

Anodic stripping voltammetry - ASV for determination of heavy metals

J Barón-Jaimez¹, M R Joya² and J Barba-Ortega²

¹ Grupo Plasnamat, Instituto de Investigaciones en Materiales, Universidad Autónoma de México, DF, México.

² Departamento de Física, Universidad Nacional de Colombia, Bogotá, Colombia.

E-mail: jairob26@hotmail.com

Abstract. Although voltammetric methods presented a number of difficulties in its early stages, nowadays "ASV" anodic stripping voltammetry is considered one of the most sensitive electro-analytical and suitable for trace-level determination of many metals and compounds in environmental samples, clinical and industrial [1, 2, 3]. Its sensitivity is attributed to the combination of a step of pre-concentration effective together with an electrochemical advanced measurement of accumulated analyte [4]. This paper presents an overview of the voltammetry, which includes a group of electro-analytical methods, in them the information about analyte is obtained from measurements of the current flowing in an electrochemical cell when applied a potential difference to an suitable electrode system.

1. Introduction

Electrochemical methods are based on the measurement of current signals associated with molecular properties or interfacial processes of the chemical species. This due to the direct transformation of desired chemical information (concentration, activity) into a current signal (potential, current, resistance and capacity) according to the method selected [5]. Although there are methods with adequate sensitivity for the determination of heavy metals such as atomic absorption, atomic emission spectrometry and ICP-MS, electrochemical methods are one of the most favorable techniques for determination of heavy metal ions because of their low cost and high sensitivity [6, 7, 8]. Electroanalytical techniques can be divided into two groups, electrodeics and ionics; the first "electrodeics" taking place at the interface metal-solution and the other "ionics" in the solution bulk (see figure 1(I)) [5]. The majority of electroanalytical methods belong to the field of electrodeics.

2. Antecedent

Historically, voltammetry was developed from polarography, which was discovered by chemist Jaroslav Heyrovsky Czechoslovak early 1920. Currently, polarography is only a branch of voltammetry; the earliest methods of voltammetry experienced a number of difficulties [2, 4, 6]. Today, stripping voltammetry is considered the most sensitive electroanalytical technique and suitable for the determination at trace levels of many metals and compounds in environmental samples, clinical and industrial [1, 3]. Its sensitivity is attributed to the combination of a step of pre-concentration effective together with an electrochemical advanced measurement of accumulated analyte [4].



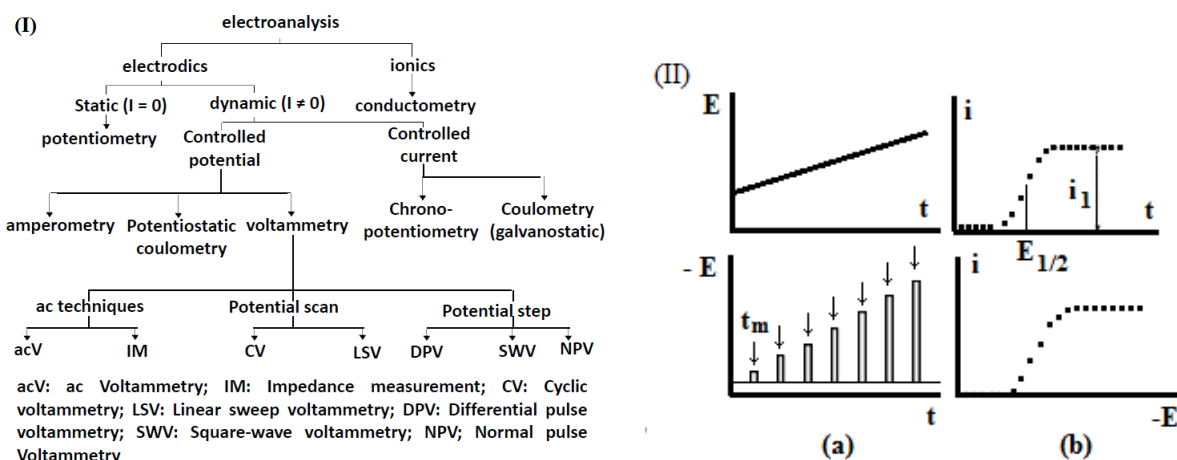


Figure 1. (I) Electro-analysis Methods and (II) two different voltammetry techniques, Linear Sweep Voltammetry (LSV) and Normal Pulse Voltammetry (NPV). a) Principal excitation and b) response curves [5].

3. Voltammetry

All voltammetry can be considered active techniques, because there is an applied potential that promotes a change in the concentration of electro-active species on the electrode surface by reduction or oxidation of the same, they can be described as a function of potential, current and time [2, 9] (see figure 1(IIa)). There are different voltammetry techniques, the difference of these, can provide a variety of chemical information, electrochemistry and physics, such as high quantitative analysis, rate constants for chemical reaction, electrons involved in redox reactions and diffusion constants [2]. We must remember, in the voltammetry there is a current signal produced by two different currents; firstly, corresponding to flow resulting of the analyte oxidation or reduction, this current is called faradic, its magnitude depends of the analytes concentrations in solution and all kinetic steps occurring on the electrode (electron-transfer process), it is based on Faraday's law [5, 9]. The other current is generated by the interface electrode-solution "electric layer double", that produce the capacitive current, it is not related to the electron transfer process, contributing in most cases only to background signals in the measurement analytical. The capacitive current must be separated from the faradic current or at least must be very small for trace analysis, this latter can be accomplished with the use of micro-electrodes and/or may be separated using techniques of step potential (eg. pulse techniques) and the advantages its different characteristics of time of fall [5].

Although there are various voltammetry techniques, the pulse voltammetry is carried out with steps and sweep combinations that improve the speed and detection limits, it can be considered as a family of techniques with adjusted potential, the current is monitored after that the potential has remained constant for a sufficient time, typically 40 milliseconds. The discrimination of the charging current is thus carried out by monitoring the current just before the end of the pulse (or the final step in the case of the stairway), where the load current "capacitive current" is negligible compared with the faradic component [10], (see figure 2(IIa)). The differential pulse voltammetry (DPV) and square wave voltammetry (SWV) improve sensitivity by subtracting the current values monitored at two different times. SWV combines the advantages of the other systems and provides significant improvements; the result is a response similar to a Gaussian signal, characterized by an excellent suppression of the background current and improves the quality of the quantitative information [10].

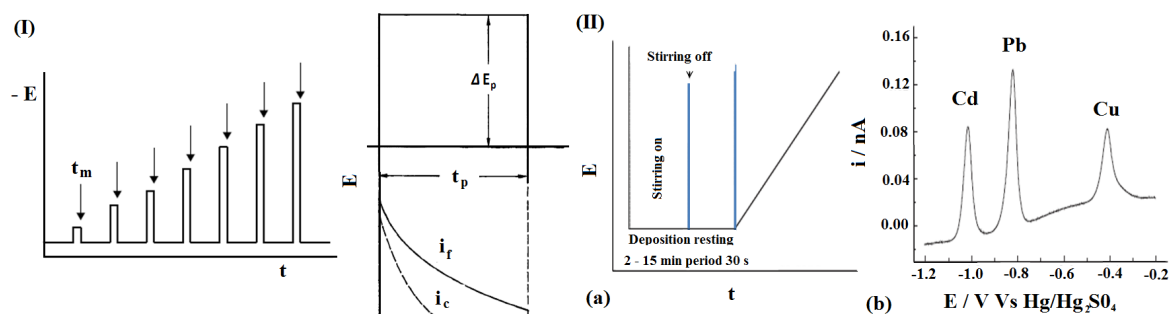


Figure 2. (I) Variation of currents i_f and i_c on the application of pulsed potential [10] and (II) Step of Stripping voltammetry (a) excitation signal (b) response curve [5].

4. Stripping voltammetry

These kinds of techniques are used in the detection and quantitative determination of metals or metal complexes, especially heavy metals in water. The techniques usually consist of a pre-concentration of the metals in the electrode surface, followed by a potential sweep (voltammetry methods) to dissolve pre-concentrated species of interest, making the quantification of them. Depending on the nature of the analyte, different modes of concentration analysis are used; the most common is the Anodic Stripping voltammetry (ASV). The stripping techniques have lower detection limit than any of the commonly used electrochemical techniques, and the preparation of the sample is low, in addition the sensitivity and the selectivity are excellent [2, 6, 9, 10]. His procedure consists of three main steps, (see figure 2(IIb)): Step of pre-concentration: This step provides different modes for pre-concentration of the analyte on the working electrode, which can be summarized by two way, electrochemically (with or without potential stimulus) and by adsorptive. Thanks to this step is achieved the species concentration in volume very much smaller compared to the volume of the solution. To achieve reproducible results is necessary control the hydrodynamic parameters (pre-concentration time, stirring, temperature, electrode area and initial potential applied [4]. The pre-concentration allows a increase of sensitivity of other 2 or 3 orders of magnitude, making it feasible to operate with analyte concentrations 10^{-10} M or even lower, sensitivities comparable with others techniques not electro-analytical characterized by high sensitivity [4]. Step of Resting: After a time perfectly measured, stops electrolysis and stirring, but remains constant initial potential. During this time, is achieved the homogenizing of the substance on the electrode and recovering the diffusion regime [4]. Step of Stripping: During this step, the deposited analyte is determined by a procedure voltammetric by stripping itself, through a potential sweep in the opposite direction to the initial. This sweep can be performed by various techniques (eg, differential pulse, square wave, linear sweep or staircase). The two most commonly used are the differential pulse and square wave, due to their advantages.

These voltammetry techniques can be classified according to the nature of the accumulation process and dissolution in anodic and cathodic tripping voltammetry, stripping potentiometric analysis or adsorptive stripping voltammetry [2, 4, 10]. Anodic Stripping Voltammetry ASV: The voltammetry is now widely recognized as a powerful tool for the analysis of metal ions and certain organic compounds in solutions. The accumulation step covers the reducing of metal cations at a constant potential for several minutes, especially assisted by convection, forming a composite or alloy (bismuth electrodes and mercury). The resulting concentration of the element to be

detected in the electrode is substantially greater than in the solution analyzed due to the volume of the electrode is much smaller in comparison with the volume of solution [5, 10]. After to finish stirring, the potential is changed to a more positive potential by means of a linear sweep voltammetry, differential pulse or square wave like described above, which results in oxidation of the metal the amalgam or alloy, returning again to the solution and recording a current peak due to this process. The current peak height reflecting the detected concentration of the material in the electrode, which is proportional to the amount of material dissolved in the solution as long as they remain appropriate experimental parameters such as the area of the electrode, potential pre-concentration time, time and potential of deposition, conditions of stirring, temperature, etc. The accumulation time necessary depends of the analyte concentration and can reach 20 minutes to a level of $10^{-9} \text{ mol dm}^{-3}$. With this technique ASV, are detected around 15 amalgams or metals alloy depending of the electrode including Ti, Cd, Zn, Cu, Bi, In and Ga. The analysis of traces of other metal ions (Hg, Au, As, Se) may be performed after they are deposited as a layer of electroplated metal in solid electrodes made of carbon or gold [5, 10].

5. Conclusions

Electrochemical methods such as ASV anodic stripping of the hand of a suitable electrode allow us to detect concentrations of heavy metals in the ppm range (single digits), this levels range allow us to be at the maximum limits for human consumption according with the World Health organization, which leads to the conclusion that it is a promise by its low cost, high sensitivity and diversity of this family electrochemical techniques.

Acknowledgements

J. Barón-Jaimez would like to thank Ana Felisa Jaimes by emotional support, J. Barba-Ortega thank to Alejandro Barba and Ely Dannier V-Niño of LNDC-UFRJ by very useful discussions.

References

- [1] C Kokinos and I Raptis 2009 *Procedia Chemistry B* **1** 1039
- [2] F Settle 1997 *Handbook of Instrumental Techniques for Analytical Chemistry* (Arlington: National Science Foundation)
- [3] C Kokinos C and A Economou 2008 *Electrochimica Acta B* **53** 5294
- [4] M Amber 1999 *Desarrollo de Técnicas Electroanalíticas Aplicables a Metales en Fluidos Biológicos de Interés Biosanitario: Determinación de Cu en LCR, Líquido Cefalorraquídeo* (España: Universidad de Cadiz)
- [5] R Cornelis 2003 *Techniques and Methodology B* **5** 429
- [6] O Hernandez 2006 *Furoiltiureas: Naturaleza de sus Complejos con CdCl_2 y HgCl_2 y su Utilización en Sensores Electroquímicos* (España: Universidad de Cadiz)
- [7] F Arduini, J Quintana, A Amine, G Palleschi and D Moscone 2010 *Trends in Analytical Chemistry B* **29** 1295
- [8] C Linyuan, J Jianbo and W Zhenhui 2008 *Electrochimica Acta B* **53** 2177
- [9] H Gunzler, A Williams 2001 *Handbook of Analytical Techniques* (Weinheim: Wiley-VCH Verlag)
- [10] C Zosky 2007 *Handbook of Electrochemistry* (Amsterdam: Elsevier)