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Article

Voltammetric Determination of Zn(II) in Zn-Fe Alloy Electroplating Baths Using Square-Wave Voltammetry

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Desenvolveu-se um método de análise de rotina para a determinação quantitativa de zinco em banhos de galvanoplastia de liga Zn-Fe através da técnica de voltametria de onda quadrada utilizando-se, como eletrodo de trabalho, o eletrodo de gota estática de mercúrio. Amostras reais de banhos de liga foram analisadas sem pré tratamento através do método de adição de padrão. Também foram feitos testes de recuperação. Estudaram-se dois eletrólitos de suporte e os melhores resultados foram obtidos nestas condições: eletrólito de NH_3 1,0 mol L^{-1}/ NH_4Cl 0,2 mol L^{-1} ; eletrólito de ácido cítrico 0,1 mol L^{-1} em pH 3, com o potencial de pico referente ao zinco, respectivamente, em -1,30V e -0,99V *vs.* Ag|AgCl (KCl saturado). Pelo método voltamétrico proposto, a faixa de resposta linear para estudo de determinação do zinco (II) nesta matriz ficou entre 1,0 x 10^{-5} and 2,2 x 10^{-4} mol L^{-1} em ambos os eletrólitos estudados a 25,0 ºC. Estudaram-se alguns interferentes metálicos, que poderiam prejudicar a eletrodeposição da liga Zn-Fe, como Cu (II), Pb (II), Cr (III) e Mn (II), e constatou-se que esses metais não apresentam interferência significativa para a análise do zinco. O teste de recuperação do zinco para o método proposto exibiu uma boa concordância com o método de referência, obtendo-se erros menores que 3%.

A routine analytical method for zinc (II) determination in Zn-Fe alloy galvanic baths was developed employing square-wave voltammetry with the static mercury drop electrode (SMDE) as working electrode. Real alloy bath samples were analyzed by the standard addition method and recovery tests were undertaken. The supporting electrolytes used in the analyses were 1.0 mol L^{-1} NH_3 / 0.2 mol L^{-1} NH_4Cl or 0.1 mol L^{-1} citric acid (pH=3), presenting peak potentials for zinc (II), respectively, at –1.30 V and -0.99 V *vs.* Ag|AgCl (saturated KCl). The proposed voltammetric method showed a linear response range at 25 ºC between 1.0 x 10^{-5} and 2.2 x 10^{-4} mol L^{-1} for zinc (II), in both electrolytes studied. The interference levels for some metals, such as Cu (II), Pb (II), Cr (III) and Mn (II), which could prejudice Zn-Fe alloy deposition, were evaluated. These ions did not present significant degrees of interference in the zinc (II) determination. The zinc (II) recovery tests for the proposed method exhibited a good agreement with the reference method, showing relative errors lower than 3.0%.

Keywords: zinc (II) determination, square-wave voltammetry, Zn-Fe alloy baths

Introduction

The requirements for good resistance to corrosion in the automotive and electronic industries have increased during recent years. Metallic electrodeposition techniques to protect the base metal from corrosion is now not sufficient. The protective layer must remain without alterations for a specific period. However, in the long-term, these materials do loose these characteristics and compromise the function of the metal piece[1]. Recently, the use of electrodeposited alloys has been developed, because this process increases the resistance of the metal to corrosion, relative to the actual processes of electrodeposition[2].

For example, we can have alloys based on Zn-Fe[3-4], Ni-Fe[5], Zn-Ni[6] and Zn-Co[7]. The Zn-Fe alloy is the most used in electroplating procedures due to its low cost. The resistance of this alloy to the corrosion process, in relation to electrodeposited layers such as zinc (II), can triple, becoming significantly advantageous. Metal resistance to corrosion occurs when these metals are in a given concentration range, but at higher or lower concentrations than those required, they present undesired effects [8]. Thus, to avoid further problems, it is necessary to carry out a periodic monitoring of the concentrations of these metals to keep them within the working limits.

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In general, zinc determination is carried out by a complex-formation titration employing EDTA[9]. It has been observed that this technique can lack precision due the presence of Fe^{3+}, Pb^{2+}, Cu^{2+} and others metals ions in the sample. Also, if the zinc (II) concentration in the alloy bath is lower than 4.0 g L^{-1}, the results obtained are also inaccurate[10]. Other analytical techniques have been used for zinc determination in alloy galvanic baths, such as potentiometric titration in zinc baths made with zinc sulphate and boric acid (known commercialy as the acid zinc bath)[11], the use of an ion selective eletrode based on tetradecylphosphonium[12] for zinc determination in cyanidric and non cyanidric baths, and flow injection analysis using as the working electrode a chloride ion selective electrode in slightly acidic zinc baths[13]. Voltammetric analysis has recently been employed in metal determinations in alloy galvanic baths because this technique is very simple, fast and has low detection limits for several metals, mainly when more than one metal coexists in the alloy bath. This coexistence occurs in alloy baths when one or more metals are in the solution, acting as contaminants in the electrodeposited layer[14-18].

The aim of this paper is to report the development of a rapid analysis method, without previous treatment, for zinc (II) in alloy galvanic baths, using the Osteryoung square-wave voltammetric technique[19], chosen due to the speed of the analysis. Different supporting electrolytes, as well different electrolyte concentrations, pH and sample volume were studied to evaluate the principal analytical parameters that could affect the voltammetric analysis.

Experimental

Reagents

The stock solution of Zn^{2+} (0.0940 mol L^{-1}) was prepared from zinc (II) chloride (*Merck*), acidified with HCl and standardized with 0.0989 mol L^{-1} EDTA[20] (disodium salt from *Merck*). The other zinc (II) standard solutions used in the experiments were prepared daily from stock solution as follows: 0.940 x 10^{-3} mol L^{-1} Zn^{2+} (dilution 1:100), 1.87 x 10^{-3} mol L^{-1} (dilution 1:50) and 3.74 x 10^{-3} mol L^{-1} (dilution 1:25). For the zinc (II) determination, 0.1 and 0.2 mol L^{-1} citric acid (*Merck*) solutions at pH values of 2.0, 3.0, 4.0 and 5.0, as well as a 1.0 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl (*Merck*) solution were used as supporting electrolytes. Standard solutions of some metallic ions for interference studies were suitably prepared using copper (II), manganese (II) and zinc (II) sulfates (C*arlo Erba*), lead (II) nitrate and chromium (III) chloride (*Vetec*).

The test alloy galvanic bath was prepared with 3.0 mol L^{-1} NaOH solution, 1.0 x 10^{-1} mol L^{-1} zinc (II) and 9.0 x 10^{-4} mol L^{-1} iron (III) solutions, besides organic additives, according to the descriptions in a Technical Bulletin from *Atotech* of Brazil[21]. The iron added to the alloy bath was as an organic iron(III) complex, combined with different organic additives. Real bath samples were obtained from the electroplating industries. All reagents utilized were of analytical grade and all solutions used in the experiments were diluted adequately in deionized water.

Apparatus

The voltammetric measurements were made with a *PAR* model 384B polarographic analyzer coupled to a *PAR* polarograph stand model 303-A, using a three electrode cell: static mercury drop electrode (SMDE) as working electrode (the large size mode of the mercury drop electrode adjusted by the polarographic stand was used), Ag|AgCl (saturated KCl) as reference electrode and a platinum wire as counter-electrode. The technique employed in the Zn^{2+} analysis was the square-wave voltammetry and the voltammograms were recorded on a DPM-40 digital plotter from *Houston Instruments*.

The pH adjustments of the solutions were performed with a *Radelkis* OP-271 pH/ion analyzer (Hungary). For pH measurements, an OP-808P *Radelkis* glass electrode (Hungary) was used. The volume additions in the polarographic cell were carried out with pipettes (*Finnpipette*) from 20 μL to 5.00 mL.

Analytical procedure

The voltammetric cells were prepared with the addition of 5.00 mL of supporting electrolyte, followed by deoxygenation of the solution by bubbling ultra-pure nitrogen for 10 min. Appropriate volumes of either Zn^{2+} standard solutions or bath samples were put into the cell followed by 2 more min of deoxygenation with nitrogen. The voltammograms were then registered over a potential range between -0.80 and –1.50 V *vs.* Ag|AgCl (satureted KCl). The optimized voltammetric conditions were: scan rate of 200 mV s^{-1}, pulse height of 20 mV, pulse frequency of 100 Hz.

Results and Discussion

Zinc voltammetric determination

The Zn-Fe alloy galvanic baths have about 15 mL per liter of organic additives, called purifiers, brightness and levellers. When the concentration of these additives are over this value they interfere in the complexometric determination of zinc using EDTA, giving rise to errors in the analysis. In the method described in this work there is no need for prior treatment to eliminate interferences, because the organic additives do not yield voltammetric peaks in the potential region near the potential of the Zn (II) voltammetric peak.

Zinc (II) generates well-defined peak potentials in different supporting electrolytes and is reduced at a more cathodic region than other metals. Thus, its determination can be easily carried out in the presence of many potentially interfering metal ions. Acidic or alkaline supporting electrolytes can be used, presenting a half-wave potential for zinc (II) between –1.0 V and –1.3 V *vs.* Ag|AgCl. In the case of electrolytes from strong acids, such as sulfuric and nitric acids, the zinc (II) half-wave potential, (or Zn (II) peak potential, depending on the polarographic or voltammetric technique used) is partially masked by the wave (or peak) due to H^+ reduction, prejudicing the electrochemical analysis[22].

Thus, the study for the determination of Zn (II) concentration in alloy electroplating baths was undertaken employing two supporting electrolytes, one with an alkaline character and other with a weak acid character. The zinc (II) concentration in the sample is high, about 0.10 mol L^{-1}, and suitable dilution in the supporting electrolytes was necessary to avoid a high diffusion current generating voltammetric peaks with low resolution or out of the linear region of the current vs. concentration analytical curves. Thus, three different dilution ratios were studied, 1:25, 1:50 and 1:100, comparing the results for both electrolytes.

i) NH_3 / NH_4Cl supporting electrolyte[23]

The voltammetric peak referring to Zn(II) obtained in this supporting electrolyte shows a good definition as can be seen in Figure 1-a.The peak potential obtained in all dilutions studied was –1.30 V *vs.* Ag/AgCl, saturated KCl, and the peak shown in Figure 1-a refers to the 1:50 dilution. The best results employing this supporting electrolyte were obtained with electrolyte concentrations of 1.00 mol L^{-1} NH_3/ 0.20 mol L^{-1} NH_4Cl . An aspect that can favor the use of this electrolyte is the fact that alkaline electrolytes are more recommended for zinc (II) determination in several matrices. Based on experimental verification that the samples and the supporting electrolyte have very close pH values, there is no necessity to evaluate the pH of the samples in the zinc (II) voltammetric determination.

Calibration curves were made for the zinc (II) concentration region of 1.0 x 10^{-5} mol L^{-1}, yielding a linear relation between the zinc (II) concentration values and peak currents. Table 1 gives the representative equations for three evaluated zinc (II) sample dilutions, as well as linear ranges and correlation coefficients. Table 2 shows the results obtained for the matrix elaborated in the laboratory, presenting relative errors lower than 3.0%, acceptable for this zinc (II) voltammetric determination and using the standard addition method in the linear region of calibration curve.

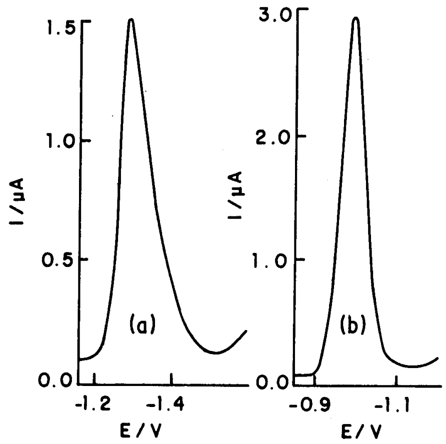

Figure 1. Square-wave voltammograms referring to the Zn(II) in the matrix. Sample aliquots of 50 µL with dilution 1:50 (1.87 x 10^{-5} mol L^{-1} Zn(II) in the voltammetric cell): **(a)** 1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl **(b)** 0.10 mol L^{-1}citric acid (pH 3).

ii) Citric acid supporting electrolyte[23]

The use of citric acid as supporting electrolyte is interesting due to its weak acid behavior, in which interference from H^+ ions can occur. In this manner, a study was carried out in the pH range from 2.0 to 5.0. The best results were obtained when the pH value was 3.0, with well-defined peaks in the square-wave voltammograms (Figure 1-b). At pH values lower than 3 the voltammetric peak of zinc(II) lost resolution due the interferences from overlapping with the voltammetric peak of H^+ reduction. For pH values higher than 3, the peak for zinc (II) was displaced toward a more negative potential region provoking a loss relative to peak definition. Thus, for further studies with this supporting electrolyte, citric acid at pH=3.0 was chosen.

The matrix used in most electroplating industries for zinc (II) deposition is very alkaline (pH=13) and, during voltammetric analysis procedures, additions of large amounts of sample in the citric acid electrolyte cause an increase in the final solution pH, prejudicing the zinc (II) determination. From matrix addition of 75 µL without dilution (about 7.4 x 10^{-5} mol L^{-1} Zn^{2+} in the voltammetric cell), the electrolyte pH displaces toward values near 10 and the peak referring to the zinc (II) disappears. With

Table 1. Representative equations for standard addition curves obtained in the zinc (II) voltammetric determination.

Dilution	[Zn(II)] (10^{-3} mol L^{-1})	Equation	Linear range (10^{-5} mol L^{-1})	Correlation coefficient
		1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl		
1:25	3.74	I = 1.29 (± 0.04) + 0.31 (± 0.01) [Zn]	5.0 to 22.0	0.9999
1:50	1.87	I = 0.59 (± 0.02) + 0.31 (± 0.01) [Zn]	2.0 to 12.0	0.9998
1:100	0.94	I = 0.39 (± 0.02) + 0.28 (± 0.01) [Zn]	1.0 to 6.0	0.9999
		0.10 mol L^{-1}citric acid (pH 3)		
1:25	3.74	I = 1.42 (± 0.09) + 0.39 (± 0.01) [Zn]	5.0 to 22.0	0.9996
1:50	1.87	I = 0.77 (± 0.05) + 0.44 (± 0.01) [Zn]	2.0 to 12.0	0.9997
1:100	0.94	I = 0.50 (± 0.01) + 0.51 (± 0.01) [Zn]	1.0 to 6.0	0.9999

I=peak current.

Table 2. Results obtained by the standard addition method in Zn(II) voltammetric determination applied in synthetic samples, employing different supporting electrolytes.

Zn(II) nominal concentration (10^{-3} mol L^{-1})	Sample dilution	Zn(II) concentration obtained by the standard addition curve* (10^{-3} mol L^{-1})	Relative error (%)$^{+}$
		1.00 mol L^{-1} NH_3/ 0.20 mol L^{-1} NH_4Cl	
3.74	1:25	3.64 ± 0.02	2.43
1.87	1:50	1.83 ± 0.03	2.10
0.94	1:100	0.93 ± 0.02	0.40
		0.10 mol L^{-1}citric acid (pH 3)	
3.74	1:25	3.65 ± 0.03	2.40
1.87	1:50	1.85 ± 0.03	1.10
0.94	1:100	0.92 ± 0.03	2.10

* Average of three determinations; $^{+}$ Relative error estimative between the nominal and obtained values in the zinc (II) determination.

sample dilutions, the results presented an improvement in the zinc (II) determination because the final pH did not suffer large pH variations. This was observed for the three evaluated dilutions. Analytical curves (standard addition method) were made for this supporting electrolyte, relative to the sample volume and zinc (II) standard concentrations, similar to the curves employing the 1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl electrolyte. Tables 1 and 2 show, respectively, the representative equations for the three studied dilutions and the data obtained for the zinc (II) synthetic matrix using citric acid as supporting electrolyte and the standard addition method in the linear region of the calibration curve.

In zinc (II) voltammetric analysis, independently of the electrolyte choice, it is desirable to dilute the samples since this metal is present in the matrix at high concentrations, in relation to the sensitivity of the voltammetric method. The dilutions done in this work provided zinc (II) concentrations of about 10^{-5} mol L^{-1}, exhibiting more accurate results in both electrolytes studied.

Interference study

Copper (II), lead (II), manganese (II) and chromium (III) were evaluated as possible interfering metallic ions (Table 3). The presence of these metals in the alloy bath can be harmful to the Zn-Fe codeposition process and consequently to the deposition quality. Lead (II) ions showed stable complexes with citrate and oxalate anions and, in these supporting electrolytes, lead (II) reduction occurred at potentials of about –0.40V and –0.50V, respectively, which does not affect the zinc (II) determination, allowing, inclusively, the simultaneous quantification of these two metals in solution when indicated (Figure 2).

Manganese (II) and chromium (III) did not present

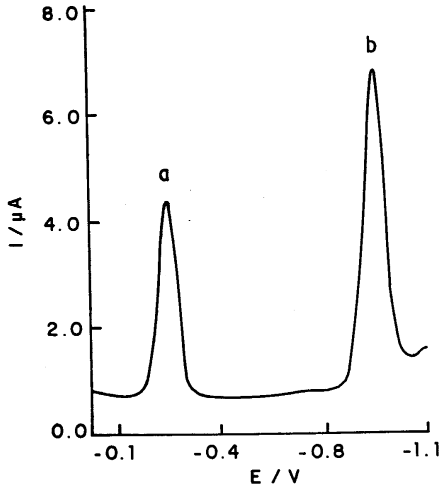

Figure 2. Square-wave voltammograms referring to **(a)** 20 µL of Pb^{2+} (4.70×10^{-3} mol L^{-1}) and **(b)** 20 µL of matrix (0.94×10^{-2}mol L^{-1} Zn(II)). General conditions: supporting electrolyte, 0.10 mol L^{-1} citric acid (pH 3); scan rate, 200 mV s^{-1}; pulse height, 20 mV; pulse frequency, 100 Hz.

Table 3. Effect of some interfering ions on zinc (II) determination using square-wave voltammetry with different supporting electrolytes.

Interfering ion [X]	Molar ratio [Zn(II)] / [X]	Relative signal (%) 1.00 mol L^{-1} NH_3/ 0.20 mol $L^{-1}$$NH_4Cl$	0.10 mol L^{-1}citric acid (pH 3)
Pb (II)	1 / 0.1	1.04	1.03
	1 / 0.5	1.01	1.07
Cr (III)	1 / 0.1	1.02	0.98
	1 / 0.5	0.98	1.05
Cu (II)	1 / 0.1	1.02	0.99
	1 / 0.5	0.98	0.99
Mn (II)	1 / 0.1	1.01	0.93
	1 / 0.5	0.98	0.99

[Zn(II)] =0.935 x 10^{-2}mol L^{-1}. The relative signal is the Zn(II) peak current ratio in the presence and absence of interfering metallic ions.

Table 4. Results found in Zn(II) determination in real alloy samples by square-wave voltammetry (proposed methods using standard addition) and by complex-formation titration (reference method).

Sample	[Zn(II)] x (10^{-2} mol L^{-1}) obtained in 1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl*	Relative error$^+$	[Zn(II)] x (10^{-2} mol L^{-1}) obtained in 0.10 mol L^{-1} citric acid (pH 3)*	Relative error$^+$	[Zn(II)] x (10^{-2} mol L^{-1}) obtained by the reference method *
1	4.80 ± 0.01^a	34.40	4.67 ± 0.03^a	30.81	3.57 ± 0.06
	4.60 ± 0.02^b	28.90	5.06 ± 0.03^b	41.70	
	4.90 ± 0.02^c	37.20	4.84 ± 0.04^c	35.50	
2	8.85 ± 0.01^a	2.74	8.90 ± 0.02^a	2.20	9.10 ± 0.03
	8.88 ± 0.03^b	2.41	8.87 ± 0.03^b	2.52	
	8.82 ± 0.02^c	3.07	8.83 ± 0.03^c	2.96	

*Average of three determinations; $^+$Relative error estimate between the proposed and reference methods in the zinc (II) determination; ^{a}(dilution 1:25); ^{b}(dilution 1:50); ^{c}(dilution 1:100)

voltammetric peaks around the zinc (II) potential range and no significant interference was observed when these metal ions were put into the solution. In the same way, copper (II) did not show voltammetric peaks in the zinc (II) potential range although, in the citric acid supporting electrolyte, a peak is observed around –0.25 V, but it is not well formed.

The presence of iron (III) in the alloy bath did not affect the proposed method. The iron (III) peak potential in the different electrolytes studied appears between –0.1V and –0.3V, which does not interfere in the zinc (II) voltammetric determination.

Analysis of real alloy bath samples

The proposed method was applied for two alloy baths extensively used in metal deposition employing electroplating procedures. Figure 3 shows the voltammograms referring to zinc (II) from one of the real samples (# 02) obtained in both supporting electrolytes evaluated. In all real samples, as with the synthetic samples, good results were obtained with standard addition curves, presenting correlation coefficients near to unit. Zinc (II) determination with the reference method employing EDTA[20] (complex-formation titration), presented high relative errors for sample 1 (Table 4), indicating that this method underwent interference, probably from iron (III) or and other impurities, since this metal and the other additives are an integral part of the alloy bath composition. The presence of organic additives in the samples interferes with the titration end point when Eriochrome black T is used as an indicator in volumetric analysis. Likewise, small quantities of iron (III), nickel (II), copper (II) and cobalt (II), commonly present in the alloy baths, can form very stable complexes with Eriochrome T and the fraction of this indicator which is complexed can not be changed by EDTA addition.

The results for Zn(II) determination in two real samples obtained by the proposed method in both supporting

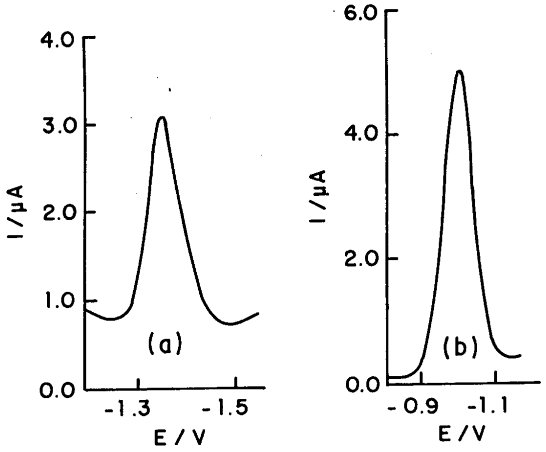

Figure 3. Square-wave voltammograms referring to Zn(II) from real sample # 02. Sample aliquots of 50 µL with dilution 1:50 (1.87 x 10^{-5} mol L^{-1} Zn(II) in the voltammetric cell): **(a)** 1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl **(b)** 0.10 mol L^{-1}citric acid (pH 3). General conditions: scan rate, 200 mV s^{-1}; pulse height, 20 mV; pulse frequency, 100 Hz.

Table 5. Zinc (II) determination in real alloy samples by square-wave voltammetry employing the recovery method. Sample dilution, 1:50.

Samples	Zn(II) obtained from the standard addition curve (mg L^{-1})	Zn(II) added in the matrix (mg L^{-1})	Zn(II) total value found (mg L^{-1})*	Recovery (%)
1.00 mol L^{-1} NH_3 / 0.20 mol L^{-1} NH_4Cl				
1	72.1	150.0	221.3 ± 0.01	99.6
2	138.3	150.0	289.5 ± 0.03	100.4
0.10 mol L^{-1} citric acid (pH 3)				
1	79.3	150.0	228.1 ± 0.02	99.4
2	137.2	150.0	286.0 ± 0.04	99.5

* *n = 6*

electrolytes and by the reference method are shown in Table 4. Table 4 also shows that, for the second sample analyzed by the reference method, even with iron (III) present and other possible metallic contaminants, the zinc (II) determination provided values closer to those obtained by voltammetry, exhibiting relative errors lower than 4.0%, because the zinc (II) concentration was higher relative to the first sample and, consequently, the influence of other interfering ions decreased.

Thus, a recovery test to validate the proposed voltammetric method was carried out, adding a specific amount of a Zn^{2+} standard solution to the sample after the Zn^{2+} determination in the same solution and calculating the recovery in terms of percentages between the added quantity and the total quantity observed for the sample (Table 5). This test is often useful in counteracting matrix effects. The data obtained confirmed the validation of the proposed method, presenting recovery values between 99.4% and 100.4% for zinc (II) determination in Zn-Fe alloy baths by square-wave voltammetry.

This new technique showed easy application, rapidity in analyses and precise results, besides selectivity in the presence of some interfering ions. The time required for each analysis was about 10 min, furnishing a zinc (II) determination method which may be utilized in routine analysis, particularly in the electroplating industries where control of the metal concentration can be very useful to the final quality of the metallic deposition.

Conclusions

The use of voltammetric techniques in the electroplating industries is very useful because through this technique it is possible to determine several metallic ions at trace levels with high precision, accuracy and rapidity. The results obtained in the zinc (II) determination allowed the application of square-wave voltammetry in real Zn-Fe alloy samples showing facility in zinc (II) quantification, while minimizing complex sample pre-treatment. In this way, new electroanalytical methods can be developed, making the use of voltammetric techniques more accessible, such as being employed for other alloy baths such as Zn-Ni and Zn-Co. Another great advantage of this technique is the low interference level, permitting recovery tests near to 100%, being less susceptible to interfering compounds by an appropriate choice of the supporting electrolyte type, concentration and pH value. The proposed method showed good agreement with the titrimetric reference method, exhibiting relative errors lower than 3.0%, when suitable sample dilutions ware made.

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