

Determination of Cu and As by Stripping Voltammetry in Utility Poles Treated with Chromated Copper Arsenate (Cca)

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Received: 19 September 2008 / Accepted: 22 October 2008 / Published: 17 November 2008

This work presents an electroanalytical method for determining the presence of Cu and As in utility poles treated with chromated copper arsenate (CCA) using anodic and cathodic stripping voltammetry in the differential pulse mode (DPASV and DPCSV) and a hanging mercury drop electrode in 1 M HCl. The effects of accumulation potential and time were investigated for both metals and the concentration of thiosulfate was optimized for the determination of total As. The copper was analyzed by anodic stripping and a preconcentration potential of -0.70 V was applied for 100s. Arsenic was detected by adsorptive cathodic stripping in the presence of 4.0 mM of $S_2O_3^{2-}$ as reducing agent, applying a potential of 0.50 V for 80s. Voltammetric peaks for Cu and As were observed at -0.24V and -0.73V (vs. Ag/AgCl), respectively. A comparison of the DPASV and DPCSV results with those obtained by atomic absorption spectroscopy revealed a good correlation.

Keywords: anodic stripping, cathodic stripping, copper, arsenic, chromated copper arsenate

1. INTRODUCTION

Chromated copper arsenate (CCA) is suitable for treating wood against fungal and insect attack.[1] CCA is chemically fixed in wood under recommended pressure schedules and the wood thus treated is used for decks, picnic tables, children's playgrounds and utility poles (telephone, electric, etc.).[2] The metal elements in CCA are usually present in the form of oxides, which are referred to as types A, B and C. However, the most commercially popular one today is type C, [3] which contains 47.5% chromium as CrO_3 , 18.5% copper as CuO , and 34.0% arsenic as As_2O_5 . [4]

Several studies have demonstrated that these metals leach out from the wood and accumulate in nearby sediments and biota. [5-9] The analysis of impregnated lumber is very important, not only because monitoring these metal ions is crucial from an environmental standpoint but also because it allows one to determine the durability of utility poles. However don't have studies of this type in Brazil, despite the existence about two million utility poles in apply. Of these elements, arsenic is especially toxic. Inorganic arsenic compounds have been recognized as human carcinogens that may cause skin or lung cancer. [1] The retention value, i.e., the mass of CCA recommended for the treatment of wood (kg CCA/m³ of wood), lies in the order of 4 to 40 kg/m³ [10]. The methods employed so far for the determination of CCA include spectrophotometric methods: Flame Atomic Absorption – Cu (FAAS), or Hydride Generation – As (HG-AAS), [6,7] Graphite Furnace Atomic Absorption (GF-AAS) [9] and Inductively Coupled Plasma Mass (ICP-MS). [5,8]

Available literature suggests than an attractive and less expensive solution to the problem is represented by electrochemical methods, in particular methods based on stripping voltammetry. Electrochemical stripping analysis has always been recognized as a powerful tool for measuring metals because of the metal's high sensitivity, specific response, and low detection limit, as well as the low cost of equipment and the technique's compatibility with other methods. [11]

Anodic stripping voltammetry (ASV) has proved useful to determine copper in honey, [12] alcoholic distillate, [13] refined beet sugar, [14] cauliflower [15] and water samples. [16-18] A critical comparison of ASV and spectrophotometric methods shows that these methods yield similar results.

The determination of arsenic in refined beet sugar, [14] natural waters, [17, 20] bovine liver, [20] biological digestion [21] and in samples of plant material has already been carried out by the cathodic stripping voltammetry (CSV) method. [22]

In this study, the Cu and As in CCA-treated utility poles were determined by stripping voltammetry in the anodic and cathodic mode, respectively, using a hanging mercury drop electrode (HMDE). The samples were mineralized by microwave irradiation.

2. EXPERIMENTAL PART

This study involved an evaluation of utility poles treated with CCA. Samples were taken from a CCA-treated utility pole in southern Brazil, from which a 60-cm section was removed at the air/soil interface. The samples were wrapped in PVC film and stored in plastics bags protected against light and humidity. In preparation for the analysis, the wood samples were cut into small pieces and the parts corresponding to the more external rings were crushed into a powder, which was then digested in an acid medium.

2.1. Digestion

A microwave digestion system (PROVETTO SISTEMAS ANALÍTICOS) equipped with a rotor for six Teflon digestion vessels was used for the samples' digestion.

Approximately 0.5 g of crushed wood was weighed and placed in a dry, clean Teflon digestion vessel, to which 5 mL of HNO₃ 65% (Merck), 1 mL of H₂O₂ 30% (Merck) and 1 mL of MilliQ water were added. The vessels were sealed and subjected to the microwave (MW) digestion cycle. After cooling, the vessels were opened and the digestion solutions completed with MilliQ water to a final volume of 25 mL. The MW digestion program was as follows: 2 min at 250 W, 2 min at 0 W, 5 min at 250 W, 5 min at 400 W and 5 min at 600 W. The cycle was performed twice.

2.2. Equipment

Voltammograms of DPCSV (differential pulse cathodic stripping voltammetry) and DPASV (differential pulse anodic stripping voltammetry) were recorded with an EG&G PARC mod. 394 voltmeter connected to an EG&G PARC mod. 303A multimode electrode used in the hanging mercury drop electrode (HMDE) mode. An Ag/AgCl (3M KCl) electrode and a platinum wire were used in the voltammetric cell as reference and auxiliary electrodes, respectively.

To validate the results obtained by the voltammetric method employed here, we used a Perkin-Elmer 4100 atomic absorption spectrophotometer with flame atomic absorption for Cu, and hydride generation for As.

2.3. Chemicals and Solutions

All the reagents were of pro-analysis grade (Merck) and the water was deionised by means of a Millipore system. All the solutions were stored in polyethylene bottles, which were thoroughly washed in water and then soaked in 1 M of nitric acid solution. Before use, the bottles were rinsed with MilliQ water.

The concentrated HCl used throughout the experiments was of p.a. plus grade, 30% w/w, $d = 1.16$, supplied by Merck.

The 1000 ppm As(III) stock solution was prepared by dissolving 0.1320 g of arsenic trioxide in 1 mL of 25% NaOH, immediately acidified with 2 mL of concentrated HCl and diluted to 100 mL with MilliQ water. The solution was stored at room temperature and remained stable for at least 1 week. The 1000 ppm As(V) and Cu(II) were prepared by dilution in "Titrisol" standard solutions (Merck). The required working solutions were prepared daily by dilution of the stock solutions.

2.4. Measurement

To determine the concentration of copper and arsenic in utility poles, an aliquot of 100 μ L of digested sample was pipetted into the voltammetric cell together with 10 mL of HCl 1M.

Copper was determined in the voltammetric cell with 10 mL of HCl 1 M and the solution was deoxygenated by purging with water-saturated nitrogen for 30 min. A new mercury drop was extruded and the plating potential was set to -0.7 V for another 100 s, after which the potential was scanned towards more positive values at a scan rate of 10 mV s⁻¹. A copper stripping peak was recorded at -

0.240 ± 0.004 V and its current used as a measure of copper concentration. The standard additions method was used to calibrate the DPASV sensitivity and to check the linearity of response.

The determination of arsenic was done in 10 mL of HCl 1 M, which was then spiked with 200 µL of 1000 ppm Cu(II) and the solution deoxygenated by purging with water-saturated nitrogen for 30 min. After the deoxygenation, S₂O₃²⁻ was added to yield a final concentration of 4 mM and the DPASV was performed 100 s after this addition. A clean mercury drop was formed and the deposition potential was set to -0.5 V for 80 s. Then, the stirring was stopped and a quiescence time of 10 s was allowed. The differential pulse scan was carried out from -0.5 to -1.0 V. The arsenic stripping peak was recorded at -0.734 ± 0.006 V and the current used as a measure of arsenic concentration. The standard additions method was used to calibrate the DPASV sensitivity and to check the linearity of response.

3. RESULTS AND DISCUSSION

The efficiency of the whole procedure depends on various parameters, such as the time and potential preconcentration for both metals. In the case of As, working conditions such as the concentration of reducing agent must be optimized. Before analyzing the samples of interest, a study was made to optimize the parameters for use in those analyses. Each measurement was made in triplicate in order to obtain the mean value of current variation. The results obtained in the optimization of the experimental parameters for each of the metals studied are given below.

3.1. Optimization of the conditions for the determination of Cu

In earlier studies, hydrochloric acid was considered the most suitable supporting electrolyte for the determination of Cu by DPASV, because it forms chlorocomplexes with this metal ion at low pH values. [16,23]

The working conditions were optimized for the DPASV determination of Cu(II) with high sensitivity. The analytical parameters were optimized using a solution of HCl 1 M in the presence of a standard solution of 10 ppm of Cu(II).

Table 1. Effect of the preconcentration potential (E_d) on the peak current (I_p) of 10 mg L⁻¹ Cu(II) in HCl 1 M.

- E_d (V)	0.5	0.6	0.7	0.8	0.9
I_p (µA)	3.504 ± 0,065	3.507 ± 0,029	3.686 ± 0,019	3.610 ± 0,011	3.539 ± 0,012

The first parameter to be analyzed was the preconcentration potential (E_d), which varied from -0.50 to -0.90 V. The mean results obtained for I (µA) are shown in Table 1. Note that there was no

significant variation in the peak current, but because the value for $E_d = -0.70$ V was slightly higher, this was the potential chosen for the preconcentration of Cu(II).

The effect of accumulation time on the peak current was studied under stirring (see Figure 1). The copper peak current increased linearly with the deposition time up to 180 s. This effect can be useful for determining copper concentrations, for sensitivity can be improved using relatively short accumulation times. A time of 100 s was selected here for routine analysis (relatively short).

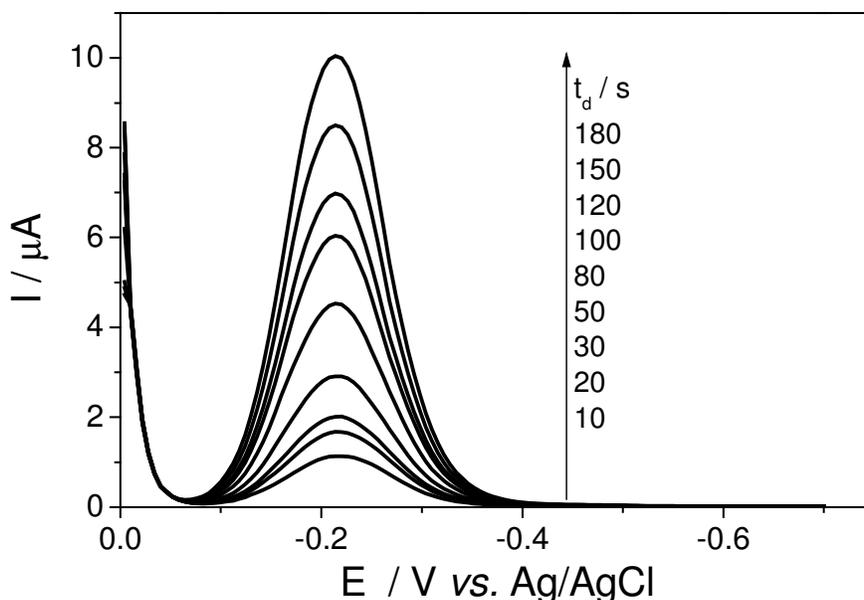
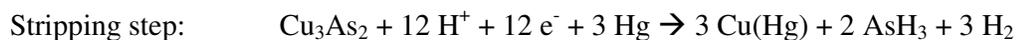
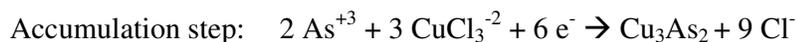


Figure 1. Effect of accumulation time on the DPASV determination of 10 mg L^{-1} of Cu(II) in HCl 1 M (E_d : -0.70 V).

3.2. Optimization of the conditions for the determination of As

To determine As in particular, the presence of Se(IV) or Cu(II) is necessary. According to Holak, some overlapping of the two peaks occurs when Se(IV) is used. [24] An alternative method is to use Cu(II). In the pre-electrolysis of As(III) in a Cu(II)-containing solution, an intermetallic compound of the Cu_xAs_y composition is probably formed on the mercury surface. The suggested electrode process during the deposition step involves the formation of a copper amalgam which subsequently reacts with arsenic to form copper arsenide. The processes that take place in HCl at HMDE using copper for As determination are well described in literature: [25-27]



In this work, the parameters were optimized aiming to determine total As in the samples.

Dependence of the peak current on the preconcentration potential of a solution of 5 mg L^{-1} As(III) in HCl and 45 ppm of Cu(II) was examined over the range of -0.30 to -0.60 V , as indicated in Table 2. A maximum value was observed when $E_d = -0.50 \text{ V}$, so this was the value chosen for the preconcentration.

Table 2. Effect of the preconcentration potential (E_d) on the peak current (I_p) of 5 mg L^{-1} of As(III) in HCl 1 M and 45 mg L^{-1} Cu(II).

$-E_d$ (V)	0.30	0.40	0.45	0.50	0.60
I_p (μA)	28.36 ± 0.68	32.93 ± 0.36	30.89 ± 0.06	36.07 ± 0.06	32.64 ± 0.32

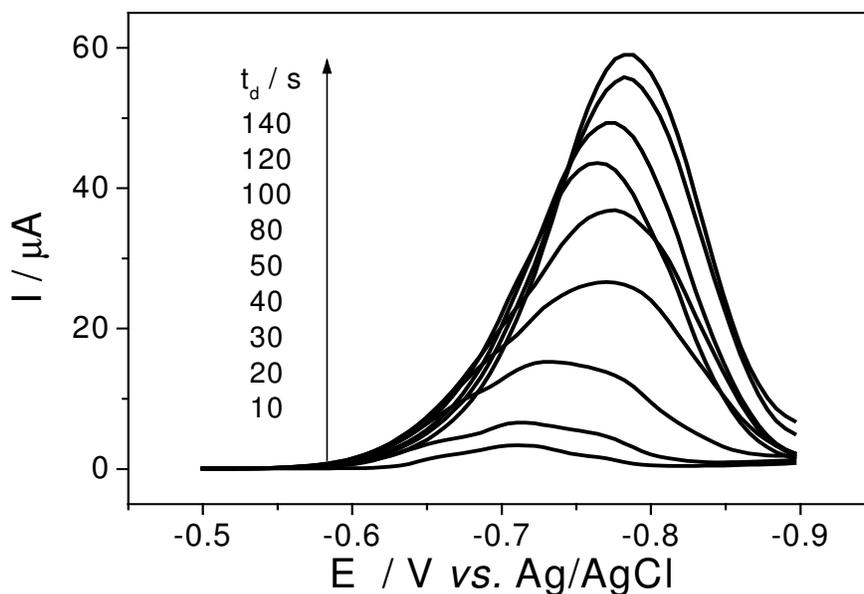


Figure 2. Effect of accumulation time on the DPCSV determination of 5 mg L^{-1} of As(III) in HCl 1 M and 45 mg L^{-1} Cu(II) (E_d : 0.50 V).

The influence of accumulation time was studied, and the peak current was found to increase continuously along with increasingly longer accumulation times (see Figure 2). An accumulation time of 80 s, which is a relatively short analysis time, was selected here for the routine analysis.

As(V) compounds do not exhibit polarographic activity in alkaline, neutral and medium-acidic media. [28,29] It is generally believed that this wave is caused by the reduction of As(V) to As(III), which undergoes further reduction at higher negative potentials. The polarographic method can be used to determine the As(V) and As(III) content when these metallic elements are present simultaneously in a solution. To this end, first the As(III) wave is obtained, then As(V) is reduced to As(III), and finally the total wave is determined. The As(V) is found from the difference. Several

reducing agents were used, such as hydrazine, [14] cysteine, [20] calcium chloride, [30] mannitol, [31] a mixture of potassium iodide and ascorbic acid, [32] and sodium thiosulfate. [18]

Ferreira and Barros tested several reducing agents to reduce As(V) to As(III) and found that the best one was thiosulfate, because it yielded a rapid and complete reduction at room temperature. [19] The efficiency of the reduction of As(V) to As(III) was studied (see Figure 3) using solutions containing 5 mg L^{-1} As(V) in 1 M HCl , 45 mg L^{-1} Cu(II). In this stage of our study, we used several concentrations of thiosulfate ranging from 0.2 to 4.8 mM. As can be seen, the peak current rose up to 4.0 mM and declined after 4.0 mM. Hence, the concentration of 4.0 mM was used for the remaining analyses.

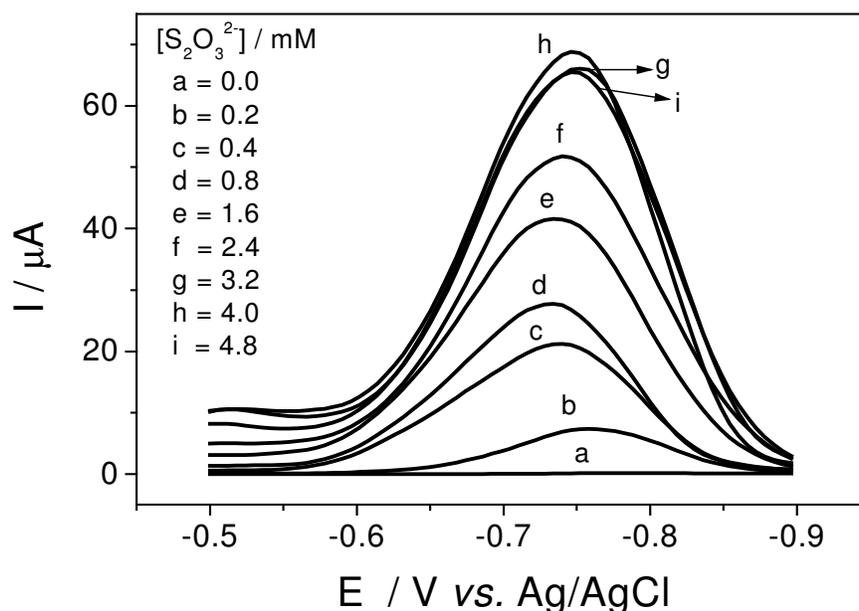


Figure 3. Effect of thiosulfate concentration on the DPCSV determination of 5 mg L^{-1} of As(V) in HCl 1 M and 45 mg L^{-1} Cu(II) (E_d : 0.50 V ; t_d : 80 s).

3.3. Determination of Cu and As in utility poles

With the optimal parameters in hand, the concentrations of Cu and As were measured by standard addition. Figure 4 shows the calibration curves in a solution of Cu(II) plus As(V). Considering that the samples treated with CCA would show the presence of Cr(VI) as well as As(V) and Cu(II), the calibration curves were obtained in the presence of this ion to verify if Cr(VI) would or would not interfere in the determination of Cu and As. Calibrations for Cu(II) in the presence of As(V) and Cr(VI) yielded a satisfactory linearity in every case under optimal conditions, Figure 4a. The calibration curves of As(V) in the presence of Cu(II) and Cr(VI), Figure 4b, yielded satisfactory linearities, which were approximated to the following straight lines: $I_p (\mu\text{A}) = 0.0037 + 1.475 [\text{Cu}]$, with $R = 0.9992$ and $I_p (\mu\text{A}) = 0.384 + 11.763 [\text{As}]$, with $R = 0.9994$, for Cu and As, respectively.

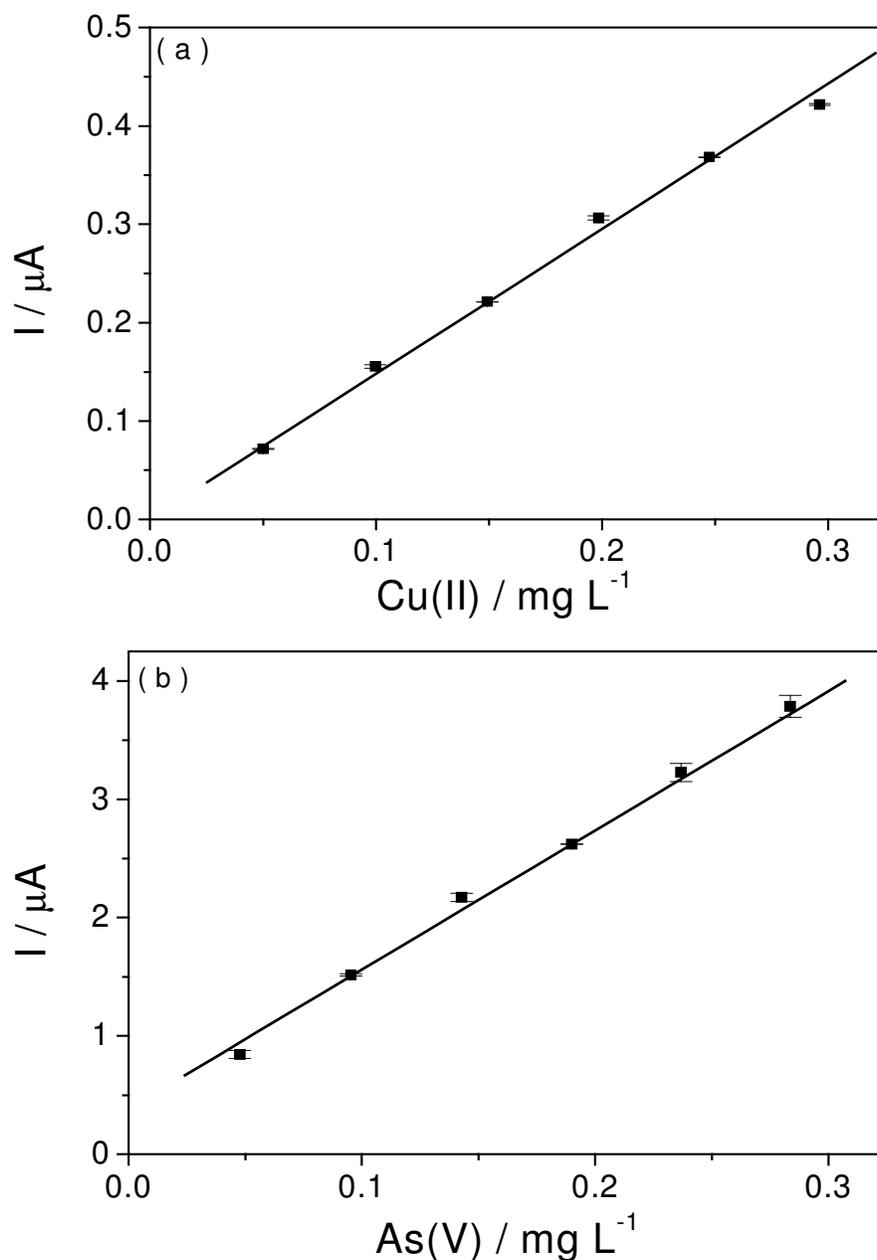


Figure 4. Analytical curves: peak current (μA) vs. concentration (mg L^{-1}). Graph for (a) copper and (b) arsenic.

After ascertaining that the determination of both As(V) and Cu(II) could be carried out in the presence of Cr(IV), the Cu(II) contained in the digested sample was determined. To this end, an aliquot of 100 μL from the digested sample, called S1, was added to the cell containing 10 mL of HCl 1 M. The DPASVs were then carried out on the S1 sample under the optimized conditions, after the addition of different standard concentrations of Cu(II). Figure 5 depicts the voltammograms obtained. Figure 6

shows the voltammograms of the digested S1 sample in solution containing standard additions, for the determination of As.

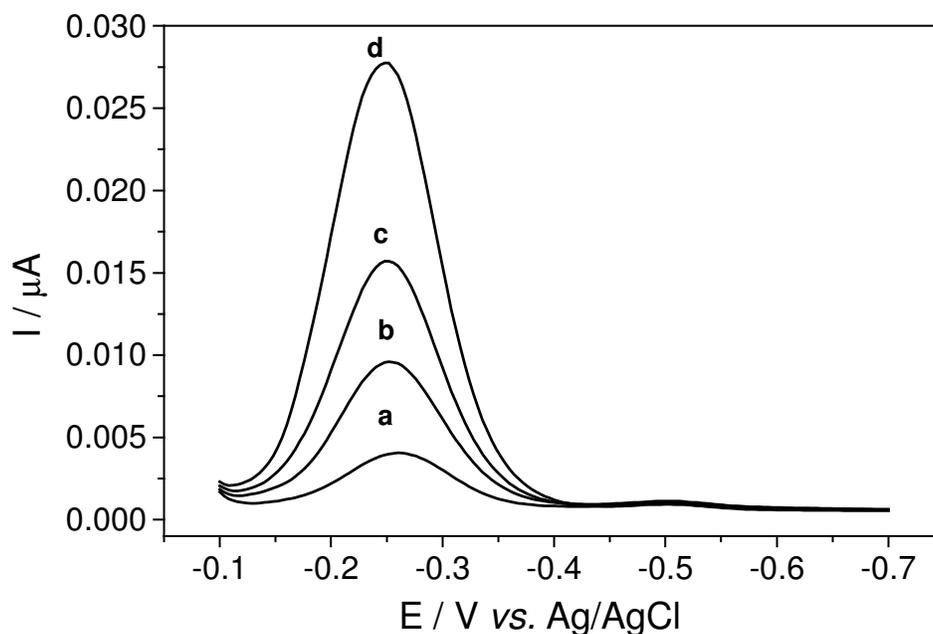


Figure 5. DPASV voltammograms of quantification of copper in utility poles C3 – 1cm (line a) by standard additions of Cu(II) – three aliquots of b = 0.5, c = 1.0 and d = 2.0 mg L⁻¹ – in the supporting electrolyte, 1 M HCl.

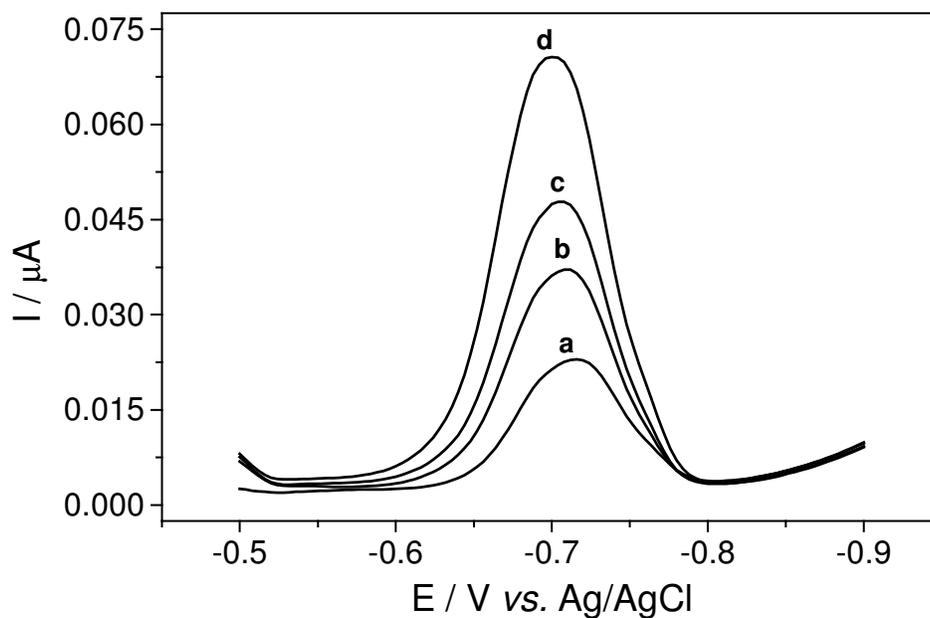


Figure 6. DPCSV voltammograms of quantification of arsenic in utility poles C3 – 1cm (line a) by standard additions of As(III) – three aliquots of b = 0.1, c = 0.2 and d = 0.4 mg L⁻¹ – in the supporting electrolyte containing 1 M HCl and 4 mM S₂O₃²⁻.

In order to validate the results obtained with the voltammetric method developed in this work, Cu and As was also determined by FAAS and GF-AAS, respectively. Table 3 shows the results obtained using these methods in the various samples analyzed. A comparison of the data in Table 3 indicates that these values are very similar, confirming the good agreement achieved by the two techniques and thus validating the proposed method.

The determination of Cu and As concentrations by the electrochemical and spectroscopic methods showed minor differences.

Table 3. Determination of Cu and As by proposed method standard method.

Sample	mg kg ⁻¹			
	Cu		As	
	DPASV	FAAS	DPCSV	GF-AAS
S1	0.569 ± 0.007	0.526	1.343 ± 0.166	1.146
S2	0.128 ± 0.005	0.118	0.184 ± 0.029	0.195
S3	1.228 ± 0.006	1.179	1.780 ± 0.089	1.766
S4	1.863 ± 0.007	1.836	1.321 ± 0.290	1.129

4. CONCLUSIONS

This paper describes a method for the determination of As and Cu in utility poles using cathodic and anodic stripping voltammetry, respectively, and a HMDE. The use of thiosulfate as a reducing agent for As(V) and the choice of HCl as the supporting electrolyte greatly simplified the voltammetric working conditions and improved the repeatability of the measurements. Cu and As in utility poles can be determined from a digested sample solution using a simple inexpensive instrumental technique. Although the experimental conditions and techniques employed in this study are described in the literature, to the best of our knowledge they have never been used for the determination of As and Cu in utility poles. The results obtained from our voltammetric experiments were in good agreement with those produced by the AAS techniques, demonstrating that DPASV and DPCSV can be used as alternative methods to AAS to evaluate the concentration of these metals in samples of CCA-treated wood. Considering that these metals leach from CCA-treated wood, impacting aquatic ecosystems and contaminating the underlying soil, the development of inexpensive and rapid techniques such as voltammetric techniques is highly relevant for environmental control. We expect this method is extendable to the analysis of soil and water samples contaminated by CCA and for Cr analysis.

ACKNOWLEDGEMENTS

The authors are grateful for Rio Grande Energia (RGE), Instituto de Tecnologia para o Desenvolvimento (LACTEC), Agência Nacional de Energia Elétrica (ANEEL) and MCT/CNPq for financially supported.

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