

Voltammetry as Analytical Technique in the Study and Quantitation of Several Food and Beverage Components: An Editorial

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Editorial

Voltammetric measurements rely on applying a controlled potential variation, and consequently recording the intensity versus potential dependence (voltammogram).

There are various ways to impose a potential variation in time, and subsequently a series of voltammetric methods. Cyclic voltammetry relies on linearly scanning the potential in time, observing a triangular waveform variation [1-3]. Differential pulse voltammetry is based on two samplings of the current intensity for each potential pulse: one measurement before applying the pulse, and the second towards the end of the pulse period. In square-wave voltammetry, a square-wave is superimposed on the potential staircase sweep, the current intensity being recorded at the end of each potential change. This potential step technique allows minimizing charging current and provides improved sensitivity, as also happens in differential pulse voltammetry [3].

These electrochemical techniques are characterized by fastness, simplicity of both the instrumentation and the applied procedure, minimum sample pre-treatment and do not involve toxic wastes. They allow the determination of a series of food and beverage components, relying on their electroactivity [4,5].

Ascorbic acid voltammetric determination is possible due to its facile oxidation to dehydroascorbic acid, involving the transfer of two protons and two electrons. Figure 1 illustrates a differential pulse voltammogram, with the obtained ascorbic acid peak.

A cyclic voltammetric method for ascorbic acid determination used single-walled carbon nanotube/ZnO modified glassy carbon electrode. The developed modified electrode exhibited better electroactivity, as well as better sensitivity and selectivity when compared to the ZnO-modified electrode or to the bare glassy carbon electrode. The reported detection limit for the modified electrode was 85 μM . The observed good linear dependence between the intensity of the anodic peak and the square root of the potential scan rate indicates that the analyte's electro-oxidation is a diffusion controlled process. The linear range of analytical response corresponded to 0.2-10 mM. Experiments performed with the single-walled carbon nanotube/ZnO modified glassy carbon electrode in 0.1 M potassium dihydrogen phosphate solution, showed that increasing the temperature within the range 20°C-85°C, resulted in an increase of the peak current [6].

A differential pulse polarographic method based on the carminic acid reduction at dropping mercury electrode was studied. Measurements were carried out in Britton-Robinson buffer solution pH=2.0. A linear dependence between the peak current intensity (obtained at -489 mV potential value) and the analyte concentration was observed in the range 1-90 μM , and the detection limit was 0.16

μM . The quantitation of carmine in spiked commercially available strawberry flavored milk was performed [7].

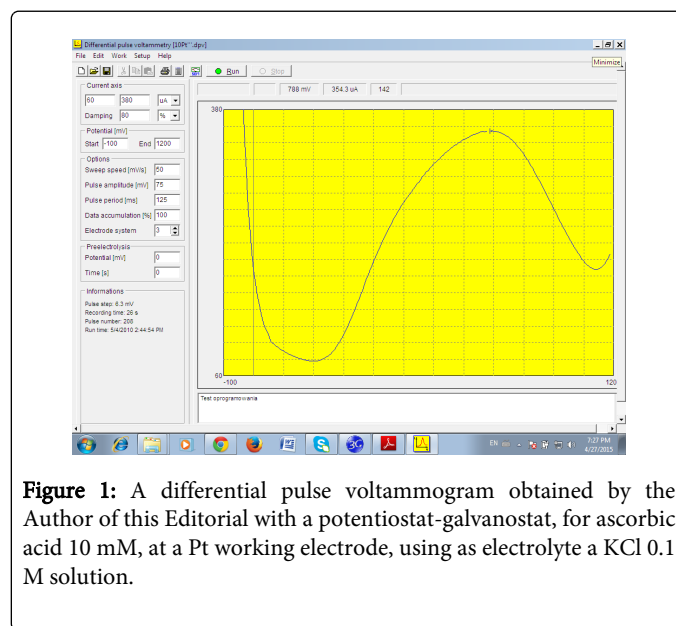


Figure 1: A differential pulse voltammogram obtained by the Author of this Editorial with a potentiostat-galvanostat, for ascorbic acid 10 mM, at a Pt working electrode, using as electrolyte a KCl 0.1 M solution.

A study of flavonoids (quercetin, rutin, epigallocatechin gallate and catechin) voltammetric behavior and of their antioxidant characteristics has been performed, by employing an electrically heated DNA-modified carbon paste electrode. Differential pulse voltammograms were obtained at both bare and DNA modified carbon paste electrodes (Figure 2). The values of the peak potentials indicate that the most electro-oxidizable is quercetin, followed by epigallocatechin gallate and catechin. Rutin proved the most difficultly electro-oxidizable. It could be noted that the modification of the carbon paste electrode resulted in a slight peak potential shift towards more positive values, pointing to a more difficult flavonoid electro-oxidation [8].

The Cu(II)-10 phenanthroline complex, in the presence of H₂O₂ and ascorbic acid, was chosen as ROS generator and DNA cleavage inducer. A positive influence of the electrode temperature within the range 20-38°C on the detection of an enhanced DNA impairment was noted. The left undamaged DNA has been assessed by employing [Co(phen)₃]³⁺ complex as redox indicator. Heating the DNA-modified carbon paste electrode during the incubation with the cleavage mixture exerted a beneficial influence on the sensitivity of assessing both DNA impairment and the protective effect imparted by flavonoid antioxidants [8].

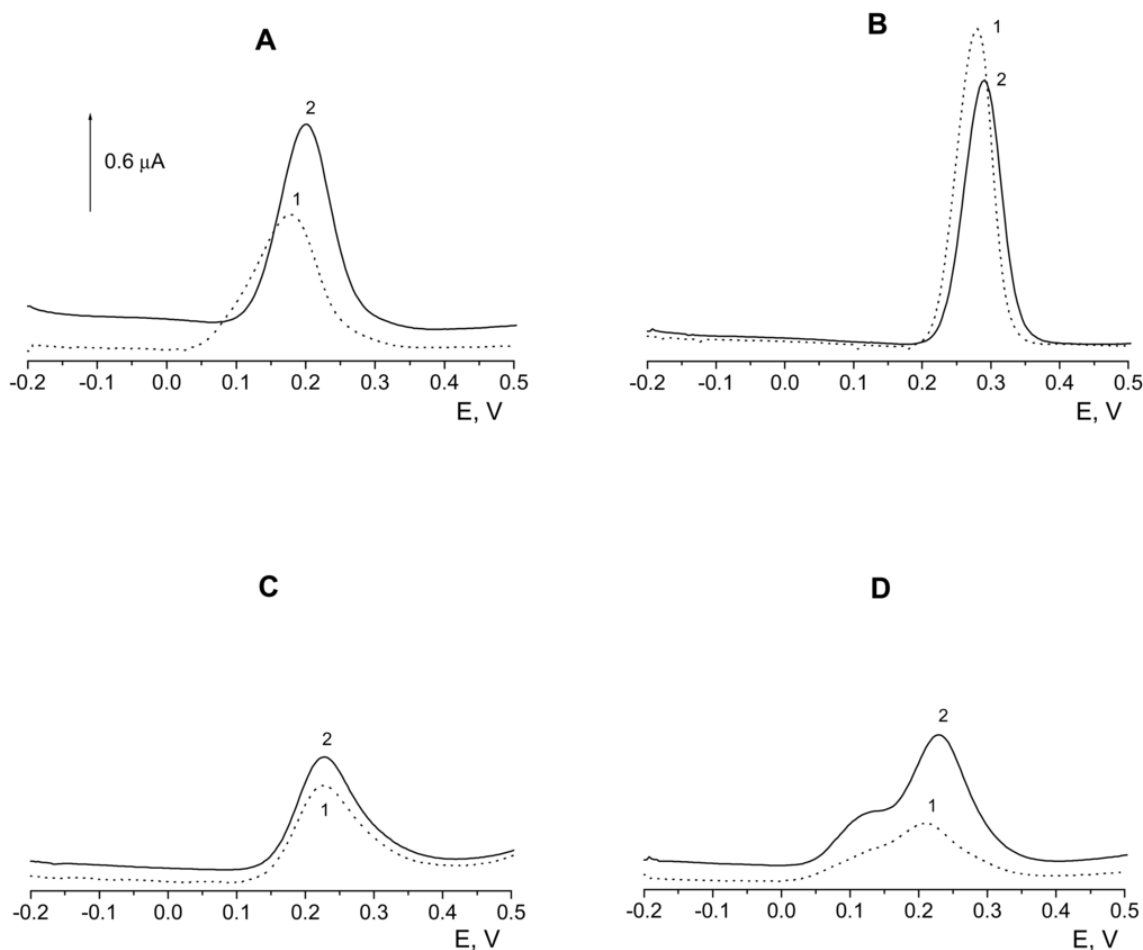


Figure 2: Differential pulse voltammograms of flavonoids, obtained at a carbon paste and a DNA modified carbon paste electrode after 5 minutes accumulation at open circuit, in solutions of: (A) 5×10^{-7} M quercetin, (B) 5×10^{-7} M rutin, (C) 5×10^{-5} M catechin and (D) 5×10^{-6} M epigallocatechin gallate. Experimental conditions: 5 mM phosphate buffer solution pH=7.0 containing 1% DMSO, pulse amplitude=100 mV, scan rate=25 mV/s, working temperature=22°C, as presented in Ref. [8].

A carbon nanotubes-modified carbon paste electrode was developed for the quantitative assessment of sulphite, relying on its electrochemical (cathodic) reduction. A linear response was obtained for $1.6\text{--}32 \text{ mg L}^{-1}$ sulphite with a detection limit of 1 mg L^{-1} . Interferent species commonly found in the analysed samples, such as ascorbic acid and sugars (fructose and sucrose) did not alter the analytical signal, allowing the determination of this preservative in beverages. Nevertheless, some red wine and red grape juice components yield a peak very close to the potential corresponding to sulphite reduction [9].

The electrochemical behavior of carmine was investigated by square-wave adsorptive voltammetry at a hanging mercury electrode, and the peak corresponding to this food dye was obtained at -350 mV , in pH=3.0 acetate buffer. The study of the analytical parameters showed a detection limit as low as 1.43 nM and a relative standard deviation of 2.2%. The developed voltammetric technique allowed for the determination of carmine in spiked commercially available ice cream and soft drinks [10].

The advantages of voltammetric methods are proved by the analytical performances obtained for a wide range of compounds present in foodstuffs and beverages. The analytical features depend on the voltammetric technique chosen, on the working electrode, as well as on the sample's composition.

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