Effect of supporting electrolytes on voltammetry with manual staircase voltage scan

Efeito de eletrólitos de suporte na voltametria com varredura manual de tensão em escada

Jorge Arce-Castro
ORCID: https://orcid.org/0000-0001-6957-5839
Universidad de Oriente, Cuba.
E-mail: jorge.arce@uo.edu.cu
Javier E. Vilasó-Cadre
ORCID: https://orcid.org/0000-0001-5172-7136
Universidad Autónoma de San Luis Potosí, México.
E-mail:jvilasocadre@gmail.com
Daniel Benítez-Fernández
ORCID: https://orcid.org/0000-0002-9303-1986
Universidad de Oriente, Cuba.
E-mail:danielbenitezf64@gmail.com
Héctor Rodríguez-de la Rosa
ORCID: https://orcid.org/0000-0002-6312-0435
Hospital Lomas de San Luis Internacional, México.
E-mail: hrodriguez2901@gmail.com
María A. Arada-Pérez
ORCID: https://orcid.org/0000-0001-9262-2066
Universidad de Oriente, Cuba.
E-mail: mayarada@uo.edu.cu

Resumo

A voltametria mínima da instrumentação com varredura manual da tensão da escada permite obter resultados eletroquímicos com equipamento não-comercial. Várias pesquisas demonstraram a sua validade analítica e metrológica; contudo, algumas variáveis não foram estudadas neste tipo de métodos, tais como o efeito do eletrólito de suporte na repetibilidade dos voltamogramas. Neste artigo, é apresentado um estudo sobre o efeito do KNO_3, KCl, $KClO_4$, K_2SO_4 e Na_2SO_3 como eletrólitos de suporte nos voltamogramas obtidos para a oxidação do KI e ácido succínico, ambos a 0.1 mol/L; ácido ascórbico 0.01 mol/L e hexacianoferrato de potássio (II) 0.08 mol/L, todos eles como modelo analítico. Foi utilizado um microdisco de grafite como eléctrodo de trabalho; uma barra do mesmo material foi utilizada como eléctrodo auxiliar. Como eléctrodo de referência foi utilizado um eléctrodo de prata. A Análise de Variância foi a ferramenta estatística para a comparação das correntes voltamétricas. Foi utilizado um Contraste de Gama Múltipla por um Teste de Fisher LSD para identificar os grupos com diferenças estatísticas. Havia diferenças estatísticas entre as correntes obtidas com diferentes eletrólitos de suporte para todas as espécies eletroativas estudadas. Os melhores resultados voltamétricos foram obtidos utilizando KCl e KNO_3 como eletrólitos de suporte.

Palavras-chave: Eletrólito de suporte. Voltametria. Grafite. Instrumentação não comercial.

Abstract

The minimal instrumentation voltammetry with manual staircase voltage scan allows to obtain electrochemical results with non-commercial equipment. Several researches have demonstrated its analytical and metrological validity; however, some variables have not been studied in this kind of methods, such as the effect of the supporting electrolyte on the repeatability of the voltammograms. In this paper, a study is presented about the effect of KNO_3, KCl, $KClO_4$, K_2SO_4 and Na_2SO_3 as supporting electrolytes on the voltammograms obtained for the oxidation of KI and succinic acid, both at 0,1 mol/L; ascorbic acid 0,01 mol/L and potassium hexacyanoferrate (II) 0,08 mol/L, all of them as an analytical model. A graphite microdisc was used as working electrode; a bar of the same material was used as the auxiliary electrode. A silver electrode was used as the reference electrode. The Analysis of Variance was the statistical tool for the comparison of the voltammetric currents. A Multiple Range Contrast by a Fisher's LSD Test was used to identify the groups with statistical differences. There were statistical differences between the currents obtained with different supporting electrolytes for all the electroactive species studied. The best voltammetric results were obtained using KCl and KNO_3 as supporting electrolytes.

Keywords: Supporting electrolyte. Voltammetry. Graphite. Non-commercial instrumentation.

1. Introduction

There are several voltammetric techniques: linear, cyclic, differential pulse, square wave, among others. These differ in the potential regime (sweep) imposed to produce the electrochemical transformation of the analyte in the electrochemical cell; in addition, pre-concentration stages can be used independently of the sweep type. Common to all these techniques is that a supporting electrolyte is always used (Han and Pan, 2021; Wang *et al.*, 2022).

The supporting electrolyte is a key component of a voltammetric cell. They are soluble substances whose ions theoretically have a high ionic mobility, allowing them to take up the charge transport by migration due to the electric field generated by the potential difference. In this way, migration transport is maximized to establish a diffusive control in the cell. All this is a result of the fact that the current that is related to concentration in voltammetry is the diffusion current, therefore, mass and charge transport by convection and migration introduce deviations from the theoretical equations governing the process, which in practice results in loss of accuracy and precision of the voltammetric quantification method (Compton and Banks, 2011; Skoog, 2017).

The preferred supporting electrolytes have been strong water-soluble salts such as KNO_3 and KCl (Kariuki and Dewald, 1997; Radhi *et al.*, 2010; Farahi *et al.*, 2015; Titretir Duran and Karagözler, 2018). However, one of the requirements of these substances is that they cannot be electroactive, and this is not always fulfilled because the electroactivity does not only depend on the salt used as a supporting electrolyte, but also on the chemical and electrochemical system, i.e. the other chemical components, the pH or the type of electrode used. Other authors have reported the use of $KClO_4$, K_2SO_4 and even H_2SO_4 (Scibioh *et al.*, 2002; Xu *et al.*, 2019; Riu *et al.*, 2020). K_2SO_3 has been used when the effect of dissolved oxygen on voltammograms is to be minimized (Farghaly *et al.*, 2014).

In a series of papers, we have reported the usefulness of non-commercial electrochemical instrumentation to develop manual staircase voltammetric methods using graphite and mercury film electrodes (Vilasó *et al.*, 2016; Vilasó Cadre *et al.*, 2019; Vilasó-Cadre *et al.*, 2020; Benítez-Fernández *et al.*, 2021). From a statistical-metrological study, the study of sweeps and their influence on voltammograms, until the application in cadmium quantification, we have shown that this type of simple instrumentation can be valid for analytical purposes. However, the effect of different supporting electrolytes on the voltammograms generated by this instrumentation and electrochemical system has not been reported.

This paper presents the effect of some supporting electrolytes on the voltammograms obtained by manual staircase voltammetry using minimal non-commercial instrumentation. This provides

further analytical, statistical and metrological elements that demonstrate the validity and scope of this type of instrumentation for practical laboratory use.

2. Materials and Methods

2.1. Reagents and electrochemical instrumentation

All reagents were purchased from Sigma Aldrich in ACS grade. All materials and measuring equipment were certified for use. The water used was double distilled and deionized.

For the voltammetric experiments, a minimal instrumentation potentiostat reported by Vilasó *et al.* (2016) was used. The schematic of the circuit is shown in Figure 1A. A current source supplies the equipment, the rheostat allows a controlled potential imposition. A graphite microdisc was used as working electrode and a graphite rod was used as an auxiliary electrode. The reference electrode was silver. The staircase potential scan is shown in Figure 1B. This perturbation program is more suitable for manual imposition and is analytically reliable as demonstrated by Vilasó-Cadre *et al.* (2020).
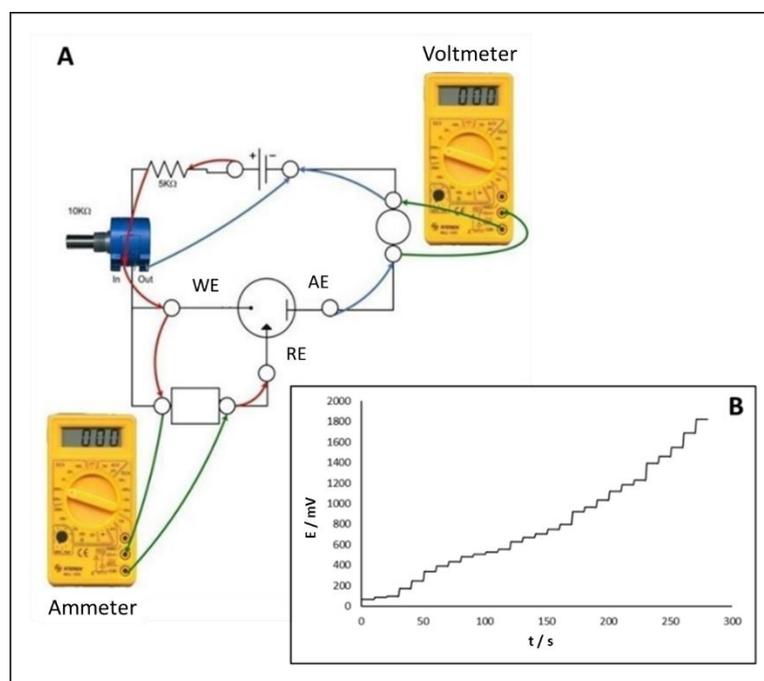
Figure 1 – A) Schematic of the potentiostatic circuit used for minimal instrumentation voltammetry (Vilasó *et al.*, 2016), B) Staircase potential scan (Vilasó-Cadre *et al.*, 2020).

2.2. Supporting electrolyte study

Analytes and supporting electrolytes: To study the effect of the supporting electrolyte on the voltammograms, the following analytes were selected: KI and succinic acid at the concentration 0.1 mol/L, ascorbic acid 0.01 mol/L and $K_4[Fe(CN)_6]$ 0.08 mol/L. KNO_3, KCl, $KClO_4$, K_2SO_4 and Na_2SO_3, all at a concentration of 1 mol/L, were used as supporting electrolytes. Voltammograms were obtained by performing anodic sweeps from 0 to 1500 mV. For each analyte, five voltammograms were obtained using each of the supports. The half-wave potential ($E_{1/2}$) and the limiting current intensity (i_{lim}) were determined according to the methodology described by Vilasó *et al.* (2016).

Comparison of the limiting currents: The limiting currents obtained from the five voltammograms were compared for each supporting electrolyte. A simple analysis of variance (ANOVA) was used for the multiple sample comparison. The groups used in the comparisons were the data corresponding to the diffusion plateau of each voltammogram which is the data series from which the limiting current is calculated. The average limiting currents of the voltammograms

corresponding to the different supports were also compared using the same statistical test. Multiple Range Contrast using a Fisher's LSD test was used to identify statistical differences between the limiting currents that were identified as non-homogeneous by ANOVA. All result processing and statistical tests were performed using Statgraphics Centurion 19 software.

3. Results and Discussion

3.1. Qualitative analysis of the effect of supporting electrolytes on voltammograms

Figure 2 shows the voltammograms for the oxidation of KI 0.1 mol/L using the supporting electrolytes: KNO_3, KCl, $KClO_4$, K_2SO_4 and Na_2SO_3, all them at 1 mol/L.
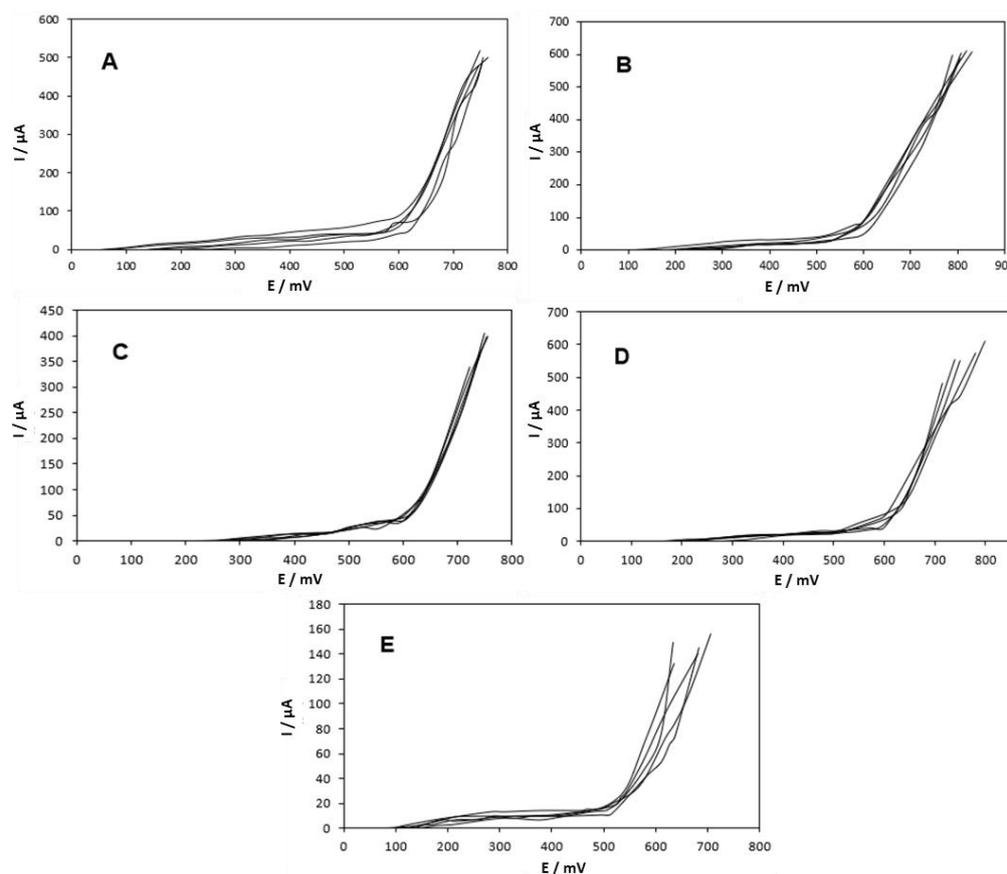
Figure 2 – Voltammograms for the oxidation of KI 0.1 mol/L on non-commercial graphite electrodes using different supporting electrolytes. A: KNO_3; B: KCl; C: $KClO_4$; D: K_2SO_4; E: Na_2SO_3.

In all cases, a diffusion plateau is observed. However, the extent of the plateau and the half-wave potential is not the same for all the supporting electrolytes. For KNO_3, KCl and K_2SO_4, little difference is observed, with $E_{1/2}$ values between 270 and 300 mV. In the case of Na_2SO_3, a shift towards lower potentials is observed with respect to the previous supporting electrolytes, with $E_{1/2}$ between 160 and 260 mV. In the case of $KClO_4$, the half-wave potential moves from 300 to 400 mV. These shifts are in correspondence with the fact that the half-wave potentials depend on the electrolysis medium, influencing by the solvent, pH and supporting electrolyte (Scibioh *et al.*, 2002; Winter, 2014). The potential corresponding to the oxidation wall of water does not shift on any support, except for Na_2SO_3 which decreases from 600 mV to 500 mV.

Figure 3 shows the voltammograms for the oxidation of succinic acid 0.1 mol/L using the different supporting electrolytes. For KNO_3 and KCl, well-defined diffusion plateaus are observed. In the case of $KClO_4$, current instability is observed throughout the voltammogram. In the case of K_2SO_4, instability is also observed, although to a lesser extent. In the case of Na_2SO_3 no

voltammogram is observed, only the water oxidation wall appears, therefore, this support is not useful to generate voltammograms for the oxidation of succinic acid. This behavior is also in correspondence with the voltammograms of KI using Na_2SO_3 (Figure 2), where the limiting current is much lower compared to the other supports. In both KCl and K_2SO_4 the half-wave potential is between 90 and 100 mV, in $KClO_4$ a shift towards 160 mV is observed, and in KNO_3 this shift is much larger, reaching 300 mV. In KNO_3 water starts to oxidize at 900 mV, in $KClO_4$ at 990 mV, while in K_2SO_4 it occurs at 970 mV. A larger shift is observed in the case of KCl, where water oxidation occurs at 1100 mV. Therefore, the latter supporting electrolyte allows a larger window of electroactivity.
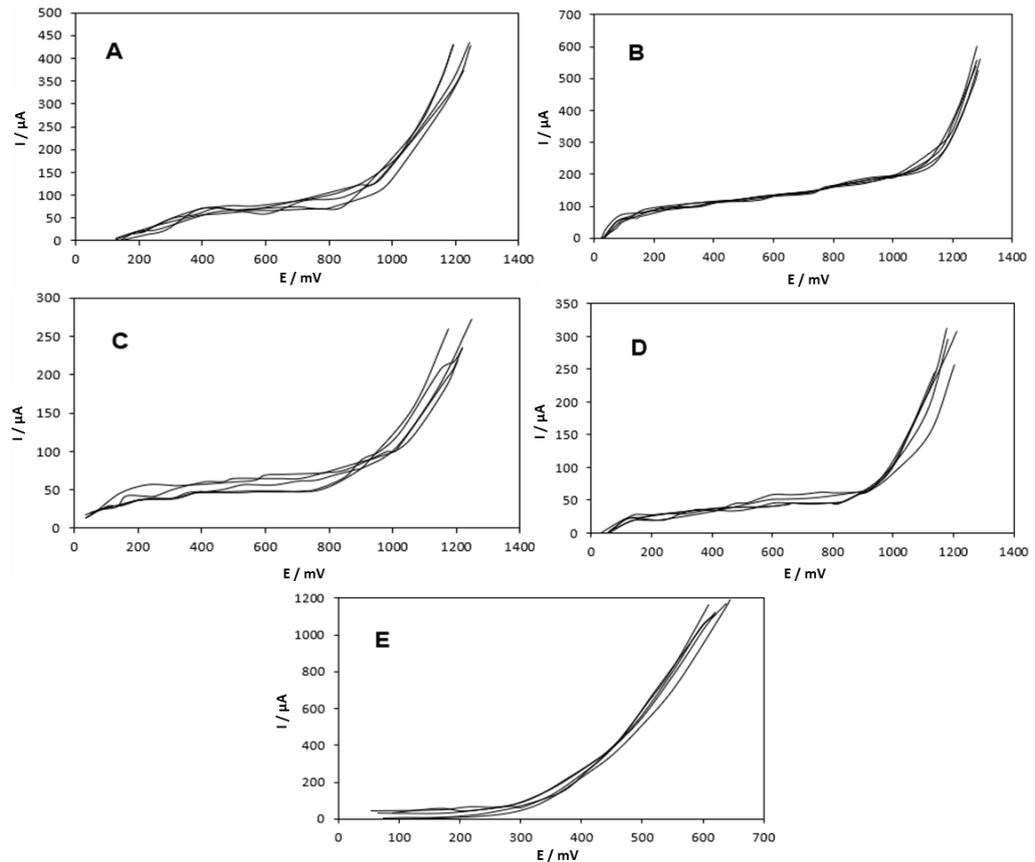
Figure 3 – Voltammograms for the oxidation of succinic acid 0.1 mol/L on non-commercial graphite electrodes using different supporting electrolytes. A: KNO_3; B: KCl; C: $KClO_4$; D: K_2SO_4; E: Na_2SO_3.

Figure 4 shows the voltammograms for the oxidation of ascorbic acid 0.01 mol/L using the supporting electrolytes. For KNO_3 and KCl, well-defined diffusion plateaus are observed. In the case of K_2SO_4, a high current instability is observed throughout the voltammogram. As for succinic acid, no voltammogram is observed when Na_2SO_3 is used, only the water oxidation wall appears, therefore, this support is not useful to generate voltammograms for the oxidation of ascorbic acid.

In KCl, $KClO_4$ and K_2SO_4 the $E_{1/2}$ is between 90 and 100 mV, in KNO_3 it is between 100 and 150 mV. In KNO_3, KCl, and $KClO_4$ water starts to oxidize at 1050 mV. In the case of K_2SO_4, a lower value is observed for the water process where oxidation occurs at 950 mV, therefore, in the latter the electroactivity window is smaller.
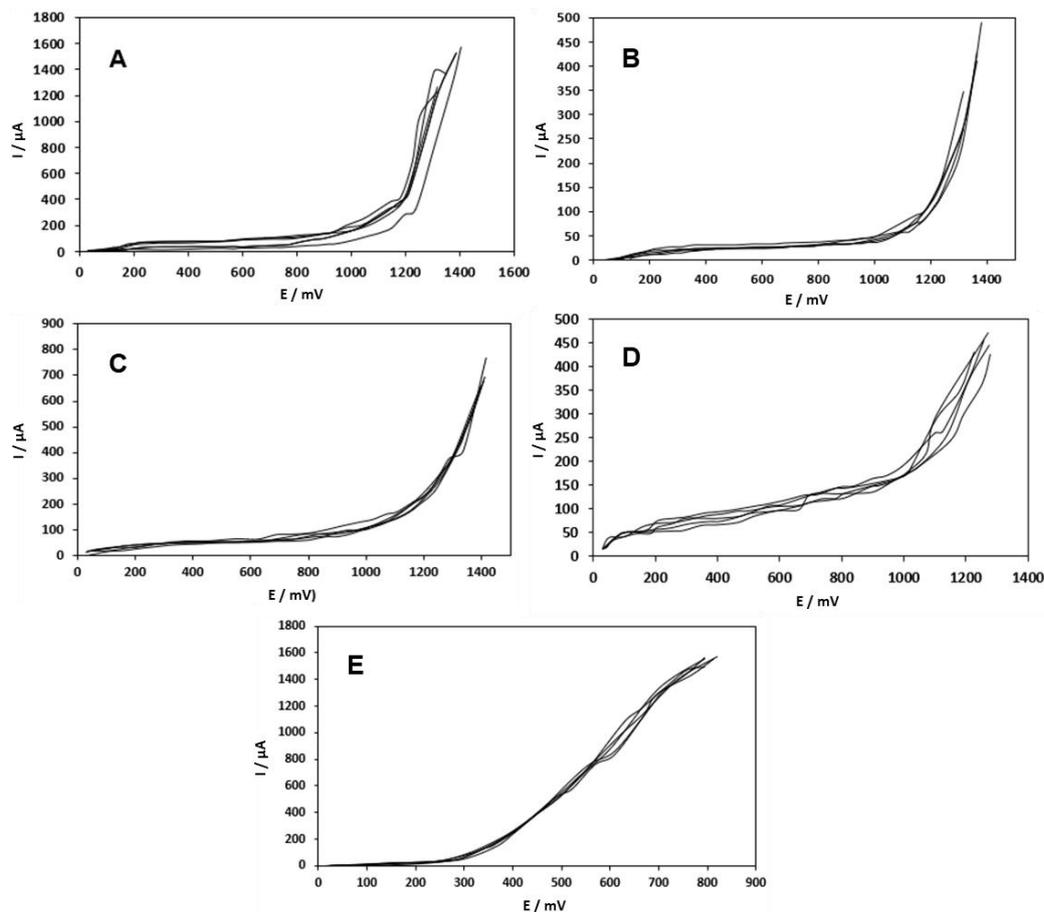
Figure 4 – Voltammograms for the oxidation of ascorbic acid 0.01 mol/L on non-commercial graphite electrodes using different supporting electrolytes. A: KNO$_3$; B: KCl; C: KClO$_4$; D: K$_2$SO$_4$; E: Na$_2$SO$_3$.

Figure 5 shows the voltammograms for the oxidation of K$_4$[Fe(CN)$_6$] 0.08 mol/L. For KCl, KNO$_3$, KClO$_4$ and K$_2$SO$_4$, well-defined diffusion plateaus with current stability are observed throughout the voltammograms. In the case of Na$_2$SO$_3$, a small diffusion plateau is observed, being the limiting current much lower compared to the other supports, so this supporting electrolyte is not useful to generate these voltammograms when a quantitative method needs to be developed.

When using KNO$_3$, KClO$_4$, and K$_2$SO$_4$ the half-wave potential is 200 mV, while in KCl a larger shift to 250 mV is observed. In KNO$_3$, K$_2$SO$_4$, and KClO$_4$ water starts to oxidize at 900 mV. A shift to a higher potential is observed for KCl, where water oxidation occurs at 1040 mV. In the case of Na$_2$SO$_3$ a shift towards a lower potential of 270 mV is observed. Therefore, the largest electroactivity window corresponds to KCl and the smallest to sodium sulfite.
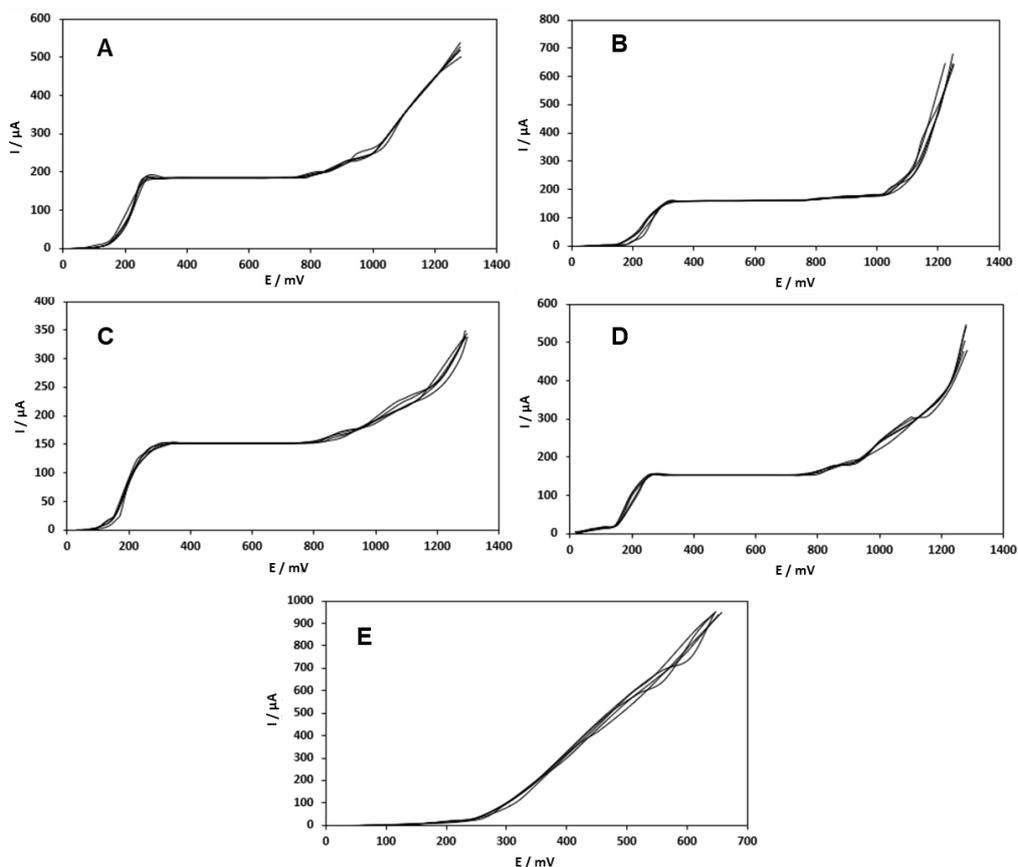
Figure 5 – Voltammograms for the oxidation of K$_4$[Fe(CN)$_6$] 0.08 mol/L on non-commercial graphite electrodes using different supporting electrolytes. A: KNO$_3$; B: KCl; C: KClO$_4$; D: K$_2$SO$_4$; E: Na$_2$SO$_3$

3.2. Analysis of diffusion currents

Table 1 shows the p-values of the ANOVA for the comparison of the limiting currents corresponding to five voltammograms in each one of the supporting electrolytes studied, the results corresponding to sodium sulfite have been excluded because in almost all the analytes no diffusion plateau was observed.

Only in the case of the oxidation of succinic acid in KClO$_4$ there are statistically significant differences between the currents because the p-value is less than the significance level ($\alpha = 0.05$) for 95% confidence. This means that there is repeatability of the voltammograms, except for succinic acid in KClO$_4$. This result is in correspondence with that observed in the voltammograms, where, as described, KClO$_4$ produces an observable instability of the current in the oxidation of succinic acid.

Table 1 – P-values of the Analysis of Variance for the comparison of the limiting currents of five voltammograms for each of the supporting electrolytes.

	Supporting electrolyte	p-value
KI	KNO_3	0.4415
	KCl	0.9591
	$KClO_4$	0.9715
	K_2SO_4	0.3450
	Na_2SO_3	0.1206
Succinic acid	KNO_3	0.8788
	KCl	0.2247
	$KClO_4$	0.0010
	K_2SO_4	0.5321
Ascorbic acid	KNO_3	0.0000
	KCl	0.6577
	$KClO_4$	0.7289
	K_2SO_4	0.9442
$K_4[Fe(CN)_6]$	KNO_3	0.9127
	KCl	0.9468
	$KClO_4$	0.9824
	K_2SO_4	0.6951

Table 2 shows the descriptive statistics for the different analytes in each of the supporting electrolytes. Results that did not show analytical usefulness in the discussion of Figures 2-5 and Table 1 have been excluded. The highest current variability in KI oxidation is observed for KNO_3, where there is the highest standard deviation and range. In the case of succinic acid oxidation, more variability is generally observed than for KI, as the standard deviations and ranges are higher. In this analyte, the highest variability corresponds to KCl. For ascorbic acid, much greater variability is observed in the currents of the voltammograms obtained in KNO_3 with respect to the other supporting electrolytes. For the oxidation of $K_4[Fe(CN)_6]$, in general, not much variability is observed in the limiting currents; the highest mean currents correspond to that obtained for this analyte with respect to the previous ones, and the supporting electrolytes with the greatest variability are KCl and K_2SO_4.

It is important to note that the larger standard deviation and larger range in the voltammograms indicate a slope of the diffusion plateau with increasing potential. This results in a deviation from the theoretical behavior (Winter, 2014). In an electrolysis where the potential increases linearly with time, a maximum current must be reached, this is because diffusion is occurring at the highest possible rate from the inside of the solution towards the electrode, this is known as diffusion limitation of the process (Henze, 2001; Skoog *et al.*, 2017). When the plateau is not constant, it means that the diffusion rate continues to increase with potential, but in a kinetically slow regime (Skoog *et al.*, 2017). Slight deviations in voltammograms from theoretical behavior are common and do not limit their analytical usefulness. For example, the diffusion plateau is often deformed and shaped more like a peak than a plateau (Silva *et al.*, 2008).

Table 2 also shows the comparison of the limiting currents by ANOVA for each analyte. It can be seen that the p-values corresponding to the calculated F-ratio are lower than the significance level ($\alpha = 0.05$). This indicates that there are statistically significant differences between the currents corresponding to the different support electrolytes for the same analyte.

Table 2 – Descriptive statistics and p-values of the comparison of the limiting currents between the different supporting electrolytes for the analytes used in the study.

	Supporting electrolyte	i_{lim}	SD	Minimum	Maximum	Range	ANOVA	
							F	Valor p
KI	KNO$_3$	30	4.27785	25.0	36.0	11.0		
	KCl	23	1.58114	21.0	25.0	4.0		
	KClO$_4$	23	1.92354	21.0	26.0	5.0	27.17	0.0000
	K$_2$SO$_4$	23	3.43511	20.0	28.0	8.0		
	Na$_2$SO$_3$	12	1.64317	11.0	14.0	3.0		
Succinic acid	KNO$_3$	72	3.80789	68.0	76.0	8.0		
	KCl	114	8.29458	103.0	125.0	22.0	151.18	0.0000
	K$_2$SO$_4$	41	3.16228	38.0	46.0	8.0		
Ascorbic acid	KNO$_3$	67.8	23.5627	38.0	93.0	55.0		
	KCl	33.4	1.14018	32.0	35.0	3.0	23.94	0.0000
	KClO$_4$	66.6	3.43511	61.0	70.0	9.0		
	K$_2$SO$_4$	98.0	3.67423	95.0	104.0	9.0		
K$_4$[Fe(CN)$_6$]	KNO$_3$	185.2	0.44721	185.0	186.0	1.0		
	KCl	164.8	0.83666	164.0	166.0	2.0	2791.5	0.0000
	KClO$_4$	152.2	0.44721	152.0	153.0	1.0		
	K$_2$SO$_4$	155.0	0.70710	154.0	156.0	2.0		

Note: i_{lim}: Mean limiting current, SD: Standard deviation, F: Fisher ratio

Table 3 shows the Multiple Range Contrasts using a Fisher's LSD test for the identification of the differences between the limiting currents for the oxidation of KI, succinic acid, ascorbic acid and K$_4$[Fe(CN)$_6$] in different supporting electrolytes.

In the case of KI, homogeneity is observed for KClO$_4$, KCl, and K$_2$SO$_4$. Na$_2$SO$_3$ and KNO$_3$ show different currents with respect to all other supports. The lowest current for this analyte corresponds to Na$_2$SO$_3$, while the highest corresponds to KNO$_3$. In the case of succinic acid, the currents of the three supports are different. The lowest corresponds to K$_2$SO$_4$ and the highest to KCl.

In ascorbic acid there is homogeneity in the currents of the voltammograms obtained with KClO$_4$ and KNO$_3$, the lowest current is for KCl and the highest for K$_2$SO$_4$, these last ones show different currents with respect to the other supports. In the case of K$_4$[Fe(CN)$_6$], much higher currents are observed than in the previous analytes and there is no homogeneity in the currents. The lowest current corresponds to KClO$_4$ and the highest to KNO$_3$. This result coincides with the study of conditions reported by Chooto *et al.* (2010), in which, when testing various supporting electrolytes for cadmium quantification, the highest current was obtained for KNO$_3$.

Table 3 – Multiple Range Contrast by Fisher's LSD test for the identification of the differences between the currents for voltammetric oxidation of the analytes studied in different supporting electrolytes.

	Soporte	Casos	Media	Grupos Homogéneos		
KI	Na_2SO_3	5	12,2	X		
	$KClO_4$	5	22,8		X	
	KCl	5	23,0		X	
	K_2SO_4	5	23,4		X	
	KNO_3	5	30,4			X
Ácido succínico	K_2SO_4	3	41,0	X		
	KNO_3	3	72,0		X	
	KCl	3	113,6			X
Ácido ascórbico	KCl	4	33,4	X		
	$KClO_4$	4	66,6		X	
	KNO_3	4	67,8		X	
	K_2SO_4	4	98,0			X
$K_4[Fe(CN)_6]$	$KClO_4$	5	152,2	X		
	KCl	5	164,8		X	
	K_2SO_4	5	155,0			X
	KNO_3	5	185,2			X

4. Conclusions

Supporting electrolyte has an important influence on the voltammograms. For all the electroactive systems studied, the best supporting electrolyte was potassium chloride, showing defined plateaus, high limiting current and lower variability. In second position is potassium nitrate, which shows acceptable results. The supporting electrolyte was shown to influence the half-wave potentials of the analyte and the oxidation potential of water. The least satisfactory results were obtained with sodium sulfite, where the current is small or even no voltammogram is recorded, making this salt unsuitable as a supporting electrolyte for the instrumentation used.

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