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Review Article

Electrochemical methods for ascorbic acid determination

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ABSTRACT

The present review focuses on electrochemical methods for ascorbic acid assessment. The occurence, role, biological importance of vitamin C, as well as the non-electrochemical methods for its assessment are firstly reviewed. The electrochemical behavior of ascorbic acid is then illustrated, followed by a description of the potentiometric, voltammetric and amperometric methods for vitamin C content estimation in various media. Different methods for the development of electrochemical sensors are reviewed, from unmodified electrodes to different composites incorporating carbon nanotubes, ionic liquids or various mediators. From this perspective, the interaction between the functional groups of the sensor's material and the analyte molecule is discussed, as it is essential for the analytical characteristics obtained. The analytical performances of the potentiometric, voltammetric or amperometric chemical and biochemical sensors (linear range of analytical response, sensitivity, precision, stability, response time etc) are highlightened. The numerous applications of ascorbic acid electrochemical sensors in fields like food, pharmaceutical or clinical analysis, where vitamin C represents a key analyte, are also presented.

Contents

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1. Introduction

Vitamin C is a hydrosoluble, antioxidant vitamin, which has a γ-lactone structure, and represents the L enantiomer of ascorbic acid, the biochemically and physiologically active form. Ascorbic acid is a hexanoic sugar acid with two dissociable protons (p*K*a 4.04 and 11.34). Therefore, under physiological conditions, it occurs as an ascorbate anion.

Ascorbic acid (AA) is known for its reductive properties, being easily oxidated to dehydroascorbic acid. It acts as a powerful antioxidant which fights against free-radical induced diseases [1–6]. Plants and most animals synthesize ascorbate from glucose. In primitive fish, amphibians and reptiles, ascorbate synthesis takes place in kidney, whereas for mammals liver is the site of synthesis, where the enzyme L-gulonolactone oxidase converts glucose to ascorbic acid [7,8]. Due to a genetic mutation that induce a L-gulonolactone oxidase deficiency, humans, some other primates, and guinea pigs are unable to synthesize ascorbic acid, so they need to take it from diet [9].

Ascorbic acid can scavenge singlet oxygen, or act as chelating agent. This is claimed as the basis of its ability to protect oxidizable constituents, including phenolic and flavor compounds, therefore being largely used as an antioxidant in foods and drinks. Studies performed on wine showed that the benefit of ascorbic acid as an antioxidant consists in its capacity to scavenge molecular oxygen, before the oxidation of phenolic compounds. Ascorbic acid also appears to be an ideal free-radical scavenger, because it reacts rapidly with hydroxyl (and other) radicals to form relatively unreactive radicals that do not readily propagate [10].

Vitamin C can be found in many biological systems and foodstuffs, namely fresh vegetables and fruits, as the most ubiquitous water-soluble vitamin ever discovered. Rich sources include blackcurrant, citrus fruit, leafy vegetables, tomatoes, green and red peppers, etc. Vitamin C is involved iron absorption, collagen synthesis and immune response activation and participates in wound healing and osteogenesis, helps maintaining capillaries, bones, and teeth [1–6].

Ascorbic acid excess can lead to gastric irritation, and one of its metabolites, oxalic acid, causes renal problems [11]. In some cases, excessive quantities of ascorbic acid may result in the inhibition of natural processes occurring in food and can contribute to taste/aroma deterioration; [12]. Another drawback of ascorbic acid excess is its ability to act as a strong antioxidant only in aqueous media and in the absence of heavy metal cations. In the presence of heavy metal cations, it can even act as a prooxidant: ascorbate ion is an excellent reducing agent that can reduce ferric (Fe^{3+}) to ferrous (Fe^{2+}) iron, while being oxidized to dehydroascorbate [7,13,14].

$$2Fe^{2+} + \text{Ascorbate} \rightarrow 2Fe^{3+} + \text{Dehydroascorbate}$$

The metal ion resulted can be subsequently reduced, reoxidated and again reduced, entering a redox cycle generating reactive oxygen species [7,13,14]. Thus, depending on the coordination environment, Fe^{2+} can react with O_2, reducing it to superoxide radical anion, which dismutes to H_2O_2 and O_2 [7].

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet -}$$

$$2O_2^{\bullet -} + 2H^+ \rightarrow O_2 + H_2O_2$$

In a classic Fenton reaction, Fe^{2+} reacts with H_2O_2 to generate Fe^{3+} and the strongest reactive oxygen species (ROS), namely the very oxidizing hydroxyl radical.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^-$$

The presence of ascorbate can allow the recycling of Fe^{3+} back to Fe^{2+}, which in turn will catalyse the formation of highly reactive oxidant species. This prooxidant activity may be displayed in the presence of heavy metal cations and in the absence of other antioxidant compounds, such as SO_2 [10].

Ascorbic acid is a labile substance as it is easily degraded by enzymes and atmospheric oxygen. Its oxidation is accelerated by excessive heat, light, and heavy metal cations [2]. Ascorbic acid is frequently used as an antioxidant in food industry to prevent unwanted changes in color or flavor. As an electron donor, ascorbic acid serves as one of most important small-molecular-weight antioxidants which contributes to the total antioxidant capacity-an important quality indicator of foods and drinks [15–17]. Due to the crucial role of vitamin C in biochemistry and in industrial applications, the determination of vitamin C still presents research interest. Quick monitoring of vitamin C levels during production and quality control stages is important [18].

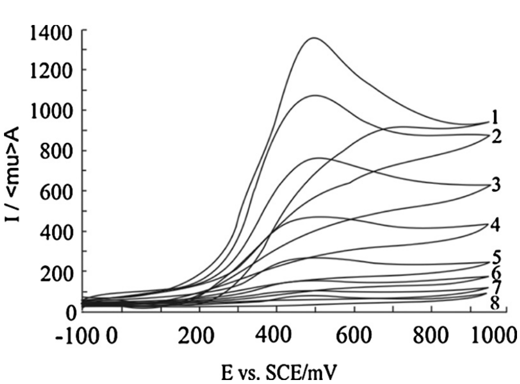

Figure 1. Cyclic voltammograms obtained with a Pt working electrode for different ascorbic acid concentrations, expressed as mmol L^{-1}: 20 (line 1), 15 (2), 10 (3), 5 (4), 2.5 (5), 1.25 (6), 0.625 (7) and 0.31 (8); potential scan rate 50 mV/s; a 0.1 mol L^{-1} KCl solution was used as supporting electrolyte [60].

2. Ascorbic acid determination by non-electrochemical techniques.

Traditional methods for ascorbic acid assessment involve titration with an oxidant solution: dichlorophenol indophenol (DCPIP) [19], potassium iodate [20] or bromate [21]. Chromatographic methods, like liquid chromatography [22–24] and particularly HPLC with electrochemical detection [25–27], have been used in ascorbic acid assessment in foodstuffs and biological fluids. Fluorimetric methods based on dehydroascorbic acid reaction with o-phenylene diamine and requiring strict control of the pH value [28,29] and UV-VIS absorbance-based determinations [30] were also applied. Ascorbic acid was assessed spectrophotometrically, based on its reaction with hexacyanoferrate (III) [31–33], on its oxidation using the Cu(II)-neocuproine complex [34], or on the determination of iodine reacted with ascorbic acid [35]. Other optical methods for vitamin C estimation include chemiluminescence [36].