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Short Review

Determination of Ascorbic Acid by Electrochemical Techniques and other Methods

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Ascorbic acid (AA) is a water-soluble vitamin essential in the human nutrition, an antioxidant, a scavenger of free radicals in biological systems and a cofactor of several enzymes. For the precise detection of AA concentration in biological samples there is important the option of the determination method. To the most common and exact methods for AA evaluation belong HPLC techniques with UV and electrochemical detection, and electrochemical methods (EM). EM are simple, sensitive, and moderate methods. For AA detection different types of electrodes are suitable, lately there are used especially various chemically modified electrodes with applied polymer films. Popular and profitable for accurate AA determination there are electrochemical biosensors and voltammetry that is reputable due to the low detection limits of AA.

Keywords: ascorbic acid, determination, electrochemical methods, electrode, polymer

1. INTRODUCTION

L-ascorbic acid (AA) is the main biologically active form of vitamin C. The biological activity of the vitamin is manifested also in its oxidation product, dehydroascorbic acid (DHA).

AA is a water-soluble vitamin essential in the human nutrition, as humans do not have the enzymes necessary to synthesize it although most animals can synthesize vitamin C from D-glucose. Enzyme l-gulono-gamma-lactone oxidase is required for the terminal step in vitamin C biosynthesis

but due to the inactivation of the gulo-gene by mutation over 40 million years ago humans have to supply this nutrient exogenously from their diet [1].

The vitamin participates in many biochemical functions as a cofactor for several enzymes in the synthesis of collagen and norepinephrine and adrenal hormones, metabolism of folic acid, tyrosine and tryptophan [2, 3]. It is also important for the absorption of iron in the gut, carnitine biosynthesis and as a reducing agent in the cellular metabolism [4].

Recommended Dietary Allowances (RDA) have been established for adult women of 75 mg/day and 90 mg/day for men [5]. Vegetables and fruits, particularly citrus fruits, green leafy vegetables, broccoli, cauliflower, Brussels sprouts, tomatoes, peppers, and potatoes, are major food sources of vitamin C [6-8]. About 80-90 % of AA is absorbed in the gastrointestinal tract and circulates in plasma, leukocytes and red blood cells and entres all tissues [9]. High levels of vitamin C are found in the pituitary and adrenal lands, leukocytes, in the brain, eye tissues and fluids [10].

AA is an excellent reducing agent, well known by its high antioxidant activity due to the neutralization of free radicals as it is a scavenger of free radicals in biological systems. It donates a hydrogen atom to an oxidizing radical to produce the ascorbate radical as an intermediate. Because ascorbate radical has its unpaired electron in a highly delocalized π-system, it is a relatively unreactive free radical that makes ascorbate a superior biological, donor antioxidant [11]. AA has the capacity to eliminate toxic free radicals and other reactive oxygen species, formed in cell metabolism, which are associated with several forms of tissue damage and diseases and keeps the membrane-bound antioxidant α-tocopherol in the reduced state [12].

AA also protects lipids in human blood plasma and LDL against detectable peroxidative damage as vitamin effectively intercepts oxidants in the aqueous phase before they can cause detectable oxidative damage to lipids [13]. By Retsky et al. [14] vitamin C protects LDL against atherogenic modification by two mechanisms, that free radical scavenging by AA prevents aqueous oxidants from attacking and oxidizing LDL, and that stable modification of LDL by DHA or decomposition products thereof imparts increased resistance to metal ion-dependent oxidation.

Due to the low stability, AA is rapidly oxidized to DHA by reason of the presence of two hydroxyl groups in its structure. It can be induced by enzyme such as ascorbate oxidase, oxygen exposure, alkaline pH, hydroxide ions, high temperature, presence of metals (copper and iron) or exposure to light and radiation [15-18]. Irreversible hydrolysis of DHA produces the biologically inactive 2,3-diketo-l-gulonic acid (DKGA), followed by its degradation to other by-products (oxalic acid, l-threonic acid, CO_2, l-xylonic acid, l-xylose). Some reducing agents can convert DHA back to AA in vivo (glutathione dehydrogenase) and in vitro systems (homocystein, dithiothreitol, dimercaptopropanol, tris(2-carboxyethyl)phosphine) [15, 19].

2. METHODS OF ASCORBIC ACID DETERMINATION

Many analytical methods have been reported for the determination of AA. Conventional titrimetric method [20], fluorimetry [21], spectrometry [22-24], chemiluminiscence [25], enzymatic

methods [26], capillary electrophoresis [27], electrochemical methods [28-30], amperometric methods [31] and HPLC [32-34] are the most common.

As the simplest techniques for ascorbic acid determination could be considered classic titration methods. To the well-known and most commonly used oxidant solution used in these determinations belongs 2,6-dichlorophenol indophenol (DCPIP) [35], potassium bromide [36], N-bromosuccinimide [37] or potassium iodate [38]. The main problem of the volumetric methods usage is the lack of specificity.

A simple fluorimetric method for the determination of AA is based on the condensation reaction between AA and o-phenylenediamine (OPDA) [39]. For the oxidation of AA to DHA and reaction with OPDA, the oxidant (DCPIP, N-bromosuccinimide and iodone) is used. The sensitivity of common OPDA method is low due to the blank effect of the oxidant. Wu and his co-workers [40] developed OPDA method when AA can react with OPDA in the absence of the oxidant at pH 9.4, so the sensitivity of the determination is better and the detection limit is lower. Fluorimetric method with 2,3-diaminonaphthalene (DAN) at pH 10.2–10.5 [41] and 2-cyanoacetamide at pH 12.9-13.3 [42] could be also used for AA analysis.

Spectrophotometric, enzymatic and chemiluminiscence analysis are time consuming methods due to the analysis duration, and in consequence of AA degradation the determined results are then overestimated.

A new spectrophotometric method measuring absorbance values at 450 nm for the reduction of the Cu(II)-neocuproine complex to Cu(I)-bis(neocuproine), and thus oxidation of AA to DHA, developed Güçlü et al. [43].

Ascorbic acid could be also evaluated by a flow injection analysis (FIA) [44, 45]. There are many modifications of this technique [46-49]. Its versatility, simplicity and reasonable costs, and possible combination of the FIA method with spectrophotometry, chemiluminescence, electrochemical methods, potentiometry, are advantageous parameters for many different analytical measurements.

2.1. Chromatographic methods for ascorbic acid determination

The accurate levels of ascorbic acid in various samples could be determined by one of the most commonly used technique – HPLC (*High*-performance liquid chromatography), with good selectivity and specificity in many modifications [50-55], using UV/DAD [56], electrochemical [57] or fluorescence detection [58].

To determine vitamin C status in different samples, AA and also its oxidation product DHA should be measured simultaneously. AA is a polar molecule with a low retention time in conventional reversed phase systems of HPLC, and hence of difficult resolution with other similar molecules such as AA epimeric - isoascorbic acid (IAA) or DHA [59, 60]. AA strongly absorbs at the wavelength 245 or 265 nm [61, 62], DHA is measured after derivatization, with 4,5-dimethyl-o-phenylenediamine (DMPD) as derivative agent, by monitoring of the UV absorbance at 360 nm [63].

AA is susceptible to oxidation in aqueous solution therefore its stability in the samples should be enhanced by addition of suitable compounds such as metaphosphoric acid (MPA) known for

decades [64]. It provides efficient extraction in samples as it prevents oxidation of AA better than other acids (e.g. trichloro acetic acid (TCA)) [65]. At low pH AA is relatively stable (fully protonated) with maximal stability at pH 4–6. Reduction of DHA could be accomplished by reducing agents including some sulphydryl compounds such as dithiothreitol (DTT), cysteine, homocysteine, glutathione, mercaptoethanol, or by tris(2-carboxyethyl) phosphine hydrochloride (TCEP) [66, 67]. Thiol-containing species are efficient only at mildly acidic and neutral pH [68].

In the presence of oxidants AA is reversibly transformed to DHA [69], so it is important to avoid degradation and oxidation of AA during sampling, sample handling and analysis, as this may misrepresent the ratio between AA and DHA [70]. Due to the low absorptivity of AA the reduction of DA to AA by means of homocysteine dithiothreitol was suggested, however this is a time consuming step [71].

HPLC with electrochemical detection is an efficient method for AA evalution in foodstuffs and biological fluids due to its simplicity, low cost, selectivity and sensitivity [72, 73]. AA is relatively reactive and easy to detect in coulometric and amperometric systems. As amperometric detector Coulochem III can be utilized [74]. Coulometric detector, such as CoulArray, was designed for the detection of electroactive species in the eluent so it measures AA before and after reduction [75]. Though electrochemical detection offers the advantages of low detection limits with high selectivity, the oxidation product of AA cannot be detected in the oxidative mode.

3. ELECTROCHEMICAL METHODS OF ASCORBIC ACID DETERMINATION

For the determination of ascorbic acid (vitamin C) in different matrices, novel electrochemical methods (EM) are lately more widely applied as they are simple, sensitive, and moderate methods.

3.1. Electrodes in the ascorbic acid determination

Electrochemical determination of this compound using electrodes has quite long continuation. For the evaluation of AA by direct electrooxidation some conventional electrodes, such as Hg [76], Au [77], Pt [78], and glassy carbon electrode (GCE) [79] has been used. However, the examination of AA on these electrodes is quite problematic due to the fouling effect on the electrode surface by oxidation [80, 81]. This problem could be solved by modification of the electrode surface electrochemically [82] as determination on unmodified electrodes has some limitations as the overlapping of oxidation potentials could be caused [83]. The problem may be also solved by pulsed laser light treatment [84], laser pulse irradiation [85], thermal treatment [86], dispersion of metal oxides particles on the electrode surface [87, 88], or by the surface modification by benzoquinone [89], ferrocene [90], TCNQ, organosulfur tetrathiafulvalene (TTF), or using 1,1-dimethylferrocene (DMFc) [91].

3.2. Electrochemical biosensors in the ascorbic acid determination

Electrochemical biosensors are very popular for the determination of various compounds such as ascorbic acid lately.

For the analysis of l-ascorbic acid a potentiometric biosensor, made by immobilization of ascorbate oxidase on polymer poly(ethylene-co-vinyl acetate) - EVA matrix, or a graphite/epoxy electrode [92] is usable. The sensor was tested for the evaluation of real samples - pharmaceuticals, without any previous treatment. Similar type of amperometric sensor, using ascorbate oxidase immobilized onto nylon net through glutaraldehyde covalent bond [93], can be also applied for the pharmaceutical samples determination. Likewise amperometric detection at a glassy carbon electrode, with ascorbate oxidase immobilized on cyanogen bromide, incorporated in FIA system is applicable for the vitamin C evaluation in fruit and vegetable juices [94]. Electrochemical biosensor based on the electrocatalytic oxidation of the GCE electrode and the MgO nanobelts, with good electrocatalytic activity, was tested for the simultaneous determination of AA, DA and UA [95]. Electrochemical biosensor based on one-step immobilization of ascorbate oxidase in the biocompatible conducting poly(3,4-ethylenedioxythiophene)-lauroylsarcosinate film was utilized for vitamin C determination for agricultural application in crops [96].

3.3. Polymers and modified polymers for the ascorbic acid determination

In the present, chemically modified electrode polymers are intensively used for the various analyses. Active particles in these electrodes are bonded three-dimensionally [97]. There are polymers such as the redox polymer [Os(bpy)2-(PVP)10Cl] containing 2,2′-bipyridine and poly(4-vinylpyridine), and the Os^{II}/Os^{III} redox couple immobilized in the polymer film [98], used as an electrochemical sensor in FIA. Lyons et al. [99] analyzed ascorbic acid by means of polymerized film containing polypyrrole with chloride and dodecylbenzene sulphonate. Ferricyanide $[Fe(CN)_6]^{3-}$ as doping anion is used as a part of a perfluoro-anionic exchange membrane in Tosflex-modified electrode [100] or for a silica sol-gel glass-coated Tosflex-modified electrode, that was examined in fruit juice, pharmaceutical tabs and human urine [101]. Also crystalline thin film of polyaniline on nickel has been studied [102]. Electropolymerized film of diphenylamine sulfonic acid (DPASA) [103], poly (m-aminobenzene sulfonic acid, m-ABSA) film [104], polymer film of 3-methylthiophene [105], aniline [106], chemically polymerised polyaniline [107] and p-nitrobenzenazo resorcinol (NBAR) polymer film [108], and poly (4-(2-pyridylazo) resorcinol) [109] were mentioned as good alternatives of polymers for AA analysis. Using surfactant and clay films, such as cetyltrimethylammonium bromide (CTAB) and hydrotalcite-like containing ferrocene, could increase the permeability and the positive surface of the film of chemically modified electrodes [110].

3.4. Determination of ascorbic acid in pharmaceutical preparations and human urine

Good electrocatalytic activity towards the oxidation of ascorbic acid has showed the cobalt hexacyanoferrate (CoHCF) modified electrode with adsorbed aniline on the surface of a graphite

electrode of amperometric sensor [111]. Practical determination of vitamin C was done in pharmaceutical tablets. Another possibility for AA analysis is the octacyanomolybdate [$Mo(CN)_8^{4-}$] and PVP (poly(4-vinylpyridine)) electrode for the electrocatalytic oxidation of l-ascorbic acid that was also applied for the evaluation in pharmaceutical pills containing vitamin C [112].

Many publications were published also for simultaneous electrochemical determination of AA in the presence of dopamine (DA) and uric acid (UA) on glassy carbon electrode, showing good selectivity, sensitivity and stability of modified electrode in human urine and pharmaceutical samples analysis.

A polymerized film of Eriochrome black T (EBT) was applied on the surface of carbon paste electrode (CPE) and showed good electrocatalytic activity towards the oxidation AA and DA compared with the bare CPE [113]. A covalently modified glassy carbon electrode with poly (vinyl alcohol) (PVA) has been also used for the electrochemical detection of AA, DA and UA [114]. Usage of a different type of electrode - exfoliated graphite electrode is suitable for simultaneous analysis of these compounds too, as the functional groups on its surface participate in the interactions well [115]. Likewise the composite carbon–polyvinylchloride (C–PVC) electrode could be used for the detection of AA, DA, and UA for its selectivity and stability. The method was practically verified by their measurement in human urine and serum samples without any preliminary pre-treatment [116]. The ascorbic acid and DA catalytic oxidation was studied also on ruthenium oxide modified electrode (RME) with good sensitivity, selectivity, rapid response and regeneration [117].

In the new electroanalysis method for the simultaneous examination of AA, DA and UA the modified glassy carbon electrode covered by polyluminol hybrid film with ZnO nanoparticles was used as working electrode [118]. ZnO/ redox mediator composite films-based sensor separated the anodic oxidation waves of analysed compounds with well-defined peak separations in their mixture solution.

The construction of a chemically modified carbon paste electrode modified with TiO_2 nanoparticles and the incorporation of 2,2′-(1,2 butanediylbis(nitriloethylidyne))-bis-hydroquinone (BBNBH) as a modifying species, was created and applied for AA and UA analysis in pharmaceutical preparations [119].

Another type of electrode – a cation surfactant (CTAB) and iron (II) phthalocyanine modified carbon paste electrode, developed by Raghavendra Naik et al. [120], could be applied to analyze AA in the presence of DA and UA with good selectivity, stability and antifouling properties. Raghavendra Naik and his co-workers [121] also prepared acetone/water modified carbon paste electrode for the separation of AA, DA and UA.

Simultaneous determination of AA, DA and UA with chitosan-graphene glassy carbon modified electrode showed high electrocatalytic activity towards oxidations of these compounds [122]. A modified glassy carbon electrode with immobilized poly 3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid (CDDA) film was an another proven electrode type for AA analysis in the presence of DA and UA [123]. A selective voltammetric method using Tiron polymer film modified on glassy carbon electrode was developed by same authors for the simultaneous determination of AA, DA, UA and was applied for the analysis of real samples - pharmaceuticals (vitamin C tablets) and urine samples without any pretreatments with satisfactory results [124]. For the

evaluation they fabricated also sulfonazo III film-modified on glassy carbon electrode with the validation for vitamin C tabs and human urine samples [125].

Sodium dodecyl sulfate (SDS) and multi-walled carbon nanotubes (MWCNT) were applied to a glass carbon electrode to analyze AA, DA and UA, with good selectivity and sensitivity of the composite electrode [126]. A multi-walled carbon nanotubes (MWNTs) bridged mesocellular graphene foam (MGF) nanocomposite modified glassy carbon electrode was proved for simultaneous determination of AA, DA, UA and tryptophan (TRP) with good stability and reproducibility [127]. A Ni/silicon microchannel plate (Ni/Si MCP) electrode modified with poly(3,4-ethylenedioxythiophene) (PEDOT) was prepared for the simultaneous determination of AA, DA and UA. The electrode was applied for their detection in urine samples [128].

3.5. Determination of vitamin C and other vitamins by EM

Electrochemical sensors with chemically modified electrodes are well applicable for ascorbic acid analysis, and also for compounds such as B group vitamins, B_2 and B_6 and some others. Nanostructured films as electrochemical sensors could be used for the determination of vitamin C. The reason of nanostructured materials usage is the fact that sensors have the advantages of p-conjugated conducting polymers such as PEDOT (poly(3,4-ethylenedioxythiophene)) with high electrical conductivity, moderate band gap and stability and also due to good electrochemical activity.

Nie et al. [129] used for vitamins C, B_2 and B_6 analysis the films prepared by incorporation of two electroactive species, ferrocenecarboxylic acid (Fc^-) and ferricyanide ($Fe(CN)_6^{4-}$) as doping anions during the electropolymerization of PEDOT at glassy carbon electrodes. Their findings demonstrated that the PEDOT/$Fe(CN)_6^{4-}$ film had better results for the determination of vitamin C and other two vitamins than PEDOT/ClO_4^- or PEDOT/Fc^- films, with no interference from other potential competing species. The practical applications were demonstrated by the analysis of vitamins in orange juice samples. These authors [130] used also poly(3,4-ethylenedioxythiophene) with Zirconia nanocomposite as an effective sensing platform for vitamins B_2, B_6 and C evaluation in honey samples.

For the simultaneous determination of vitamins C, B_2, B_6 could be utilized electrochemically pretreated glassy carbon electrode (PGCE) too. Vitamins B_2 and B_6 could be adsorbed at PGCE and vitamin C proceeded with an electrocatalytic process. The method was tested in real samples, multivitamin tablets [131].

Stable voltammetric signals for vitamin C, riboflavin (B_2), and folic acid (B_9) have been presented in the novel simultaneous determination using the electropolymerized film of 3-amino-5-mercapto-1,2,4-triazole (p-AMTa) modified glassy carbon electrode [132]. The utilization was verified by the determination of the vitamins concentrations in human plasma samples.

3.6. Voltammetry in the ascorbic acid determination

Voltammetry becomes popular technique for the ascorbic acid determination as it is an inexpensive, modest and fast method that is reputable also due to the low detection limits.

Cyclic voltammetry technique was used for AA determination with the surface of MgB_2-MWCNT mixture modified glassy carbon electrode showing good reproducibility and recovery rate for AA in real samples [133]. Voltammetry was also successfully applied to AA analysis at a glassy carbon electrode modified with single-walled carbon nanotube/zinc oxide (SWCNT/ZnO) [134]. The cyclic voltammetry method using a glassy carbon as working electrode, Ag/AgCl as reference and Pt as the auxiliary electrode was utilized for the analysis of AA in real samples of tropical fruits [37].

4. CONCLUSIONS

For the accurate AA detection and concentration measurement in various samples the HPLC techniques and electrochemical methods could be used. As for electrochemical techniques different types of electrodes are suitable in the determination, lately there are used especially various chemically modified electrodes with applied polymer films. Also electrochemical biosensors, utilising a biological system with AA, and voltammetric methods with low detection limits of AA are of great interest in the AA evaluation.

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