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Applying Platinum Microelectrodes as a Sensor for Heterocyclic-Based Compounds Corrosion Inhibitors

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An electroanalytical method based on differential pulse voltammetry was developed using a platinum electrode to monitor the quality and quantity of morpholine-based commercial inhibitors used in the oil industry. The voltammetric method presented a strong linear correlation coefficient with a linear response over a concentration range of 20 to 80 mg L^{-1} and detection limit of 12 mg L^{-1}. In addition, the method has been shown to be precise, linear and homoscedastic. The recovery for the voltammetric method was 102 ± 4%, and the recovery for the commercial inhibitor samples fortified with morpholine was 102 ± 4%.

Keywords: Platinum microeletrodes, corrosion inhibitors, morpholine

1. INTRODUCTION

Heterocyclic compounds are classified as effective corrosion inhibitors [1, 2]. Their high inhibition efficiencies are directly related to the presence of electronegative functional groups and to π-electrons found in triple bonds or conjugated double bonds. Aromatic rings and heteroatoms (e.g., sulphur, phosphorus, nitrogen and oxygen) are crucial for the molecules' inhibitory capacity because they act as optimal adsorption sites, and the mechanism of inhibition occurs primarily through a

surface adsorption process [3, 4].

Consequently, morpholine and its derivatives are considered to be excellent corrosion inhibitors and are used as components in commercially available corrosion inhibitors [5, 6]. The addition of corrosion inhibitors such as morpholine and its derivatives is essential to avoid both general and pitting corrosion of pipelines, which are covered by oil and hydrogen sulphide-containing water, formation water with high salinity or seawater at high temperatures, which all act as highly corrosive media [7]. Therefore, it is necessary to build a sensor with a long-term stability that should be able to determine heterocyclic-based compounds inhibitors through the entire pipeline [8].

In this way, corrosion is a major problem faced in the oil industry, especially in steam generation and pipeline systems. The corrosion of metallic materials is commonly caused by pH variations and the presence of oxidising media, which exist in both the vapour and liquid phases. Thus, the use of corrosion inhibitors is essential to mitigate the premature degradation of industrial equipment [9].

Therefore, it is clear that a fast and reliable method to monitor the concentration of an inhibitor (e.g., morpholine) is fully required. Among some analytical techniques, such as direct titration, colorimetric methods, spectrophotometry and electrochemical methods still are being used for the determination and quantification of morpholine. Moreover, ion-exchange chromatography (IEC) [10, 11], gas chromatography (GC) [12, 13] and high-performance liquid chromatography (HPLC) [14, 15] are also being used for this purpose. Although these classical methods are useful, they are still time-consuming for routine analysis when compared with electrochemical methods.

For these goals, electrochemical methods (i.e., electroanalytical techniques) are suitable for trace analysis and are an interesting alternative to identify and quantify compounds in industrial water in terms of high sensitivity, fast response time and low cost [16]. Their advantages arise from their capability for direct, in situ usage without the need for sample pre-treatment compared to the aforementioned chromatographic techniques [17].

Focusing on electrochemical systems, some of us have recently suggested [18] flow injection analysis method to determine morpholine in gas condensate samples. The method presented a good recovery for both real and synthetic samples showing to have suitable precision and accuracy. For the condensate samples in the field the use of miniaturized system is required. By the way, the use of microelectrodes can be considered for this purpose since a disposable device can be readily assembled.

The aim of this work is to develop an electroanalytical method based on differential pulse voltammetry using a platinum microelectrode to monitor the quality of morpholine-based commercial inhibitors and residual inhibitors used to control internal corrosion in oil industry pipelines. Moreover, a statistical analysis was done to validate our electrochemical method. In the light of metrology, such results highlight statically the confidence of purposed electrochemical methods mostly used.

2. EXPERIMENTAL

2.1. Reagents and supporting electrolyte solutions

All reagents used in this work were of analytical grade, and all solutions were prepared in water

purified by the Milli-Q Millipore system (resistivity ≥18 MΩ cm^2).

Morpholine (ACS reagent) was purchased from Sigma-Aldrich (Duque de Caxias, Brazil). The supporting electrolyte solution used for the analytical studies consisted of 0.1 mol L^{-1} $LiClO_4$ in acetonitrile. The analytical curves were constructed by adding different aliquots of 10000 mg L^{-1} morpholine standard solution to the electrochemical cell containing 10 mL of the blank electrolyte solution, with the final concentrations between 20 and 80 mg L^{-1}. All experiments were carried out, at least, three times in order to perform statistical analysis. Solutions of morpholine and electrolyte solution were freshly prepared.

2.2. Electrochemical Instrumentation

All measurements were performed using an Autolab potentiostat (model PGSTAT 128, Eco Chemie B.V.; The Netherlands) with a current amplifier module controlled by GPES 4.9 software. All experiments were carried out at 25 ºC in a Faraday cage to eliminate any noise current. The differential pulse voltammetry technique was used, and the curves were obtained with 50 mV potential step (E_{step}) and 10 mV pulse amplitude (a) at potential scan rate (v) equal to 20 mV s^{-1}.

The electrochemical experiments were carried out with a conventional electrochemical cell with three electrodes. The working electrode was a homemade platinum microelectrode, a platinum wire was employed as a counter electrode and the reference electrode was Ag/AgCl/LiCl saturated in ethanol. The platinum microelectrode was prepared using a platinum wire with a diameter of 300 μm (purchased from Heraeus Vectra) was sealed directly into soft glass. The tip of the Pt microelectrode was abraded with emery paper 400 and 600 grit emery paper until a metal microdisc was exposed at the surface. Prior to each experiment, the surface was mechanically abraded with 1000, 1500 and 2000 grit emery paper and cleaned with purified water.

The cleanness of the electrochemical apparatus was checked from successive cyclic voltammograms between −0.4 and 1.75 V at 0.5 V s^{-1} in acidic media until the characteristic voltammetric profile for the polycrystalline platinum microelectrode in acid media was observed (cf. Ref. [19]).

3. STATISTICAL ANALYSIS

The validation of the voltammetric method for the quantitative determination of morpholine was performed via several steps, which were important to ensure the reliability of the obtained results [20] and [21].

3.1. Linearity and homoscedasticity

The analytical curve (peak current vs. morpholine concentration) was acquired by fitting the data obtained with morpholine standard samples to the linear regression model. The Cochran test was

applied to the curve to evaluate the bilateral deviation of the variances to a 5% significance level. Moreover, a residue graph was constructed to evaluate the homoscedasticity of the method. The residue graph was generated from the differences between the values calculated from the straight line of the analytical curves and the values obtained experimentally. The results of any quantitative method that can be described by a linear regression model should present analytical curves with significantly constant (homogenous) variances.

3.2. Detection and quantification limits

The detection limits (DL) for the voltammetric methods were obtained from the experimental data according to three statistical criteria: $3.3\sigma_c/b$, $3\sigma_b/b$ and $3\sigma_b + X_b$, wherein b is the slope of the linear analytical curve, σ_c is an estimate of the standard deviation of the analytical curve, σ_b is an estimate of the standard deviation of the blank sample response and X_b is the average value for a blank sample. Eight blank samples of the electrolyte solution were analysed to determine the detection limits. Grubb's test was used to check for possible outliers, and all measurements lay within a 95% confidence interval. The detection limit was also determined experimentally from the lowest peak current of morpholine oxidation that was still significantly different from the blank sample.

3.3. Recovery Study

The recovery of the method was tested with synthetic samples as well as commercial inhibitor samples (containing morpholine) fortified with 75 mg L^{-1} (0.86 mmol L^{-1}) of morpholine.

Synthetic samples were obtained by addition of aliquots of morpholine standard solution (concentration range: 20 – 80 mg L^{-1}) in an electrochemical cell containing 0.1 mol L^{-1} $LiClO_4$ in acetonitrile. Then, electrochemical measurements (differential pulse voltammetry) were carried out and current peaks were observed. From these current peaks the synthetic samples concentrations were calculated, using the analytical curve (see 3.1), and the recovery was obtained by the ratio between nominal and calculated concentrations.

A commercial inhibitor sample was aliquoted and then added in an electrochemical cell containing 0.1 mol L^{-1} $LiClO_4$ in acetonitrile. Then, an electrochemical measurement (differential pulse voltammetry) was carried out and current peak was observed. The same sample was fortified with morpholine standard solution (75 mg L^{-1}). The electrochemical measurement was carried out again and new peak current was observed. The concentration of morpholine added was calculated by the difference between the current peaks before and after the fortification step. The recovery was obtained by the ratio between nominal and calculated concentrations.

3.4. Precision

Precision was determined based on the repeatability of the analysis, which was evaluated from the standard deviations obtained in triplicate from an analytical curve constructed with the same

instrument. The intermediary precision was evaluated by comparing the analytic curves from different days and with different analysts. A sequence of statistical calculations was performed to compare the slope of the analytical curves, which were obtained from distinct operators at different days.

3.5. Study of the matrix effect

The matrix effect on an analytical method is due to the effect of all other components of the sample except the specific compound to be quantified.

The matrix effect in the voltammetric method was measured by the statistical comparison of the analytical curves performed with a synthetic morpholine solution containing 0.1 mol L^{-1} $LiClO_4$ in acetonitrile in the absence and presence of the morpholine-based commercial inhibitor sample provided by Cenpes/Petrobras.

A sequence of statistical calculations was necessary to evaluate the slopes of the two analytical curves, which were obtained from distinct matrices. First, the residual variance (Se^2) was determined for each analytical curve. Then, the Cochran test was applied to verify if the residual variances were significantly different [20, 21].

3.6. Comparison of different analytical curves

To evaluate the slope of the two analytical curves, which were obtained from distinct matrices, a sequence of statistical calculations was necessary. First, the residual grouped variance was determined for each analytical curve. When the calculated *F*-value (F_{cal}) was lower than the critical *F*-value (F_{crit}), the variances were considered to be statistically equivalent. In the second step, the grouped variance was calculated for each calibration curve. In the last step, the calculated *t*-value (t_{cal}) was obtained and compared with the critical *t*-value (t_{crit}) for a 5% significance level. If t_{cal} was lower than t_{crit}, then the slopes of the two calibration curves were considered to be statistically equivalent [20, 21].

4. RESULTS AND DISCUSSION

4.1. Electroactivity

The electroactivity of morpholine was investigated over a potential range of 0.0 to 2.0 V vs Ag/AgCl. Figure 1 shows the voltammograms obtained in the absence (blank) and presence of 80 mg L^{-1} of morpholine in 0.1 mol L^{-1} $LiClO_4$ in acetonitrile. In these voltammograms, one peak at approximately 1.1 V vs. Ag/AgCl was observed. This peak can be correlated with an anodic process, which is characteristic of morpholine oxidation. Similar electro-oxidation behaviour was previously observed using carbon screen-printed electrode in aqueous media [18].

To the best of our knowledge, there is no mechanism for morpholine's electro-oxidation. Nevertheless, several papers deal with the biodegradation of morpholine using Mycobacterium [22-26]

or Arthrobacter, and Gram-negative bacteria [27]. It is considered that the bacterial oxidation of morpholine involves the Cytochrome P450 enzyme and takes place initially at the αC of the nitrogen atom by a hydrogen abstraction followed by rebound OH insertion to form the 2-hydroxymorpholine [28]. A thorough mechanistic study of morpholine's electro-oxidation is yet to be performed by our group.

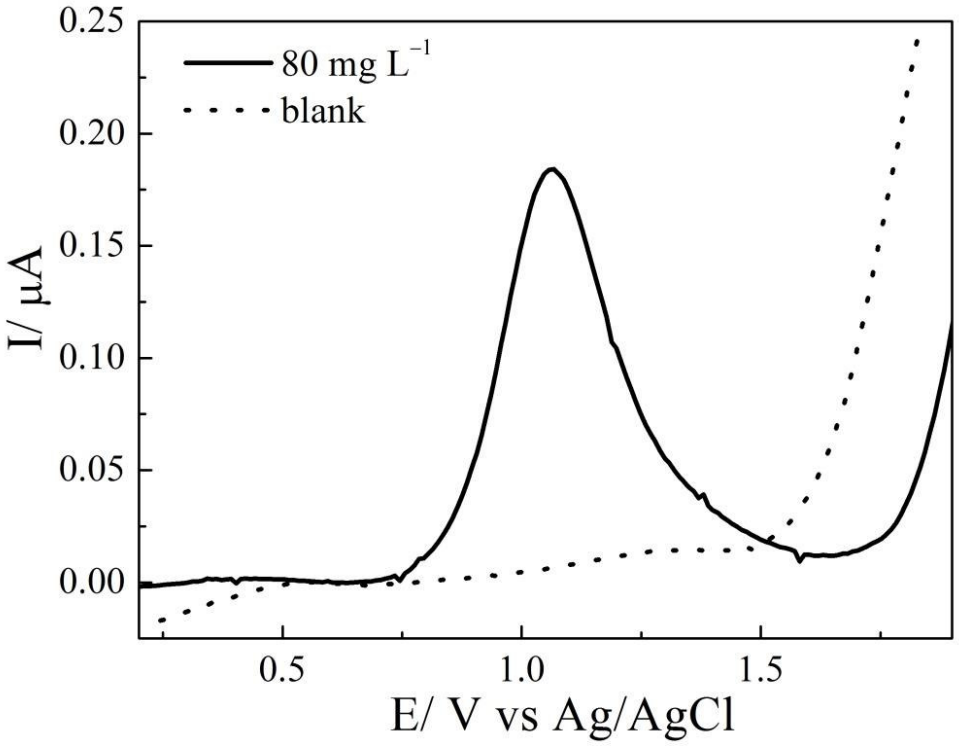

Figure 1. Voltammograms obtained by differential pulse voltammetry (E_{step} = 50 mV, a = 10 mV and v = 20 mV s^{-1}) in the absence and presence of 80 mg L^{-1} morpholine in 0.1 mol L^{-1} $LiClO_4$ in acetonitrile using a platinum microelectrode.

4.2. Linearity and homoscedasticity

Figure 2 depicts the relationship between the peak currents and the morpholine range concentration (20 and 80 mg L^{-1}). The curve presents a good correlation coefficient (r = 0.9986). It can be observed that the fitting line does not pass through the origin. This indicates that there probably is a cumulative contribution of capacitive current (ca. 0.005 μA) from blank voltammogram (cf. Figure 1), shifting the best-fitting from the origin.

The homoscedasticity of the method was determined by applying the Cochran test to the analytical curve shown in Figure 2 and by analysing the residue graph. The calculated Cochran value (0.546) obtained by the Cochran test was less than the critical value (0.561) with 5% significance level, indicating the homoscedasticity of the method. The residue graph constructed from the differences in current values from the analytical curve and the experimental values is shown in Figure 3.

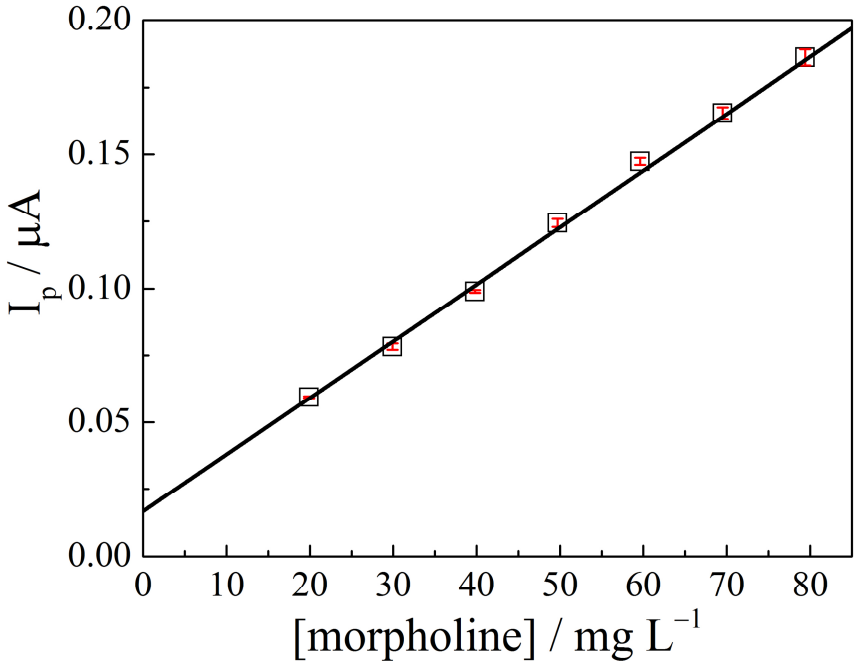

Figure 2. Analytical curve obtained for morpholine electro-oxidation showing a linear response range from 20 to 80 mg L^{-1}. Electrolyte solution: 0.1 mol L^{-1} $LiClO_4$ in acetonitrile.

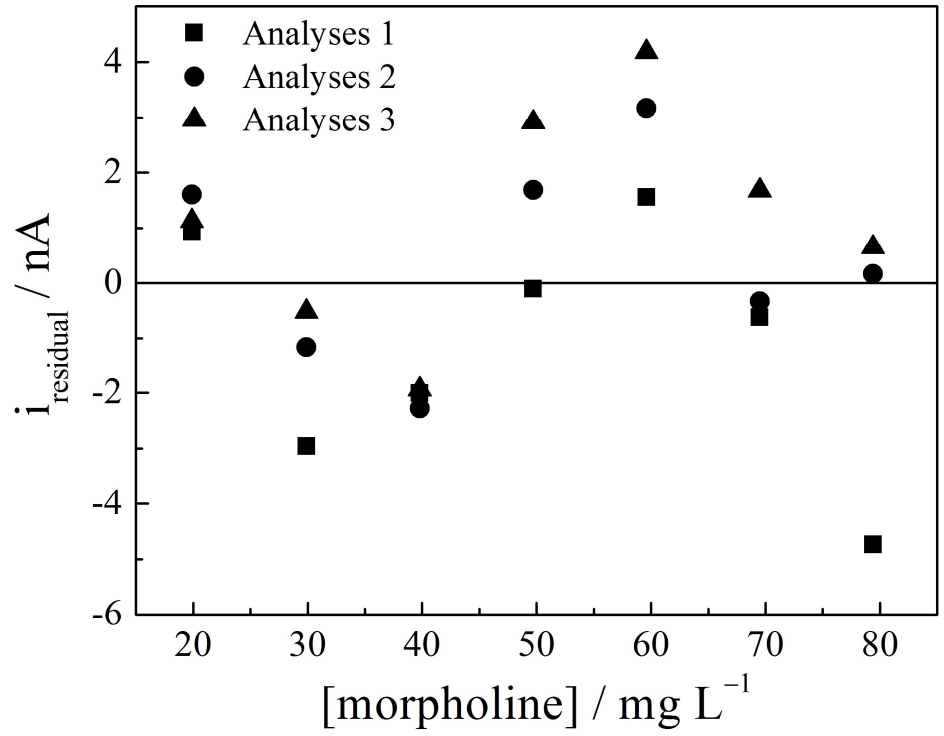

Figure 3. Residue graph constructed using values from the analytical curve of Figure 2.

According to the residual plot, the residuals fell into a random distribution around the zero line (straight line), and no pattern was observed. This result indicates that the suggested linear model was adequate to describe our data. The linear regression model was considered correct because the residues did not exceed 5 nA, which was close to the baseline noise.

4.3. Recovery Study

Table 1 shows the recovery of the method obtained from synthetic morpholine samples with different concentrations. The voltammetric method presented a recovery value of 102 ± 4%.

Table 1. Results from the method recovery determined by differential pulse voltammetry in the conditions described in Fig.1.

$[Morpholine]_{added}$ / mg L^{-1}	$[Morpholine]_{found}$ / mg L^{-1}	Recovery (%)
20.0	20.1	101
29.6	29.1	98
35.4	38.8	110
49.6	50.8	102
60.0	61.6	103
69.6	70.2	101
78.3	79.9	102

Table 2 shows the recovery results obtained from real commercial inhibitor samples fortified with the morpholine standard.

Table 2. Results from the sample recovery.

[Morpholine]added / mg L^{-1}	[Morpholine]found / mg L^{-1}	Recovery (%)
74.8	77.4	103
74.8	79.1	105
74.8	73.1	97

The results presented in Table 2 showed an average recovery of the sample of 102 ± 4%. These results suggest viable recovery performance and also indicate that there is no matrix interference.

4.4. Limits of detection and quantification

The mean values and standard deviation of all blank sample analyses were used to calculate the detection and quantification limits. The detection and quantification limits based on different criteria ($3.3\sigma_c/b$, $3\sigma_b/b$ and $3\sigma_b + X_b$) are shown in Table 3. The experimental detection limit was 12 mg L^{-1},

and the quantification limit was 36 mg L^{-1}.

Table 3. Detection (DL) and quantification (QL) limits by different criteria.

Criterion	DL / mg L^{-1}	QL / mg L^{-1}
$3.3\sigma_c/b$	4.35	11.3
$3\sigma_b/b$	2.61	7.83
$3\sigma_b + X_b$	13.0	20.0
Experimental	12.2	35.7

The compound of interest (morpholine) can be analyzed by an array of analytical techniques such as high-pressure liquid chromatography [15, 30, 31], ion chromatography [10, 32] or spectrophotometry [33] with detection limits in the low part-per-million (ppm) range. However, using a simple electrochemical setup and approach, we observed results that could be compared with some classical techniques; considering comparable detection limits (Table 4).

Table 4. Summary of methods and techniques used for morpholine determination.

Technique	Detection Limit	Matrices	Linearity range	Pre-treatment	Reference
Amperometric measurements	12 ppm	organic	20 to 80 ppm	No	This work
IEC	0.1 ppm	aqueous	0.1 to 20 ppm	No	[10]
IEC suppressed electric conductivity detection	No specified	aqueous	100 ppm	No	[11]
GC	2 ppm	aqueous	2.0 ppm*	No	[12]
GC	0.1 ppm	aqueous	0.1 to 100 ppm	No	[13]
GC/MS and HPLC - fluorescence detection	5×10^{-5} mg L^{-1}	aqueous	5×10^{-5} to 1×10^{-3} ppm	Yes	[14]
HPLC Spectrophotometric detection	0.01 ppm	aqueous	0.01 a 10 ppm	Yes	[15]
Amperometric coupled with FIA using carbon SPE	10 ppm	aqueous	20 to 120 ppm	No	[18]
RF HPLC Spectrophotometric detection	0.03 ppm	aqueous	0.25 a 10 ppm	Yes	[37]

*Morpholine can be detected either directly (if >2.0 ppm) or by quantitative preconcentration ([Morpholine] << 2.0 ppm)

4.5. Precision

The voltametric method precision was evaluated based on the repeatability of the method by observing the standard deviation obtained with each concentration of analyte in the range of 20 to 80 mg L^{-1}. A good repeatability was verified (i.e., there were only small variations in the results of the analyses performed in triplicate within a short time using the same conditions). The relative standard deviation values did not exceed 1.6 % variability (Table 5), which is considered acceptable for this type of technique.

Table 5. Data for analytical curve obtained from different standard concentrations of morpholine in electrolyte solution by the differential pulse voltammetry method using Pt microelectrode.

Morpholine concentration (mg L^{-1})	1st signal (µA)	2nd signal (µA)	3rd signal (µA)	$\bar{X}$	SD	RSD (%)
20.0	0.0591	0.0598	0.0593	0.0594	0.0004	0.6
29.6	0.0769	0.0787	0.0794	0.0784	0.0013	1.6
35.4	0.0984	0.0991	0.0995	0.09899	0.0006	0.6
49.6	0.1228	0.1246	0.1258	0.1244	0.0015	1.2
60.0	0.1460	0.1476	0.1486	0.1474	0.0013	0.9
69.6	0.1633	0.1656	0.1676	0.1655	0.0022	1.3

The intermediary precision was evaluated by the comparison of analytical curves constructed on different days and by different analysts (Fig. 4). Comparing the variances obtained from the analytical curves by differential pulse voltammetry on different days, it was observed that the calculated *F*–value (1.57) was lower than the critical *F*–value (5.82) for the 95% confidence level, which indicates equal variances. The slopes of the analytical curves were also compared, and the calculated *t*–value (0.53) was lower than the critical *t*–value (2.23) for the 95% confidence level, showing equal slopes for these two curves.

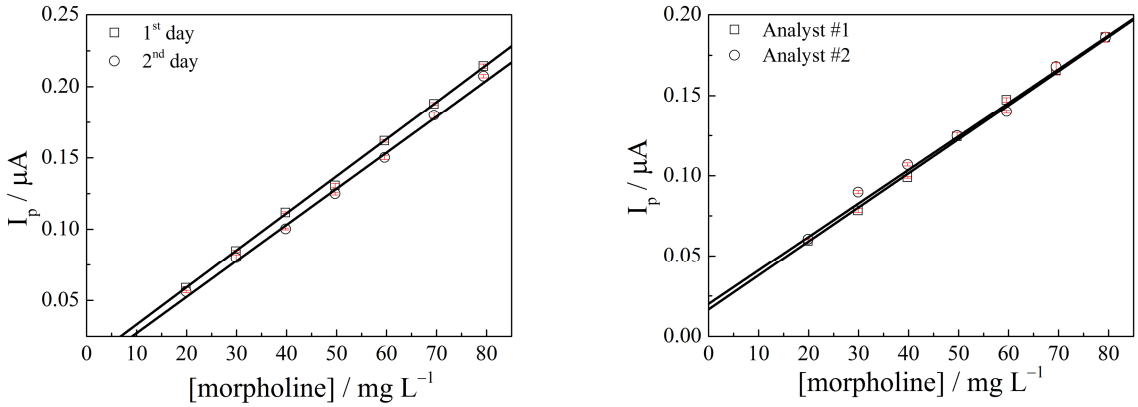

Figure 4. Analytical curves constructed on different days and by different analysts.

Comparing the variances obtained for the analytical curves from different analysts, it was observed that the calculated *F*–value (1.01) was lower than the critical *F*–value (5.82) for the 95% confidence level, which indicates equal variances. The slopes of the analytical curves were also compared, and the calculated *t*–value (0.53) was lower than the critical *t*–value (2.23) for the 95% confidence level, showing equal slopes for these two curves.

Thus, the proposed method can be considered to have good precision considering the type of analysis employed.

4.6. Study of the matrix effect

The ability to analyze morpholine compounds by other methods has historically been difficult at the detection limits similar to the aforementioned techniques (parts-per-million) due to the matrix effects involved in aqueous samples [12, 34-36]. In this way, the analyses of morpholine in aqueous media represents a challenge due to matrix effect and in the present paper we showed by comparative statistical analysis that our data can be compared with techniques that require pre-treatments or long-time of analyses.

The matrix effect of the proposed method was evaluated by comparing the analytical curves obtained in the presence and absence of the commercial inhibitor sample (Fig. 5). The variances obtained by voltammetry showed that the calculated *F*–value (2.71) was lower than the critical *F*–value (5.82) for the 95% confidence level, indicating that the variances were equal. The slopes of the analytical curves were also compared, and the calculated *t*–value (0.69) was lower than the critical *t*–value (2.23) for the 95% confidence level. Thus, these two curves present equal slopes, and the analysis is not subjected to matrix effects.

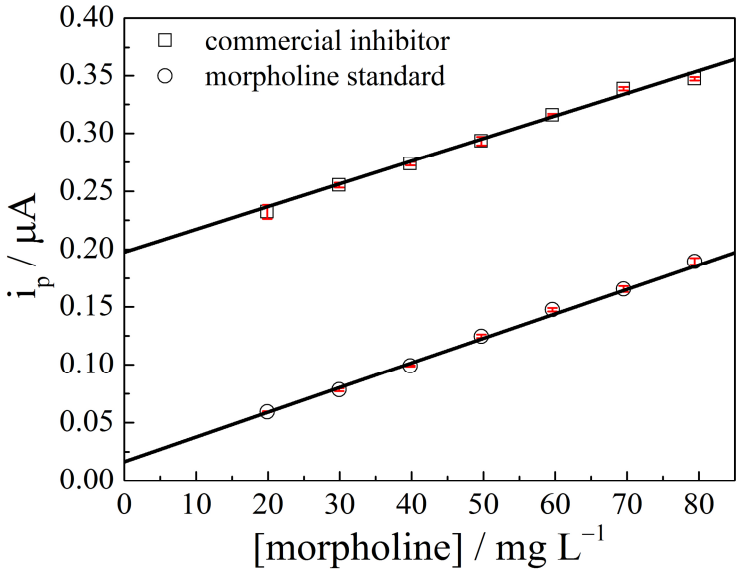

Figure 5. Analytical curves obtained obtained in the absence and presence of the commercial inhibitor sample showing a linear response range from 20 to 80 mg L^{-1}. Electrolyte solution: 0.1 mol L^{-1} $LiClO_4$ in acetonitrile.

It can be observed, again, that the fitting line did not pass through the origin for both in the presence and absence of commercial morpholine. In the case of the sample that already contains morpholine (commercial inhibitor sample), the presence of some excipients distorted the baseline in the differential pulse voltammogram (data not shown) and raised the peak currents, increasing the capacitive current. Even some matrix effect can be observed, the slope of the analytical curve almost did not change, showing that our suggested method can be used directly in the pipelines.

5. CONCLUSIONS

The proposed voltammetric method using a platinum microelectrode can be used for morpholine determination in field samples. This method is linear in the concentration range studied (from 20 to 80 mg L^{-1}), homoscedastic and presents 12 mg L^{-1} and 36 mg L^{-1} as experimental detection and quantification limits, respectively. Moreover, it showed adequate recovery for both real and synthetic samples (102 ± 4%), precision (considering inter-day analysis and by different analysts) and accuracy. It was shown that this method can be used to quantify morpholine in commercial morpholine-based inhibitor samples since it presented low detection limit, showed no matrix effect in the sensitivity of the method, allowed faster analysis, did not require pre-treatment of the samples and/or preliminary preparation of the working electrode and had a low cost for both instrumentation and maintenance.

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