SIMULTANEOUS DETERMINATION OF LEAD, THALLIUM AND INDIUM MIXTURES BY ANODIC STRIPPING VOLTAMMETRY USING CHEMOMETRIC METHODS

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Abstract

The simultaneous determination of Tl, In and Pb by differential pulse anodic stripping voltammetry was carried out using multivariate calibration methods. The ability of this methodology to overcome the problem of overlapping signals is demonstrated. The method was applied to analysis of ternary mixtures of these ions with successful results.

Key words: Multivariate calibration; voltammetric analysis; overlapping signals.

Introduction

Chemometric methods, namely multivariate calibration methods, have been applied to electroanalysis to perform the quantitative determinations of several electroactive species when overlapping signals are observed [1-3].

In general, the application of multivariate calibration in voltammetry involves the preparation of a set of calibration mixtures with known concentrations of the elements under study. The voltammograms of each mixture are measured and multivariate calibration techniques are employed to construct a calibration model; this model is subsequently used to predict the concentration of unknown mixtures from their voltammograms.

The aim of this work is to investigate the performance of multivariate calibration in the simultaneous determination of Tl, In and Pb by anodic stripping voltammetry.

Material and Methods

Reagents

All reagents were of analytical grade (Merck) and all solutions were prepared with deionized water. Stock solutions of Pb(II), Tl(I) and In(III) were prepared from $Pb(NO_3)_2$, $TlNO_3$ and $InCl_3$, respectively. Calibration and synthetic mixtures were prepared by dilution of these stock solutions.

Apparatus and software

Voltammetric measurements were made with a polarographic analyser type EGMA (Tacussel) equiped with a hanging mercury drop electrode (HMDE) as working electrode, an Ag/AgCl (in 3M KCl) electrode as reference electrode and a platinum wire as auxiliary electrode.

The voltammograms were digitized with a software UN-SCAN-IT v3.0 [4], and the calculations associated to the multivariate calibration techniques was performed with UnscramblerII v3.5 [5].

Chemometric methods

In this study three chemometric methods are discussed: partial least square regression (PLSR-1 and PLSR-2), and principal component regression (PCR). PLSR and PCR methods use all information of the analytical signal to define a subset of variables (designed by factor or principal components) which extract the most relevant chemical information to build a calibration model. The main difference between those methods lays in the different way to select the principal components.

The chemometric methods employed are described in the detail elsewhere [6,7]. Only a brief description will be given here. Nomenclature adopted in this work: capital, italic bold face letters are used for matrices, small italic bold letters are used for vectors and small italic characters are used for scalars. The number of samples, components, potential values and factors are denoted by m, l, k and a, respectively.

Principal Component Regression (PCR) [8-10]

The PCR method is a two step process. The first step consists in the determination of the number of principal components, using the principal component analysis method. This information is used to decompose the voltammetric-response data X matrix into the product of two smaller matrices:

$$X(m,k) = T(m,a)\, P(a,k) + E(m,k) \tag{1}$$

where T is the score matrix, P is the loading matrix and E is the residual matrix.

The second step involves a multilinear regression between the concentration matrix, Y, and the score matrix, T, to calculate the matrix of regression coefficients, B:

$$Y(m,l) = T(m,a)\, B(a,l) + E'(m,l) \tag{2}$$

Matrix B is used to estimate the unknown concentration for a given voltammogram:

$$y' = x\, P'\, B \tag{3}$$

where P' (transpose of matrix P) and B can be obtained from the calibration process, x is the voltammogram of the unknown mixture and y' the estimated concentration.

Partial Least Square Regression (PLSR) [8-10]

The PLSR method uses the information of matrix X and matrix C to estimate the number of factors. In this method the decomposition of matrix X and matrix C is performed simultaneously:

$$X(m,k) = T(m,a)\, P(a,k) + E(m,k) \tag{4}$$

$$Y(m,j) = U(m,a)\, Q(a,j) + F(m,j) \tag{5}$$

where U and Q are the score and loading matrices of Y and F is the residual matrix.

The number of factors are determined in such way that maximize the correlation between the two matrices. Thus regression coefficients, b, for each factor, h, are obtained from the equation:

$$u_h = b_h\, t_h \tag{6}$$

A prediction equation is obtained by replacing U in the Eq. (5) by TB:

$$Y' = TBQ \tag{7}$$

There are two versions of the PLSR algorithm: PLSR-1 and PLSR-2. The PLSR-1 performs the decomposition and regression for only one analyte at a time so the method estimates a calibration model for each analyte under study. The PLSR-2 uses all analytes simultaneously.

Results and Discussion

Typical voltammograms of separate solutions containing Pb(II), Tl(I) or In(III) as well a mixture containing the three ions are shown is Fig. 1.

As can be seen the closeness between the E_p originates a strong overlapping of the peaks hindering simultaneous determination of Pb(II), Tl(I) and In(III) in mixtures by differential anodic stripping voltammetry.

Therefore, to overcome the lack of selectivity, the analysis of ternary mixtures of these ions was carried out by multivariate methods.

The first step in the simultaneous determination of these ions by multivariate calibration methodology
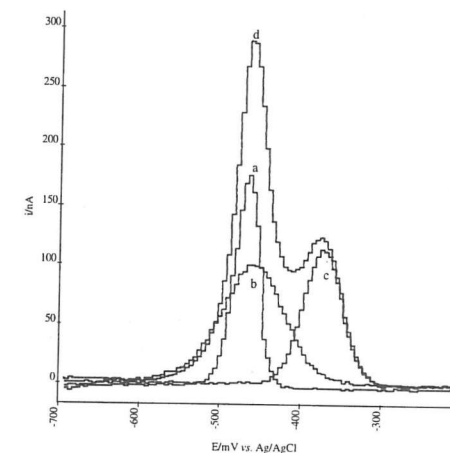

Fig. 1 – Differential pulse anodic stripping voltammograms of solution containing (a) In³⁺ (50 µg/L), (b) Tl⁺ (100 µg/L), (c) Pb²⁺ (60 µg/L) and (d) Pb²⁺ + In³⁺ + Tl⁺ at indicated concentrations. E_d = -900 mV *vs.* Ag/AgCl; t_d = 60 s; Pulse height = 50 mV; scan rate = 5 mV/s; Supporting electrolyte: HNO₃ 0.1M

involves the preparation of a training set.

Fig. 2 illustrates experimental design and composition of the calibration mixtures used to prepare the training set.

In this study the training set is formed by thirteen standard mixtures in the following concentration ranges: 50-200, 25-175 and 50-200 µgL^{-1} for Pb, In and Tl, respectively.

The voltammograms obtained for each mixture were digitized in the potential range from -630 to -290 mV, resulting 69 points per voltammogram. From these data two matrices are built: the information about voltammetric signals was represented in a X(13x69) matrix (each row corresponds to a voltammogram of a standard mixture and each column correspond a standard mixture and each column correspond

Fig. 2 – Training set experimental design.
● - calibration mixtures; ○ - synthetic mixtures
Number in parenthesis correspond to the concentration
of Pb, In and Tl (µgL^{-1}) in the mixtures

to the current intensities values at same potential) and the composition was collect in a Y(13x3) matrix (each row corresponds to the number of standard mixtures and each column corresponds to the number of analytes).

The three multivariate calibration methods were used to develop calibration models that related the voltammetric data with ion concentrations.

One important step in the construction of a calibration model is the determination of the number of factors which ensures the minimum prediction error. From the various criteria available to select the optimum number of factors we used the cross validation method [11]. The optimum number suggested by the program Unscrumbler II [5] on the basis of a minimum for the y-residual variance for each case is indicated in Table 1.

Resolution of Synthetic Mixtures

A set synthetic mixtures containing the three ions in variable proportions was prepared and analysed in order to compare the performances of PCR, PLSR-1 and PLSR-2 in the simultaneous determination of Tl, Pb and In.

Table 1 shows the results obtained in the analysis of the synthetic mixtures using the three proposed methods. The precision of each multivariate calibration technique is expressed here in terms of relative standard error of prediction (RSEP):

$$RSEP(\%) = \sqrt{\frac{\sum_{1}^{N}(C_{found} - C_{added})^2}{\sum_{1}^{N}C_{added}^2}} \qquad (8)$$

where C_{found} is the concentration estimated from the model, C_{added} is the concentration present in the mixture and N is the number of mixtures.
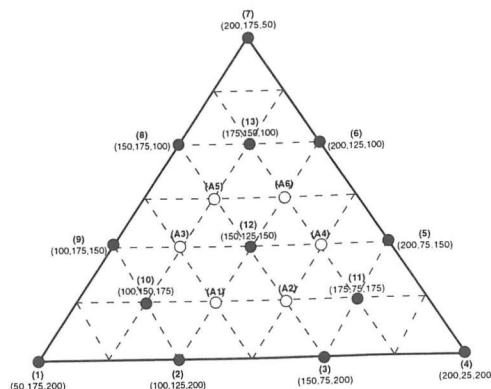
Table 1 – Results obtained for the simultaneous determination of Pb, In and Tl in different synthetic mixtures using PLSR-1, PLSR-2 and PCR

Added Concentration (µgL^{-1})			Estimated Concentration by PLSR-1 (µgL^{-1})			Estimated Concentration by PLSR-2 (µgL^{-1})			Estimated Concentration by PCR (µgL^{-1})		
Pb	In	Tl	Pb	In	Tl	Pb	In	Tl	Pb	In	Tl
126.0	135.3	175.8	121.9	137.2	179.8	127.4	141.2	170.0	124.9	141.2	173.5
151.9	108.2	175.8	152.7	107.3	176.7	152.9	104.4	178.9	152.8	104.2	179.1
126.1	162.7	150.8	134.1	153.0	156.4	130.6	162.1	140.6	135.3	162.1	142.4
176.2	108.6	151.8	171.8	109.6	153.3	173.4	116.0	148.2	177.0	116.0	144.3
150.8	162.7	126.2	143.5	165.5	130.6	152.1	181.5	108.1	146.1	181.5	114.2
176.0	135.7	125.7	195.7	136.9	104.3	196.0	129.8	111.2	198.9	129.8	107.8
RSEP (%)			6.2 (4)	3.1 (5)	6.2 (4)	6.1 (5)	6.6 (5)	7.1 (5)	6.7 (5)	6.6 (5)	6.6 (5)

Values in parenthesis are the number of factor.

The results obtained indicate a reasonable agreement between the concentration added and the concentration estimated by the three methods. However a closer inspection of individual results shows some discrepancy which can be attributed to the relative contribution of each ion to the overall analytical signal: because a strong overlapping of peaks is observed that contribution is important and, in general, the prediction of the minor component is estimated with the largest errors. The values of RSEP show that there are no significant differences in the precision of PLSR-1, PLSR-2 and PCR in the resolution of ternary mixtures.

Conclusions

The performance of PCR, PLSR-1 and PLSR-2 was compared in the determination of Tl, Pb and In in mixtures. Results indicated that multivariate calibration techniques can be a practical alternative procedure for multielementar voltammetric analysis when there is strong overlapping of peaks. Both techniques PLSR and PCR predicted the concentration of Pb, In and Tl in different mixtures with reasonable agreement.

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