

## Square-Wave Voltammetric Determination of Ascorbic Acid Based on its Electrocatalytic Oxidation at Zeolite-Modified Carbon-Paste Electrodes

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Carbon-paste electrodes modified with Fe(III)-Y zeolite have been used to study the electrocatalytic oxidation of ascorbic acid. The ion-exchange behavior of the modified electrodes in different supporting electrolytes was investigated. Maximum cathodic current due to reduction of the exchanged Fe(III) ions was observed in phosphate buffer, pH 5. The modified electrode acts as a catalyst for electrooxidation of ascorbic acid, lowering the overpotential of the reaction by ~200 mV. The faster rate of electron transfer results in a great enhancement of the cathodic peak current compared to those observed for the unmodified electrode. The effect of several parameters such as pH and concentration of the supporting electrolyte was investigated. The square-wave voltammetric response of the electrode to ascorbic acid is linear in the range  $4.0 \times 10^{-7}$  to  $1.2 \times 10^{-3}$  M with a detection limit of  $2 \times 10^{-8}$  M. The interfering effect of several cationic species and organic compounds was investigated and tolerance limits were obtained. The method was applied to the determination of ascorbic acid in citrus fruits.

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**Keywords:** Fe(III)-Y zeolite; Modified electrode; Ascorbic acid; Square-wave voltammetry; Electrocatalysis

### 1. INTRODUCTION

Zeolites are an important group of crystalline aluminosilicates currently available for various fields of applications. These minerals are widely used as sorbents, ion exchangers, catalysts and catalyst supports [1-4]. The catalytic nature and activity, and other properties of zeolites can be greatly improved by cation-exchange. The versatile cation-exchange behavior of zeolites allows a large number of metal ions and complexes to be incorporated into these materials [5-8]. These characteristics of zeolites, together with their low cost and resistance to various chemical environments have made them useful for electroanalytical applications [9]. Several reviews cover the general

interests in zeolites as materials useful for electrochemical environments [10-13]. Applications of zeolites in various electroanalytical fields such as potentiometry [14,15], voltammetry and amperometry [16-18], voltammetry after preconcentration [19,20], and especially electrocatalysis [4-6,21] have stimulated a wide variety of research. Almost all of these applications are based on the use of zeolites in chemically modified electrodes. Due to their unique characteristics including molecular sieving selectivity [11] based on the size and shape of the molecules, charge selectivity, high ion-exchange capacity [22,23], inherent catalytic activity [17], possibility of improving their catalytic properties and their analyte preconcentration ability [19,20], zeolites possess outstanding potentialities for use as the modifying agents for chemically-modified electrodes, and as such, have drawn considerable attention of electrochemists during the past years [24-27].

Several methods have been used for incorporation of zeolite particles into electrodes. These include the use of a polymer layer containing zeolite [28,29], pressed zeolite pellets [30], carbon-paste mixed with zeolite particles [31,32], zeolite-carbon composites [33], and co-deposition of zeolite with organic salts [34]. For analytical applications, it is highly desirable to develop robust modified electrodes that can be prepared easily and reproducibly. Additionally, by using a suitable modifier, it is desirable to improve sensitivity, detection limit and selectivity [5]. Jiang *et al.* [2] have reported on the use of a graphite-zeolite-modified electrode doped with iron(III) for the catalytic oxidation of ascorbic acid. They have prepared their modified electrode by applying a suspension of zeolite-graphite mixture containing polystyrene and carried out their electrochemical studies using cyclic voltammetry and constant potential amperometry. In the present work, we have attempted to improve the response characteristics of the Fe(III)-Y-zeolite by incorporating the modifier in carbon-paste matrix. A simple electrode was designed with a reservoir for holding the carbon-paste. The electrode surface can be renewed very easily for a large number of times over a long period. The use of carbon-paste matrix, besides renewability by a simple polishing, offers several other advantages including easy preparation, uniform distribution of the catalyst into the paste, better reproducibility and stability, and adequate robustness in aqueous solutions. The electrochemical response characteristics of the modified electrode were investigated. The influences of several alkali ion electrolytes, pH, modifier concentration and instrumental parameters on the response characteristics of the electrodes were studied and the optimum operating conditions established. The modified electrodes were used for the electrocatalytic oxidation of ascorbic acid using square-wave voltammetry.

## 2. EXPERIMENTAL PART

### 2.1. Reagents and chemicals

The sodium-Y (NaY) zeolite (Cat. No. 33444-8) and spectroscopic grade mineral oil (Nujol) were obtained from Aldrich. Graphite powder, ascorbic acid, sodium dihydrogen phosphate, tetrabutylammonium perchlorate (TBAP), lithium, potassium, and sodium nitrates, and all other chemicals were of analytical reagent grade from Merck. Doubly distilled, deionized water was used for preparing all solutions and throughout the experiments. Ascorbic acid solutions were freshly prepared as required and protected from light during the investigation. Phosphate buffer was prepared from 0.1

M sodium dihydrogen phosphate and the desirable pH was adjusted by addition of sodium hydroxide or phosphoric acid solution as appropriate.

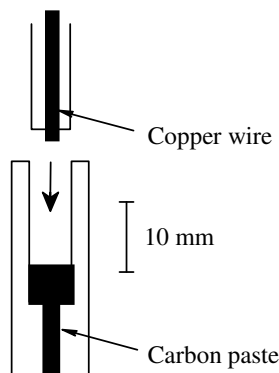
The Fe(III)-Y zeolite was prepared according to a previously reported method [2]. The NaY zeolite (0.5 g) was lightly ground, mixed with 100 ml 0.01 M FeCl<sub>3</sub> solution and stirred on a magnetic stirrer for 24 h. The exchanged zeolite was washed with dilute HCl solution to remove the adsorbed matter, then washed with water till free of chloride and dried in open air.

## 2.2. Apparatus

Electrochemical experiments were carried out using a 746 VA Trace Analyzer (Metrohm) equipped with a 747 VA Stand. A conventional three electrode system was employed incorporating a zeolite-modified carbon-paste electrode, a saturated Ag/AgCl reference electrode and a Pt wire counter electrode. All potentials are reported vs. Ag/AgCl reference electrode. The pH measurements were performed using a Corning model 125 pH meter equipped with a combined glass electrode.

## 2.3. Modified electrode preparation

The zeolite-modified carbon-paste electrodes were prepared according to the following procedure. An appropriate amount of the Fe(III)-exchanged zeolite (5–20 weight% with respect to graphite) was mixed with 100 mg graphite powder and then Nujol was added. After thorough hand mixing in a mortar to obtain a fine paste, a portion of the composite mixture was packed into the end of a polyethylene tube. The electrode body (see Fig. 1) was made by drilling a bore with 2.5 mm diameter through 1/3 of a solid polyethylene rod of 3 cm length and 11 mm diameter. In the opposite end, a bore with 6 mm diameter was drilled. The modified carbon-paste was inserted from the wider side and pressed down using a rod of the same diameter. In this way the carbon-paste is packed into the short diameter side of the electrode. Electrical contact was made by forcing a copper wire of ~1 mm diameter, positioned into a glass tubing of 6 mm diameter, down the polyethylene tube and into back of the paste. Unmodified electrodes were prepared in a similar way, using a carbon-paste with unmodified zeolite (NaY). The electrode surface was polished using a soft paper and then rinsed with ethanol and distilled water, respectively.



**Figure 1.** Schematic drawing of the modified electrode.

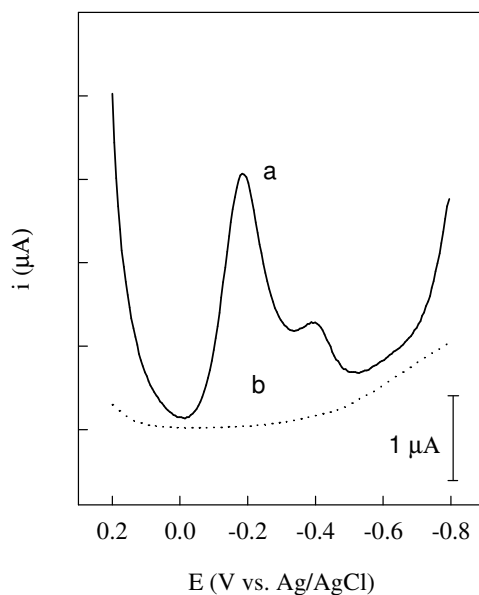
## 2.4. Procedure

The supporting electrolyte, 20 mL phosphate buffer, pH 5, was placed in the cell and an appropriate amount of standard or the measuring solution containing ascorbic acid was added. The solution was degassed with pure argon for at least 10 min. The inert gas was passed over the solution during all the voltammetric measurements. The modified carbon-paste electrode was polished on a soft paper and rinsed with ethanol and distilled water. This electrode together with the reference and the counter electrodes were immersed into the measuring solution and the potential was scanned from 0.1 to +0.8 V vs. Ag/AgCl using square-wave voltammetry. The peak current was appeared at a potential of  $\sim 0.42$  V vs. Ag/AgCl. All electrochemical measurements were conducted at room temperature. The electrodes were kept in open air when not in use. A series of optimization studies were made on the square-wave voltammetric parameters; optimized values of the parameters were: pulse height ( $\Delta E_p$ ), 20 mV; pulse width ( $t_{step}$ ), 50 ms; measuring time ( $t_{meas}$ ), 2 ms; modulation frequency, 50 Hz; step potential ( $E_{step}$ ), 2–12 mV. Scan rate was varied by changing either  $E_{step}$  or  $t_{step}$ .

## 3. RESULTS AND DISCUSSION

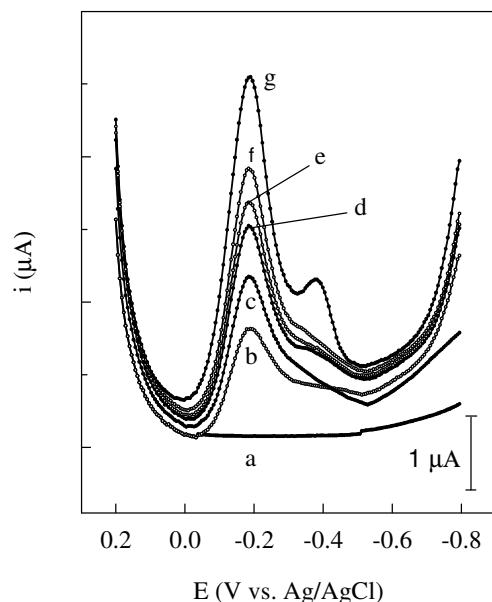
### 3.1. Voltammetric response of the Fe(III)-Y-modified electrode

The voltammograms of the unmodified and Fe(III)-Y-modified carbon-paste electrodes were recorded in phosphate buffer, pH 5, at a scan rate of  $240 \text{ mV s}^{-1}$ . Fig. 2 shows the resulting voltammograms, recorded after several preliminary scans. No voltammetric response is observed for the unmodified electrode (Fig. 2b). However, a well defined reduction peak with a peak potential at  $-0.2$  V was observed for the Fe(III)-Y-modified electrode (Fig. 2a).



**Figure 2.** Square-wave voltammograms obtained in phosphate buffer, pH 5, for (a) the reduction of Fe(III)-Y zeolite at the modified carbon-paste electrode and (b) the same voltammogram run at the unmodified electrode. Modifier concentration, 15%; scan rate  $240 \text{ mV s}^{-1}$ .

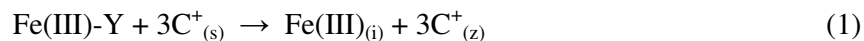
Experimental results showed that the square-wave voltammetric peak height at the modified electrode depends strongly on the type of supporting electrolyte. Several electrolytes, including 0.02 M TBAP, 0.1 M LiNO<sub>3</sub>, 0.01 M NaNO<sub>3</sub>, 0.01 M KNO<sub>3</sub>, 0.1 M NaNO<sub>3</sub>, 0.1 M KNO<sub>3</sub>, and phosphate buffer, pH 5 were investigated. There was no wave in the presence of TBAP. However, well defined reduction peaks were observed in the other electrolytes (Fig. 3).



**Figure 3.** Square-wave voltammograms for the reduction of Fe(III)-Y zeolite in different supporting electrolytes; (a) 0.02 M TBAP, (b) 0.1 M LiNO<sub>3</sub>, (c) 0.01 M NaNO<sub>3</sub>, (d) 0.01 M KNO<sub>3</sub>, (e) 0.1 M NaNO<sub>3</sub>, (f) 0.1 M KNO<sub>3</sub>, and (g) phosphate buffer, pH 5. Other conditions same as Fig. 2.

These observations can be described on the basis of possible mechanisms for the electrochemical processes at zeolite-modified electrodes. Two possible mechanisms have been considered [5]: one where the electrochemical process takes place while the electroactive species is resident inside the zeolite; the other where such a process occurs after the electroactive species exits the zeolite through ion exchange or desorption. These mechanisms are known as intrazeolite and extrazeolite electron transfer processes, respectively [6]. The latter calls for electron transfer to occur at the electrode solution interface. This is the mechanism which has been shown to be operative in most cases [5,6]. From Fig. 3a, it is clear that no electrochemical reaction occurs in the presence of TBAP electrolyte because the TBA<sup>+</sup> cation is size excluded from the Y-zeolite pore system. Therefore, no ion exchange occurs and all the Fe(III) species are located in the interior of the zeolite which is not conducive for the electrochemical reaction to take place. It should be mentioned that no iron species is initially present at the electrode surface, because as described in the experimental section, the Fe(III)-Y zeolite, after preparation, was thoroughly washed with dilute HCl solution to remove the surface adsorbed species. However, ion exchange occurs between the intrazeolite Fe<sup>3+</sup> ions and the electrolyte cations in the electrolytes with small cations. This ion exchange process results in transport of Fe(III) to the electrode surface where they can approach the conductive parts of the electrode surface, and therefore, extrazeolite electrochemical mechanism becomes operative. Based on the results presented

in Figs. 2 and 3, and in the light of previous works [5,6], the electrochemical process for the reduction of Fe(III) at the modified electrode can be represented by the following reactions,



where  $\text{C}^+$  stands for a singly charged cation and the descriptors z, s and i stand for zeolite, solution, and zeolite-solution interface, respectively. It is clear that  $\text{TBA}^+$  cation is size excluded from the Y-zeolite pore system. The  $\text{Fe}^{3+}$  ions leaving the zeolite pores are reduced at the electrode-solution interface.

As can be seen in Fig. 3, the response of the electrode depends both on the type of cation (size selectivity) and its concentration in the supporting electrolyte solution. The current observed for the reduction of Fe(III) was highest when the zeolite was exposed to phosphate buffer solution, pH 5, containing  $\sim 0.1 \text{ M Na}^+$  (Fig. 3g). The current observed in this solution is more than that observed for the neutral  $0.1 \text{ M NaNO}_3$  electrolyte with about the same concentration of  $\text{Na}^+$  (Fig. 3f). This can be related to cooperation of hydronium ion in displacing Fe(III) from zeolite pores. The voltammogram g in Fig. 3 shows an extra peak at  $-0.4 \text{ V}$ . This is due to the reduction of Fe(III) from its phosphate complex, because the peak shifts to more negative potentials and its intensity increases by increasing phosphate concentration in the supporting electrolyte.

Voltammetric responses of the modified electrodes with 5, 10, 15 and 20% (w/w, with respect to graphite) Fe(III)-Y zeolite were examined by square-wave voltammetry in phosphate buffer, pH 5 using the same instrumental parameters. The results of this study revealed that the optimum proportion of zeolite to graphite was 15:85. Lower amounts of the modifier decrease the extent of ion exchange and higher amounts increase the resistance of the electrode, both of which decrease the sensitivity of the electrode response.

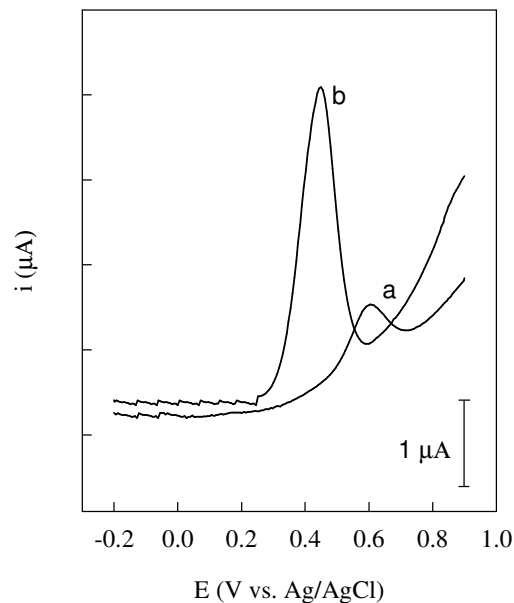
The Fe(III)-Y-modified electrode with the above characteristics was successfully applied for the electrocatalytic oxidation of ascorbic acid, the results of which are presented in the following sections.

### 3.2. Electrocatalytic oxidation of ascorbic acid at the Fe(III)-Y-modified electrode

Carbon-paste electrodes modified with transition metal complexes have the ability to catalyze the oxidation or reduction of solute species. The major effect of the modifier consists of lowering the potential required for the catalyzed redox systems, which is generally accompanied with a considerable increase in sensitivity. Among the transition metal ions, cobalt and iron complexes show the highest electrocatalytic activity and have shown great promise for the electrocatalytic determination of many organic and biologically important compounds [35-38]: Here, we used the Fe(III)-Y zeolite as a modifier in carbon-paste electrode as a square-wave voltammetric sensor to study the electrocatalytic oxidation of ascorbic acid.

The electrocatalytic function of the Fe(III)-Y-modified electrode for the electrochemical oxidation of AA is demonstrated in Fig. 4 by square-wave voltammograms of  $1 \times 10^{-4} \text{ M}$  ascorbic acid

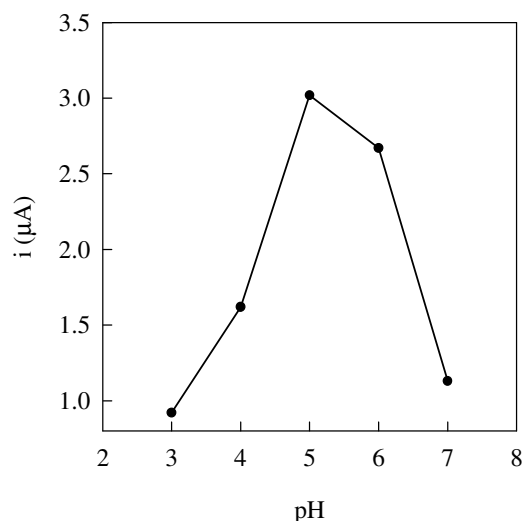
obtained in phosphate buffer, pH 5. Under the same experimental conditions, the direct oxidation of ascorbic acid at the unmodified carbon-paste electrode showed relatively weak anodic peak (Fig. 4a). The corresponding voltammogram for the oxidation of ascorbic acid at the modified electrode gives rise to electrocatalytic responses with an anodic peak current that is greatly enhanced over that observed for the unmodified electrode (Fig. 4b). Maximum current for the oxidation of ascorbic acid at the modified electrodes occurred at potentials about 200 mV more negative than those obtained in the absence of the modifier. This behavior, which was observed at several concentrations and at different potential scan rates, clearly demonstrates the electrocatalytic function of the modified electrode toward ascorbic acid oxidation.



**Figure 4.** Anodic square-wave voltammograms for the oxidation of  $2 \times 10^{-4}$  M ascorbic acid in phosphate buffer, pH 5 at (a) unmodified and (b) modified electrodes. Other conditions same as Fig. 2.

The influence of pH on the catalytic oxidation of ascorbic acid was investigated in the range 3–7. In all cases the concentration of  $\text{Na}^+$  in the phosphate buffer was maintained at  $\sim 0.1$  M and voltammograms were obtained using  $1 \times 10^{-4}$  M ascorbic acid at a scan rate of  $240 \text{ mV s}^{-1}$ . The results indicated that the peak potential,  $E_p$ , shifts to more negative values with increasing pH. Such a behavior suggests that the acidic dissociation of ascorbic acid occurs at or before the rate determining step [35]. In addition, the square-wave voltammetric peak heights for the electrocatalytic oxidation of ascorbic acid also are strongly affected by the solution pH as shown in Fig. 5; highest sensitivity was observed at pH 5. Therefore, all subsequent measurements were performed at pH 5. This pH is also suitable for better stability of ascorbic acid, because it has been suggested that for maximum stability, ascorbic acid solutions should be buffered to  $\text{pH} \leq 5.4$  [39]. Ascorbic acid can be oxidized by dissolved oxygen present as an impurity in solutions [40]; and this effect is intensified under alkaline conditions. Lower electrocatalytic currents observed at  $\text{pH} < 5$  can be related to the formation of undissociated form of ascorbic acid.

The effect of supporting electrolyte concentration, phosphate buffer (pH 5), on the electrocatalytic oxidation of ascorbic acid was investigated at 0.02, 0.05, 0.1 and 0.15 M. Highest sensitivity was observed with 0.1 M phosphate buffer, containing  $\sim 0.1$  M  $\text{Na}^+$ .



**Figure 5.** Effect of pH on the square-wave voltammetric peak height for the determination of ascorbic acid at the Fe(III)-Y-modified electrode.

The voltammetric peak current at the modified electrode was linearly proportional to the square root of scan rate, illustrating that the process of ascorbic acid oxidation is diffusion controlled.

On the basis of our results and previous works [2,5,6,36], the electrocatalytic oxidation of ascorbic acid at the surface of the zeolite-modified electrode, following Eq. (1), can be explained by a two step process; oxidation of AA by Fe(III) and subsequent reoxidation of the resulting Fe(II) at the electrode surface. All these processes occur at the electrode solution interface, where  $\text{Fe}^{3+}$  is released through the ion-exchange with  $\text{Na}^+$  ions.

Calibration was performed using square-wave voltammetry with increasing concentration of ascorbic acid. The peak current is linearly related to the concentration of ascorbic acid in the range  $4.0 \times 10^{-7}$ – $1.2 \times 10^{-3}$  M, with a least squares fit of  $i$  ( $\mu\text{A}$ ) =  $0.3375 + 2.857 \times 10^4 C_{\text{AA}}$  ( $\mu\text{M}$ ), and a correlation coefficients of 0.9995 ( $n=12$ ).

Long term stability was investigated by taking the response of the modified electrode in a period of 10 months. The electrode was stored in open air when not in use. Voltammetric measurements and calibration were performed every three days during the first month and then every week for the rest of the period. The electrode retained its full activity during this period; it was only necessary to renew the surface by a slight rubbing of the electrode on a soft paper, whenever the electrode response diminished. The reproducibility of the voltammetric response of the modified electrode was investigated by carrying the measurements on five independent electrodes with the same composition. The relative standard deviation (between electrode variation) thus obtained was less than 4%. The relative standard deviations of 10 replicate measurements performed on a single electrode (within electrode variation) at several ascorbic acid concentrations between  $2 \times 10^{-3}$  to  $1 \times 10^{-6}$  M



were between 1.0 to 2.4%. A detection limit of  $2 \times 10^{-8}$  M was estimated considering a signal/noise ratio of 3.

The influence of several metal ions and organic compounds were tested on the voltammetric response of the electrode in solutions containing  $5 \times 10^{-4}$  M ascorbic acid. The results are presented in Table 1. The tolerance limits, given in Table 1, are the molar ratio of interfering species/ascorbic acid which caused an error of  $\leq \pm 2\%$  in the measurement of ascorbic acid. It was found that several organic compounds including benzoic acid, tartaric acid, citric acid, glucose, urea, acetate, and a number of metal ions  $\text{Ca}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Sn}^{2+}$  have no effect even when their concentration exceeds  $\sim 200$  fold of ascorbic acid. Oxalic acid interferes in the determination if its concentration is more than 30 fold of ascorbic acid, which can be related to formation of a relatively strong complex with Fe(III) at pH 5.

**Table 1.** Molar tolerance ratio of several metal ions and organic compounds on the voltammetric response of  $5 \times 10^{-4}$  M ascorbic acid.

Species	Molar tolerance ratio (species/AA)	
	This work	Reference 2
Benzoic acid	240	100
Tartaric acid	240	100
Citric acid	200	100
Sodium acetate	160	-
Oxalic acid	30	10
Glucose	280	100
Urea	240	100
Uric acid	18	10
Vitamin A	200	-
$\text{Ca}^{2+}$	220	100
$\text{Cs}^+$	240	-
$\text{Cu}^{2+}$	190	100
$\text{Mg}^{2+}$	230	100
$\text{Al}^{3+}$	220	100
$\text{Sr}^{2+}$	240	-
$\text{Sn}^{2+}$	220	100
$\text{Ce}^{3+}$	260	-

The proposed electrode shows lower detection limit, higher precision and higher selectivity compared to the Fe(III)-Y modified electrode reported by Jiang *et al.* [2], which is based on applying a suspension of zeolite and graphite in polystyrene matrix to the electrode surface. Higher precision,

which is reflected in lower detection limit and high stability of the electrode, can be related to the carbon paste characteristics and uniform distribution of the electrocatalyst in the paste. Further, carbon-paste-based electrodes show rather low background current compared to solid electrodes [41]. Higher selectivity of the present electrode can be related to the lower peak potential observed for the electrocatalytic oxidation of ascorbic acid, which was 0.4 V vs. Ag/AgCl ( $\sim 0.6$  V vs. SHE), compared to the value of 0.55 V vs. SCE ( $\sim 0.8$  V vs. SHE) used by Jiang *et al.* [2]. Lower potential resulted in higher selectivity of the electrode with respect to several metal ions and organic compounds, as indicated by the higher tolerance limits given in Table 1.

The modified electrode was applied to the determination of ascorbic acid concentration in freshly squeezed citrus fruits according to the procedure described in the experimental section, using the standard addition method. The method of US Association of Official Analytical Chemists (AOAC) [42] was used as the reference method. The results of the analysis are presented in Table 2, indicating a close agreement between the proposed and the reference method ( $t_{\text{calc}} = 0.58$  to 1.70,  $n = 3$ ,  $t_{0.05,2} = 4.30$ ).

**Table 2.** The results of analysis of citrus fruit juices for determination of vitamin C.

Sample	Amount of ascorbic acid (mM) ( $\pm$ RSD%, $n=3$ )		
	Voltammetric method	Reference method	$t$ statistics $t_{0.05,2} = 4.30$
Orange juice	3.72 (2.4)	3.75 (1.5)	0.58
Sweet lemon juice	3.34 (3.2)	3.30 (1.4)	0.65
Sour orange juice	1.97 (4.2)	2.0 (2.7)	0.63
Sour lemon juice	4.27 (2.9)	4.15 (2.3)	1.70

#### 4. CONCLUSIONS

The results of this study demonstrate the suitability of the Fe(III)-Y-modified carbon-paste electrode for square-wave voltammetric determination of ascorbic acid. The electrocatalytic behavior of the electrode together with its long term stability, high sensitivity, low detection limit, wide dynamic range, easy preparation, relatively high selectivity, and easy regeneration by a simple polishing of the electrode surface, make it a useful device for determination of vitamin C in different samples.

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