

## APPLICATION OF MICROELECTRODES ON ENVIRONMENTAL ANALYSIS: IRON DETERMINATION

*José L. F.C. Lima\**, *Cristina M. Delerue-Matos\**, *Aida M.S.Roque da Silva\**  
and *João P. Sousa\*\**

\*CEQUP/Departamento de Química Física, Fac. de Farmácia da Universidade do Porto, Rua Aníbal Cunha 164, 4050 Porto- Portugal.

\*\*Departamento de Engenharia Química, Fac. de Engenharia da Universidade do Porto, Rua dos Bragas, 4099 Porto Codex- Portugal

### ABSTRACT:

An electroanalytical procedure for total iron determination in waste water samples based on adsorptive cathodic stripping voltammetry using mercury film microelectrodes is described. Iron was determined using cathecol, as the metal ligand agent, being the chelator adsorbed at the mercury film surface by imposition of a potential of -1.8 V and the reduction current measured. The results obtained by this procedure were compared to those obtained by atomic absorption spectrometry to evaluate the quality of the electrochemical method.

**Keywords:** iron, gold / mercury coated microelectrode, square wave voltammetry.

### INTRODUCTION:

Significant advances have recently been made in electroanalytical methods towards determination and speciation of metallic species in water and biological samples. It has been reported in the literature [1-2] that adsorptive cathodic stripping voltammetry (AdCSV) is a reliable procedure (e.g. high data sensitivity, accuracy, precision and shorter analysis time) when an appropriate metal ligand is used to form a chelator. This technique has been used by several research teams [3-4] to determine iron in aqueous solutions in the presence of cathecol, solochrome violet RS and 1-nitroso-2-naphthol.

The use of mercury film microelectrodes (MFM) coupled with AdCSV enabled to determine metallic species such as Fe, Ni, Cu, Co and Cr in biological samples [5-6], using cathecol as the ligand in a buffered medium. This procedure was optimized to determine total iron content in composed waste water samples collected from a winery residual water treatment station. The iron levels in these waste water samples were determined by AdCSV and by atomic absorption spectrometry (AAS), allowing to compare the accuracy of the attained experimental data.

**EXPERIMENTAL :**

The composed waste water samples were collected daily during a week from both entrance and exit of the treatment station. During this period of time distillation of white wine was being carried at the winery which should account for a higher metallic content of species and organic matter in the residual waters.

The mercury film microelectrode was prepared by electrodeposition of a mercury film onto a gold microdisk ( $\varnothing = 25 \mu\text{m}$ ) at a constant potential of 0.00 V (versus AgCl/Ag) during a deposition time of 100 seconds. The mercury solution, containing  $1.00 \text{ molL}^{-1} \text{ KNO}_3$ ,  $5.70 \times 10^{-3} \text{ molL}^{-1} \text{ Hg}(\text{NO}_3)_2$  and 0.50 % (v/v) concentrated nitric acid, was previously deoxygenated by purging argon during 20 minutes.

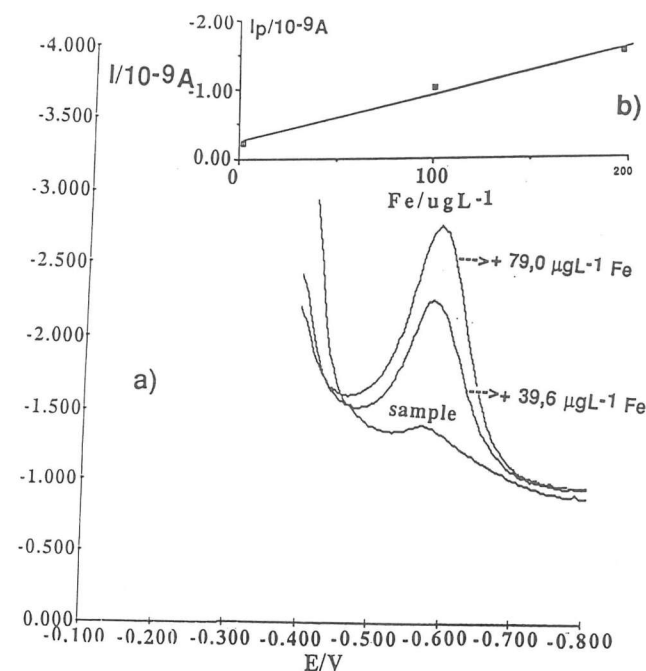
A buffer solution of  $0.010 \text{ molL}^{-1}$  PIPES (piperazine-N-N'-bis-2-ethane sulphonic acid) with a pH value ca 8.0 was prepared in  $0.50 \text{ molL}^{-1} \text{ NH}_4\text{OH}$  and cathecol  $5.0 \times 10^{-4} \text{ molL}^{-1}$  in the absence of oxygen. A volume of 5.0 mL of the waste water samples was placed inside of the electrochemical cell having a final volume of 10.0 mL.

The square wave voltammetry studies were performed using an AUTOLAB potentiostat/galvanostat Model PSTAT 10 coupled with a microelectrode ECD Module; the electrodes were a cylindrical carbon counter electrode, an AgCl/Ag reference electrode and a MFM working electrode. Scans were preceded by a deposition step at -1.80 V during 30 seconds to promote the cathecol-iron complex adsorption at the mercury surface. The working parameters were a frequency of 50 Hz, an amplitude of 20 mV and a staircase step of 4 mV.

**RESULTS AND DISCUSSION:**

The inherent sensitivity of the procedure allows to use the standard addition method to detect low concentrations of iron in waste water samples. Furthermore, the analyzed samples have a complex matrix containing species which may interfere with the iron peak, and the use of this method minimizes the interferences effects.

A well-defined peak appears at -0.58 V when a waste water sample is subjected to AdCSV after cathecol has been added. Examples of such voltammograms are given in Fig. 1. These results were obtained for a sample collected at the entrance of the waste water treatment station. The peak height increases linearly with increasing iron concentration.



**Figure 1** - Determination of total iron in waste water samples obtained by AdCSV using MFM; (a) Voltammograms of a water sample collected at the entrance of the treatment station and iron additions after an adsorption time of 30 s at -1.8 V; (b) The resulting standard additions plot.

Fig. 2 shows linear voltammograms obtained for a water sample collected after the treatment process. The iron cathecol complex yields a well-defined peak at a potential of -0.53 V. The slight shift of potential observed between entrance and after treatment water samples can be

attributed to the presence of other adsorbing substances that compete for sites at the mercury film surface.

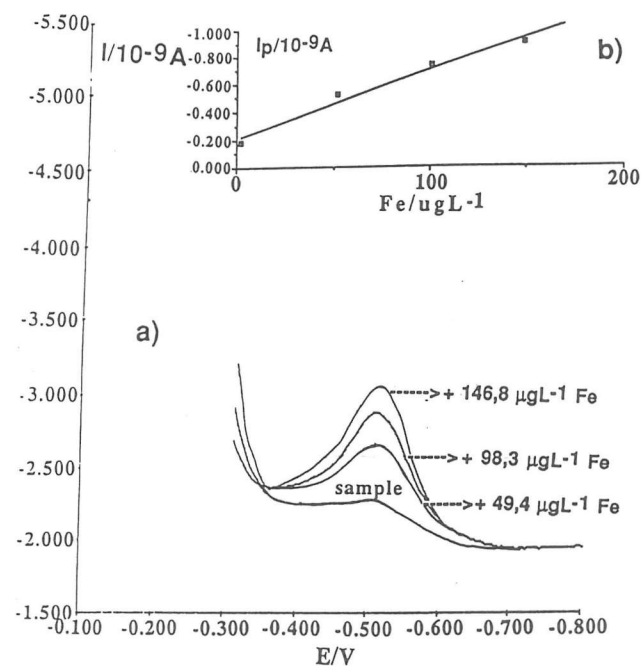


Figure 2 - (a) Voltammograms obtained for an after treatment water sample under the conditions described in Fig. 1; (b) Resulting standard additions graph.

The accuracy of the MFM using AdCSV to determine iron in waste water samples was tested by comparison with the results obtained by AAS. As can be seen from Table 1 there is no significant discrepancies between the results. However, it should be noted that the waste water samples were analysed as collected, i. e., no previous digestion stages of the organic matter was performed. The presence of the organic matter as well as other metallic species may interfere with the iron peak height in different ways. The values obtained by AdCSV and AAS do not differ more than 3.0 % indicating that the electroanalytical method is appropriate for the determination of iron in environmental analysis. A further conclusion can be drawn from Table 1 which is that the iron content decreases with the treatment process being incorporated in the sludges, indicating that the station is labouring properly.

When comparing the iron contents measured in the after treatment water samples with those stipulated by law ( 5-20 mgL<sup>-1</sup>), one can observe that they are far from reaching such values and, therefore, the residual water coming out of the station will not contaminate the surrounding soils in what concerns to the iron species.

Table 1 - Comparison of results for iron in waste water samples collected at the entrance and after treatment at the station, obtained by AdCSV and AAS.

SAMPLE / TECHNIQUE	AdCSV (mgL <sup>-1</sup> )	AAS (mgL <sup>-1</sup> )
A <sub>1</sub> - Entrance	0.096	0.086
A <sub>1</sub> - After treatment	0.043	0.040
A <sub>2</sub> - Entrance	0.086	0.085
A <sub>2</sub> - After treatment	0.075	0.068
A <sub>3</sub> - Entrance	0.158	0.200
A <sub>3</sub> - After treatment	0.074	0.070

ACKNOWLEDGEMENTS:

The authors are thankful to JNICT for the financial support (project PEAM/SEL/516/95) and to Lic. Agostinho Almeida for the AAS analysis.

REFERENCES:

1. J. Wang, *Am. Lab.*, 17 (1985) 41.
2. C.M.G. van der Berg, N. Nimmo, O. Abbulino and E. Mentasti, *Electroanalysis*, 3 (1991) 47.
3. J. Wang and S. Mannino, *Analyst*, 114 (1989) 643.
4. C.M.G. van der Berg and Z.Q. Huang, *J. Electroanal. Chem.*, 177 (1984) 269.
5. M. L. Pereira, M.C. Pereira and J. P. Sousa, *Biomedical Letters*, 52 (1995) 235.
6. S. Morais, G. S. Carvalho and J. P. Sousa, *Electroanalysis*, in press (1996).