

## Study of the potential sweeps in the manual staircase voltammetry

### Estudio de los barridos de potencial en la voltamperometría manual de barrido en escalera

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#### ABSTRACT

Voltammetry can be developed using manual potentiostats. This study focuses on the potential sweeps and its influence on the voltammograms in the manual staircase voltammetry. Oxidations of potassium ferrocyanide, potassium iodide, ascorbic acid and succinic acid were used for the study. Five voltammograms were generated for each analyte. A mathematical approximation of the scans to a linear sweep was used for the quantitative description. The scan rate was the slope of the linear regression. The sweeps were compared to evaluate their repeatability. The influence of the repeatability of the sweeps was checked comparing the limiting currents of the voltammograms for each analyte. The results showed that the manual staircase potential sweeps are generated at random, with a high tendency to be non-repeatable. The scan rates were in correspondence with the common values reported. Although not repeatable manual voltage scans were used, the voltammograms did not show statistical differences.

**Keywords:** manual staircase voltammetry; potential sweep; voltammograms repeatability.

## RESUMEN

Es posible desarrollar el método voltamperométrico utilizando potencióstatos manuales. Este estudio se centra en los barridos de potenciales manuales de escalera y su influencia en los voltamperogramas. Las oxidaciones de ferrocianuro de potasio, yoduro de potasio, ácido ascórbico y ácido succínico se utilizaron para el estudio. Se generaron cinco voltamogramas para cada analito y se utilizó una aproximación matemática a un barrido lineal, para la descripción cuantitativa. La velocidad de barrido se calculó como la pendiente de la regresión. Los barridos se compararon para evaluar su repetibilidad. Se comprobó la influencia de la repetibilidad de los barridos comparando las corrientes limitantes de los voltamogramas. Los resultados mostraron que los barridos de escalera se generan al azar, con tendencia a no repetirse. Las velocidades de barrido estuvieron en correspondencia con los valores reportados. A pesar de la baja repetibilidad de los barridos, los voltamperogramas no mostraron diferencias estadísticamente significativas.

**Palabras clave:** voltamperometría manual de barrido en escalera; barrido de potencial; repetibilidad de los voltamperogramas.

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## Introduction

Voltammetry is an electroanalytical method based on the measurement of the current intensity that flows in an electrolytic cell when the analyte is transformed into a microelectrode by a potential difference imposed. This potential difference should be variable in time, and it is known as the perturbation program. When a substance is transformed during an electrolytic process, its concentration reduces in the area near to the electrode and gradients of concentration will appear, which causes the diffusion of the ions from the bulk solution to the electrode. This diffusion generates a current, which is denominated diffusion current and it is related to the concentration of the substance. The pattern of response in voltammetry is the voltammogram. It represents the relationship between the current and the imposed potential.<sup>(1,2)</sup>

Some authors have demonstrated the possibility of developing voltammetric techniques using non-commercial potentiostats without automatization to impose the perturbation program. These instruments are known as manual potentiostats,<sup>(2-4)</sup> and, in these cases, the substitution of the classical linear perturbation for a staircase potential sweep is convenient. In the classical linear sweep voltammetry (LSV), the potential perturbation program is a linear relationship between potential and time. The potential is fixed and the current is immediately sampled. In the staircase voltammetry (SV), the perturbation program is made using potential steps. The current is measured some time after the potential imposition, and then, a new potential is

imposed /5, 6/. Quantitatively, a staircase scan is equivalent to a linear scan, because in both the potential increases linearly in time /1, 5, 6/. The only difference is the potential step, for that, the staircase potential sweep could be described by an approximation to a linear potential scan. Even, the linear digital sweeps in modern instrumentation is made in a staircase form, but the steps are very short.<sup>(5-6)</sup>

For a manual voltammetry, the substitution of the classical linear sweep is necessary due to the instability of the current and the potential. Similar to LSV, in SV the Cottrell equation (equation 1) describes the relationship between current and other chemical-physical magnitudes.

$$i_{lim} = \frac{nFAD^{1/2}c}{(\pi t)^{1/2}} \quad (1)$$

According to this equation, when a potential is imposed, the current falls with the inverse of the square root of the time; this has been widely demonstrated using chronoamperometry.<sup>(1,2,6)</sup> Therefore, right after the potential is imposed, the current will be unstable and it may influence the repeatability of the voltammograms. This instability is more significant in manual voltammetry due to the simple potentiostatic circuit that is used. This perturbation program has also some electrochemical advantages because it discriminates against charging current.<sup>(6)</sup> At the end of the potential step, the background charging current has decayed to a negligible value; for this reason, the contribution of the residual current is minimal.<sup>(1)</sup>

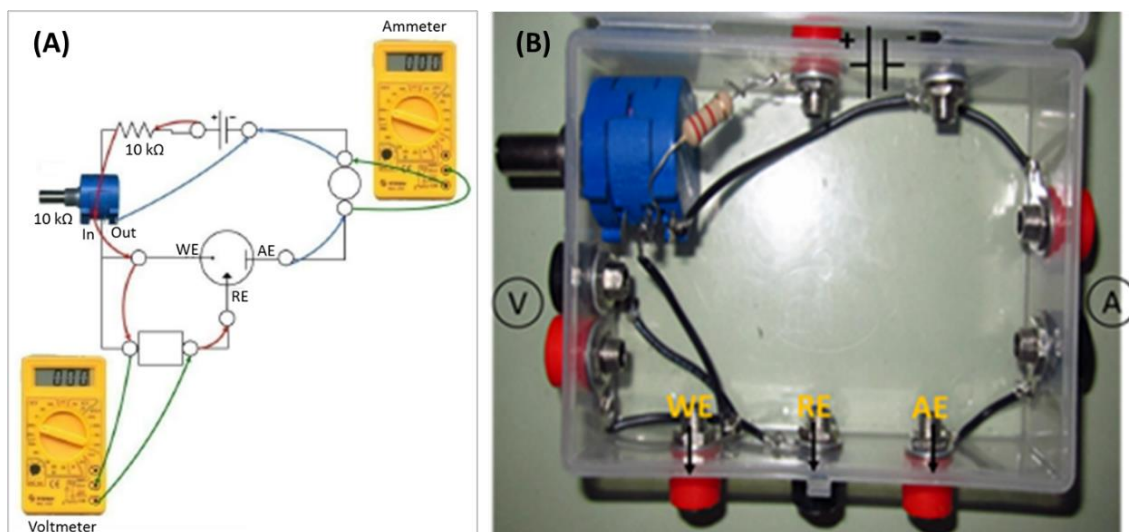
General aspects about the manual staircase potential sweeps have been little described in the bibliography and one of the questionable points of this kind of potential perturbation program is that the scan rate and linear correlation potential-time cannot be controlled and this may influence the voltammograms and the limiting current repeatability. In this work, a study of the manual voltammetric staircase sweep was conducted by splitting a mathematical approximation to the LSV; then, the influence of the sweeps on the diffusion current was analyzed. The research contributes to demonstrate that the minimal instrumentation voltammetric methods allow to obtain reliable results for its application in environmental and industrial laboratories of low economic resources.

## Material and methods

### Electrochemical instrumentation and reagents

A minimal instrumentation micropotentiostat was employed for the voltammetry (figure 1).<sup>(4)</sup> The working electrode (WE) was a carbon microdisc ( $d = 2,03 \text{ mm}$ ) and the auxiliary electrode (AE) was a carbon bar.<sup>(4,7,8)</sup> The step period in the staircase potential sweeps was 10 s; it also corresponds with the current sampling time.<sup>(4,7)</sup> Time was measured using a chronometer.

The oxidations of potassium ferrocyanide, ascorbic acid, potassium iodide and succinic acid were considered for the study. All the reagents were Merk Pure for Analysis quality.



**Fig. 1** - Circuit design (A) and photograph (B) of the minimal instrumentation micropotentiostat employed<sup>(4)</sup>

### Conditions for the voltammograms registration

Five voltammograms for the oxidation of each analyte were registered under specific conditions:

- Potassium ferrocyanide oxidation was studied at 0,08 mol/L. A copper electrode ( $\text{Cu}|\text{Cu}^{2+}||$ ) was used as reference (RE). The supporting electrolyte was  $\text{KNO}_3$  1,0 mol/L.
- Ascorbic acid oxidation was achieved at 0,1 mol/L. The electrolysis medium was a buffer acetate/acetic acid pH 5 and KCl 1.0 mol/L as supporting.
- Potassium iodide oxidation was studied at 0,1 mol/L in  $\text{Na}_2\text{SO}_3$  1,0 mol/L as supporting electrolyte.
- Succinic acid was oxidized at 0,1 mol/L in  $\text{KNO}_3$  1,0 mol/L; the medium was acidified to pH 2,0 using nitric acid.
- A silver wire was used as reference electrode for the oxidation of potassium ferrocyanide, potassium iodide and succinic acid.

### Study of the manual potential sweeps and its influence on the limiting current

For the staircase sweep the scan rate can be calculated using the equation 2.<sup>(4,5)</sup>

$$v = \Delta E / \tau \quad (2)$$

Where  $\Delta E$  is the height of the potential step and  $\tau$  is the step period. The velocity is given in mV/s.

However, imposing the same step height in the manual staircase potential sweep at all times is not possible; therefore, this equation cannot be used. For that reason, an approximation to a linear potential sweep was necessary for the quantitative description of the manual staircase program perturbation.

The only difference between both perturbation programs is the step period, as  $\tau$  gets close to zero, the staircase approximates to a linear plot.<sup>(4,5)</sup> Assuming that  $\tau = 0$ , the potentials which correspond to the measurement time of the current were taken as the points of a linear plot; then, the linear regression was made. The slope and the correlation coefficient were used for the quantitative description of the program perturbation. As in the LSV, the slope of the regression was considered as the scan rate.<sup>(1,2,5)</sup>

The scan rates were compared using a Regression Curves Comparison by a Simple Analysis of Variance (ANOVA) ( $\alpha = 0,1$ ). The comparison was conducted using 10 combinatory pairs. The influence of the scan rate on the limiting current was studied by checking the repeatability of the currents obtained from the voltammograms. The comparison was done for each analyte using an ANOVA for the Comparison of Multiple Samples ( $\alpha = 0,05$ ).

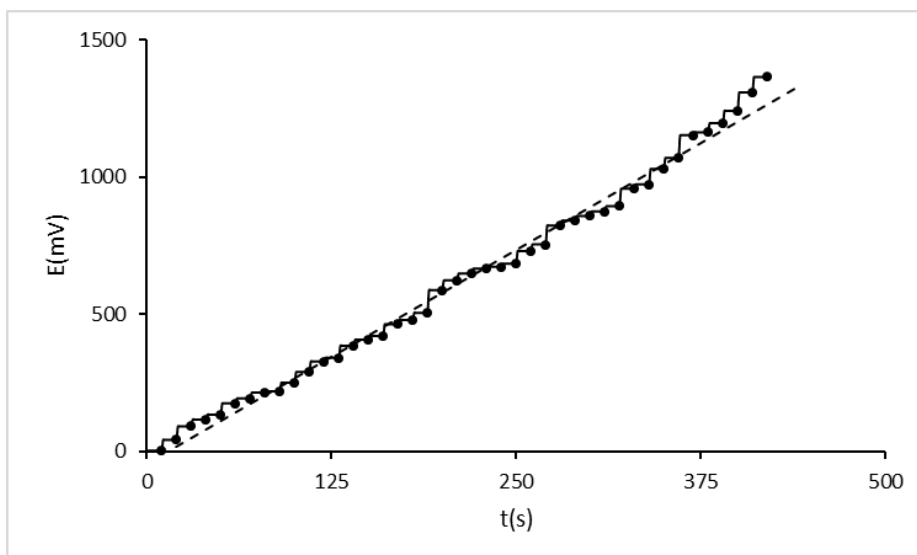
For all the ANOVAs conducted, a p-value higher than the significance level was used as the acceptance criterion for the null hypothesis.

### **Data processing and statistical tests software**

Microsoft Office Excel 2016 and Statgraphics Centurion XV were used for the data processing and the statistical tests.

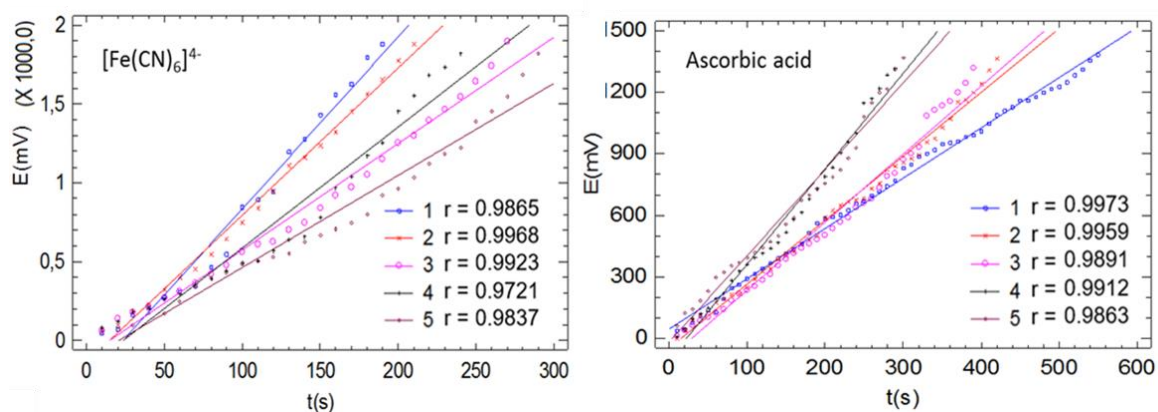
## **Results and discussion**

Figure 2 shows the approximation of the staircase scan to a linear potential sweep for ascorbic acid oxidation. The same approximation was used for all sweeps.



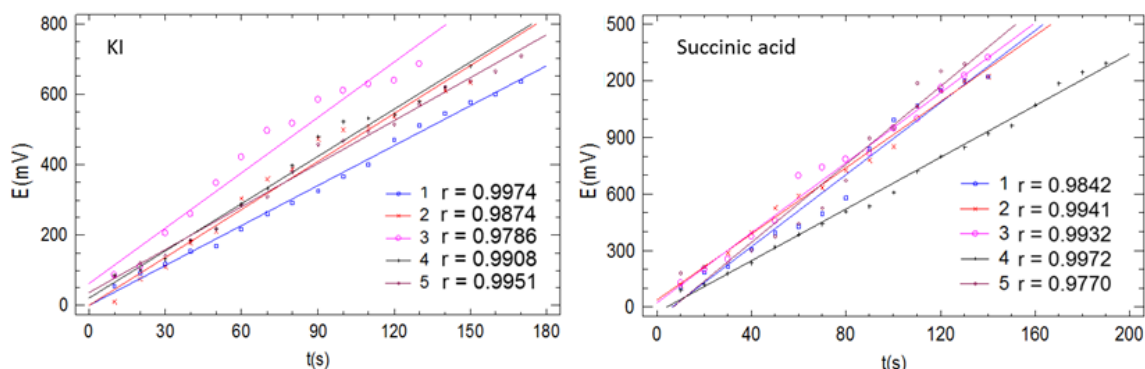
**Fig. 2** - Manual staircase potential sweep for the ascorbic acid oxidation, its approximation to a linear sweep and the linear regression curve

Figure 3 shows the E-t plots of five potential sweeps for the oxidation of potassium ferrocyanide and ascorbic acid. The linear correlation coefficients are shown as well. The values of correlation range go from 97, 21 to 99,68 % for the ferrocyanide oxidation; from 98,63 to 99,73 % for the ascorbic acid. All the sweeps present a strong and directly E-t correlation, however, notable differences in the slopes exists between them.



**Fig. 3** - Potential sweeps for the oxidation of potassium ferrocyanide (0,08 mol/L) and ascorbic acid (0, 1 mol/L)

Figure 4 shows the potential sweeps for potassium iodide and succinic acid. For these, the correlation coefficients go from 97, 86 to 99,74 % and from 97,70 to 99,72 % respectively. All the sweeps show a strong and directly E-t correlation.



**Fig. 4** - Potential sweeps for the oxidation of potassium iodide (0,1 mol/L) and succinic acid (0,1 mol/L)

The repeatability of the sweeps depends on the potentials fixed during the perturbation, and a quantitative analysis can be accomplished by comparing the scan rates. Table 1 shows the p-values corresponding to the ANOVAs for the comparison per pairs of the linear scan rates. All p-values lower than 0,1 ( $\alpha$ ) indicate statistically significant differences. All the sweeps are different for the potassium ferrocyanide and the ascorbic acid oxidation. Only sweeps 2 and 4 do not show differences for the potassium iodide. For these analytes, almost all the sweeps are different; however, this behavior differs for the succinic acid. In this case, all the sweeps are statistically equal, except number 4. As a general tendency, these manual sweeps are not repeatable. These results allow corroborating the fact that the manual perturbation programs are generated at random due to the instrumental impossibility to fix the same potential steps between different sweeps.

The range of scan rates goes from 2,45 to 10,90 mV/s. Such values correspond with the ones used in the LSV, which commonly range from 1 to 50 mV/s.<sup>(9-10)</sup>

**Table 1** - P-values corresponding to the ANOVAs ( $\alpha = 0,1$ ) to compare the linear scan rates for the oxidation of potassium ferrocyanide, ascorbic acid, potassium iodide and succinic acid.

	Sweep pairs	Linear scan rate (mV/s)	p-value
Potassium ferrocyanide	1-2	10,90-9,34	0,001 1
	1-3	10,90-6,75	0,000 0
	1-4	10,90-7,66	0,000 0
	1-5	10,90-5,84	0.000 0
	2-3	9.34-6,75	0,000 0
	2-4	9,34-7,66	0,001 2
	2-5	9,34-5,84	0,000 0
	3-4	6,75-7,66	0,028 1
	3-5	6,75-5,84	0,001 5
	4-5	7,66-5,84	0,000 1
Ascorbic acid	1-2	2,45-3,11	0,000 0
	1-3	2,45-3,32	0,000 0

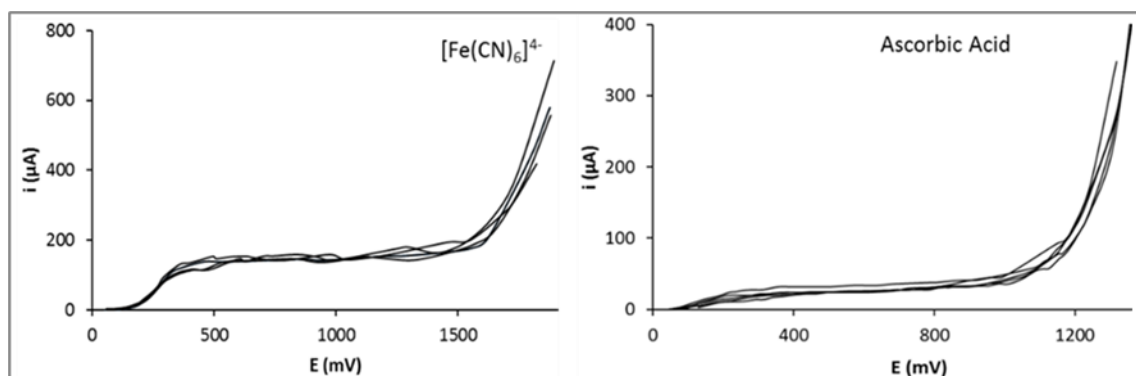
	1-4	2,45-4,66	0,000 0
	1-5	2,45-4,20	0,000 0
	2-3	3,11-3,32	0,026 7
	2-4	3,11-4,66	0,000 0
	2-5	3,11-4,20	0,000 0
	3-4	3,32-4,66	0,000 0
	3-5	3,32-4,20	0,000 0
	4-5	4,66-4,20	0,014 7
KI	1-2	3,76-4,54	0,000 5
	1-3	3,76-5,23	0,000 0
	1-4	3,76-4,46	0,000 3
	1-5	3,76-4,04	0,035 2
	2-3	4,54-5,23	0,075 3
	2-4	4,54-4,46	0,762 8
	2-5	4,54-4,04	0,027 9
	3-4	5,23-4,46	0,036 7
	3-5	5,23-4,04	0,000 4
	4-5	4,46-4,04	0,037 4
Succinic acid	1-2	9,57-8,74	0,158 3
	1-3	9,57-9,25	0,589 0
	1-4	9,57-6,86	0,000 0
	1-5	9,57-10,35	0,358 5
	2-3	8,74-9,25	0,234 8
	2-4	8,74-6,86	0,000 0
	2-5	8,74-10,35	0,310 0
	3-4	9,25-6,86	0,000 0
	3-5	9,25-10,35	0,138 6
	4-5	6,86-10,35	0,000 0

Figure 5 shows the voltammograms for the oxidation of ferrocyanide 0,08 mol/L and ascorbic acid 0,1 mol/L. The sigmoid form of the linear voltammograms is observed. The current increases with the potential, until a constant value is reached. At this point, the diffusion of the analyte from the bulk solution to the electrode surface is maximum, the electrochemical process has been limited by the diffusion and the current cannot continue increasing its values.<sup>(1,2)</sup> The current which corresponds with the diffusion plateau is the analytical parameter of quantitative interest.<sup>(2)</sup>

For ferrocyanide, some instability in the currents for the same i-E curve is observed, it can be associated with the carbon working electrode employed. Carbon electrodes shows tendency to develop unstable currents because their non-homogeneous surface.<sup>(1,4)</sup> However, current instability is not observed in all analytes, because it depends too of the electrolysis conditions.



For the ascorbic acid the currents in the same voltammogram show more stability. Some instability is observed in the zone when solvent begins to oxidize, but for quantitative applications it has no importance because the diffusion plateau is large and stable. The voltammograms show a good correspondence between them for both analytes.

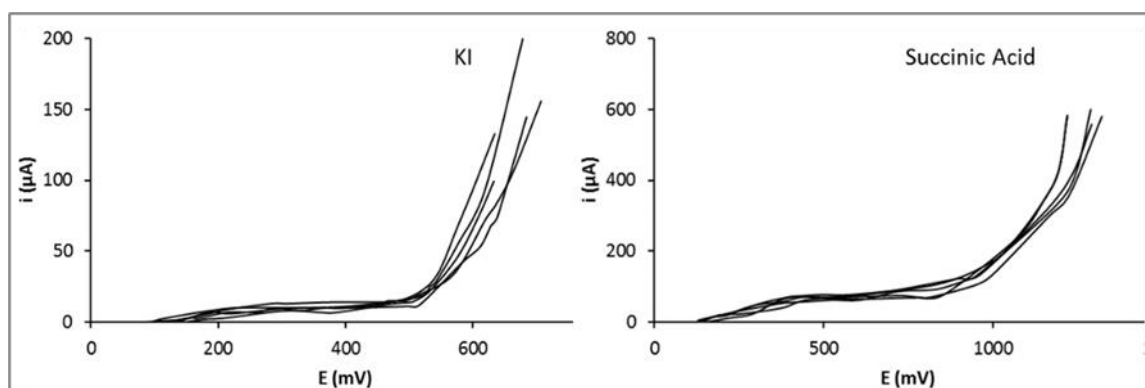


**Fig. 5** - Voltammograms for the oxidation of potassium ferrocyanide (0,08 mol/L) and ascorbic acid (0,1 mol/L) in repeatability conditions

Figure 6 shows the voltammograms for the oxidation of potassium iodide and succinic acid, both 0.1 mol/L. Voltammograms for KI are stable, however, a little dispersion between them is observed. The dispersion in the wall of oxidation of water has not importance for quantitative applications. This can be associated again with the carbon electrodes used for the voltammetry.<sup>(4)</sup>

Stability of the current is observed for the succinic acid. The voltammograms show correspondence except for the zone where water begins to oxidize. A shorter diffusion plateau is observed for both analytes.

The observed deviations between some voltammograms should be analyzed by statistical method because the differences are in a range of a few microamperes, and they could not be significative.



**Fig 6** - Voltammograms for the oxidation of potassium iodide (0.1 mol/L) and succinic acid (0,1 mol/L) in repeatability conditions

Some changes in the voltammograms depending on the linear scan rate have been reported by other authors. Hassan H.H. *et al.*<sup>(12)</sup> reports deformations of the voltammograms when high scan rates are used. Voltammograms show the common sigmoidal shape under 100 mV/s, but when the value is higher, the diffusion plateau disappears and the current never limits. A similar behavior has also been predicted by Klymenko *et al.*<sup>(13)</sup> for the LSV when using a wall tube electrode. By means of a mathematical simulation, these authors show how the voltammograms suffer deformations due to the increasing of the scan rate. At high velocities, voltammograms show peaks, and the limiting current is substituted by the current peak, similar to the cyclic voltammetry.

For a serious comparison of the voltammograms, statistical tests should be applied. Table 2 shows the statistical parameters of the limiting currents which corresponds to the five voltammograms per analyte and the p-values for the comparison of these currents. Low ranges are observed for all analytes; this indicates slight differences between the limiting currents, and for this reason, the standard deviations show low values in comparison with the average of the limiting currents. All these results evidence the repeatability of the limiting currents generated by using statically different potential sweeps.

**Table 2** - Statistical parameters for the limiting currents of the voltammograms and p-values for the comparison for each analyte using ANOVA ( $\alpha = 0,05$ ).

Analyte	$i_{\text{average}}(\mu\text{A})$	$i_{\text{min}}(\mu\text{A})$	$i_{\text{max}}(\mu\text{A})$	Range	SD	p-value
$[\text{Fe}(\text{CN})_6]^{4-}$	140,4	139,0	141,0	2,0	0,89	0,990 4
Ascorbic acid	34,0	33,0	35,0	2,0	0,71	0,6577
KI	11,0	9,0	14,0	5,0	1,87	0,109,3
Succinic acid	69,8	67,0	74,0	7,0	2,77	0,820 0

All the p-values are higher than 0,05; this demonstrates that there are not statistically significant differences between the limiting currents, and the correspondence among the voltammograms generated by the manual random perturbation programs is corroborated.

## Conclusions

The staircase sweeps in manual voltammetry have tendency to be not repeatable. The scan rates are in the range commonly reported in the linear scan voltammetry. Although non-repeatable perturbation programs are used in manual voltammetry, it has no influence in the repeatability of the voltammograms.

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### **Conflict of interest**

The authors express that there are no conflicts of interest in the submitted manuscript.

### **Author's contribution**

Javier Ernesto Vilasó Cadre: Discussion of the results. Revision and approbation of the final version of the manuscript.

Jorge Arce Castro: Discussion of the results.

María de los Ángeles Arada Pérez: Revision and approbation of the final version of the manuscript.

José Alejandro Baeza Reyes: Revision and approbation of the final version of the manuscript.