

Amperometric determination of rutin on carbon paste electrodes

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Received: 25 October 2010 / Received in revised form: 13 August 2011, Accepted: 25 August 2011, Published: 25 October 2011
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Abstract

Three different carbon paste electrodes (i.e. unmodified, iron phthalocyanine and ionic liquid modified) were tested to determine rutin by amperometry. The widest linear concentration range and lowest detection limit were obtained with unmodified carbon paste electrode.

Keywords: Rutin, carbon paste electrodes, pulse amperometric technique

Introduction

Rutin (Fig 1) is a bioactive flavonoid, naturally occurring in plants and it is generally present in the common human diet. Numerous analytical methods have been applied to determine rutin, such as voltammetric techniques (Ghica and Brett 2005), capillary electrophoresis (Chen et al. 2000), HPLC (Liu et al. 2008), spectrophotometry (Hassan et al. 1999) and chemiluminescence (Song and Hou 2002).

Electrochemical behavior of rutin is characterized by two oxidative signals. The first reversible anodic signal corresponds to two-electron oxidation of -OH groups at positions 3' and 4' forming an *o*-quinone. The second, irreversible anodic signal is presumably caused by oxidation on the ring A (Ghica and Brett 2005).

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In the literature, a considerable number of the use of amperometric techniques can be found, such as pulse amperometric detection for separation techniques (Ruiz MA et al. 1999) and various amperometric biosensors (Granero AM et al. 2010). Amperometric measurements with various modified carbon paste electrodes (CPEs) are often used for analysis of biological active substances (Forzani et al. 1997). In this work, an amperometric determination of rutin using different modified CPEs is described for the first time.

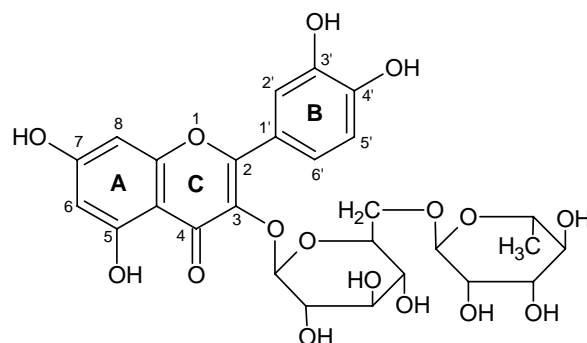


Figure 1: Chemical structure of rutin

Materials and methods

Amperometric measurements in stirred solution were done with CH660 electrochemical workstation (CH Instruments, U.S.A.). The three electrode system involved saturated Ag/AgCl reference electrode, a platinum wire auxiliary electrode and three different carbon paste electrodes as working electrodes, i.e. unmodified CPE, CPE modified with iron phthalocyanine (~90 %, Fluka) (IP/CPE) and CPE modified by 1-hexyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide [hmim][Tf₂N] ionic liquid (≥98.0 %, Merck) (IL/CPE).

The carbon paste was prepared by mixing 200 mg of graphite flakes (Sigma-Aldrich) with 80 µL of paraffin oil. IP/CPE was prepared by replacement of 10 % (by weight) of graphite flakes by iron (II) phthalocyanine. IL/CPE was prepared from 200 mg graphite and 100 µL [hmim][Tf₂N]. Each mixture was homogenized in an agate mortar until a cohesive substance was formed. The paste was filled

into the teflon electrode body equipped with a piston (inner diameter 2 mm).

The measurements were carried out in acetate buffer pH=4 prepared from acetic acid (0.1 M) and sodium hydroxide (0.2 M) (both Lachema, Czech Republic). The aliquots (50 μ L) of 1 mmol/L rutin standard solution (≥ 94 %, Sigma-Aldrich) were introduced into electrochemical cell containing 20 mL of base electrolyte using a home-made autosampler. A constant potential was set to 600 mV vs. Ag/AgCl.

Results and Discussion

After repeated injections of rutin standard solutions an increased noise in the corresponding amperometric response appeared for all electrodes, which may be caused by adsorption of rutin or its oxidation products on the electrode surface (Fig 2). The highest level of noise even in low rutin concentration of 5 μ mol/L exhibited the IL/CPE electrode, which made it unsuitable for rutin analysis. We have found that significant improvement of signal to noise ratio is achieved, if a pulse technique involving cleaning step at -300 mV for 30 s is used. The detection limits using the pulse technique were 0.32 μ mol/L for unmodified CPE, somewhat higher for IP/CPE (0.50 μ mol/L) and ten times higher detection limit was determined for IL/CPE (3.07 μ mol/L). The widest linear concentration range was found for unmodified CPE (0.25–33.8 μ mol/L) and the narrowest one was found for IL/CPE (2.5–12.4 μ mol/L).

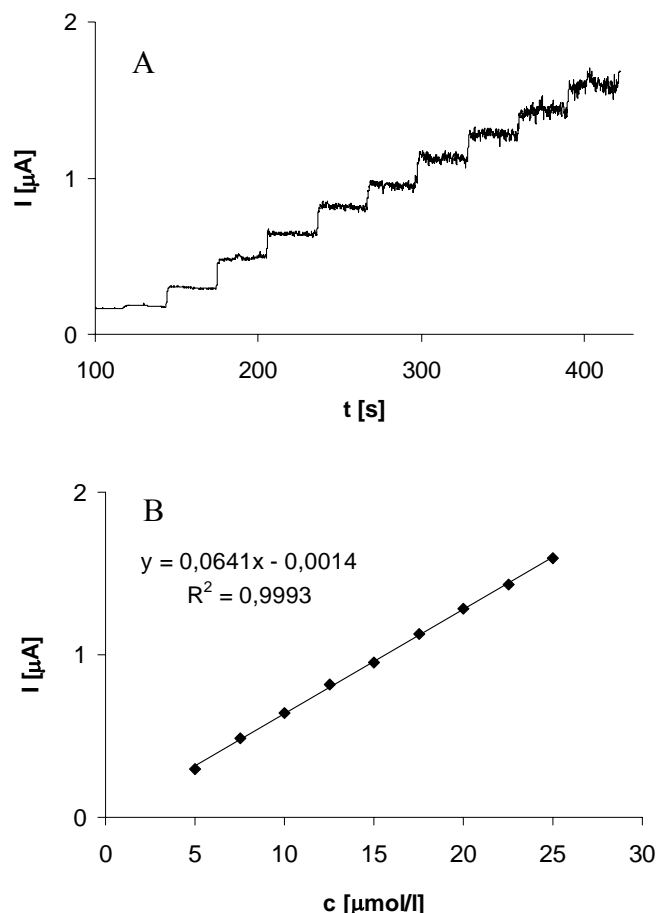


Figure 2: Amperogram (A) and a corresponding calibration curve (B) of rutin. Unmodified CPE, base electrolyte: acetate buffer pH 4, applied potential: 600 mV, stirred solution.

Conclusion

We have developed pulse amperometric technique to determine rutin using carbon paste electrodes.

Acknowledgement

The authors gratefully acknowledge the support by the Ministry of Education, Youth and Sports of the Czech Republic (projects CZ.1.05/2.1.00/03.0058 of Operational Program Research and Development for Innovations - European Social Fund and MSM6198959216). The work has been also supported by the project of Palacky University in Olomouc PRF_2011_025.

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