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Biamperometric Applications to Antioxidant Content and Total Antioxidant Capacity Assessment: An Editorial

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Oxidative stress can be regarded as the lack of balance between the reactive oxygen/nitrogen species (hydrogen peroxide H_2O_2, superoxide radical anion $O_2^{\cdot-}$, singlet oxygen O_2, hydroxyl radical HO·, hydroperoxyl radical HO_2·, hypochlorous acid HOCl, nitric oxide NO, peroxynitrite ONOO–) production and the organism's defense ability exerted by the antioxidant system [1]. Reactive oxygen species can promote structure alterations in all classes of biomolecules. Lipids are the most prone to oxidation: polyunsaturated fatty acids oxidation implies formation of carbonylated final products, such as malonyl dialdehyde and 4-hydroxynonenal. The backbone and the side chain of proteins can be attacked by reactive oxygen species, and alteration in purine and pyridine bases structure results in DNA mutations [2]. Moreover, oxidative stress has been viewed as more complex than mere radical overproduction, being reconsidered as a perturbation of redox signaling pathways in the cell [3-5].

The intake of plant-sourced antioxidants contained in fruits and vegetables leads to lowering oxidative stress-related pathology, and this fact has been confirmed by epidemiological studies, hence the interest in applying performant methodologies to assess the total antioxidant capacity as quality index of foodstuffs [6].

The application of electrochemical techniques in antioxidant and antioxidant capacity determination is characterized by sensitivity, fastness, simple and relatively unexpensive instrumentation, small volumes of samples, with improvement of research resources use. The analytical signal does not depend on the distance that radiation travels in the analytical cell or on the turbidity, and the dynamic range is large [7-12].

The biamperometric method relies on recording the current intensity between two identical working electrodes at a small potential difference, and found in a solution where a reversible redox couple is present. The analyte reacts with the indicating redox couple (Fe^{3+}/Fe^{2+}, I_2/I^-, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$), the selectivity of the technique depending on the specificity of the reaction involving the oxidized form of the redox pair and the antioxidant. In DPPH·/DPPH biamperometry, antioxidants react with DPPH· (radical form) decreasing its concentration, and generating DPPH (reduced form). When employed working conditions are as such, for the radical form concentration to be smaller than one proper to the molecular form, cathodic current is limited by the lower concentration of DPPH· radical in the indicating mixture [13,14].

DPPH•/DPPH biamperometry was employed in the analysis of fruit juices for their total antioxidant capacity, using two identical Pt electrodes [13] and also tea, wine and coffee using glassy carbon electrodes [14]. The most significant values of the total antioxidant capacity were proper to juices freshly obtained from fruits, namely 9.07 mM Trolox for orange juice and 6.25 mM Trolox for lemon juice [13]. $ABTS^{+\cdot}$/ABTS is a redox pair also extensively applied to biamperometric antioxidant capacity evaluation. A peroxidase-relying flow system was responsible for the cation radical formation, enabling analysis of juices, tea and wine using interdigitated microelectrodes [15]. $ABTS^{+\cdot}$ was also obtained by glucose oxidase - peroxidase, for the analysis of wine and spirits with excellent sensitivity, 0.165 nA/μM Trolox [16].

Samples of Brazilian woods, cabreuva (Myrocarpus frondosus), cabreuvavermelha (Myroxylon balsamum), imbuia (Octea porosa) and pequi (Caryocar brasiliense), and oak (Quercus sp.) extracts were subject to ceric reducing antioxidant capacity (CRAC) analysis, relying on Ce^{4+}/Ce^{3+} redox couple. Chronoamperometric determinations enabled quantification of the decrease of Ce^{4+} concentration, that was caused by its reduction by antioxidants present in the sample. The Ce^{4+}/Ce^{3+} redox pair being characterized by an elevated value of the redox potential, it allows determinations at a boron-doped diamond film electrode, with results given as Trolox equivalents, that illustrated the variation of the antioxidant activity of analysed extracts: oak (1.73) > cabreuva-vermelha (1.05) > cabreuva (0.90) > imbuia (0.71)> pequi (0.31) [17].

The ceric reducing antioxidant capacity assay was also exploited by virtue of its direct electron transfer facility, for determining the antioxidant capacity of eight antioxidant compounds, also based on the capacity to reduce the oxidized form of the redox couple [18]. The developed technique was based on observing the decrease of the Ce^{4+} concentration after its reaction with tested antioxidants. The current intensity decreased in time after imposing the due potential step, and this was described by Cottrell law. The following trend of variation of antioxidant capacities resulted from this comparative investigation that relied on chronoamperometric measurements: tannic acid > quercetin > rutin > gallic acid ≈ catechin > ascorbic acid > butylated hydroxyanisole > Trolox. The results were consistent with those furnished by previous studies, and by the applied conventional FRAP assay [18].

Biamperometry integrated in a flow injection analysis (FIA) setup was also applied to antioxidant assessment. This technique involves the valve injection of a liquid sample, in an inert, unsegmented carrier flow. Peristaltic pumps are responsible for the transport of the sample and reagents and the detection is ensured, at the end of the experimental setup, by various methods: photometric, electrochemical, mass spectrometrical [19,20]. Vitamin C assessment relied on the oxidation of the analyte at acidic pH, by I_2/I^- employed as oxidizing agent. The biamperometric detection of the amount of iodine consumed, allowed for the assessment of vitamin C with a linear range of analytical response comprised between 5×10^{-5} and 5×10^{-4} M, a 1.08% RSD (n=10; c= 2.5×10^{-4} M) and high throughput of 60 samples h^{-1} [21].

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It can be concluded that, with a rigorous control of the operational parameters such as the molar ratio between the oxidized and the reduced form of the redox couple, and the potential value applied, biamperometry can constitute a viable method in antioxidant content and total antioxidant capacity determination in foodstuffs.

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