex [1]. Moreover, when all-solid-state ISE's are considered, the variety of processes involved both in the inner set of solid conductors and in the membrane/support interface isresponsible for further complexity. Indeed, previous work [2 and references therein] showed that the effect of the temperature on the response of all-solid-state ISE's with conductive epoxy supports depends on a large variety of factors, for instance, the type of membrane, the nature of the internal contact, the metal used as conductive filling of the epoxy, the sensor system, etc. The purpose of such work was to improve the construction procedure of electrodes with conductive epoxy supports to bring the concentration of the isopotential point into the operational range. This purpose was not reached because the

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