Voltammetric Behavior of a Modified Electrode With Azide Copper Octa(3-Aminopropyl)Octasilsesquioxane Composite in the Oxidation of Ascorbic Acid

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A novel nanostructured composite, azide copper octa (3-aminopropyl)octasilsesquioxane (ASCA) was incorporated into a graphite paste electrode and the electrochemical studies were conducted with cyclic voltammetry. The cyclic voltammogram of the modified graphite paste electrode with ASCA (GPE-ASCA), showed one redox couple with formal potential \( E^\circ = 0.30 \) V and an irreversible process at 1.1 V (vs Ag/AgCl; NaCl 1.0 mol L\(^{-1}\); \( v = 20 \) mV s\(^{-1}\)). The redox couple with \( E^\circ = 0.30 \)V presents an electrocatalytic response for determination of ascorbic acid. The modified electrode gives a linear range from \( 1.0 \times 10^{-4} \) – \( 1.0 \times 10^{-3} \) mol L\(^{-1}\) (\( r = 0.998 \)) for the determination of ascorbic acid with detection limit of \( 6.9 \times 10^{-5} \) mol L\(^{-1}\) and standard deviation of 2.3% for \( n = 3 \). The amperometric sensitivity was 122.1 mA/mol L\(^{-1}\) for ascorbic acid. The application this electrode was tested and ascorbic acid in three commercial pharmaceutical product (Cebion, Cewin and Redoxon) have been determined.

Keywords: Silsesquioxane, ascorbic acid, graphite paste electrode, voltammetry, modified electrode

1. INTRODUCTION

Cubic silsesquioxanes (cubes) and the related polyhedral oligomeric silsesquioxanes (POSS) are nano-sized inorganic materials with a silica core and reactive functional groups on the surface. The silsesquioxane [1,2] has an empiric formula \( (RSiO_{1.5})_n \), where R may be a hydrogen or some organic group such as alkyl, methyl, aryl, vinyl, phenyl or any organofunctional derivative from these organic
groups. Each silicon atom is, on average, connected to 1.5 oxygen atoms and to an R group (hydrocarbon). When \( n = 4,6,8,10; \ (n \geq 4) \), the resulting compounds are called polyhedral oligomeric silsesquioxanes [3,4] (POSS).

The strong intermolecular forces between their constituent molecules and neighbors, as well as their strong framework with their shorter bond lengths make these silica nanocomposites even more resistant to chemical degradation. The POSS molecule is in the cubic octameric form (T8) with well-defined nanoclusters having an inorganic silica-like core surrounded by eight organic corner groups, which can be replaced by same or different functional groups to form to multifunctional materials with intermediate properties between those of organic polymers and of ceramics. Cubic silsesquioxanes, \( R_8Si_8O_{12} \), consist of a rigid, crystalline silica-like core that is perfectly defined spatially (0.5-0.7 nm) and that can be linked covalently to eight R groups. In addition, the silsesquioxane structure (\( Si_8O_{12}^- \)) is an electron acceptor in such way that it has been compared to the group \( CF_3^- \) [5].

The most common applications are those that have technological significance, such as: additives [6-10] (crossed bonds agents and thermal and viscosity modifiers); precursory for polymer dendrimers and transition metal complex octafunctional silsesquioxanes [11-17] (medical materials, advanced plastics and elastomeric resins); liquid crystals [18,19]; electroactive films [20]; biosensors [21] precursory for silicon interface [22]; glass and ceramic matrixes [23], homogenous and heterogeneous catalysts [24,25] and more recently material for biomedical applications [26].

In electroanalytical chemistry, the chemical modification of electrodes is a growing field that has been extensively developed because chemically modified electrodes possess distinct advantages over conventional electrodes in numerous application areas including electrocatalysis and electrochemical sensors. Recent developments in chemically modified electrodes (CMEs) towards analytical applications was published in a review [27]. One of the important properties of the chemical modified electrodes (CMEs), which has been the subject of considerable study is ability to facilitate charge transfer process catalysing the oxidation and reduction of solute species which exhibit high overpotential at unmodified electrode surfaces. This away CMEs contribute to decrease overpotential often required to perform electrochemical and increasing sensitivity and selectivity of some electroactives species. In addition, CME possess distinct advantages over mercury electrodes because of their possible toxicity or because of rapid deterioration of electrode response [28]. Platinum and gold electrodes form surface oxide, causing complications with analytical applications also [29]. In this viewpoint the graphite paste electrode offers advantages over methods of modification above mentioned.

Within this context, particularly our interest in the silsesquioxane chemistry is to prepare multifunctional nanostructured materials that can be used as electrochemical sensors. The objective of this work was test a novel composite the azide copper octa(3-aminopropyl)octasilsesquioxane [30] (Figure1) freshly prepared as a sensor for biological substances of interest, for instance, ascorbic acid. The increasing use of pharmaceuticals and other natural samples containing vitamin C has necessitated the development of an accurate and specific procedure for its determination. Determination of ascorbic acid (AA) by voltammetric methods has received much attention in recent years [31]. It has been shown that content of AA in biological fluids can be used to access the amount of oxidation stress in human metabolism and excessive oxidative stress has been linked to cancer, diabetes and hepatic
disease [32]. It is known that accurate determination of AA using conventional electrodes is very difficult because of its high overpotential, poor reproducibility due to fouling effect caused by the oxidized products of AA, low selectivity, and low sensitivity. As a direct application of electrocatalytic properties of the azide copper octa(3-aminopropyl)octasilsesquioxane at pharmaceutical products (Cebion, Cewin, Redoxon) were determined.

![Figure 1. Schematic representation of ASCA](image)

### 2. EXPERIMENTAL

#### 2.1. Reagents and solutions

All reagents solutions and supporting electrolytes were prepared using Milli-Q water. Ascorbic acid were used without further purification and all reagents and solvents were of analytical grade (Merck or Aldrich) and were used as purchased. All solutions and supporting electrolytes were prepared using Milli-Q water. The ascorbic acid solutions were prepared immediately before use and were deaerated with purified nitrogen. This procedure was adopted because this species can be oxidized to ascorbate by atmospheric oxygen.
2.2. Preparation of Octa (3-aminopropyl)octasilsesquioxane (AC)

Octa(3-aminopropyl)octasilsesquioxane (AC) was prepared according to the procedure described in the literature [30] with some modifications.

The preparation of octa (3-aminopropyl)octasilsesquioxane used a two-step process:

Step 1: Concentrated HCl (200 mL) was carefully added, under stirring, to a solution. A 150 mL syringe containing γ-aminopropyltriethoxysilane ($\text{H}_2\text{NCH}_2\text{CH}_2\text{Si(OEt)}_3$) was slowly added to methanol anhydrous (3.6 L) in a 4.0 L three-neck round bottom flask. The bottle was capped and allowed to stand for 6 weeks at 30 °C. The product usually begins to crystallize from the reaction mixture after 3-4 weeks. A solution of octahydrochloride salt in ~ 31%, was obtained and washed with cold methanol and then dried at room temperature. The resulting product, the octahydrochloride salt, was designated (1).

Step 2: a neutralization of (1). Amberlite IRA-400 (Cl) ion-exchange resin (37 g) was prepared by successive washing with water (4 × 200 mL), 1 M NaOH (3 × 200 mL), water (6 × 200 mL). The resin was suspended in an eluent and chilled (-10°C; 2 h.) before use. Half of the resin beads were loaded onto a column (3.5 cm outside diameter); the other half was used to dissolve a suspension of (1). The elution across the column produced a stock solution that was tested negative for chloride. To avoid decomposition the amine should be prepared immediately before use and stored in methanol solutions at -35°C. The purity and identity of these compounds was confirmed by conventional analytical methods (microanalysis (C, N, H), infrared (FTIR) and absorption spectroscopy) [30]. The Table 1 presents a summary these preparation.

Table 1. Main spectroscopic data for $[\text{NH}_2(\text{CH}_2)_3\text{SiO}_{1.5}]_8$

<table>
<thead>
<tr>
<th>FTIR (cm$^{-1}$)</th>
<th>$^{13}$C NMR (ppm)</th>
<th>$^{13}$Si NMR (ppm)</th>
<th>$^1$H NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Si 1110-1130</td>
<td>α-C 10.18</td>
<td>SiO₂ -66.5</td>
<td>a-NH$_2$ 7.8</td>
</tr>
<tr>
<td>N-H 1650-3500</td>
<td>β-C 21.67</td>
<td></td>
<td>b-CH$_2$ 2.9</td>
</tr>
<tr>
<td>C-N 1490</td>
<td>γ-C 43.19</td>
<td></td>
<td>c - CH$_2$ 1.8</td>
</tr>
<tr>
<td>C-Si 1253</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Si 765</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H 2950</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H 1387-1408</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3. Preparation of azide copper octa (3-aminopropyl)octasilsesquioxane

The compound copper octa (3-aminopropyl)octasilsesquioxane was prepared by the following procedure [30]: 163 mg of CuCl$_2$.5H$_2$O was added to a methanolic solution of $[\text{H}_2\text{N(CH}_2)_3]_8\text{Si}_8\text{O}_{12}$ (10 mL), and the blue transparent solution was stirred for 2.5 h at room temperature, next, a solution of 74 μL of saturated sodium azide was added to form a green precipitate (Caution! Azide complexes are potentially explosive. Only a small amount of the material should be prepared and always handled with care). In order to prevent a possible thermal degradation, this gelatinous green precipitate was filtered through a celite bed, washed with methanol and water five times, respectively and finally lyophilized (s...
the azide compound is thermally unstable). The dried product was stored and sheltered from light. The resulting composite was designated as ASCA.

2.4. Electrochemical Measurements

Cyclic voltammograms were performed using the Microquimica (MQP1- PGST) potentiostat. The three electrode systems used in these studies consisted of a modified working electrode (graphite paste electrode) an Ag/AgCl reference electrode, and a platinum wire as the auxiliary electrode. The measurements were carried out at 25°C.

2.5. Preparation of the graphite paste electrode modified with ASCA

The graphite paste electrode modified with ASCA (GPE-ASCA) was prepared by mixing 20 mg of ASCA with 90 mg of graphite (Aldrich) and 50 µL of mineral oil. The electrode body was produced from a glass tube of 3 mm i.d. and 14 cm height, containing graphite paste. A copper wire was inserted through the opposite end of the glass tube to establish electrical contact. After homogenizing the mixture, the modified paste was carefully positioned on the tube tip to avoid possible air gaps, which often enhances electrode resistance. The external surface of the electrode was smoothed on soft paper. A new surface can be produced by scraping out the old surface and replacing the graphite paste.

2.6. Procedure

Initially, cyclic voltammograms were recorded for study the sensibility of ascorbic acid, by graphite paste electrode modified with ASCA. The supra analite solutions were prepared immediately before use and were deaerated with nitrogen. In most of the experiments, 1.0 mol L⁻¹ NaCl (pH ~ 6.7) was used as the supporting electrolyte. The catalytic and or sensibility current was estimated by the difference between the electrode current in the presence of analite compounds and that which is established in the blank solution.

2.7. Voltammetric determination procedure of pharmaceutical products

In this study, we have applied the modified electrode to the determination of ascorbic acid at three pharmaceutical products (Cebion, Cewin and Redoxon). A standard aqueous solution of ascorbic acid and 0.1 mol L⁻¹ (stock solution) were prepared in water. The standard addition method was employed for the quantification of ascorbic acid, where in an electrochemical cell filled with 20 mL 1.0 mol L⁻¹ NaCl (pH 7.1), suitable aliquots of the sample (500 µL) were immediately taken into cell and the curve were registered after successively added 200 µL of the standard solution of ascorbic acid (0.1 mol L⁻¹). The experiments were preformatted in triplicate.
3. RESULTS AND DISCUSSION

The effect of the graphite paste composition on the voltammetric response of the working electrode (GPE-ASCA) was evaluated.

![Figure 2](image1.png)

**Figure 2.** Influence of percentage mixture of ASCA and graphite on the anodic current intensity

The cyclic voltammogram of graphite paste electrode containing ASCA (Figure 3a) shows a redox couple and an irreversible process for different electrolytes. The Table 2 list the main electrochemical parameters for this experiment.

![Figure 3](image2.png)

**Figure 3.** Cyclic voltammograms of GPE-ASCA in various 1.0M aqueous solutions of alkali metal chloride: a NaCl; b LiCl; c KCl; d NH₄Cl. Scan rate 20 mV s⁻¹
Ten working electrodes in the percentage varying from 20% to 80% (m/m) of graphite/ASCA and a fixed oil (nujol) volume (25 µL) were prepared and examined for their voltammetric signals under identical conditions. As can be seen in Fig. 2 the anodic intensity current signal of ASCA decreased (~ 37%) with increasing ASCA percentage up to 20% and leveled off at higher percentage. Hence an electrode containing 20% ASCA/graphite (m/m) was employed for all subsequent experiments. The intensity current decrease from 20% (m/m) because probably the insulator nature of silicate cage presents in ASCA.

The formal potential \( E^\theta \) where \( E^\theta = E_{pa} + E_{pc} / 2 \) and \( E_{pa} \) = anodic peak potential and \( E_{pc} \) = cathodic peak potential was 0.30 V and the irreversible process occur at 1.1 V (vs Ag/AgCl; NaCl 1.0 M; \( v = 20 \text{ mV s}^{-1} \)). We found that the cation nature of the supporting electrolytes interfere formal potential (Figure 3). The first and the second process were described by equation (1) and (2) respectively [30].

\[
\begin{align*}
\text{Cu}^{(I)}(N_3)_2 & \Leftrightarrow \text{Cu}^{(II)}(N_3)_{2} + e^- \quad (0.30 \text{ V}) \quad (1) \\
\text{Cu}^{(III)}(N_3)_2 & \Leftrightarrow \text{Cu}^{(II)} + 3N_2 + 2e^- \quad (1.1 \text{ V}) \quad (2)
\end{align*}
\]

The ratio of the currents, \( I_{rev}/I_{fwd} \), can be conveniently measured by the empirical method of Nicholson [33], which requires the evaluation of \( I_{pa} \), \( I_{pc} \), and \( I_\lambda \), where \( I_\lambda \) is the value of the current at the switching potential \( E_\lambda \) (where the direction of the CV scan is reversed). These quantities are then used to obtain the current ratio, \( I_{rev}/I_{fwd} \) in equation 3.

\[
\left| \frac{I_{rev}}{I_{fwd}} \right| = \frac{I_{pc}}{I_{pa}} + \frac{0.485 \times (I_\lambda)}{I_{pa}} + 0.086
\]

The \( I_{rev}/I_{fwd} \) and \( \Delta E_p \) values were characteristic of a quasi-reversible redox process. Table 2 lists the main electrochemical parameters for these studies. For this attribution an electro inactivity nature of silicate cage was considered [34]. From these experiments we conclude that NaCl was the best electrolyte and based on the results above, was chosen NaCl (1.0 mol L\(^{-1}\), pH 6.8) to be used in subsequent voltammetric investigation.

The intensity current is dependent of concentration of NaCl as showed by Figure 4. With increase of bulky cations concentrations the charge propagation is increased to active copper center of ASCA. It must be noted that, when electrode is transfered through 0.1 mol L\(^{-1}\) electrolyte solution to 1.0 mol L\(^{-1}\) the voltammogram is restored.
Table 2. Electrochemical parameters of GPE-ASCA in several electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_a$</th>
<th>$E_c$</th>
<th>$I_{pa}$</th>
<th>$I_{pc}$</th>
<th>($I_{pa}$)$_0$</th>
<th>($I_{pc}$)$_0$</th>
<th>$\Delta E_p$</th>
<th>$I_{pa}/I_{pc}$</th>
<th>$E^\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>381</td>
<td>228</td>
<td>44.23</td>
<td>-48.70</td>
<td>57.44</td>
<td>-24.18</td>
<td>153</td>
<td>1.18</td>
<td>304.5</td>
</tr>
<tr>
<td>LiCl</td>
<td>384</td>
<td>219</td>
<td>34.88</td>
<td>-44.86</td>
<td>53.11</td>
<td>-25.08</td>
<td>165</td>
<td>1.18</td>
<td>301.5</td>
</tr>
<tr>
<td>KCl</td>
<td>371</td>
<td>231</td>
<td>37.40</td>
<td>-49.75</td>
<td>55.88</td>
<td>-25.48</td>
<td>140</td>
<td>1.12</td>
<td>301.0</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>367</td>
<td>180</td>
<td>51.44</td>
<td>-78.27</td>
<td>90.56</td>
<td>-54.44</td>
<td>187</td>
<td>1.16</td>
<td>273.5</td>
</tr>
</tbody>
</table>

Figure 4. Cyclic voltammogram of graphite paste electrode modified with ASCA in NaCl concentration: a 1.0; b 0.5; c 0.1 mol L$^{-1}$. Scan rate 20 mV s$^{-1}$

Electrochemical behavior of ASCA was studied in pH range 3 to 8. As can be seen in Figure 5 with an increasing pH, the anodic peak potential shift about 50 mV and the current intensity decreased. With increasing pH values, there is a slower penetration (charge propagation) of H$^+$. The reason for the depletion in rate of charge transfer and decrease in intensity peak currents, is not clear, but can be due a cupric hydroxide formed on the material surface. The anodic current intensity is kept in the pH 3-8 range. Although the oxidation reaction may be accelerated by protons, we selected pH 6.8 for investigation due its possible applications in biological samples analysis.
Figure 5. Variation of anodic peak potential with the pH of electrolyte solution at the GPE-ASCA modified electrode, NaCl 1.0 M. Scan rate 20 mV s⁻¹

It can be seen in Figure 6 shows the cyclic voltammogram graphite paste electrode with ASCA at various scan rates (v = 20 – 200 mVs⁻¹). The peak separation potential (ΔEₚ) is greater than 59/n mV (n = 1) as expected for a system which shows quasi reversible behavior for the Cu⁺ / Cu²⁺ redox system. In addition, the plots of the anodic and cathodic peak currents were linearly depended on the square root of scan rate (graph inset). This behavior indicates that the redox process is diffusion-controlled [35].

Figure 6. Cyclic voltammogram of ASCA at different scan rates: 20-200 mV s⁻¹; (KCl 1.0 mol L⁻¹; pH 7.0). (Graph inserted: Dependence of current peak I (anodic and cathodic) with the square root of scan rate)
In order to verify the electrocatalytic activity of ASCA for ascorbic acid (AA) oxidation, the electrochemical experiments in the presence of AA were carried out. Due its biological importance, the electrocatalytic activity was tested in pH near 7.0.

The electrocatalysis of graphite paste electrode modified with ASCA for electro-oxidation of ascorbic acid in a 1.0 mol L\(^{-1}\) NaCl solution (pH 6.8) is showed in Figure 7.

Figure 7 displays cyclic voltammograms of ASCA in absence (curve B) and presence (curve C) of ascorbic acid. After the addition of this compound, a substantial enhancement of the anodic peak current is observed (curve C). The anodic peak current increased in proportion to the analyte concentration.

![Cyclic voltammogram of ASCA](image)

**Figure 7.** Cyclic voltammogram of: a Graphite paste electrode (GPE) with 1.0×10\(^{-3}\) mol L\(^{-1}\) ascorbic acid; b ASCA modified graphite paste electrode (GPE-ASCA) in absence of ascorbic acid; c GPE-ASCA with 1.0×10\(^{-4}\) mol L\(^{-1}\); d 2.5×10\(^{-4}\); e 5.0×10\(^{-4}\); f 7.5×10\(^{-4}\) and g 1.0×10\(^{-3}\) mol L\(^{-1}\) of ascorbic acid (1.0 mol L\(^{-1}\) NaCl; Scan rate 20 mV s\(^{-1}\)).

This increase in anodic current indicates the electrocatalytic oxidation of ascorbic acid compound by ASCA. The Cu(II) produced during the anodic scan chemically oxidises these compounds while it is reduced to the Cu(I), which will be again oxidised to the Cu(II) electrochemically. Ascorbic acid is easily oxidized to dehydroascorbic acid, which undergoes further chemical reaction to form the gem-diol. The chemically oxidation step of ascorbic acid can be described by equation 4.

\[
\text{Cu}^{(II)}(N_3)_2 + \text{AA}^- \rightarrow \text{Cu}^{(I)}(N_3)_2 + \text{DAA}^- + \text{H}^+ (0.35V)
\] (4)
Where AA\(^{-}\) e DAA\(^{-}\) correspond to dissociate forme of ascorbic acid and dehydroascorbic acid respectively.

Thus ascorbic acid electrocatalytically oxidised at the electrode surface and the oxidation process stars at 0.30 V. In the graphite paste electrode the ascorbic acid oxidation occur at 0.45 V (Figure 7a) showing a decrease of potential of 100 mV.

The potential peak, for analite were not affected by ascorbic acid concentration and the \(I_{pa}\) was proportional to the square root of the scan rate over the range 20 – 100 mV s\(^{-1}\) (results not showed). This behavior, suggests that the electrocatalytic process is controlled by diffusion [36]. In comparison, differently of Prussian Blue film, [37] that the film disintegrates by hydrolysis in solutions of higher pH than 5 this hydrolysis in ASCA happen at pH > 10. In a different way of Fe(II)NP [38] modified electrode the ASCA utility is not affected for high hidrogenionic concentration (pH < 2.5). A calibration graph for the amount of ascorbic acid versus anodic current are shown in Figure 8.

![Figure 8](image)

**Figure 8.** Calibration plot for determination of the ascorbic acid, 1.0 mol L\(^{-1}\) NaCl. Scan rate 20 mV.s\(^{-1}\).

The modified electrode gives a linear range from 1.0\(\times\)10\(^{-4}\) – 1.0\(\times\)10\(^{-3}\) mol L\(^{-1}\) \((r = 0.998\) for the determination of ascorbic acid with detection limit of 6.9\(\times\)10\(^{-5}\) mol L\(^{-1}\), standard deviation of 2.3\% for \(n = 3\) and the amperometric sensitivity was 122.1 mA / mol L\(^{-1}\).

The linear dependence of the calibration curve in Figure 8 suggest that the response of modified electrode is appropriated for quantitative ascorbic acid determination even in the millimolar concentration range. Such a wide concentration range of analytical useful response was also reported for ascorbic acid determination by chemically modified electrodes using voltammetric technique [39, 40].

In a similar way when compared to the methods involving mercury electrodes, the calibration plot crosses the abscissa, presumably owing to the interference of trace heavy metal. The reproducibility is satisfactory for the investigated concentration range (RSD 2.3\%) for ascorbic acid.
The influence of others biological substances, on the electrode response was examined. Interference studies were carried out by exposing the GPE-ASCA and 100 fold Glucose, dopamine, oxalic acid, citric acid, maltose, levulose, sucrose, and tartaric acid but is stronger influenced by nitrite concentrations (< 1 fold). The applicability of the modified electrode was confirmed by using this modified electrode for the determination of AA in the pharmaceutical formulations, using standard addition method. The ascorbic acid content for each sample (Cebion, Cewin and Redoxon) was determined, and the obtained experimental results are presented in Figure 9.

![Figure 9. Application of the standard addition method for determination of ascorbic acid in: a Cebion; b Cewin and c Redoxon.](image)

The AA content of the same sample was estimated alternately by a titrimetric method with 2,6-dichlorophenolindophenol as a titrant and visual end-point detection (Association of Official Analytical Chemists (AOAC) method) [41] was used as the reference method. An intercomparison of data from both the electrochemical and titrimetric methods indicates that the amount of ascorbic acid by the two methods agrees with each other. The results of the determination are given in Table 4. The main analytical parameters of these studies are listed in Table 4. These results for the determination of ascorbic acid in the samples (Cebion, Cewin and Redoxon) are a good evidence of the accuracy and absence of matrix effects at ascorbic acid determination by the proposed.

The main electrochemical characteristic of ASCA modified paste electrode is that it could be used for followed an unique washing with Milli-Q water, is not necessary remove the electrode surface. In addition, after using the modified GPE-ASCA, and after storage for two months at room temperature, it could retain the initial voltammetric response upon the continuous cyclic voltammetric sweep in neutral pH.
Table 3. Ascorbic acid determination in pharmaceutical products and standard deviations (n=3) as determined by proposed procedure and triiodite procedure (w/v)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proposed Method (mg/mL)</th>
<th>Triiodite procedure (mg/mL)</th>
<th>Declared (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cebion*</td>
<td>199.35 ± 0.03</td>
<td>196.84 ± 0.03</td>
<td>200</td>
</tr>
<tr>
<td>Cewin**</td>
<td>197.22 ± 0.04</td>
<td>198.52 ± 0.05</td>
<td>200</td>
</tr>
<tr>
<td>Redoxon***</td>
<td>196.96 ± 0.03</td>
<td>197.73 ± 0.03</td>
<td>200</td>
</tr>
</tbody>
</table>

* excipients (cherry flavor, sodium benzoate, caramel, double-distilled glycerin, sodium saccharin, sodium hydroxide solution  
** Oral solution containing sorbitol, methylparaben, sodium hydroxide, sucrose, riboflavin 5-phosphate, ethyl alcohol, artificial aroma of caramel  
*** Sodium saccharin, methylparaben, propylparaben, caramel concentrated essence of caramel essence of plum, sweet orange aroma and demineralized water

5. CONCLUSIONS

The cyclic voltammogram of the modified graphite paste electrode with azide copper octa(3-aminopropyl)octasilsesquioxane (GPE-ASCA), showed one redox couple with formal potential ($E^{0v}$) = 0.30V and an irreversible process at 1.1 V (vs Ag/AgCl; NaCl 1.0 M; $v = 20$ mV s$^{-1}$).

The redox couple presents electrocatalytic property for ascorbic acid. Quantitation in millimolar range of ascorbic acid in pharmaceutical products (Cebion, Cewin and Redoxon) can be achieved using GPE-ASCA. This method is very simple convenient, economical and no separation step and elimination of specie strangers is required.

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