

residual current [8-9]. In this work, the square-wave voltammetry together with the cyclic voltammetry is utilized for the characterization of the redox properties as well as for the quantitative determination of both *cis* and *trans* aconitic acid at a hanging mercury drop electrode (HMDE) in aqueous medium.

Experimental

All chemicals were of analytical grade (MERCK). The stock solution of aconitic acid was prepared with dissolution of an appropriate amount of aconitic acid in twice distilled water. All measurements were performed by a Polarographic Analyzer Princeton Applied Research Model 384 B. The working electrode was a hanging mercury drop (HMDE) with a surface area of 0.0149 cm², Ag/AgCl (saturated KCl) was the reference and Pt wire was used as a counter. The pure nitrogen was used for deoxygenization of working solutions. All experiments were done at room temperature.

Results and discussion

Several chemicals with different pH values were tested as supporting electrolytes for aconitic acid. The data for peak potential, peak current as well as half-peak width of the SW signal of aconitic acid in each of these supporting electrolytes are listed in Table I. It can be seen that the aconitic acid is an electroactive compound only in neutral and acid media. Table I

Data for the supporting electrolytes.
 $c(\text{aconitic acid}) = 5 \cdot 10^{-5} \text{ mol/L}$; $f = 120 \text{ Hz}$; $E_{sw} = 20 \text{ mV}$; $dE = 4 \text{ mV}$

Supporting electrolyte	E_p/V	i_p/mA	$\Delta E_{p/2}/\text{mV}$	$i_p/\Delta E_{p/2} \times 100/\mu\text{A mV}^{-1}$
0.1 mol/L KI	-1.15	1.07	110	0.97
0.1 mol/L ammonia buffer pH = 9.1	/	/	/	/
0.1 mol/L KNO ₃	-1.10	0.95	175	0.54
0.1 mol/L acetate buffer pH = 3	-1.02	1	140	
0.1 mol/L acetate buffer pH = 3.5	-1.05	0.83	150	0.71
0.1 mol/L acetate buffer pH = 4.9	-1.19	0.35	100	0.35
0.1 mol/L HCl	-0.830	1.32	110	1.2
0.1 mol/L borax	/	/	/	/

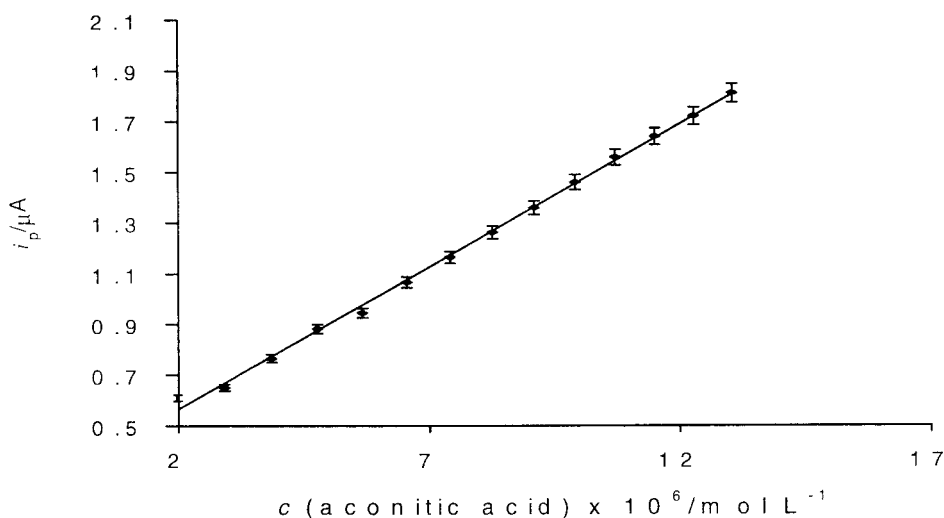
The ratio peak current-half-peak width ($i_p/\Delta E_{p/2}$) for aconitic acid has a maximum when 0.1 mol/L hydrochloric acid is used as a supporting electrolyte. The square-wave voltammogram of aconitic acid recorded in 0.1 mol/L HCl is well shaped, with peak potential of -0.832 V and half-peak width of 140 mV. The redox process of aconitic acid at HMD electrode is completely irreversible and, according to the literature data for the reduction of unsaturated dicarboxylic acid with one double bond (fumaric and maleic acid) at a mercury electrode [7], it could be presented with the following equation:



The linearity between the peak potential and frequency of the excitement signal ranges from 40 to 120 Hz. Frequency of 120 Hz was found to be suitable for quantitative determination of aconitic acid. The peak potential as well as the peak current of aconitic acid are affected significantly by the amplitude of the SW signal.

For SW amplitude value from 10 to 80 mV, the peak current enhances proportionally to the SW amplitude. The half-peak width is also sensitive to the variation of the SW amplitude. The ratio $i_p/\Delta E_{p/2}$ reaches a maximum at SW amplitude of 40 mV. It means that amplitude of 40 mV is the most suitable for analytical purposes in the case of aconitic acid. The calibration curve ($R^2 = 0.999$) of aconitic acid was constructed over the concentration range from 2×10^{-6} mol/L to 1.4×10^{-5} mol/L (see figure 2).

Figure 2. Relationship between peak current and concentration of aconitic acid in 0.1 mol/L HCL as a



supporting electrolyte. Frequency $f = 120$ Hz, SW amplitude $E_{sw} = 40$ mV, scan increment $dE = 4$ mV.

The effect of the interference compounds which are usually presented in the fruit samples together with aconitic acid on its SW voltammetric response is investigated.

Table II

Tolerance limit of some interference on the SW voltammetric response of aconitic acid.
 c (aconitic acid) = 5×10^{-6} mol/L. *

Interference	Tolerance limit ($c(i)/c(\text{aconitic acid})$)	Potential of reduction/ V (in 0.1 mol HCl)
Malic acid	1	-0.740
Fumaric acid	3	-0.756

* Other conditions are as in the Table I

It should be noted that vitamin C, succinic, tartaric, acetic, citric and oxalic acid do not interfere with the voltammetric response of aconitic acid, except maleic and fumaric acid whose electrochemical behaviour is similar with that for aconitic acid (see Table II).

The detection limit is estimated as 1×10^{-6} mol/L (0.184 μ g/mL).

The sensitivity of the method expressed as a slope of calibration curve is about 0.112 μ A L/ μ mol. The recovery of the method varied from 0.1 to 1.2 % (n = 10)

In summary, square-wave voltammetry is a sensitive, rapid, precise, and accurate analytical technique for determination of aconitic acid, and by extension of other organic compounds. This technique is also attractive due to the relatively low cost of the instrumentation and short time required for the analysis. The disadvantages of this approach are addressed to the problems presented by complex sample types. In principle, the problem of interference can be dissolved by separation techniques (i.e. chromatography) case by case, according to the specific nature and the type of the sample.

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Апстракт

Аконитната киселина претставува незаситена трикарбоксилна органска киселина, присутна најчесто во растителни плодови. Електрохемиски е активна во кисела и неутрална средина. За нејзино квантитативно определување, разработена е квадратно-бранова волтаметриска метода на висечка живина капка. Оптималните услови за квантитативно определување се: основен електролит 0,1 mol/L HCl, фреквенција $f = 120$ Hz, амплитуда $E_{sw} = 40$ mV и потенцијален инкремент $dE = 4$ mV. Испитано е влијанието на некои органски супстанции врз волтаметрискиот одговор. Границата на детекција изнесува 1×10^{-6} mol/L. Репродуцибилноста на методата изразена преку релативната стандардна девијација се движи од 0,1 до 1,2 %.