



**EVALUATION OF ANTIOXIDANT ACTIVITY OF AGRI-FOOD BY-PRODUCTS
EXTRACT AND SEVERAL MIXTURES OF THEIR MAINE COMPOUNDS BY AN
ELECTROCHEMICAL METHOD**

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Introduction. Agri-food by-products extract can be used as antioxidants, as potential “eco-friendly reductants” to obtain nanoscale materials, for inhibition of corrosion of metals in corrosive media [1–3]. Phenolic compounds and flavonoids, organic acids, and terpenoid compounds are the most abundant secondary metabolites of the fruits pomace and have drawn increasing attention due to connection with the possibility of use in various fields of chemical technology [4–9]. Evaluation of their redox propertie is an important study for further application in various fields of chemical technology. A multitude of chemical assays based on spectrometry have been developed for characterizing antioxidants/redox characteristics. But all of them are based on the use of a wide range of organic substances/radicals (DPHH, ABTS), which complicates the use of these methods. Electrochemical research methods are often used to determine antioxidant properties. Thus, cyclic voltammetry, flow-injection amperometry and differential pulse voltammetry were applied to investigate of antioxidative property/redox characteristics.

Therefore, the objectives of this study were to evaluate of redox reaction and the electrochemical behaviour of the agri-food by-products extract (apricot, black currant, grape pomace extracts) and several mixtures of their some compounds by use of cyclic voltammetry technique.

Cyclic voltammetry testing. Application of cyclic voltammetry to the reduction processes investigation in different organic compounds is based on the ability of these compounds to donate electrons. In this approach, the oxidation peak potentials $E_{p.a.}$ in the forward anodic scan are taken into consideration in order to rank the reducing capacity of compounds, the lower the $E_{p.a.}$ value, the easier the oxidation and therefore the more potent the reductant is.

The electrochemical measurements were conducted in the three-electrode cell of 50 cm³ volume. The working electrode was a glassy carbon electrode of 2 mm in diameter. The surface of the electrode prior to testing was rinsed with organic solvent and dried with filter paper. The auxiliary electrode was a platinum plate and the reference electrode was the saturated silver chloride electrode (SSCE) attached to the cell through a salt bridge. The water extract or individual compound solution was mixed with acetate buffer (pH 4) and NaClO₄ in the following mass ratio 70:28:2 and placed into the cell. The cell was thermostated in water bath at 25 °C. Total 3 extracts and 6 mixtures were tested in concentration of 0.5 mM/L. The potential scan range was 0...1 V/SSCE with a scan rate of 100 mV/s. The scan started from the OCP in cathodic direction and reversed once the potential reached 1

V/SSCE. Total 5 cycles were measured in each solution to ensure data convergence. The values of oxidation peak potentials $E_{p.a.}$, reduction peak potentials $E_{p.c.}$, anodic, and cathodic peak currents were determined from cyclic curves.

Results and Discussion. The cyclic voltammograms for the apricot, black currant, and grape pomace extracts are given in fig. 1. Voltammograms for mixture compounds are shown in Fig. 2. The top scan represents the oxidation of the compounds that are contained in the extracts, generating a positive (anodic) current $I_{p.a.} = 2.3\text{-}3.5 \mu\text{A}$, peaking at a particular electrode potential $E_{p.a.1} = 0.54 \text{ V/SSCE}$, $E_{p.a.1} = 0.51 \text{ V/SSCE}$ and $E_{p.a.1} = 0.48 \text{ V/SSCE}$ for black currant, apricot and grape pomace extracts, respectively. On the reverse scan a negative (cathodic) peak is reproduced for black currant and grape pomace extracts at $E_{p.c.1} = 0.28 \text{ V/SSCE}$ and $E_{p.c.1} = 0.44 \text{ V/SSCE}$. The absence of a cathodic peak in the reverse scan for apricot pomace extract gives information about the non-reversibility of the redox reaction of the oxidized compound generated in the forward scan.

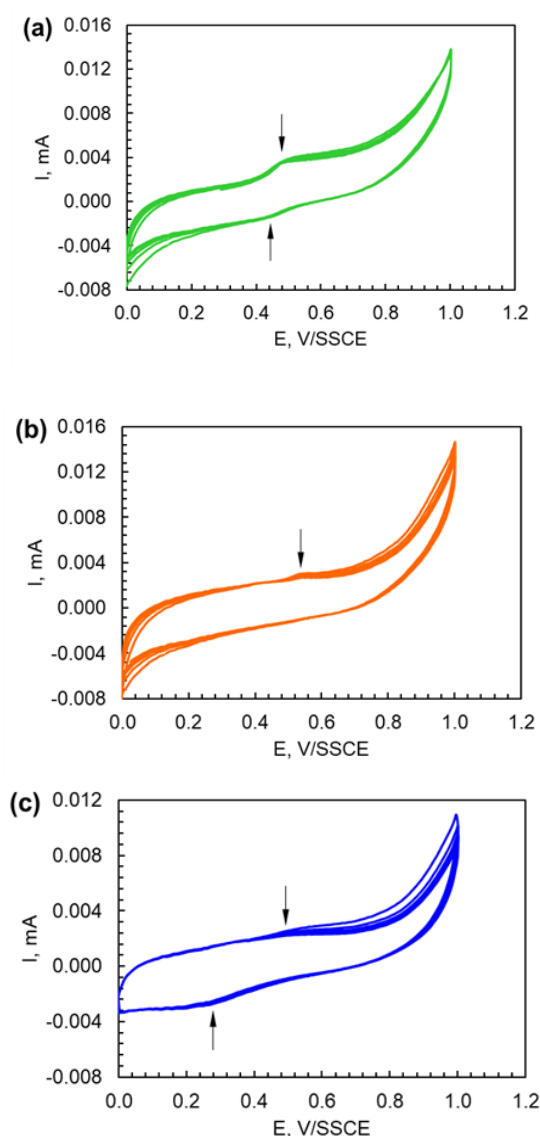


Figure 1. Cyclic voltammograms for the grape (a), apricot (b), and black currant (c) pomace extracts

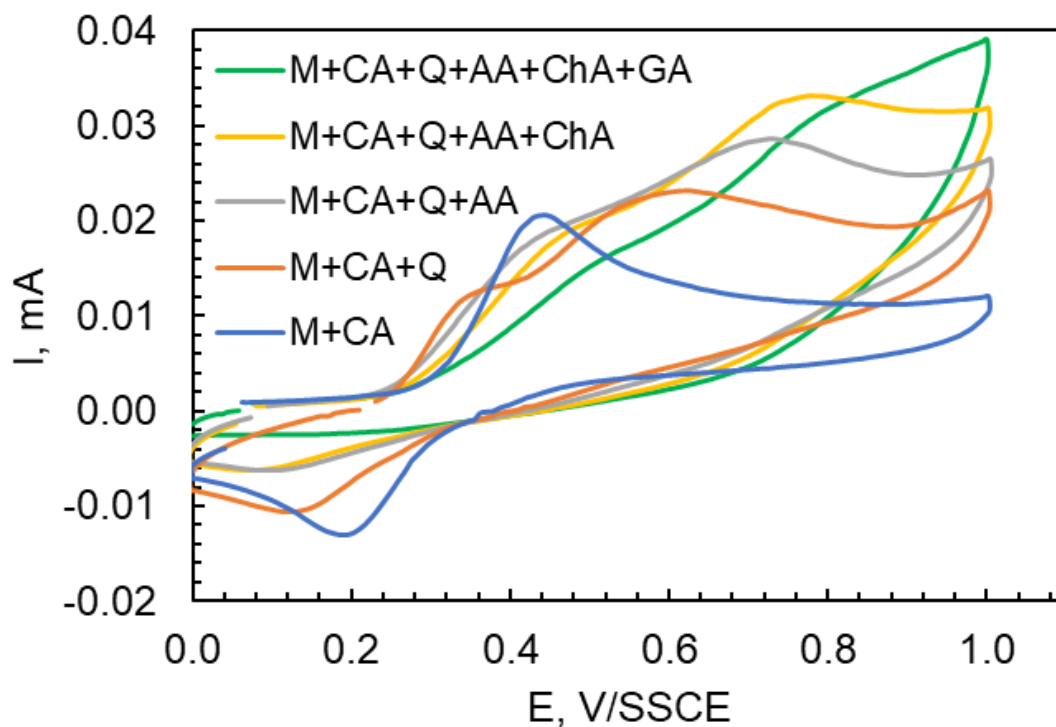


Figure 2. Cyclic voltammograms of a mixture of phenolic acids and monoterpenoid phenols at 0.5 mM/L concentration in acetate buffer 0.1 M (pH 4) and NaClO₄ (70:28:2). M – menthol; CA – caffeic acid; Q – quercetin; AA – ascorbic acid; ChA – chlorogenic acid; GA – gallic acid. Scan rate of 100 mVs⁻¹.

Thus, the reducing capacity of tested extracts decreases as follows: grape pomace extract > apricot pomace extract > black currant pomace extract. Cyclic voltammetry has been used to evaluate redox reaction and the electrochemical behavior of several polyphenols mixtures (Caffeic acid and (+)-Catechin) and non-polyphenolic compounds (cysteine and L-ascorbic acid). The antioxidant properties of some binary mixtures (gallic acid/caffeic acid; gallic acid/chlorogenic acid; gallic acid/quercetin; caffeic acid/quercetin; caffeic acid/chlorogenic acid; chlorogenic acid/quercetin; (-)-catechin/caffeic acid Caffeic acid/quercetin) have been studied. A mixture of Menthol+ Caffeic acid exhibits two peaks, one with an oxidation potential of 0.43 V and another at a reduction potential of 0.2 V; meanwhile, Caffeic acid alone is reduced at 0.27 V. For a mixture additionally containing Ascorbic acid and Quercetin, the oxidation part of the curve contains two anodic peaks and the potentials value are approximately close to the one of individual compounds. The mixture of Menthol (M)+Caffeic acid (CA) + Quercetin (Q) + L-ascorbic acid (AA)+ Chlorogenic acid (ChA) exhibits two peaks, one with an Ep.a.1 of 0.47 V and another at Ep.c.2 of 0.76 V. The Ep.a.1 value of the mixture is the same as for Chlorogenic acid, while the Ep.c.2 is slightly different (Ep.c.2 = 0.65 V/SSCE). Gallic acid added to the mixture increased reducing power and this correlates with the cyclic voltammogram for the pomaces extracts that have a similar monotonic course of curves. This observation shows that there is no interaction between the oxidation processes when the compounds are present in a mixture. Alternate mixing of components and the formation of a multicomponent mixture did not show any effect of pronounced synergy.

Conclusions. The voltammetric profile of the extracts was similar to the mixes of the main compounds. The voltammograms for the extracts showed a broad anodic peak with similar (anodic) current $I_{p.a.} = 3 \mu\text{A}$ for all apricot, black currant, and grape pomace extracts.

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