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**QUANTITATIVE DETERMINATION OF CITRACONIC AND MESAONIC ACID IN MIXTURES USING THE SQUARE-WAVE VOLTAMMETRY**

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Skopje, REPUBLIC OF MACEDONIA\***Introduction**

Mesaconic and citraconic acid are known as starting materials for the preparation of polymers with various characteristics [1] and, hence, there is an interest in the developments of methods for their quantitative determination. Since these two acids are geometric isomers, they are often found together and the analytical method for their quantitative determination must be such as to permit their simultaneous determination in mixtures.

The presence of a double C=C bond, conjugated with the acid carbonyl groups makes the *cis-trans* isomers citraconic and mesaconic acids polarographically active compounds. In our previous work, a polarographic method was developed for the simultaneous determination of the two mentioned acids in dioxane–water mixture [2]. In the present paper we report the results of our investigation of the voltammetric behavior of citraconic and mesaconic acid aimed to the development of an analytical method for their quantitative determination. As far as we know, no such studies have been performed so far.

**Experimental**

The stock solutions of citraconic and mesaconic acid, as well as all other solutions used for voltammetric measurement were prepared with twice distilled water. The general voltammetric behavior of citraconic and mesaconic acid has been investigated in various supporting electrolytes (HCl, KNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub> and citric acid, acetic acid) with different pH values.

All measurements were performed by a Polarographic Analyzer Princeton Applied Research Model 384B. The working electrode was a hanging mercury drop (HMDE) with a surface area of 0.0149 cm<sup>2</sup>, an Ag/AgCl (saturated KCl) was the reference electrode and Pt wire was used as a counter electrode. The solutions were degassed with high-purity nitrogen for 8 min prior to the measurements and for additional 20 s before each scan.

All experiments were done at room temperature and all chemicals were of analytical grade (Merck).

**Results and Discussion**

In an attempt to select the optimal supporting electrolyte, solutions of different compounds with known pH values were tested. The data for the peak potential and peak current as well as the half-peak width of the SW signal of citraconic and mesaconic acid are listed in Table 1.

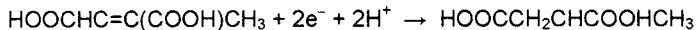
From the data given in Table 1, it can be calculated that the ratio peak current-half-peak width ( $I_p/dE_{p/2}$ ) for citraconic and mesaconic acid has a maximum when 0.1 mol/L hydrochloric acid is used as a supporting electrolyte and the square-wave voltammograms are well shaped (see Fig. 1 and Fig. 2). In 0.1 mol/L citric acid buffered to pH = 3.8 with Na<sub>2</sub>HPO<sub>4</sub>, the above mentioned ratio has a higher value than in the other electrolytes and, furthermore, the peaks of the two acids are well separated (see Fig. 3).

The redox process of citraconic and mesaconic acid at the HMD electrode is completely irreversible and, according to the literature data for the reduction of unsaturated dicarboxylic acid

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\* Editorial note: Recognized by Greece as FYROM.

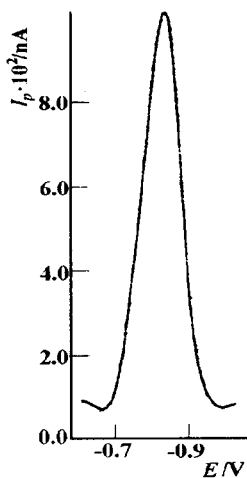
with one double bond at the mercury electrode [3]), it could be represented by the following equation:



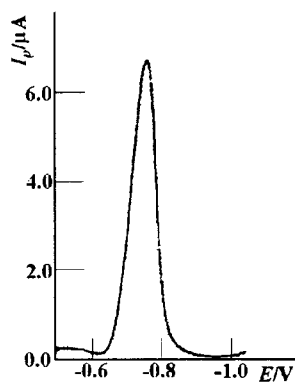
**Table 1.** The SW voltammetric response parameters as a function of the supporting electrolytes tested for citraconic\* and mesaconic acid :  $c_{\text{acid}} = 1 \cdot 10^{-4}$  mol/L;  $f = 120\text{Hz}$ ;  $E_{\text{sw}} = 20$  mV and  $dE = 4$  mV.

Supporting electrolyte	$I_p/\mu\text{A}$		$E_p/\text{V}$		$dE_{p/2}/\text{mV}$	
0.1 mol/L $\text{KNO}_3$ , buffered to pH = 4.2	4.260	0.789	-1.226	-1.304	100	110
0.1 mol/L $\text{Na}_2\text{SO}_4$ , buffered to pH = 4.4	1.980	0.585	-1.236	-1.320	100	150
0.1 mol/L HCl	5.890	1.524	-0.750	-0.840	100	120
0.1 mol/L $\text{CH}_3\text{COOH}$	3.110	1.246	-0.848	-0.944	100	170
0.1 mol/L citric acid buffered to pH = 2 with $\text{Na}_2\text{HPO}_4$	4.000	1.430	-0.844	-0.968	100	130
0.1 mol/L citric acid buffered to pH = 3.8 with $\text{Na}_2\text{HPO}_4$	3.600	1.104	-1.250	-1.368	100	110

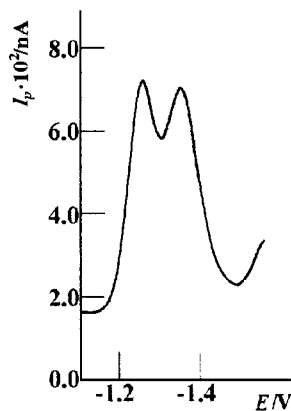
\*The numbers in the first columns are for citraconic acid.



**Figure 1.** Square-wave voltammogram of mesaconic acid in HCl ( $c_{\text{HCl}} = 0.1$  mol/L);  $c_{\text{acid}} = 1.0 \cdot 10^{-4}$  mol/L;  $f = 120$  Hz;  $E_{\text{sw}} = 20$  mV;  $dE = 4$  mV.



**Figure 2.** Square-wave voltammogram of citraconic acid in HCl ( $c_{\text{HCl}} = 0.1$  mol/L);  $c_{\text{acid}} = 1.0 \cdot 10^{-4}$  mol/L;  $f = 120$  Hz;  $E_{\text{sw}} = 20$  mV;  $dE = 4$  mV.



**Figure 3.** Square-wave voltammogram of citraconic (a) and mesaconic (b) acid in citric acid ( $c_{\text{cit.ac.}} = 0.1$  mol/L) buffered to pH = 3.8 with  $\text{Na}_2\text{HPO}_4$ :  $c_{\text{cit.acid}} = 4.0 \cdot 10^{-5}$  mol/L;  $c_{\text{mes.acid}} = 6.0 \cdot 10^{-5}$  mol/L;  $f = 120$  Hz;  $E_{\text{sw}} = 20$  mV;  $dE = 4$  mV.

After choosing the supporting electrolyte (0.1 mol/L citric acid buffered to pH = 3.8 with Na<sub>2</sub>HPO<sub>4</sub>) the next step was to define the optimal experimental data. The frequency of 120 Hz; SW amplitude of 20 mV and scan increment of 4 mV were found by varying the values of the frequency from 10 Hz to 120 Hz, the SW amplitude from 10 to 100 mV and the scan increment from 2 mV to 6 mV. The reaction is going on without preconcentration (the deposition time is 0 s).

The dependence of the peak current and the concentration of the two acids  $\{I_p = f(c_{acid})\}$  is linear in the concentration range from 1.5·10<sup>-5</sup> mol/L to 9.0·10<sup>-5</sup> mol/L for citraconic acid and from 3.5·10<sup>-5</sup> mol/L to 9.0·10<sup>-5</sup> mol/L for mesaconic acid.

The linear dependence are associated with following regression equations:

$$I_p/\mu A = 0.1105 \cdot c_{cit. ac} \times 10^{-6}/\text{mol L}^{-1} + 0.448 \quad (R^2 = 0.996)$$

$$I_p/\mu A = 0.0361 \cdot c_{mes. ac} \times 10^{-6}/\text{mol L}^{-1} + 0.173 \quad (R^2 = 0.998)$$

The detection limit (three times to noise) of 3.1·10<sup>-6</sup> mol/L, for citraconic acid, and of 2.7·10<sup>-6</sup> mol/L for mesaconic acid was estimated.

The recovery of the method varied from 96.3 % to 103.2 %.

## Conclusion

Square-wave voltammetry is a sensitive, rapid, precise and accurate technique for determination of citraconic and mesaconic acid. It is also attractive due to the relatively low cost of the instrumentation and the short time required for the analysis. The disadvantages of this approach are related to the problems present in the case of complex samples. In principle, the problem of interference can be overcome by separation techniques on a case by case basis, depending to the specific nature and the type of the sample.

## References

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