

Quantification of Iron using its Amine Complexes by Square Wave Voltammetry in Alkaline Solutions

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This work presents an electrochemical method for detecting iron, derived from corrosion processes in carbon steel structures, based on its complex ability with some organic molecules. The square wave voltammetry technique was applied using glassy carbon as a solid working electrode, and five amines were tested as complexing agents: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoethylamine (MELA) and triethylamine (TELA). Electrochemical tests showed peak oxidation in the presence of Fe⁽²⁺⁾ for these amines, except MELA. However, TEA was the only one to present a satisfactory determination coefficient ($R^2 = 0.9946$). The essays were performed to determine the optimal analysis conditions for frequency, pulse height and step potential. The optimized parameters were 60 Hz, 75 mV and 10 mV, respectively. Also, the results indicated that Fe^(2+/3+)-TEA complex could be applied in the chemical speciation of iron to determine the corrosion rate of carbon steel.

Keywords: Analytical Methods, Fe^(2+/3+), Amines, Square Wave Voltammetry.

1. INTRODUCTION

Among the minerals on earth, iron is highlighted due to its commercial value. Iron ore has a broad industrial application, mainly carbon steel production. Methods of iron detection are necessary and recommended since this metal is present in many environments [1,2].

In aqueous media, several techniques are useful: atomic absorption spectrometry, capillary zone electrophoresis, ion chromatography, and polarography. The latter is the most applied voltammetric method, using dripping mercury as a working electrode (HMDE). Despite many advantages, mercury presents high toxicity levels. So, significant efforts have been made to develop an alternative method to polarography using solid working electrodes but maintaining the sensitivity and response time of techniques [3-7].

Verma [8] and Ferreira [9] report the use of complexing agents as alternatives to mercury, applying more practical and less harmful to the environment electrodes, such as graphite, glassy carbon, and diamond. The complexing agent most reported is EDTA since it can chelate with a wide range of metals, forming stable complexes. However, the use of EDTA in voltammetric processes is limited by its non-selectivity to ferrous ions.

This study proposes an alternative iron detection method that includes voltammetry using a glassy carbon (without *ex-situ* modification) as a working electrode. The technique is effective even in environments with a high concentration of iron ions, being useful to quantify and perform speciation of these ions from corrosion processes.

The proposed catalytic system encompasses the formation of a $\text{Fe}^{(2+/3+)}$ complex with amines that present high selectivity as complexing agents. The composition of the electrolytic solution (sodium hydroxide (NaOH) and sodium chloride (NaCl)) has been extensively applied due to its good response in the quantification of $\text{Fe}^{(2+/3+)}$ with other working electrodes. Square wave voltammetry (SWV) was used in this study since it is a consolidated and sensitive electrochemical technique [10, 11].

The organic substances applied in this study as complexing agents are TEA, MEA, DEA, MELA, and TELA [12-16].

The amine-Fe complexes' reversibility was analyzed aiming the chemical speciation since the ions generated by corrosion processes may present different oxidation states. Kindra and Lê report detections of iron in solution as $\text{Fe}^{(2+)}$ or $\text{Fe}^{(3+)}$ [17,18]. However, few studies in the literature present chemical speciation, as Verma [8] and Zhu [19]. Based on this scenario, the reversibility, or chemical speciation, was assessed in this study through square wave cyclic voltammetry (SWCV).

2. EXPERIMENTAL PROCEDURES

2.1 SWV

The electrochemical experiments were carried out at 25°C under argon atmosphere in a three-electrode cell (volume of 15 mL), using a potentiostat/galvanostat Autolab PGSTAT 128N (Metrohm) and NOVA software (v.2.1.4) as an operational interface. The electrochemical system was composed of a glassy carbon electrode (GCE 3.0 mm in diameter) as working electrode, a platinum wire (1 mm in diameter) as counter electrode, and silver/silver chloride (Ag/AgCl) as reference electrode. The GCE was polished with alumina 1.0 and 0.4 μM , submitted to ultrasonic bath for 5 min in a 10% v/v HCl solution, and rinsed with ultrapure water. The following parameters range were applied in SWV tests: frequency (f): 10 to 90 Hz; pulse height (E_{sw}): 10 to 200 mV; step potential (ΔE): 1 to 10 mV.

2.2 Complexing Agents

The redox process, complexing capacity and quantification response of amines were tested individually by SWV. All the amine solutions (20% v/v) were prepared by dissolving 20 mL of amine (MEA, DEA, and TEA - Sigma-Aldrich®; MELA and TELA - Vetec®) in 80 mL of deionized water.

2.3 General Electroanalytical Procedure

The electrochemical cell consisted of 10 mL of electrolytic solution (1.17 mol.L⁻¹ NaOH and 1.37 mol.L⁻¹ NaCl at pH = 13.7 deaerated with pure argon 5 min. The amines were individually analyzed by the addition of 200 μL of 20% v/v solution with 0.36 mmol.L⁻¹ of Fe⁽²⁺⁾ ions.

2.4 Reversibility

SWCV assessed the reversibility applied to 10 mL of supporting solution, 200 μL of the amine solution, which seems to be the most adequate for the proposed system and 0.018 mmol.L⁻¹ of Fe⁽²⁺⁾ [20]. The potential was varied anodically from -1.5 to -0.9 V, which caused oxidation of Fe⁽²⁺⁾ to Fe⁽³⁺⁾ followed by a variation in the cathodic direction in the same range, causing the reduction of such species.

2.5 Validation of the method

Aiming to validate the electrochemical test applied to iron ions detection, corrosion tests were performed on a lab-scale. For that purpose, a gravimetric test was carried out according to the ASTM G31 standard [21].

Carbon steel specimens (triplicate) were immersed for 24 hours in synthetic seawater (ASTM D1141-98 standard) when they were removed and pickled in Clark solution to assess the mass variation. The corrosion rate, in milligrams by decimeter square, was determined by Eq. 1, where Δm represents the mass variation in milligrams; A dm² represents the exposed area of the specimen in decimeters square and t represents the immersion period in days. After the tests, the solutions were evaluated through SWCV for comparison [22].

$$CR = \Delta m / A.t \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Electrochemical Characterization

Cyclic Voltammetry (CV) evaluation, presented in detail in Fig. S1 (Supporting Information), indicated -1.8 and +1.0 V as the working potential range for the proposed method, useful for analyses of about 2.8 V [23].

The proposed electroanalytical system can evaluate compounds that present very negative or very positive potentials without water electrolysis interference. The glassy carbon electrode and the supporting solution showed a high working potential range. Since iron redox reactions occur in high cathodic potential, the system is expected to detect iron effectively [19,20,24].

3.2 Electrochemical Behavior of Complexing Agents

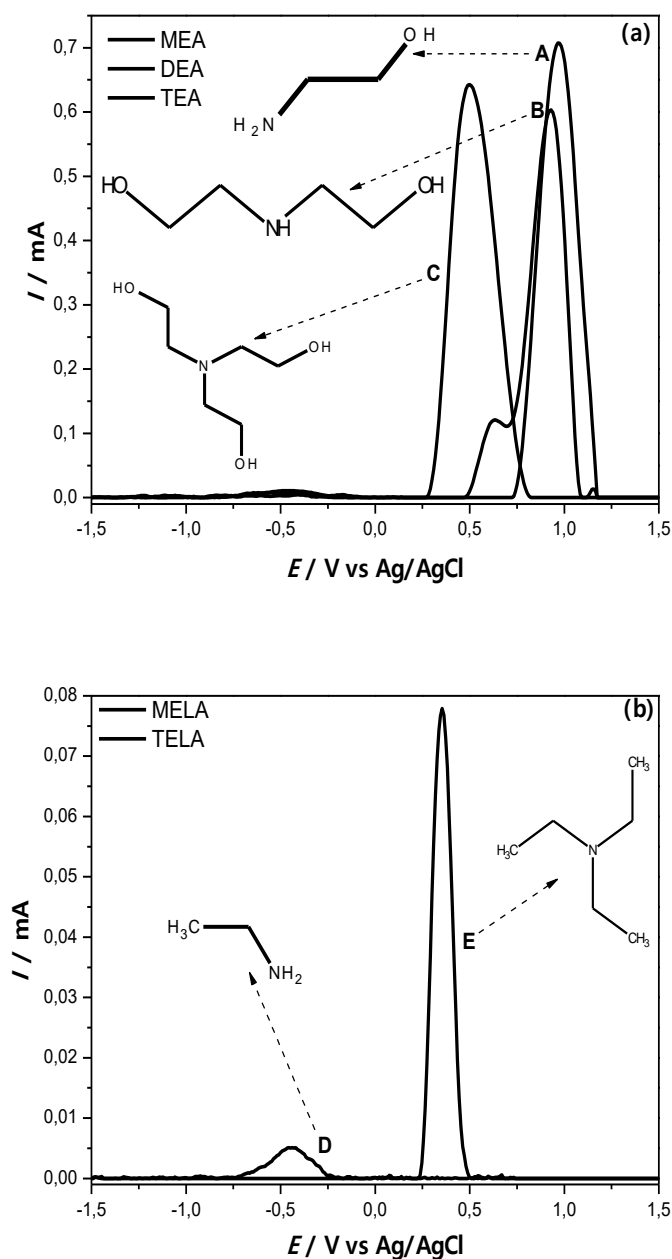


Figure 1. SWV of amines (a) (A) MEA (6.5 mmol.L⁻¹), (B) DEA (4.1 mmol.L⁻¹), (C) TEA (3.0 mmol.L⁻¹), (b) (D) MELA (13.0 mmol.L⁻¹) e (E) TELA (2.8 mmol.L⁻¹) in electrolytic solution (pH = 13.7). E_i : -1.5 V; E_f : 1.5 V; f : 60 Hz; E_{sw} : 100 mV; ΔE : 5 mV.

SWV investigated the electrochemical behavior of the studied amines in a GCE. Fig. 1a and 1b show the oxidation peaks of MEA ($E_p = +0.98$ V), DEA ($E_p = +0.93$ V), TEA ($E_p = +0.49$ V), and TELA ($E_p = +0.35$ V). The oxidation peaks are related to the amine group and not to the presence of the hydroxyl group. As presented by Deelod, TEA in ethanolic solutions presented an oxidation peak in the anodic range (1.53V) and with a peak intensity higher than of the metallic complex [25].

The oxidation response of amines, except for MELA, indicates complexes' formation with higher stability and higher current responses. Nonetheless, as some of these complexes are not reported in the literature, tests were performed to evaluate if these amines present redox peaks when chelating iron ions.

3.3 Electrochemical Characterization of amine- $Fe^{(2+/3+)}$ complexes

As noted in the SWV test, MELA was not capable of forming complexes with $Fe^{(2+)}$ ions. Moreover, due to its alkalinity, the addition of $Fe^{(2+)}$ ions to the supporting solution causes hydrolyzes and precipitation.

Some studies on metal complex such as MEA and DEA are reported in the literature as electrocatalysts. Hanaoka report that Co(II)-MEA and Co(II)-TEA complexes can be used as catalysis enhancing reagents for H_2O_2 detection. Pirsky report in their work on the efficient coordination of nickel and cobalt with MEA [26,27]. However, for detection iron ions the $Fe^{(2+/3+)}-MEA$ and $Fe^{(2+/3+)}-DEA$ complexes present non-linear responses when standard $Fe^{(2+)}$ ions are successively added to the catalytic solution. Therefore, SWV can not be applied to quantify the complexes, although the qualification is possible, as shown in Fig. S2 (Supporting Information).

Since $Fe^{(2+/3+)}-TEA$ and $Fe^{(2+/3+)}-TELA$ complexes presented a linear tendency when standard $Fe^{(2+)}$ ions were successively added, a further study of ΔE , f , and E_{sw} took place. These parameters were established in univariate evaluations in the presence of $Fe^{(2+)}$ ions. $Fe^{(2+/3+)}-TEA$ and $Fe^{(2+/3+)}-TELA$ complexes showed redox peaks in -1.06 V and -1.03 V, respectively. Kothari presented, in 2006, $Fe-TEA$ oxidation peak at -1.13 V by CV [28]. Furthermore, the oxidation peak at -1.06 V and -1.03V presented by SWV of the $Fe^{(2+/3+)}-TEA$ and $Fe^{(2+/3+)}-TELA$ complexes are not exactly the oxidation of the metal itself, but the oxidation of complex, therefore, the $Fe^{(2+)}/Fe^{(3+)}$ oxidation process that occurred in the iron complexes depends on the coordinated ligands.

The increase of step potential up to 10 mV contributed to heighten the peaks amplification, increasing the analytical selectivity. In this way, an increase to 10 mV was chosen to perform the voltammetric analysis (Shown more details Fig. S3, Supporting Information). The increase in frequency caused an increase in current values throughout the studied range. Since noise was observed for values above 60 Hz (Fig. S4, Supporting Information), a frequency of 60 Hz was applied. Increasing the pulse height caused an increase in the voltammetric response. However, for values higher than 75 mV, a loss in analytical selectivity was observed (Fig. S5, Supporting Information).

According to SWV theory, for species-diffusion-controlled systems, the current peak intensity varies linearly with the pulse frequency's square root. Fig. 2 illustrates the current peak behavior for $Fe^{(2+/3+)}-TEA$ and $Fe^{(2+/3+)}-TELA$ complexes. The intensity of the current peak also varies linearly with the square wave frequency's square root, indicating that the diffusion of species regulates the redox process of complexes containing $Fe^{(2+/3+)}$ [29].

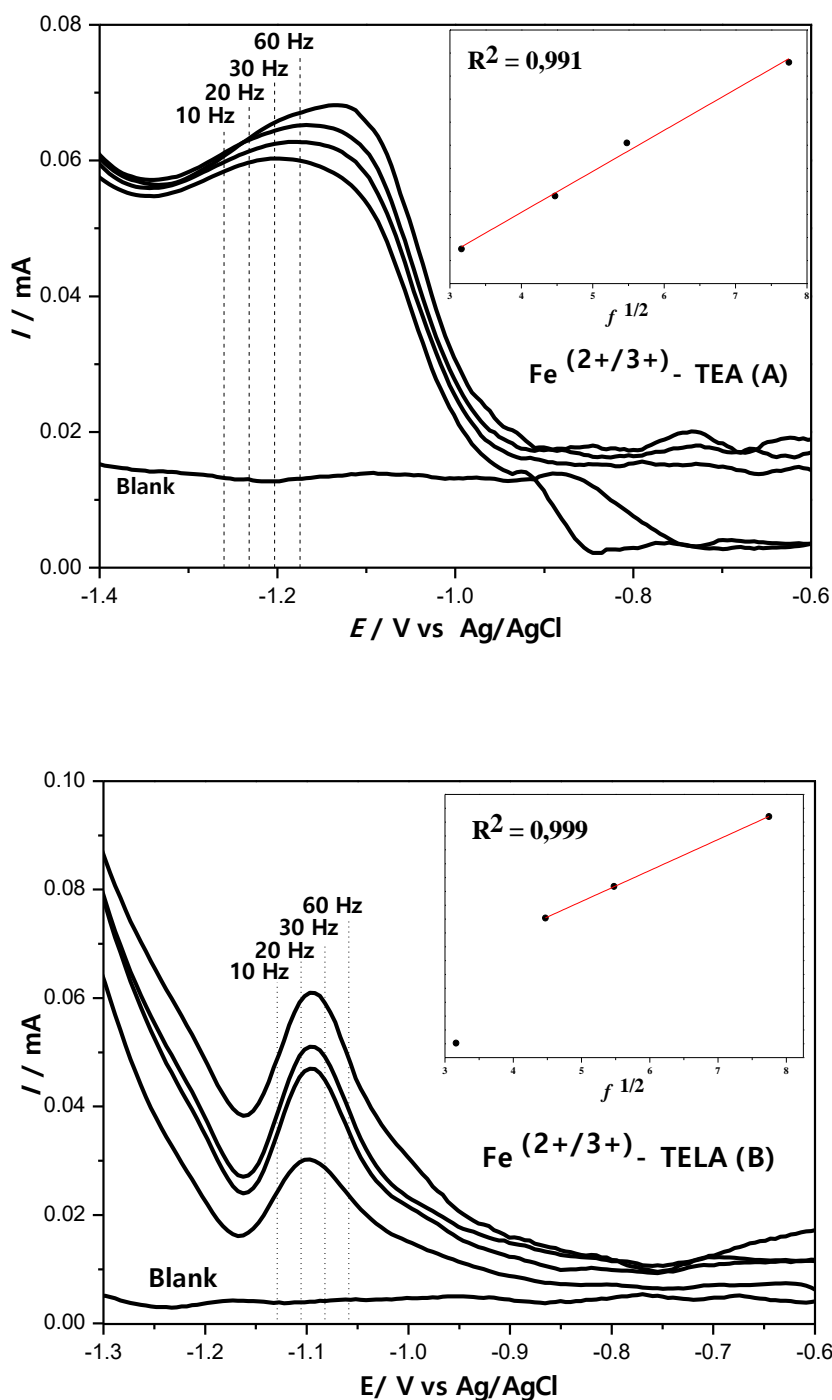


Figure 2. SWV for (A) Fe^(2+/3+)-TEA and (B) Fe^(2+/3+)-TELA complexes at different frequencies of potential pulses at pH 13.7 in an electrolytic solution. E_{sw} : 75 mV; ΔE : 10 mV. Highlights: current peak as a function of square wave frequency's square root.

According to these electroanalytical experiments, there was a decrease in the oxidation analytical signal after successive measurements, suggesting that adsorption is caused by such analyte, not by reaction products. The linear relation between the current peak and square root of frequency indicates

that the complexes exhibit reversible processes. For frequencies below 30 Hz, the linearity deviations can also occur due to the noise from the electronic circuit, and at such low speeds, more substantial interference can be noticed in the voltammetric response. Thus, 10 Hz frequency was disregarded in determining the linearity [30].

3.4 Analytical Performance

After optimizing the square wave voltammetry parameters, analytical curves were constructed by adding small volumes of $\text{Fe}^{(2+)}$ standard solution in the electrolytic solution containing TEA or TELA. A series of voltammetric responses to different concentrations of $\text{Fe}^{(2+)}$ with TEA and TELA amines are presented in Fig. 3 and 4, respectively.

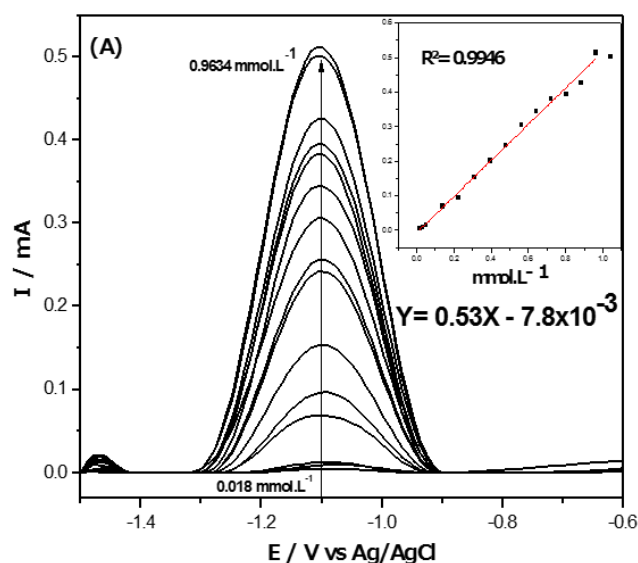


Figure 3. Calibration curve of $\text{Fe}^{(2+/3+)}\text{-TEA}$ from $0.018 \text{ mmol.L}^{-1}$ to $1.042 \text{ mmol.L}^{-1}$ in an electrolytic solution ($\text{pH} = 13.7$). f : 60 Hz; E_{sw} : 75 mV; ΔE : 10 mV.

Voltammetric peak signals and concentrations presented linear relation for $\text{Fe}^{(2+/3+)}\text{-TEA}$ and $\text{Fe}^{(2+/3+)}\text{-TELA}$ complexes for the studied concentration range. The calculated values for the limit of detection (LOD) and limit of quantification (LOQ) for the complexes are shown in Table 1.

Table 1. LOD, LOQ and R^2 of $\text{Fe}^{(2+/3+)}\text{-TEA}$ and $\text{Fe}^{(2+/3+)}\text{-TELA}$ complexes.

	$\text{Fe}^{(2+/3+)}\text{-TEA}$	$\text{Fe}^{(2+/3+)}\text{-TELA}$
LOD	$0.038 \text{ mmol.L}^{-1}$	$0.044 \text{ mmol.L}^{-1}$
LOQ	$0.128 \text{ mmol.L}^{-1}$	$0.148 \text{ mmol.L}^{-1}$
R^2	0.9946	0.9802

LOD and LOQ were calculated as 3 and 10 times, respectively, the intercept's standard deviation over the calibration curve slope. After automatic background subtraction, the presented voltammograms were obtained. The calibration plot of $\text{Fe}^{(2+/3+)}$ -TEA was linear from 0.018 to 0.963 mmol.L^{-1} and agreed with equation $y=(0.52 \pm 0.012)x-(7.8e^{-3} \pm 6.6e^{-3})$, where y and x represent peak current (mA) and $\text{Fe}^{(2+)}$ concentration (mmol.L^{-1}), respectively. While, the calibration plot of $\text{Fe}^{(2+/3+)}$ -TELA was linear 0.018 to 0.395 mmol.L^{-1} and agreed with equation $y=(2,7e^{-4} \pm 1,7e^{-5})x+(1,8e^{-5} \pm 4,0e^{-6})$.

Fig. 3 and 4 show that $\text{Fe}^{(2+/3+)}$ -TEA has presented better linearity than $\text{Fe}^{(2+/3+)}$ -TELA. Such linearity indicates the formation of $\text{Fe}^{(2+/3+)}$ -TEA complexes to be used as an alternative method for analyzing iron in solution. According to the curve slope, it was possible to affirm that the proposed method is sensitive to $\text{Fe}^{(2+/3+)}$ -TEA detection with a sensitivity of 0.53 ± 0.012 (mmol.L^{-1}).

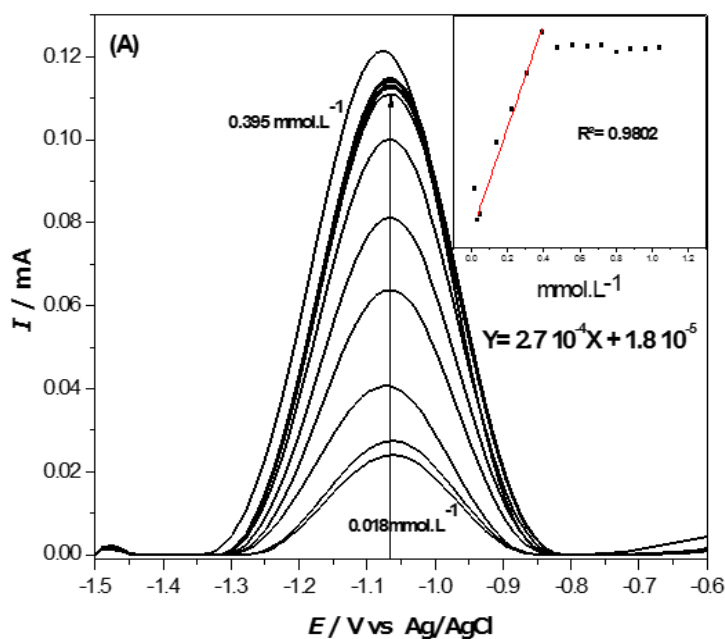


Figure 4. Calibration curve of $\text{Fe}^{(2+/3+)}$ -TELA from 0.018 mmol.L^{-1} to 0.395 mmol.L^{-1} in an electrolytic solution ($\text{pH} = 13.7$). f : 60 Hz; E_{sw} : 75 mV; ΔE : 10 mV.

Since only $\text{Fe}^{(2+/3+)}$ -TEA complex showed significant linearity for the proposed methodology, this complex's degree of reversibility was evaluated applying the SWV in the cathodic sense, as seen in Fig. 5. After oxidation of $\text{Fe}^{(2+)}$ -TEA to $\text{Fe}^{(3+)}$ -TEA through anodic scanning, the cathodic scanning converts the complex to its original state without loss of efficiency, indicating that iron speciation can be analyzed by this method.

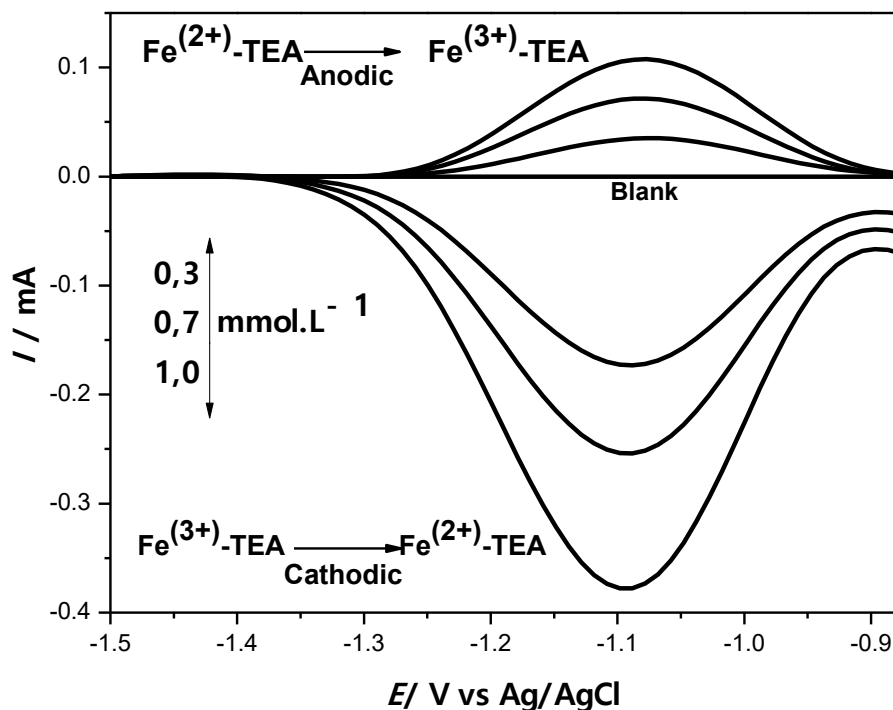


Figure 5. Evaluation of reversibility of redox reaction $\text{Fe}^{(2+/3+)}\text{-TEA}$ in an electrolytic solution ($\text{pH} = 13.7$). f : 60 Hz; E_{sw} : 75 mV; ΔE : 10 mV.

3.5 Tolerance to Interfering Species

Possible interferences in detecting $\text{Fe}^{(2+/3+)}$ from corrosion products in actual samples were evaluated under optimized experimental conditions. The metal ions that could potentially interfere due to their presence in the synthetic seawater were examined: Mn^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , and Ag^+ . No interference was observed in the potential range of -1.5 to -0.6 V after automatic background subtraction.

The SWV voltammogram shown in Fig. 6 shows the presence of only two significant current signal peaks. The peak in the anodic region (-1.1 V) is due to the $\text{Fe}^{(2+/3+)}\text{-TEA}$ complex oxidation. The peak current in the cathodic region (+0.6 V) is due to the TEA molecule oxidation, as previously seen in Fig. 1a.

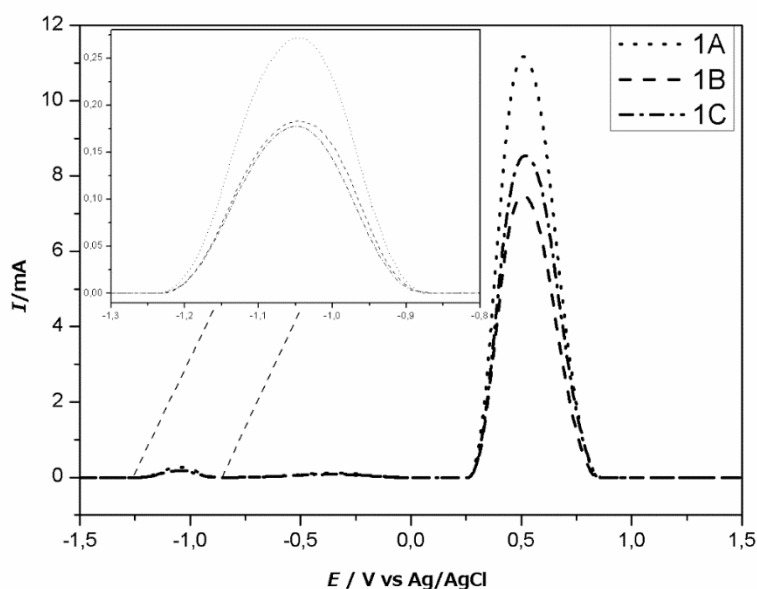


Figure 6. SWV of Sample-TEA in an electrolytic solution (pH = 13.7). f : 60 Hz; E_{sw} : 75 mV; ΔE : 10 mV.

3.6 Validation of the method

The corrosion rates obtained by the gravimetric analysis were 36.4, 40.7, and 40.3 mdd. Since 1020 carbon steel is about 99,9% composed of iron, iron concentrations found in the gravimetric analysis were 1.164, 1.253, and 1.343 mmol.L⁻¹. According to the Eh-pH diagram (Pourbaix diagram) and with the initial and final values of potential and pH, presented in Fig. S6 (Supporting Information), it is supposed that the corrosion process occurs in the region where there is a thermodynamic prevalence of Fe⁽²⁺⁾ generation. So, corrosion evaluation by SWCV was performed only in the anodic direction [31].

Finally, the synthetic sea water medium was analyzed by SWV to provide data for comparison with the gravimetric analysis and also to study the influence of interfering compounds in the technique proposed. The aqueous media were diluted 2 times for this analysis. Fig. 6 shows the voltammogram for the samples in the potential range between -1.3 and -0.8 V.

The voltammogram indicates that the use of SWV in the Fe^(2+/3+)-TEA complex is selective and shows good replicability even when applied to a diverse matrix-like synthetic sea water, which presents relevant concentrations of interfering metals, such as Mn²⁺, Cu²⁺, Zn²⁺, Pb²⁺ e Ag⁺ as well as free chlorine ions. The voltammetric profile presented few noise areas, and, from the peak currents, the Fe⁽²⁺⁾ concentration through the linear regression of the calibration curve was estimated. The concentrations estimated by this method for the samples showed in the Table 2.

Table 2. Comparison of de concentration iron by SWV and mass loss.

Sample	Concentration ^a of Fe _{total} (mmol.L ⁻¹)	Concentration ^b of Fe _{total} (mmol.L ⁻¹)	Accuracy (%)
1A	1.148	1.164	98.6
1B	1.267	1.253	101.1
1C	1.363	1.343	101.5

a –

Concentration of Fe_{total} by SWVb – Concentration of Fe_{total} by mass loss

Comparing the results from both methods there was high similarity for the three samples, the accuracy of the new developed methodology is confirmed. The accuracy of the new method was also verified through the coefficient of variation in different calibration curves, which was 0.4%, demonstrating, once again, the capability of quantifying iron in solution in this concentration range. Therefore, the method can be applied to assess carbon steel corrosion.

The comparison of corrosion detection methodology through the Fe^(2+/3+)-TEA complex and the methods described in the literature for the last five years (Shown more details Table 3) these also aimed at the qualification/quantification of the corrosion product using ions iron as an analyst. We can say that the methodology developed here, besides being the only one capable of carrying out chemical speciation, among those listed, of the iron element when necessary, is also capable of quantifying the iron ions selectively and with good reproducibility.

Table 3. Comparison between different methodologies for detecting corrosion by quantification of the chemical element iron.

Method	Linear Range [mol/L]	LOD [mol/L]	Ref
Raman Spectroscopy	-	-	25
Infrared Spectroscopy	1.13 to 5.64	2.3x10 ⁻¹	26
Spectrophotometry	1.8x10 ⁻⁷ to 9.0x10 ⁻⁶	-	27
Raman Spectroscopy	Qualitative	-	28
Permanganometry	-	-	29
ICP-MS	-	-	30
Raman Spectroscopy	5.4x10 ⁻⁶ to 1.1x10 ⁻¹	-	31
Fluorescent Spectrophotometry	1.0x10 ⁻⁷ to 1.0x10 ⁻⁶	3.5x10 ⁻⁸	32
SWV	1.8x10 ⁻⁵ to 9.6x10 ⁻⁴	3.0x10 ⁻⁵	This Work

4. CONCLUSIONS

A new voltammetric method for iron ions detection was developed using glassy carbon as a working electrode and complexing agents to form Fe^(2+/3+)-amines complexes. Among the five amines

evaluated in this study, MEA, DEA, TEA, MELA and TELA, only the $\text{Fe}^{(2+/3+)}$ -TEA complex presented linear tendency, accuracy, and precision for the proposed method.

The electrochemical tests show the following ideal parameters for this analysis: frequency of 60 Hz, pulse height of 75 mV, and a step potential of 10 mV. $\text{Fe}^{(2+/3+)}$ -TEA complex exhibited good analytical properties and, therefore, could be considered as an effective alternative method for detection and speciation of iron in solution.

The comparison to the gravimetric analysis results suggests that the developed SWV method shows good accuracy and precision for quantifying iron ions in practical samples since the most significant error with the gravimetric method was 1.5%. Therefore, this new methodology represents an alternative for detecting corrosion in carbon steel since it is efficient and selective to iron.

SUPPLEMENTARY INFORMATION

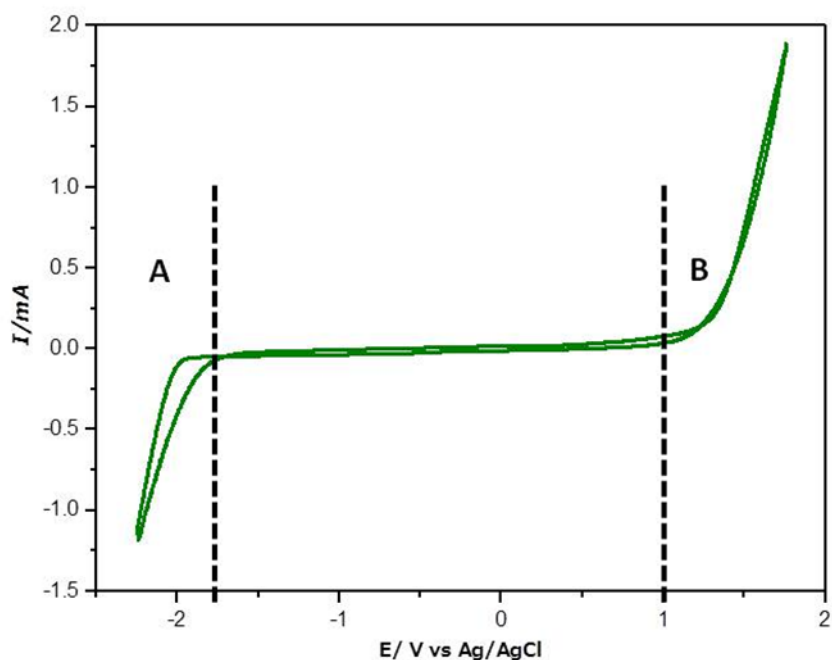


Fig. S1. Cyclic voltammetry of electrolytic solution (1.17 mol.L^{-1} NaOH and 1.37 mol.L^{-1} NaCl at $\text{pH} = 13.7$) scan rate of 30 mV.s^{-1} . Regions A and B, water oxidation and reduction processes.

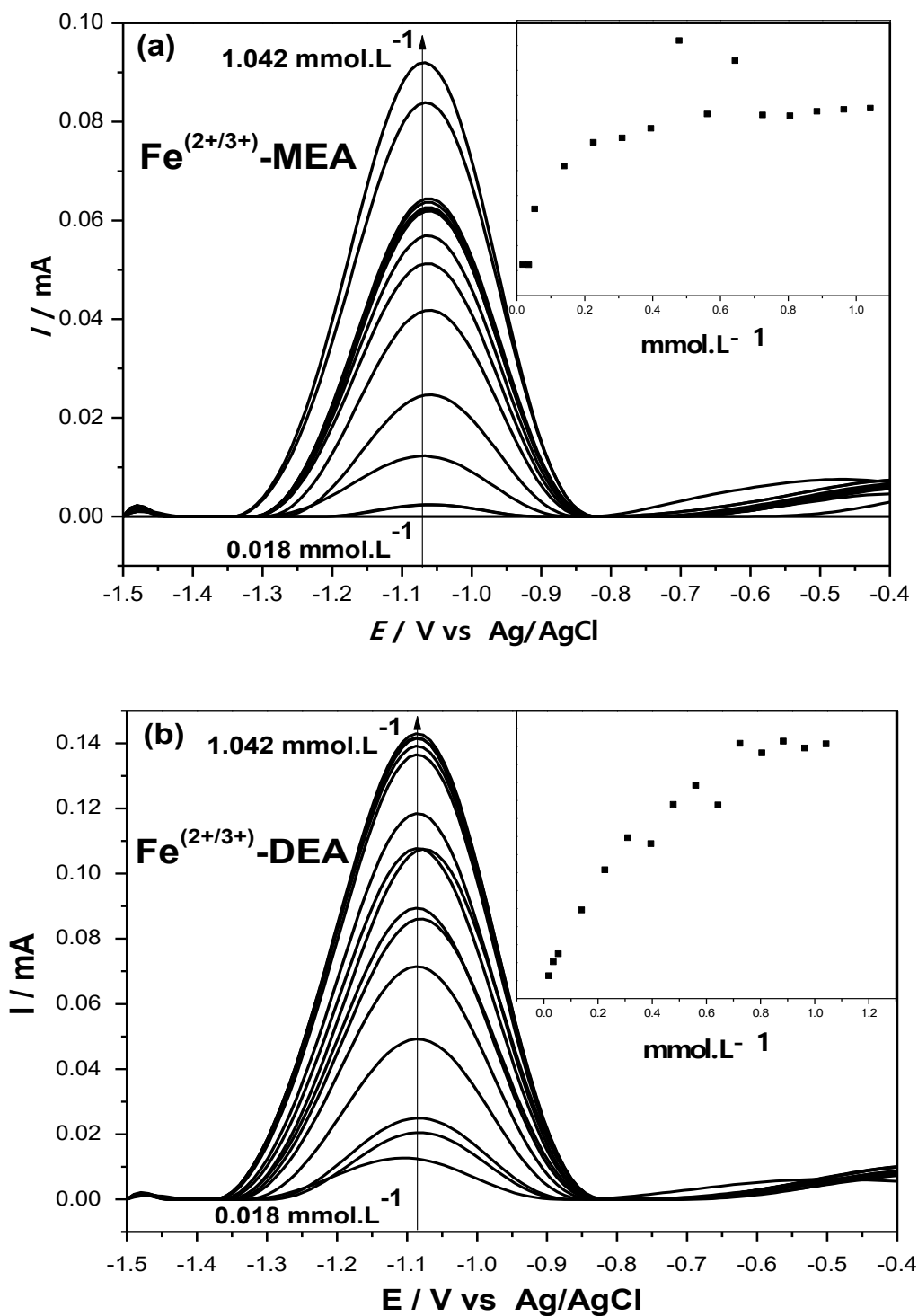


Fig. S2. SWV of (a) $\text{Fe}^{(2+/3+)}\text{-MEA}$ complex and (b) $\text{Fe}^{(2+/3+)}\text{-DEA}$ complex. In electrolytic solution, f : 60 Hz; E_{sw} : 100 mV; ΔE : 5 mV.

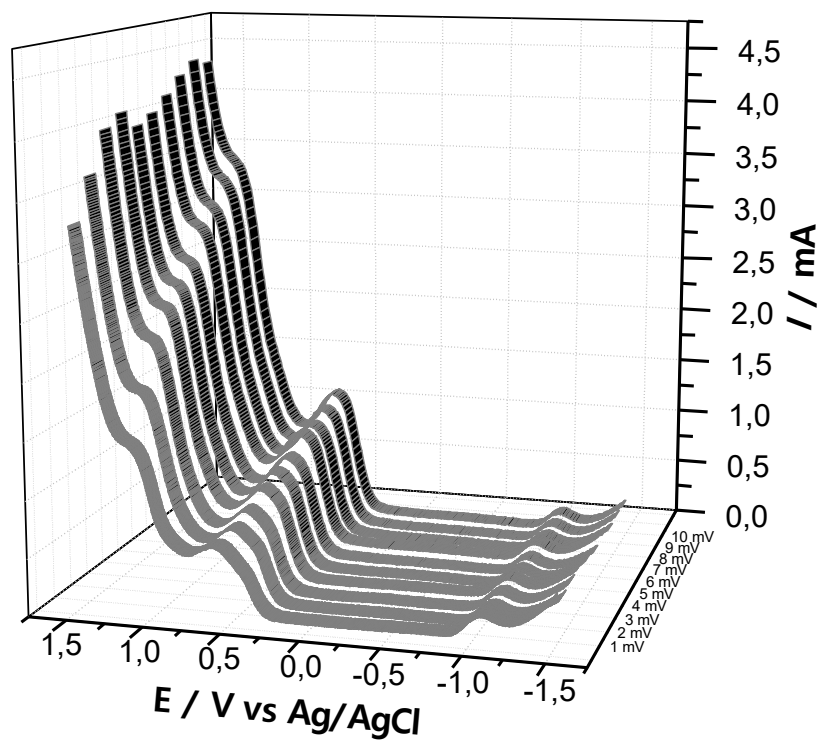


Fig. S3. Variation of step potential (ΔE : 1 to 10 mV) of $\text{Fe}^{(2+/3+)}$ -TEA complex. SWV in electrolytic solution, f : 60 Hz; E_{sw} : 100 mV.

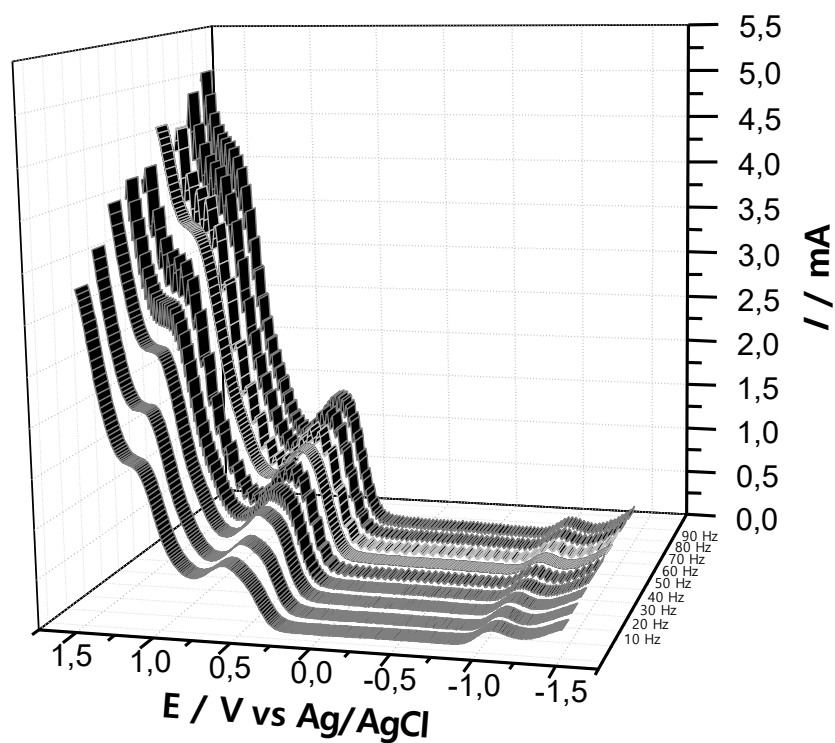


Fig. S4. Variation of frequency (f : 10 to 90 Hz) of Fe^(2+/3+)-TEA complex. SWV in electrolytic solution, E_{sw} : 100 mV; ΔE : 10 mV.

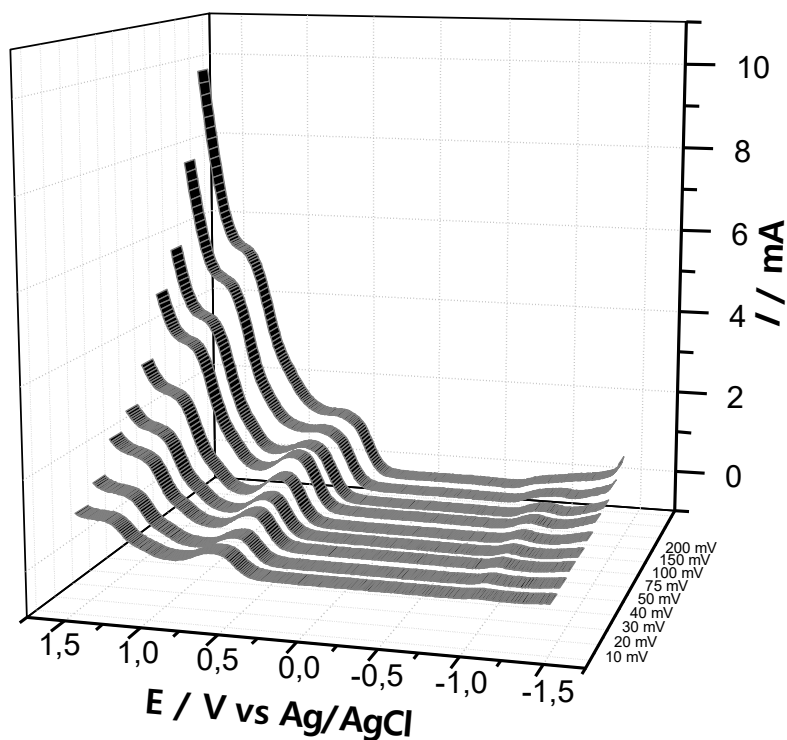


Fig. S5. Variation of pulse height (E_{sw} : 10 to 200 mV) of $Fe^{(2+/3+)}$ -TEA complex. SWV in electrolytic solution, f : 60 Hz; ΔE : 10 mV.

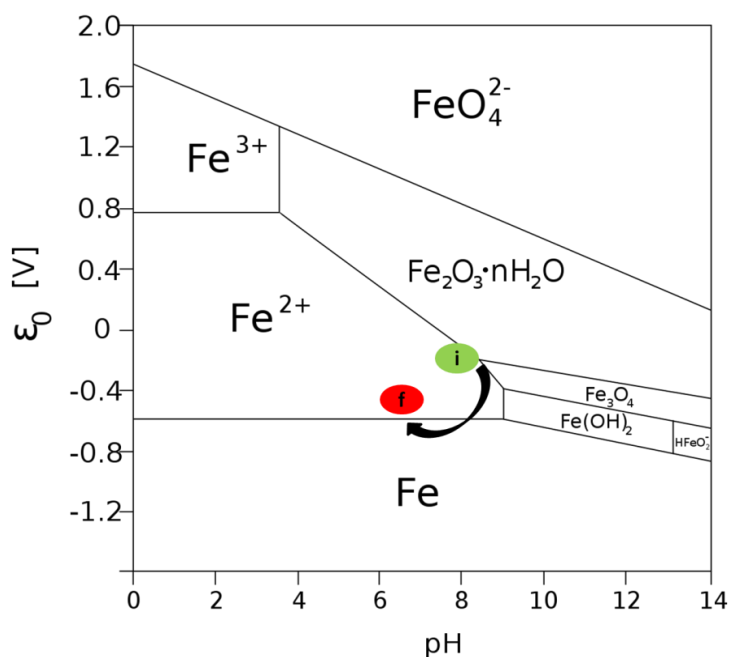


Fig. S6. Pourbaix diagram of the iron, where “i” stands for the initial state and “f” for the final state. Source: *Atlas of electrochemical equilibria in aqueous solutions*, NACE. 1974.

References

1. S.H. Jeon, G.D. Song, and D.H. Hur, *Mater. Trans.*, 56 (2015) 1107.
2. H. Heli, S. Majdi, N. Sattarahmady, and A. Parsaei, *J. Solid State Electrochem.*, 14 (2010) 1637.
3. L. Kozak, P. Niedzielski, and W. Wachowiak, *Microchem. J.*, 110 (2013) 54.
4. R. Gotti, J. Fiori, L. Liverani, and F. Spelta, *Electrophoresis*, 36 (2015) 2820.
5. S. Chen, N. Li, X. Zhang, D. Yang, and H. Jiang, *Spectrochim. Acta, Part A*, 138 (2015) 375.
6. Y.H. Xu, H.F. Li, C.P. Chu, P. Huang, and C.A. Ma, *Ind. Eng. Chem. Res.*, 53 (2014) 10637.
7. G. Somer, A.C. Çalışkan, and O. Şendil, *J. Anal. Chem.*, 69 (2014) 1083.
8. P.S. Verma, R.C. Saxena, and A. Jayaraman, *Fresenius J. Anal. Chem.*, 357 (1997) 56.
9. R.D. Ferreira, M.R. Baldan, N.G. Ferreira, and N.A. Braga, *Rev. Bras. Apl. Vacuo*, 35 (2016) 1.
10. Y.P. Dong, H. Cui, and C.M. Wang, *J. Phys. Chem. B*, 110 (2006) 18408.
11. L.M. Laglera, S. Caprara, and D. Monticelli, *Talanta*, 150 (2016) 449.
12. V. Mirceski, B. Mitrova, V. Ivanovski, N. Mitreska, A. Aleksavska, and R. Gulaboski, *J. Solid State Electrochem.*, 19 (2015), 2331.
13. X. Hu, D. Pan, M. Lin, H. Han, and F. Li, *Microchim. Acta*, 183 (2016) 855.
14. C. Göde, M.L. Yola, A. Yılmaz, N. Atar, and S. Wang, *J. Colloid Interface Sci.*, 508 (2017) 525.
15. E. Safaei, N. Naghdi, A. Wojtczak, and Z. Jagličić, *Polyhedron*, 109 (2016) 190.
16. T. Karimpour, E. Safaei, A. Wojtczak, Z. Jagličić, and A. Kozakiewicz, *Inorg. Chim. Acta*, 395 (2013) 124.
17. L.R. Kindra, C.J. Eggers, A.T. Liu, K. Mendoza, J. Mendoza, A.R. Klein Myers, and R.M. Penner, *Anal. Chem.*, 87 (2015) 11492.
18. A. Lê, D. Floner, T. Roisnel, O. Cador, L. Chancelier, and F. Geneste, *Electrochim. Acta*, 301 (2019) 472.
19. Y. Zhu, X. Hu, D. Pan, H. Han, M. Lin, Y. Lu, and R. Zhu, *Sci. Rep.*, 8 (2018) 1.
20. Y.H. Wen, H.M. Zhang, P. Qian, H.T. Zhou, P. Zhao, B.L. Yi, and Y.S. Yang, *Electrochim. Acta*, 51 (2006) 3769.
21. ASTM G31-72: Standard Practice for Laboratory Immersion Corrosion Testing of Metals. *ASTM Int.*, (2014) United State.
22. ASTM D1141-98. Standard practice for the preparation of substitute ocean water. *ASTM Int.*, (2008) United State.
23. S.O. Fatin, H.N. Lim, W.T. Tan, and N.M. Huang, *Int. J. Electrochem. Sci.*, 7 (2012) 9074.
24. A. Bobrowski, K. Nowak, and J. Zarębski, *Anal. Bioanal. Chem.*, 382 (2005) 1691.
25. W. Deeloed, S. Wannapaiboon, P. Pansiri, P. Kumpeerakij, K. Phomphrai, A. Laobuthee, Y. Hanlumyuang, S. Suramitr, P. Pinyou, and W. Wattanathana, *Crystals*, 10 (2020) 474.
26. S. Hanaoka, J.M. Lin, and M. Yamada, *Anal. Chem. Acta*, 426 (2001) 57.
27. Y. Pirskyy, N. Murafa, O.M. Korduban, and J. Šubrt, *J. Appl. Electrochem.*, 44 (2014) 1193.
28. H.M. Kothari, E.A. Kulp, S.J. Limmer, P. Poizot, E.W. Bohannon, and J.A. Switzer, *J. Mater. Res.*, 21 (2006) 293.
29. M. Bouroushian, T. Kosanovic, Z. Loizos, and N. Spyrellis, *J. Solid State Electrochem.*, 6 (2002) 272.
30. D. Badocco, V. Di Marco, A. Mondin, and P. Pastore, *J. Chem. Eng. Data*, 60 (2015) 895.
31. M. Pourbaix, "Atlas of electrochemical equilibria in aqueous solutions", 307 (1974) NACE.
32. O. Toshiaki, *Surf. Sci.*, 36 (2015) 12.
33. D. Turkmen, C. Dettenrieder, P. Forsberg, A. Mattsson, and F. Nikolajeff, *ACS Sens.*, 19 (2019) 3373.
34. L.K. Wu, J.M. Hu, J.Q. Zhang, *Corros. Sci.*, 59 (2012) 348.
35. J.I. Iribarren, F. Liesa, A. Meneguzzi, C. Alemán, and E. Armelin, *J. Cult. Heritage*, 42 (2020) 240.
36. S. Fedosov, V. Roumyantseva, and V. Konovalova, Phosphate coatings as a way to protect steel reinforcement from corrosion, In: MATEC Web of Conferences. *EDP Sciences*, 2019, 126.
37. R. Ayers, M. Miller, J. Schowinsky, E. Burger V. Patel, and C. Kleck, *J. Mater. Sci.: Mater. Med.*, 29

(2018) 3.

38. C. Remazeilles, F. Leveque, E. Conforto, L. Meunier, and P. Refait, *Microchem. J.*, 148 (2019) 10.
39. Z. Yan, L. Hu, J. You, *Anal. Methods*, 8 (2016) 5738.
40. P. Ugo, L.M. Moretto, D. Rudello, E. Birriel, and J. Chevalent, *Electroanalysis*, 13 (2001) 661.
41. D.V. Thomaz, K.D.S. Leite, E.K.G. Moreno, L.F. Garcia, M.F. Alecrim, I.Y.L. Macêdo, and E.D.S. Gil, *Int. J. Electrochem. Sci.*, 13 (2018) 5433.
42. S.O. Fatin, H.N. Lim, W.T. Tan, and N.M. Huang, *Int. J. Electrochem. Sci.*, 7 (2012) 9074.

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