



Voltammetric behavior of Pb(II), Tl(I) and Cd(II), in gradient of EDTA in continuous flow by Evolving Factors Analysis

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ABSTRACT: The fundamental idea of Evolving Factor Analysis is to follow the evolution of the weights of a data matrix, in this case the concentrations of Cd(II), Tl(I) and Pb(II) as a function of an ordered variable, which is the EDTA gradient. The mixture of Cd(II), Tl(I) and Pb(II) is not easily resolved by voltammetry as the peak potentials are close together and thus the voltammograms overlap considerably. As the complexations of these ions with EDTA are different, it is possible to obtain differences in the data. So scans were made with the differential pulse technique, in a system in flow where there is variation in the concentration of EDTA. It was possible to observe the presence of three species in the EDTA gradient, confirming the possibility of quantification by multivariate calibration.

KEYWORDS: Voltammetry, Heavy metals, Factor analysis, Flow analysis.

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I. INTRODUCTION

Extracting information from the results of an experiment very often involves the analysis of a considerable number of variables. Often a small number of these variables can contain a lot of chemical information, while most add little or nothing to what is interpreted in chemical terms. With the ever-increasing sophistication of instrumental techniques, driven by the wide availability of microprocessors and microcomputers in the chemical laboratory, more complex data processing from a mathematical and statistical point of view becomes necessary, in order to relate the signals obtained (intensities, for example) with the desired results (concentrations). Much emphasis has been given to multivariate systems, in which many variables can be measured simultaneously (or sequentially, with great efficiency) when studying any sample.

A substantial part of the activities in chemometrics is focused on solving overlapping peaks, both in the analysis of pure substances and mixtures. The multivariate method of principal component analysis has become the standard method for separating overlapping peaks in analysis of mixtures of many components. Multivariate chemical data can be arranged in the form of a data matrix, where objects are arranged in rows and variables in columns. The objects are often chemical compounds, and the varying values of concentrations, pH, conductivity, times in flow systems, heights (or areas) of spectra or chromatographic peaks [1].

The resolution of overlapping signals is a general problem, but in electroanalysis this is not the most severe problem because it can be minimized by shifting the analytical signal, for example, by changing the pH, electrolyte, etc. Even having these instrumental possibilities, it is important to consider the mathematical means for solving superimposed signals. Differential pulse voltammetry is an analytical technique characterized by its selectivity and sensitivity and is therefore frequently used for the determination of heavy metals in different matrices without prior separation. On the other hand, in certain cases, the selectivity of this technique is not enough to solve mixtures of metal ions such as Cd(II), Pb(II) and Tl(I) because the peak potentials of these ions are very close and consequently the voltammograms are considerably overlapping [2, 3].

Evolving Factor Analysis is a powerful method for analyzing multivariate data that have an intrinsic order, such as speciation in multiple equilibrium systems using, for example, spectrophotometric titration. Data can be listed, according to pH values, from lowest to highest. The first columns can contain the data measured at low pH values and the last columns those obtained at high pH values. The method is based on repetitive analysis of the dataset during the evolutionary process performed on a series of matrices, which are constructed by successive additions of data to the previous matrix. This process called singular value decomposition (SVD)

consists of factoring a matrix, with several important applications, such as in instrumental signal processing, as advanced [4, 5].

The singular values obtained in matrix processing are plotted on a logarithmic scale against an ordered variable. To make the graph clearer, all points calculated for the first singular value are connected with a line; similarly lines are also drawn to connect the second singular value and so on. On the ordinate variable axis where the singular value stands out beyond the noise level, a new species appears. For example, when the line describing the first singular value stands out from the noise, detection of the first species starts in the system under investigation. The point where the second singular value stands out from the noise indicates the presence of the second species, and so on. Thus the number of species can be easily determined by inspecting the Evolving Factor Analysis graphs. The number of singular values above the noise level, ie the weight of the data matrix, is equal to the number of implicit species.

II. MATERIAL AND METHODS

Analytical grade chemical reagents and deionized water were used in all solution preparations. Stock solutions of Pb(II), Cd(II) and Tl(I) were prepared at a concentration of 5.0 mmol L^{-1} in HNO_3 1.0 mmol L^{-1} . Acetate buffer solution (pH 4.85) was prepared from 0.1 mol L^{-1} acetic acid and 0.1 mol L^{-1} sodium acetate solutions. A 0.05 mol L^{-1} EDTA stock solution was also prepared.

Figure 1 shows the constructed electrode array, consisting of 31 electrodes in which each individual electrode is formed by an array of five copper wires per electrode, each with a diameter of $55 \mu\text{m}$. In this way, the array was formed, totaling 155 electrodes. At one end, the five wires of each sub-array were joined and soldered to an Alphicon-type connector to allow the electrodes to be independently accessed by the multichannel instrument [6].

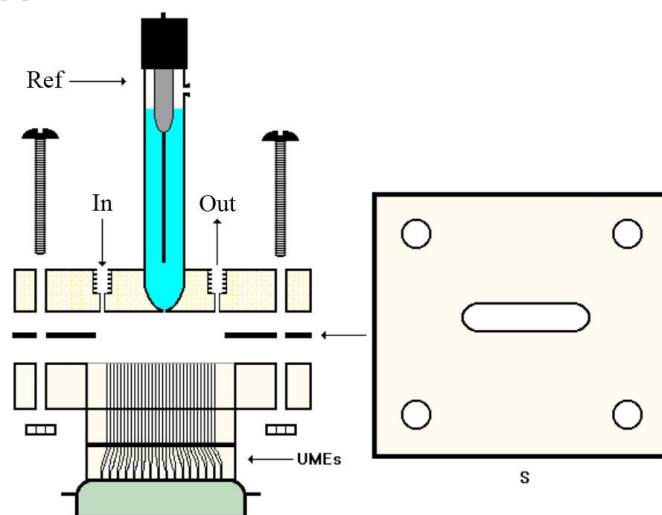


Figure 1: Multiple electrode assembly as a laminar flow cell; S - Rubber separator with a thickness of 0.5 mm; Ref - Ag/AgCl reference electrode ($\text{KCl } 3 \text{ mol L}^{-1}$); UMES - Ultramicroelectrode set.

The matrix was polished with abrasives of decreasing particle sizes. The last two were 1.0 and 0.3 mm alumina. The exposed surfaces of the copper wires (disks) were washed with deionized water, immersed in a 60% v/v phosphoric acid solution for 1 minute and washed again with deionized water. Immediately, the matrix was immersed for 10 min in a solution of $\text{Hg}(\text{NO}_3)_2$, which allows a spontaneous deposition of mercury film on the 155 copper discs of the matrix. The electrode array was stored in a deoxygenated solution of 1.0 mmol L^{-1} HNO_3 and, before use, it was subjected to 60 voltammetric cycles in the range of -250 to -850 mV , with a scan rate of 100 mV s^{-1} in HNO_3 0.1 mol L^{-1} to homogenize the mercury film on the copper substrate.

Figure 2 shows the flow system used in which the solutions, after being deoxygenated by a flow of N_2 , are pumped at a rate of 1.0 ml min^{-1} . An acetate buffer solution (pH 4.85) and the 0.01 mol L^{-1} HNO_3 acidified solution of Pb(II), Cd(II) and Tl(I) ions separately or in mixture are continuously pumped in two separate lines. Then, a volume of $200 \mu\text{l}$ of a 0.05 mol L^{-1} EDTA solution in acetate buffer (pH 4.85) is injected into the acetate buffer solution line (pH 4.85) for a sampling device built with four electromechanical Teflon® micro-valves (V1 - V4) and transported to the mixing chamber [5].

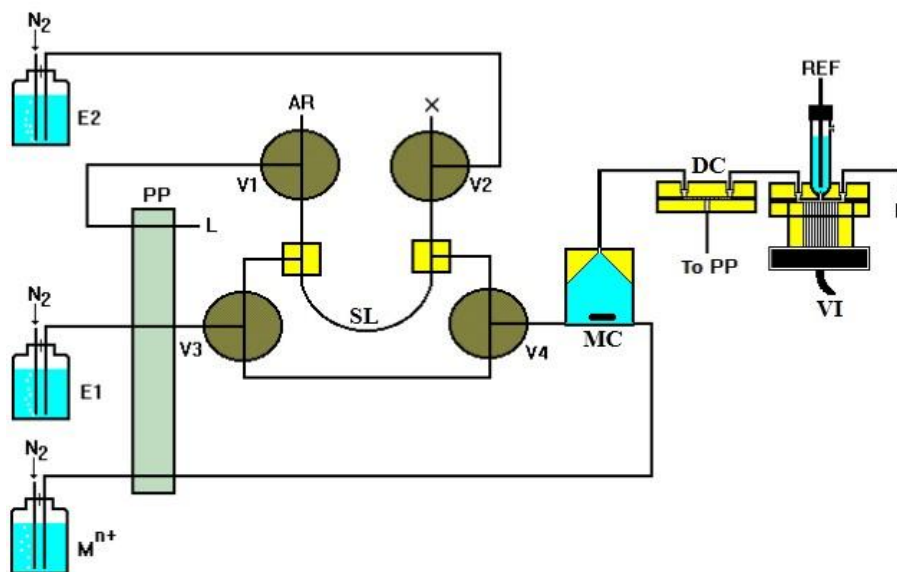


Figure 2: Flow analysis system. E1 - H₃CCOOH/H₃CCOONa buffer pH 4.85, E2 - 0.05 mol L⁻¹ EDTA solution in H₃CCOOH/H₃CCOONa pH 4.85 buffer; Mⁿ⁺ - Solution of Pb(II), Tl(I) or Cd(II) or mixture of the three ions in HNO₃ 0.01 mol L⁻¹; V1, V2, V3, V4 - Teflon solenoid valves; L - Discard; PP - Peristaltic pump; MC - Mixing chamber; AR - Connection of valve V1 open to the environment; X - Connection of valve V2 closed to the environment; VI - Multi cable for connection to the voltammetric instrument; DC - Degassing chamber; SL - 200 µL sampling loop.

As EDTA is injected in a discrete volume and not continuously, an EDTA gradient is generated in the mixing chamber and sequentially voltammetric scanning is performed in the range of -250 to -850 mV against an Ag/AgCl reference electrode.

The voltammetric technique used was the differential pulse, with a pulse width of 50 ms and a height of 50 mV, with a sweep speed of 175 mV s⁻¹. The flow cell with the ultramicroelectrode array has an interior volume of 30 µL. All electrodes are connected to a multichannel voltammetric instrument [6, 7]. After 15 s interval of EDTA solution injection, 80 scans were performed every 2 s on the gradient flowing through the flow cell. The initial hold time ensures that the EDTA concentration in the chamber reaches the maximum and the subsequent 80 scans are taken on the decreasing EDTA gradient. The total time for the acquisition of 80 voltammograms, considering the waiting time and the time of each voltammogram, was 450 s (7.5 min).

Control of instrument functions and data acquisition were performed using a program developed in Quickbasic 4.5. The chemometric analysis of the data was performed using Evolving Factor Analysis programs available in the Chemometric ToolBox 3.0 [8], which operates in the MatLab [9] environment.

III. RESULTS AND DISCUSSION

In the potential range studied, which goes from -250 to -850 mV, the Pb(II), Tl(I) and Cd(II) ions presented the following peak potentials, against the reference electrode of Ag/AgCl in KCl 3,0 mol L⁻¹:

$$\text{Pb(II)} = -450 \text{ mV} \quad \text{Tl(I)} = -570 \text{ mV} \quad \text{Cd(II)} = -620 \text{ mV}$$

Voltammetric data were obtained for 31 different potential values equally spaced in the studied range. The moving average of the current was calculated for every five consecutive values to improve the presentation of the voltammograms. The central value in the moving average calculation has a weight of three, its two nearest neighbors have a weight of two and the farthest one has a weight of one, according to the equation:

$$I_m = (I_{n-2} + 2 \cdot I_{n-1} + 3 \cdot I_n + 2 \cdot I_{n+1} + I_{n+2}) / 9$$

where:

I_m = Estimated current value (moving average)

I_n = Current values found

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

The data acquired with the voltammetric instrument were stored in files in ASCII format. These files were worked within the Origin program. To this end, each original matrix of the data obtained, consisting of 2160 lines and 1 column, which is formed by 80 scans under 27 potential values, moving averages of the 31 initial potential values referring to the 31 electrodes, was initially transformed into an 80 x 27 matrix, for later visualization of the surface, as for example, in figure 3.

From the voltammograms of the three individual ions at a concentration of $60 \mu\text{g mL}^{-1}$, it can be seen that while the voltammetric waves of the Cd(II) and Pb(II) ions are narrower, the same does not occur with the voltammetric wave of the Tl(I) ion. Tl(I) which occupies practically the entire range studied, for the electrolyte used (Figure 3).

As can be seen, EDTA, at this pH value, apparently does not complex the Tl(I) ion and therefore does not affect the waveform for this ion over the 80 scans. On the other hand, it affects Pb(II) and Cd(II) ions a little differently. This is due to the intensity of complexation for these two ions, since the formation constants for Cd is equal to 2.9×10^{16} and that of Pb is equal to 1.1×10^{18} .

With the differences in the formation constants of the studied ions, Pb(II) and Cd(II) with EDTA, the order in which the complexes appear can be inferred, or in the specific case of this experiment, the order in which they disappear and the ions are free. In the case of Tl(I), as there is apparently no complexation at this pH value, thus, the voltammetric waveform for this ion remains constant along the created gradient (Figure 3a).

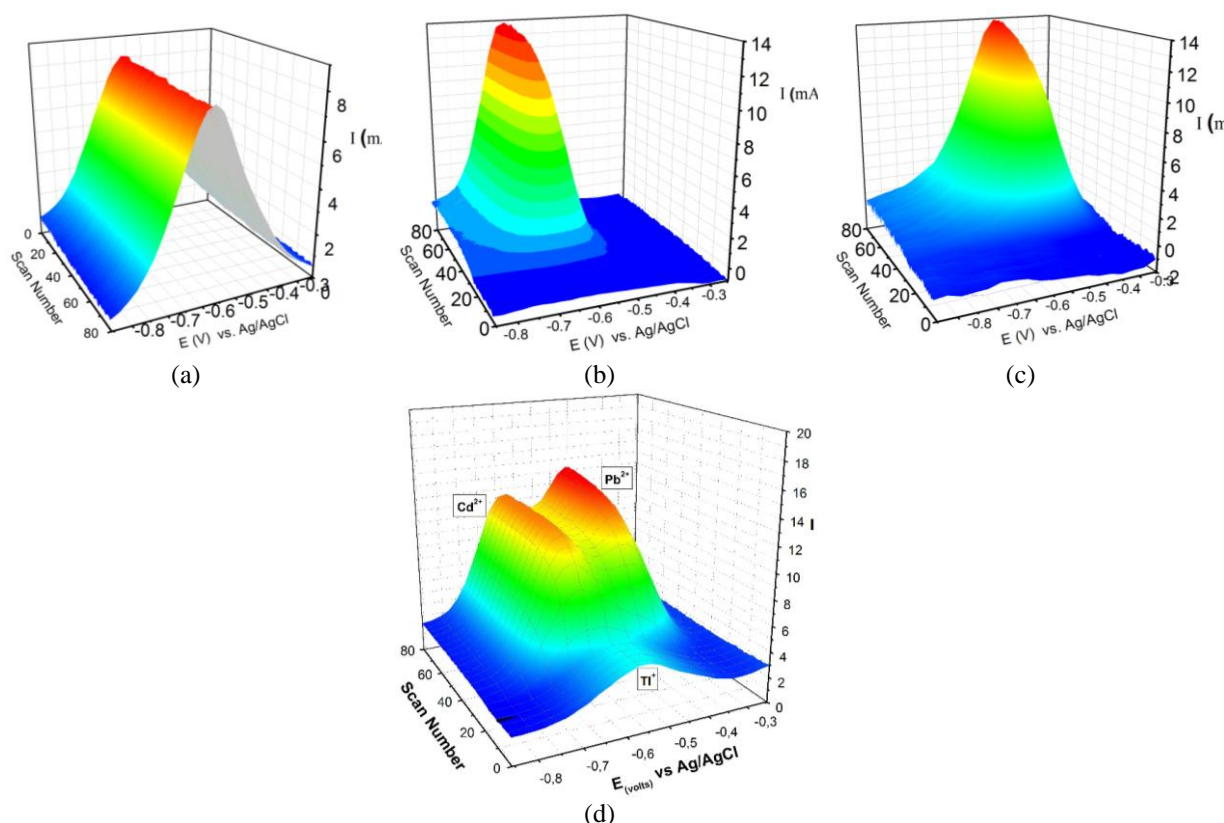


Figure 3: Voltammograms of the separated ions (a) Tl(I) = $60 \mu\text{g mL}^{-1}$, (b) Cd(II) = $60 \mu\text{g mL}^{-1}$, (c) Pb(II) = $60 \mu\text{g mL}^{-1}$ and (d) in Pb(II) mixture = $47.0 \mu\text{g mL}^{-1}$, Tl(I) = $26.0 \mu\text{g mL}^{-1}$, Cd(II) = $47.0 \mu\text{g mL}^{-1}$. Maximum current potentials: Pb(II) = -450 mV ; Tl(I) = -570 mV ; Cd(II) = -620 mV .

For the cases of Pb(II) and Cd(II) ions, as the complexation constant with EDTA for Pb(II) is greater than that for Cd(II), decomplexation to Cd(II) occurs first (Figure 3b) followed by lead (Figure 3c). By differentiating the degree of complexation of the three species as a function of the varying concentration of EDTA created by the gradient, it is possible to improve individual determinations of the species in a mixture using multivariate calibration. For this, not only data from a voltammogram at a given concentration of EDTA or in its absence are used, but all data from a voltammogram at various concentrations of EDTA in the created gradient. The results show that the EDTA gradient is effective in generating the complexes for Cd(II) and Pb(II) at different time intervals due to the differences in their complexation constants. On the other hand, if Tl(I) does not react with EDTA at the employed pH, the voltammetric signal remains practically constant throughout the entire data acquisition process, as already mentioned.

Applying the Evolving Factors Analysis to the data matrices, the evolution of the number of free species in solution was initially verified as a function of the EDTA gradient, in a direct analysis of the data, since at the end of the gradient the EDTA concentration is practically equal to zero and all species are present in the free form (Figure 4).

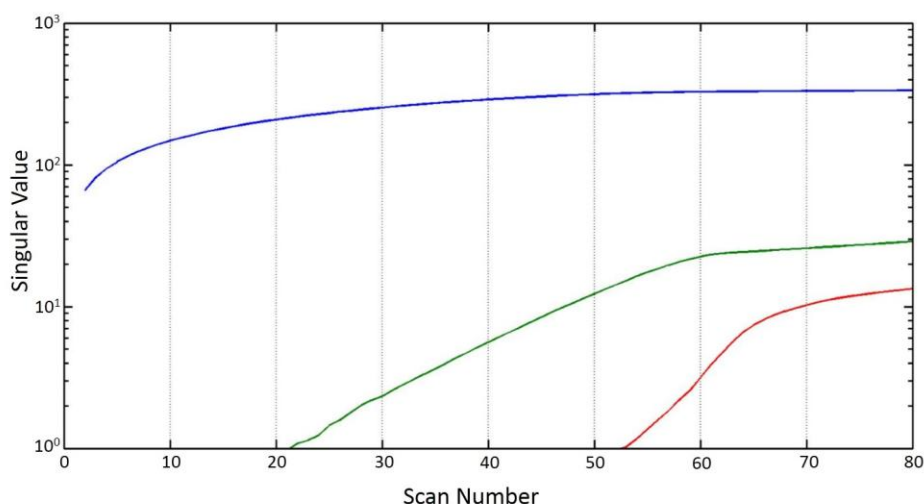


Figure 4: Evolving Factors Analysis directly for the mixture of Pb(II) $10 \mu\text{g mL}^{-1}$, Cd(II) $32.5 \mu\text{g mL}^{-1}$ and Tl(I) $57.5 \mu\text{g mL}^{-1}$, in supporting electrolyte of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$, at pH 4.85, in an EDTA gradient.

In figure 4 it is possible to observe that only three species are present, standing out above the noise, which corresponds to the three free ions Pb(II), Cd(II) and Tl(I). The time of appearance of each species is different, depending on the variation of the EDTA concentration and the complexation constant of each species. It is observed that the first species exists since the beginning of the scans, corresponding to Tl(I), since this ion is not affected by the presence of EDTA. The second species appears since scan number 20 and depending on the value of the complexation constant with EDTA, it is verified that it corresponds to the Cd(II) ion. And finally, the last species to appear approximately after scan number 50 is Pb(II) which has the highest EDTA complexation constant.

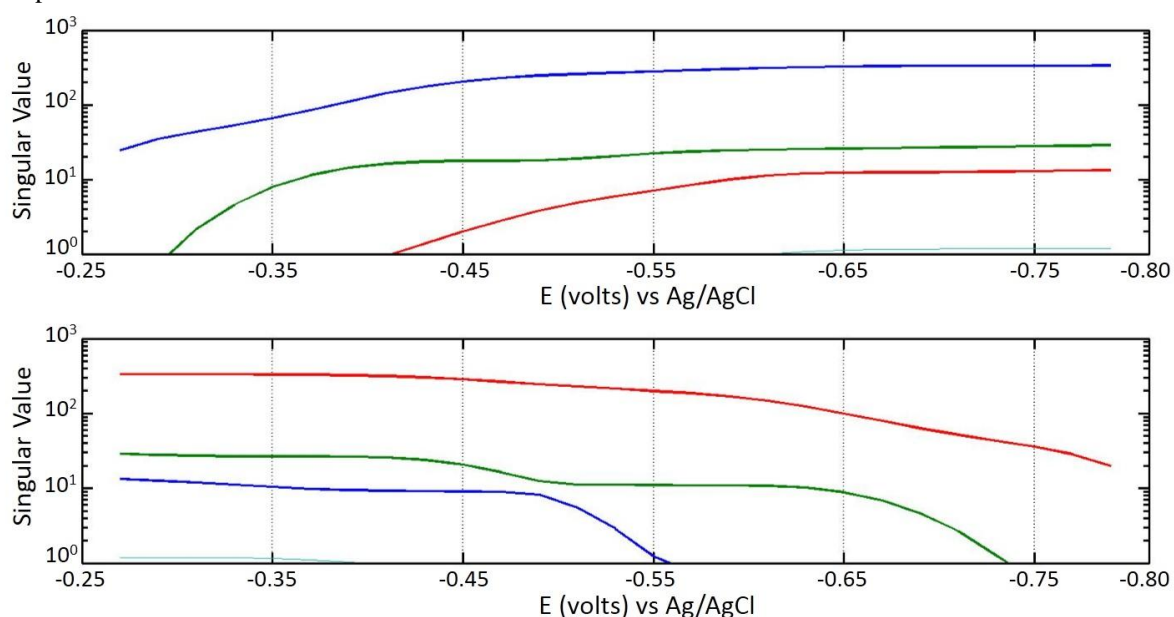


Figure 5: Forward and Reverse Evolving Factors Analysis for the mixture of Pb(II) $10 \mu\text{g mL}^{-1}$, Cd(II) $32.5 \mu\text{g mL}^{-1}$ and Tl(I) $57.5 \mu\text{g mL}^{-1}$, in electrolyte support $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$, at pH 4.85, in a potential sweep from -250 to -850 mV versus Ag/AgCl reference electrode.

Performing the Evolving Factors Analysis in a direct and reverse way (Figure 5), depending on the potential difference, it is possible to verify in the concentration window, which is the region of existence of each of the species, the presence of the three species in the explored potential range. Thus, to correctly associate the appearance of a given species with its disappearance, it must be assumed that the first species to appear will be the first to disappear, the second species to be the next to disappear, and so on.

Thus it is observed that the first species appears at the potential of -250 mV disappears at -550 mV, the second species appears at -300 mV and disappears at -700 mV and finally the third species appears at -410 mV

and disappears at -800 mV. Thus, it is possible to verify that the second species, which corresponds to the Tl(I) ion, presents a voltammetric wave that overlaps the two voltammetric waves corresponding to the Pb(II) and Cd(II) ions, respectively.

It is evident that by observing the profiles of the voltammetric waves of the mixture in figure 3, it is possible to infer about the existence of three species present, but it is important to emphasize the possibilities of this mathematical technique of identifying species in mixture, when the existence of species in equilibrium, or not, are present in mixtures is not so evident.

IV. CONCLUSION

From the voltammograms of the three individual ions it can be seen that the voltammetric waves of the Cd(II) and Pb(II) ions are narrower, the same does not occur with the voltammetric wave of Tl(I) which occupies practically the entire explored range.

On the other hand, over the 80 scans at this pH value, EDTA apparently does not complex the Tl(I) ion and therefore does not affect the waveform for this ion, only differently affecting the Pb(II) and Cd(II) ions. The EDTA gradient is effective in generating complexes for Cd(II) and Pb(II) at different time intervals due to differences in their complexation constants.

Performing the Evolving Factors Analysis directly along the EDTA gradient, it is verified that the moment of appearance of each species is different, depending on the variation of the EDTA concentration and the complexation constant of each species. It is observed that the first species exists since the beginning of the scans, corresponding to Tl(I), since this ion is not affected by the presence of EDTA. Depending on the maximum current potentials and the values of the complexation constants with EDTA, the second species to appear is Cd(II) and finally the last species to appear is Pb(II).

When the Evolving Factors Analysis is carried out in a direct and reverse way, as a function of the potential difference, it is possible to verify the region of existence of each of the species. Thus, to correctly associate the appearance of a given species with its disappearance, it must be assumed that the first species to appear will be the first to disappear, the second species to be the next to disappear, and so on.

In this case, by visually observing the profiles of the voltammetric waves, it is possible to infer about the existence of the three species present, noting that the possibilities of Evolving Factors Analysis go further when applied to mixed species when the visualization is not so evident.

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