

# Multielement Determination in Voltammetry using Flow Injection Generated Reagent Gradient and Multi-Way PLS

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## Abstract

A system for continuous flow analysis with a voltammetric detector was developed, employing a multichannel polarograph, capable of operating with an assembly of 31 working ultramicroelectrodes (UMEs).

The flow analysis system was based on the development of an EDTA gradient on a line containing the support electrolyte and Pb(II), Cd(II) and Tl(I) ions. With the differential complexation of each ion, promoted by the EDTA gradient, differentiations in the voltamograms were observed, which makes possible the use of a multivariate calibration, since the investigated ions presented overlapping voltammetric waves.

**Keywords:** Flow voltammetry, three way PLS, Tl, Pb and Cd.

## 1. Introduction

Hydrodynamic voltammetry is the use of voltammetric and amperometric techniques in a flow of electroactive analytes in such a way to maintain the electrode work on conditions of convection and diffusion well defined [1].

When the electrodes in an array have their size reduced from millimeter to micrometer dimensions, the electrochemical behavior shows improved characteristics [2, 3]. However, it is important to point out the lower capacitive current, smaller ohmic drop and faster achievement of mass transport in a stationary diffusion state, followed by a higher current density, compared with electrodes of conventional size [4].

In this present work, a multichannel polarograph [2] and a set of microelectrodes working with a flow parallel to the their surface was proposed to increase the information available for multivariate calibration in voltammetry by inducing a reaction between the analytes and a gradient of a reagent produced in a flow injection manifold. The products of such reaction are not electroactive in the potential range scanned or are active only in a potential value different from that one of the free analyte. Therefore a third dependence parameter is established in relation to the voltammetric response and multivariate calibration is performed in a three dimensional space (current vs potential vs time).

## 2. Experimental

### 2.1. Reagents and standard solution

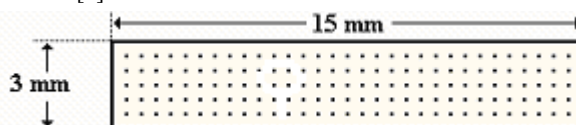
Analytical reagent grade chemicals and freshly distilled, deionized water were employed throughout. Lead(II), cadmium(II) and thallium(I) solutions were prepared respectively from 5.0 mmol l<sup>-1</sup> stock standard solutions in 1.0 mmol l<sup>-1</sup> HNO<sub>3</sub> solution. Acetate buffer solution (pH 4.85) was prepared from 0.1 mol L<sup>-1</sup> acetic acid and 0.1 mol l<sup>-1</sup> sodium acetate solution. A 0.05 mol l<sup>-1</sup> EDTA stock solution and a 0.01 mol l<sup>-1</sup> Hg(II)

solution in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub> were prepared.

### 2.2. Electrode array

Electrical isolation and mechanical stability of the array were achieved by encasing the array in a polyester resin placed in a rectangular container and cured for 24 h. The distances between adjacent electrodes in the array were set to 10 times their diameter. Figure 2 shows the constructed electrode array. An array made of 31 individual copper wires was arranged in a rectangular format, the arrangement was assembled employing sub-arrays of five copper wires per electrode, each with a diameter of 55 μm, as shown in the figure 1. At one end, the five wires of each sub-array were joined and welded to a male Alphicon type 36-way connector to allow the electrodes to be accessed independently by the multichannel instrument. So, an arrangement of 31 electrodes was mounted so that each electrode is formed by 5 sub-electrodes, giving a total of 155 electrodes.

The array was polished using abrasives of decreasing particle size. The last two ones were alumina of 1.0 and 0.3 mm. The exposed surfaces of the copper wires (discs) were washed with deionized water, immersed in 60% v/v phosphoric acid solution for 1 min and washed again with deionized water. Immediately, the array was immersed during 10 min in a Hg(NO<sub>3</sub>)<sub>2</sub> solution, which allows a spontaneous mercury film deposition on the 155 copper discs of the array. The array was stored in a 0.001 mol l<sup>-1</sup> HNO<sub>3</sub> solution (oxygen free). Before the use, the array was submitted to 60 voltammetric cycles applying a potential in the range of 0.2 to -1.2 v at a 100 mv s<sup>-1</sup> scan rate in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub> solution to homogenize the mercury film on the copper substrate [2].



**Figure 1.** View of the spatial distribution of the copper microelectrodes. Five copper wires are joined to each electrode

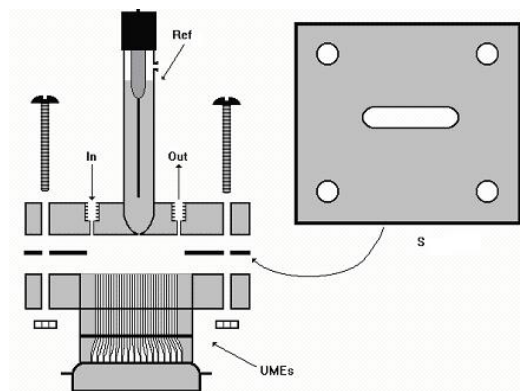
of the 31 ones present in the array.

### 2.3. Instrumental

Figure 3 shows the flow manifold employed. Under computer control, 200  $\mu\text{l}$  of a 0.05  $\text{mol l}^{-1}$  EDTA solution in an acetate buffer (pH=4.85) is introduced by a sampling device constructed with four electromechanical Teflon<sup>®</sup> micro-valves ( $V_1 - V_4$ ).

An EDTA sample solution is carried out to a magnetically stirring gradient chamber (acrylic made, volume of 1.5 ml) by an acetate buffer solution. In the chamber, the solution is mixed to sample solutions containing Pb(II), Cd(II) e Tl(I) ions in a 0.01  $\text{mol l}^{-1}$   $\text{HNO}_3$  solution (Table 1), which are continuously pumped. The solutions were pumped at 1.0  $\text{ml min}^{-1}$  and were deoxygenated by a  $\text{N}_2$  stream. The chamber generates a EDTA gradient and the voltammetric scan is performed in the range of -0.25 to -0.85 v against Ag/AgCl reference electrode, using the differential pulse voltammetry, with pulse width of 50 ms and height of 50 mv, with the scanning speed of 175  $\text{mv s}^{-1}$ . The flow cell with the array of ultramicroelectrodes has an inner volume of 30  $\mu\text{l}$ .

All electrodes are connected together and a home-made voltammetric multichannel electrode instruments were employed [2]. After 15 s of interval of EDTA solution injection, 80 scans were performed every 2 s, over the gradient flowing through the flow cell. The waiting time ensures that the concentration of EDTA had reached its maximum and the 80 scans were obtained in the decreasing gradient concentration of the tail. The total time for acquisition of the 80 voltammograms, counting the waiting time and the time of each voltammogram was in the order of 450 s (7.5 min).



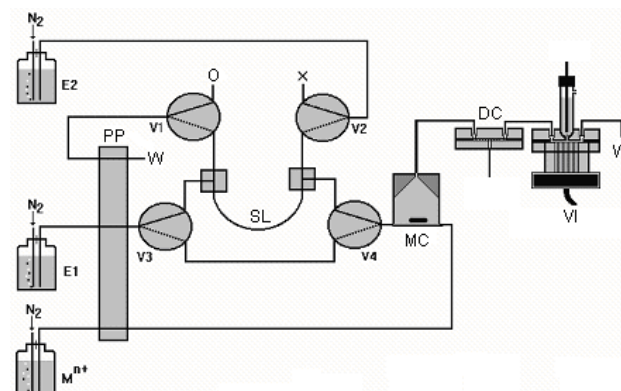
**Figure 2.** Multiple electrode set as a laminar flow cell; S: Rubber tab with thickness of 0.5 mm; Ref: Ag/AgCl reference electrode; UMEs: Set of ultramicroelectrodes.

An IBM PC standard compatible computer was used to control the functions of the instrument and to do the data acquisition, using a program developed in Quickbasic 4.5. The data chemometric analysis was done using the two and three way PLS programs [5, 6] available in the Chemometric ToolBox 3.0 package [7], which operate in MatLab [8].

### 3. Results and Discussion

Voltammetric data were obtained to 31 different values of potential equally spaced. The moving average is calculated between five consecutive points and applied to improve the presentation of the voltammograms, the central value has weight

three, its two closest neighbours have weight two and the most



**Figure 3.** Flow analysis system. E1: Acetate buffer solution, E2: EDTA solution in acetate buffer solution;  $M^{n+}$ : Solution of Pb(II), Cd(II), Tl(II),  $V_1, V_2, V_3, V_4$ : Solenoid valves of teflon; W: Waste; PP: Peristaltic pump; MC: Mixture chamber; O: Connection of the opened  $V_1$  valve; X: Connection of the closed  $V_2$  valve; VI: Connection of the cell with the UMEs arrangement and the Ag/AgCl reference electrode to the voltammetric instrument; DC: Degassing chamber; SL: Sampling loop of 200  $\mu\text{l}$ .

**Table 1.** Experimental Planning for the standard mixtures of Pb(II), Cd(II) e Tl(I).

Sample	Concentration ( $\mu\text{g mL}^{-1}$ )		
	Pb(II)	Cd(II)	Tl(II)
1	80.00	10.00	10.00
2	10.00	80.00	10.00
3	10.00	10.00	80.00
4	32.50	10.00	57.50
5	57.50	10.00	32.50
6	57.50	32.50	10.00
7	32.50	57.50	10.00
8	10.00	57.50	32.50
9	10.00	32.50	57.50
10	26.50	26.50	47.00
11	40.00	20.00	40.00
12	47.00	26.50	26.50
13	40.00	40.00	20.00
14	26.50	47.00	26.50
15	20.00	40.00	40.00
16	33.33	33.33	33.33

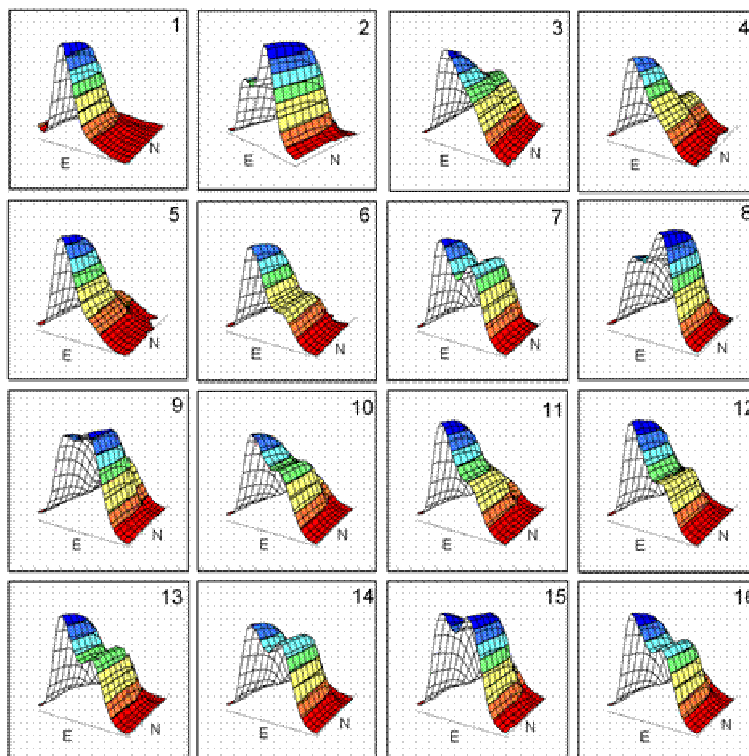
distant has weight one [9]. The mathematical relations are:

$$I_m = (i_{n-2} + 2i_{n-1} + 3i_n + 2i_{n+1} + i_{n+2}) / 9$$

where:

$$I_m = \text{Estimated current values}$$

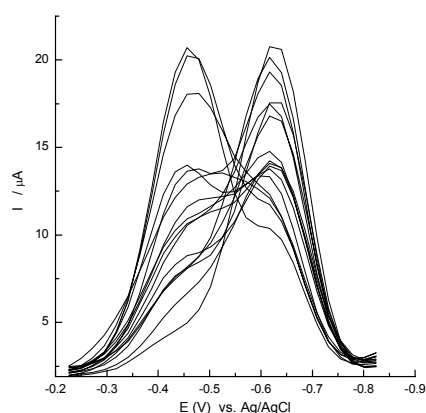
$$i_n = \text{Found current values}$$



**Figure 4.** Voltammograms of Pb(II), Cd(II) and Tl(I) mixtures in acetate buffer support electrolyte in an EDTA gradient, as the experimental planning. E: Potential (v) vs Ag/AgCl; N: Scan number (0 to 80).

Thus, all matrices of data presented 27 values of current after this operation for each voltammogram.

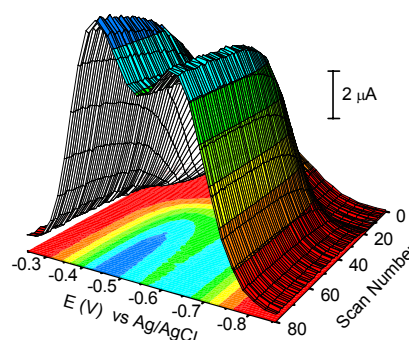
The voltammetric readings for the 16 mixtures (Table 1), taken in duplicates, used in the multivariate calibration for the two and three way PLS, were performed in a random order. In the first case, the last voltammogram of the set of 80 potential scans in the EDTA gradient for each sample was used. The results of the voltammetric readings for these mixtures, in an EDTA gradient, can be seen in the figure 4, and the last scan of each mixture can be seen in the figure 5. The figure 6 shows in more details the voltammograms of one of the mixtures used in the experimental planning.



**Figure 5.** Scan number 80 for each of the 16 experimental planning mixtures.

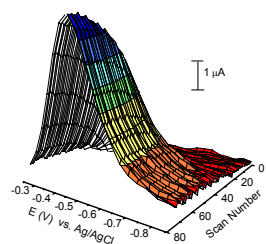
Previous readings showed that the current peaks for Pb(II), Tl(I) and Cd(II) occur, respectively, in the potentials of -0.45 v, -0.57 v and -0.62 v (Figures 7, 8 and 9). The differences in

potential peak for the three species are small, so, there is an overlap of the voltammograms of Tl(I) with Cd(II) and Tl(I) with Pb(II), what results in non-differentiated responses of the three, in the absence of the EDTA gradient. This fact makes impossible the simultaneous determination of these ions when in mixtures without use of chemometric calibration techniques. The EDTA gradient improves the differentiation which along with the techniques of multivariate calibration leads to the achievement of better results.

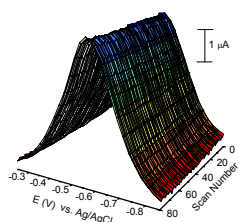


**Figure 6.** Voltammograms of the mixture number 14, in acetate buffer support electrolyte, in an EDTA gradient.

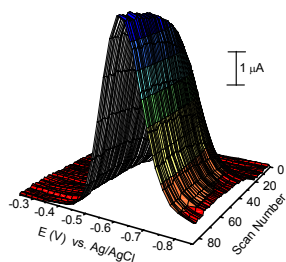
As the complexation constants of the studied ions, Pb(II), Cd(II) and Tl(I) with EDTA, the order that the complex appears can be inferred, or in the specific case of this experiment, the order in which them disappear. In the case of Tl(I), in this pH value, there is no apparently complexation and thus the voltammetric wave to this ion remains constant throughout the created gradient (Figure 8). For the cases of Pb(II) and Cd(II)



**Figure 7.** Voltammograms of Pb(II) solution  $60 \mu\text{g mL}^{-1}$ , in acetate buffer support electrolyte, in an EDTA gradient.



**Figure 8.** Voltammograms of Tl(I) solution  $60 \mu\text{g mL}^{-1}$ , in acetate buffer support electrolyte, in an EDTA gradient.



**Figure 9.** Voltammograms of Cd(II) solution  $60 \mu\text{g mL}^{-1}$ , in acetate buffer support electrolyte, in an EDTA gradient.

ions, as the complexation constant with EDTA for Pb(II) is greater than the one for Cd(II) [9], there is a first decomplexation for cadmium (Figure 9) followed for lead (Figure 7).

With the differentiation in the complexation degree of the three species as a function of the variable EDTA concentration created by the gradient, it is possible to improve the individual determinations of the species in a mixture using the three way PLS. For this, not only the data of a voltammogram in a defined EDTA concentration or in its absence is used, but all voltammograms in various EDTA concentrations in the created gradient.

The set of 16 Pb(II), Cd(II) and Tl(I) standard mixtures, according to the experimental planning (Table 1) generated the total of 16 matrices, 27 values of current obtained in function of the potential versus 80 scans, or 2160 values of current for each standard; these matrices combined resulted in a matrix 16 (number of mixing standards) vs 2160 (potential vs number of scans in an EDTA gradient) with a total of 34.560 values of current, used in the three way PLS.

Besides the greater volume of information in this case related to the bidimensional case, the power of differentiation between species increases with the differentiation of the voltammograms in EDTA gradient.

The obtained results, according to table 2, attest to a great improvement for the calibration using the three-way PLS in relation to the two-way PLS, for the three studied ions, in the concentrations of the table 1, using cross-validation.

#### 4. Conclusions

The results show that the EDTA gradient is effective in generate the complexes for Cd(II) and Pb(II) in different intervals of time due the differences in their stability constants. On the other hand, Tl(I) does not react with EDTA at the pH employed and its voltammetric signal remains practically constant over the entire data acquisition process.

Two and three-way PLS program were employed for multivariate calibration in order to observe the contribution of the multidimensional approach to the multielement determination of Pb(II), Cd(II) and Tl(II). The results show a substantial reduction in the REP for the three elements obtained by using the three-way PLS when compared with the two-way PLS elements obtained by using the three-way PLS.

**Table 2.** Implementation of the PLS for the set of 16 standard mixtures using cross-validation.

Ion	PLS			
	Two way		Three Way	
	R *	REP (%) **	R	REP (%)
Cd(II)	0.828	33.02	0.978	12.30
Pb(II)	0.970	14.17	0.994	6.42
Tl(I)	0.906	24.73	0.997	4.12

(\*) R: Correlation coefficient; (\*\*) REP: Estimate average error.

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