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Short communication

Sensitive voltammetric determination of rutin at an in situ plated lead film electrode

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ABSTRACT

A highly sensitive sensor for the determination of rutin by adsorptive stripping voltammetry was described. It consists of a lead film modified glassy carbon electrode (LF/GCE). In the proposed procedure rutin was accumulated by adsorption on the lead film electrode and then during the stripping step a lead film and the accumulated rutin were oxidised. The electrochemical behaviour of rutin at the lead film electrode was investigated by square-wave voltammetry. In the optimal conditions the anodic peak currents (measured by square-wave voltammetry) increased linearly with the concentration of rutin in the range of 5×10^{-10} to 1×10^{-8} mol L^{-1}. The detection limit for rutin following 30 s of accumulation time was equal to 2.5×10^{-10} mol L^{-1}. The method was successfully applied to the determination of rutin content in the tablets without previous separation.

1. Introduction

Rutin (3′, 4′, 5, 7-terahydroxyflurone-3β-D-rutinoside) is a very important bioactive flavonoid also known as vitamin P; its molecular structure is shown in Fig. 1. Flavonoid rutin, a natural flavone derivative, presents a wide spectrum of biochemical and pharmacological activities, including antibacterial, anti-inflammatory and antitumor [1–6]. It is also thought to be an activating factor for vitamin C [7]. Rutin is an oral capillary preservatory drug usually used for the therapy of chronic venous insufficiency and is also an ingredient in a large number of multivitamin preparations and herbal remedies [8,9].

The electrochemical determination of rutin was mostly based on its adsorptive property at carbon electrodes [10–17] or carbon nanotube-modified electrodes [18–21]. Among these, the lowest detection limit was 1.0×10^{-9} mol L^{-1} [15]. A lower detection limit of 5.0×10^{-10} mol L^{-1} was achieved at the hanging mercury drop electrode [22]. However, the toxicity of the mercury was the greatest drawback in the practical application of this electrode.

The aim of this paper was to show a new procedure for determination of rutin based on its adsorption on the lead film electrode in the accumulation step and next oxidation of lead film and then rutin. Till now the lead film electrode has been used for the determination of inorganic ions such as Ni(II), Co(II), U(VI), Mo(VI) [23–26] and organic compounds such as folic acid [27], trimethoprim [28] and testosterone [29]. This kind of the electrode can be easily regenerated by stripping the lead film after a preceding measurement and formation of a new film before each measurement. Although lead compounds used for plating a lead film are toxic their toxicity and volatility is lower as compared to mercury and mercury compounds used for the preparation of mercury electrodes. For example the maximum contaminant level in drinking water recommended by EPA for lead was equal 15 μg L^{-1} while for mercury 2 μg L^{-1} [30].

2. Experimental

2.1. Apparatus

All measurements were performed using a μAutolab analyser made by Eco Chemie, the Netherlands. A classical three-electrode quartz cell of volume 10 mL was used. A glassy carbon electrode (GCE) of diameter 1 mm was polished daily using 0.3 μm alumina slurry on a Buehler polishing pad. Pt wire and Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.2. Reagents

An acetate buffer, used as a supporting electrolyte, was prepared from CH_3COOH and NaOH obtained from Merck. The standard of rutin was obtained from Sigma and was not purified further. A stock standard solution of rutin (10^{-3} mol L^{-1}) was prepared by a dissolving reagent in methanol and stored in a refrigerator

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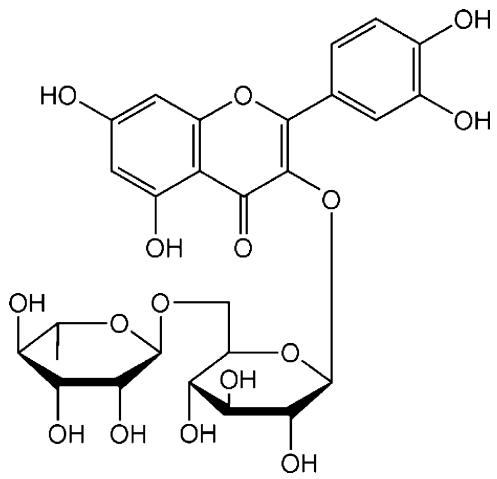

Fig. 1. Chemical structure of the rutin molecule.

in the dark until used. Methanol was also used for further dilution. The reagents used to study the interference effect were obtained from Sigma. All solutions were prepared in triply distilled water.

2.3. Standard procedure of measurements

In the optimised conditions of measurements a 0.075 mol L^{-1} acetate buffer (pH 4.6) was used as a supporting electrolyte. The concentration of $Pb(NO_3)_2$ added to the electrolyte was 7.5×10^{-6} mol L^{-1}. In the course of rutin determination the potential of the electrode was changed in the following sequence: 0.5 V for 10 s; −1.15 V for 25 s and −0.75 V for 30 s. The first step was applied to clean the electrode from a lead remaining after the preceding measurement. During the second and third steps a lead film was plated on a glassy carbon electrode and rutin was accumulated by adsorption on the electrode, respectively. During all three steps the solution was stirred using a magnetic stirring bar. Then after a rest period of 5 s a square-wave voltammogram was recorded at a frequency of 200 Hz, while the potential was scanned from −0.75 to 1.0 V. The amplitude was 50 mV. In the course of the stripping step lead film and then rutin were oxidised. The measurements were carried out in undeaerated solutions. The oxidation peak current of lead was much larger than the oxidation peak current of rutin, so the recorded voltammograms were cut in the potential range from 0.25 to 1.0 V. Then after the setting potential window of the blank square voltammogram and the voltammograms in the presence of rutin, the value of the current of the former (background current) was subtracted from the current values of the latter. The square-wave voltammograms obtained for solution containing rutin at a concentration of 5×10^{-9} mol L^{-1} are presented in Fig. 2. Fig. 2a presents the voltammogram in the potential window from −0.75 to 1.0 V and Fig. 2b shows the voltammogram in the potential window from 0.25 to 1.0 V after the subtracting the background current.

2.4. Sample preparation

The pharmaceutical preparation analysed were Rutinoscorbin tablets produced by GlaxoSmithKline Pharmaceuticals S.A., Poland, containing 25 mg of rutin and 100 mg of ascorbic acid per tablet. The pharmaceutical was prepared by the following procedure. Ten tablets were weighed and then the average mass per tablet was determined. The tablets were carefully grounded to a fine powder, and then a quantity of homogeneous powder equivalent to 25 mg of rutin was transferred into a 25 mL volume calibrated flask. The flask was filled to the mark with methanol and mixed. The desired concentration of rutin was obtained by accurate dilution with methanol. The sample solution so prepared was added to the supporting electrolyte in the voltammetric cell and adsorptive stripping voltammetric measurements were carried out under the optimal conditions.

3. Results and discussion

3.1. Voltammetric behaviour of rutin at the lead film electrode

Preliminary electrochemical measurements were carried out in order to identify the general behaviour of rutin in the presence and the absence of the lead film plated on a glassy carbon electrode. Fig. 3 shows electrochemical responses of a GCE and a LF/GCE in 3×10^{-8} mol L^{-1} rutin + 0.1 mol L^{-1} acetate buffer solution (pH 4.6), respectively. At the GCE and the LF/GCE, rutin showed a well-defined oxidation peak at +0.425 V. However, the peak current of rutin at the LF/GCE was much larger than that at the GCE, it was about three times higher than that obtained at the GCE by square-wave voltammetry. At the GCE and LF/GCE no a reduction peak of rutin was observed. Above experimental results indicated the advantages of the use of the lead film as a modifier of a glassy carbon electrode, so such prepared electrode was used in further measurements.

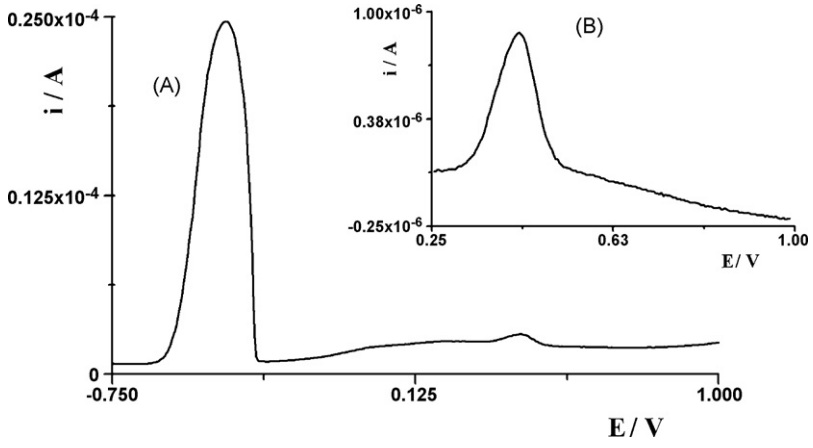

Fig. 2. Square-wave voltammograms obtained for solution containing rutin at a concentration of 5×10^{-9} mol L^{-1}: (a) potential window from −0.75 to 1.0 V, (b) potential window from 0.25 to 1.0 V. Rutin was accumulated for 30 s at −0.75 V. The lead film was deposited for 25 s at −1.15 V.

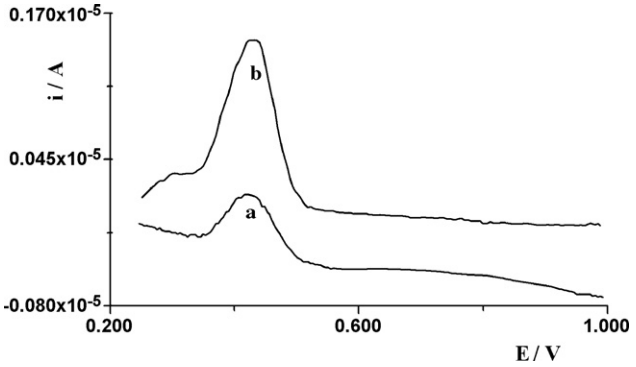

Fig. 3. Anodic square-wave voltammograms of 3×10^{-8} mol L^{-1} rutin at (a) GCE and (b) LF/GCE in the potential window from 0.25 to 1 V. Rutin was accumulated for 30 s at −0.8 V. The lead film was deposited for 10 s at −1.2 V.

3.2. Composition and pH of the supporting electrolyte

For determination of organic compounds at the lead film electrode an acetate buffer is usually used as the supporting electrolyte so $CH_3COONa + CH_3COOH$ was chosen for this study. Concentrations of the acetate buffer and $Pb(NO_3)_2$ were 0.1 and 1×10^{-5} mol L^{-1}, respectively. The pH of the solution was changed in the range from 4.0 to 6.0. For further study the pH of 4.6 was chosen as at such a pH the peak current of the studied compound attains the maximal value. In addition, at such a pH analytical signals of the oxidised lead and rutin are well separated. The concentration of the acetate buffer was changed in the range from 0.025 to 0.20 mol L^{-1} and its influence on the 5×10^{-9} mol L^{-1} rutin signal was studied. It was found that the current of the rutin peak increased as the concentration of the acetate buffer increased to 0.075 mol L^{-1} and then decreased. For further study the concentration of the acetate buffer of 0.075 mol L^{-1} was used.

3.3. Optimisation of the experimental conditions of the lead film formation

Three parameters were optimised: concentration of Pb(II) ions added to the electrolyte, the potential and the time of the lead film formation. A concentration of $Pb(NO_3)_2$ influences the quality of the lead film formed before each measurement and so the reproducibility of the rutin signal. The concentration of $Pb(NO_3)_2$ added to the solution was changed in the range from 0 to 5×10^{-5} mol L^{-1} and its influence on the rutin signal added to the solution to concentration of 5×10^{-9} mol L^{-1} was studied. It was found that in the absence of Pb(II) the peak of rutin was observed on the voltammogram because it was adsorbed on the GC support. However, the current of the rutin peak increased as the concentration of the Pb(II) increased and attained the maximal and stable value in the range of the concentration of the Pb(II) from 5×10^{-6} to 1×10^{-5} mol L^{-1}. The presence of the lead film on the GC support was necessary to obtain more than three times higher the analytical signal for rutin compared to the bare GCE. For further study the concentration of Pb(II) added to the electrolyte of 7.5×10^{-6} mol L^{-1} was chosen. Next, the potential of the deposition of lead film was changed in the range from −0.8 to −1.2 V and its influence on the peak current of rutin was studied. The potential of rutin accumulation in these experiments was equal to −0.8 V. The rutin peak current attained a maximal value as the deposition potential of the lead film was −1,15 V, so for further study this potential was chosen. Next, the time of the deposition of the lead film on the glassy carbon electrode was changed in the range from 0 to 60 s and its influence on the rutin signal was studied. The concentration of rutin added to the supporting electrolyte was equal to 2×10^{-9} mol L^{-1}. It was observed that the peak current of rutin attained a maximal and stable value as the lead film was deposited for 20–60 s. For further measurements the deposition time of the lead film of 25 s was used.

3.4. Optimisation of the experimental conditions of rutin accumulation

The influence of the accumulation potential on the rutin peak current was studied for a rutin concentration of 2×10^{-9} mol L^{-1}. The results indicate that the highest efficiency of the accumulation of rutin is obtained if the accumulation potential is in the range between −0.70 and −0.80 V. For further studies the accumulation potential of −0.75 V was chosen. The effect of the accumulation time was studied for a rutin concentration of 1×10^{-9} mol L^{-1}. The accumulation time was changed in the range from 0 to 120 s. It was observed that the rutin peak current increased linearly with the prolongation of the accumulation time to 90 s.

3.5. Calibration graph, repeatability and reproducibility

The calibration graph for the accumulation time of 30 s was linear from 5×10^{-10} to 1×10^{-8} mol L^{-1} and obeyed the equation $y = 168x + 0.0063$, where y and x are the peak current (μA) and rutin concentration (μmol L^{-1}), respectively. The correlation coefficient r was 0.999. The relative standard deviation for a rutin concentration of 5×10^{-9} mol L^{-1} was 3.9% ($n = 5$). The detection and quantification limits for an accumulation time of 30 s estimated from 3 to 10 times the standard deviation for the lowest determined concentration of rutin were about 2.5×10^{-10} and 8.3×10^{-10} mol L^{-1}, respectively. The voltammograms obtained for the increasing concentrations of rutin are presented in Fig. 4.

The repeatability of the rutin signal at the LF/GCE was evaluated measuring the peak current of 5×10^{-9} mol L^{-1} rutin five times using the same electrode regenerated electrochemically before each measurement. The relative standard deviation was 3.9%, indicating that the results obtained with the proposed modified electrode have a good repeatability. The electrode-to-electrode reproducibility was examined on three modified electrodes prepared independently. An acceptable reproducibility with a relative standard deviation of 4.9% was obtained for measurements carried out in 5×10^{-9} mol L^{-1} rutin solution.

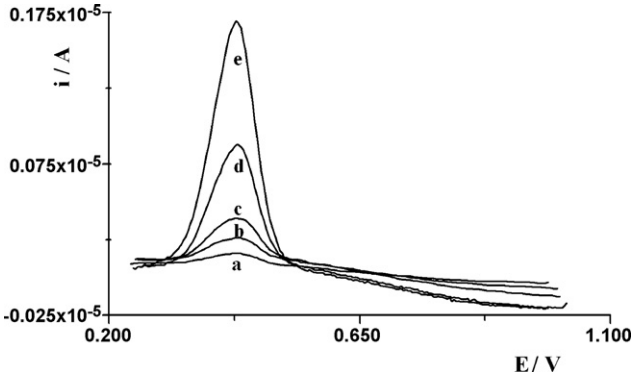

Fig. 4. Square-wave voltammograms obtained for solutions containing increasing concentrations of rutin: (a) 5×10^{-10} mol L^{-1}; (b) 1×10^{-9} mol L^{-1}; (c) 2×10^{-9} mol L^{-1}; (d) 5×10^{-9} mol L^{-1}; and (e) 1×10^{-8} mol L^{-1}. Rutin was accumulated for 30 s at −0.75 V. The lead film was deposited for 25 s at −1.15 V.

3.6. Interferences

The effects of inorganic ions and organic compounds on the determination of 5×10^{-9} mol L^{-1} rutin were studied. The determination of rutin following accumulation for 30 s was not influenced by a 100-fold excess of Cu^{2+}, Ca^{2+}, Fe^{3+}, Zn^{2+}, Na^{+}, K^{+}, ascorbic acid, glucose, vitamin B_1, lactic acid, folic acid, adenine, 50-fold excess of dopamine and epinephrine.

3.7. Analytical applications

The in situ plated lead film electrode was applied to the rutin determination by adsorptive stripping voltammetry in the tablets (label amount: 25 mg/tablet) without any matrix effects. The recovery of the proposed procedure was conducted to evaluate the accuracy of the method. The recovery of five-independent experiments was 102% with relative standard deviation (R.S.D.) of 3.9%, demonstrating the accuracy of the proposed method. The quantitative results obtained for the tablets were in agreement with the data supplied by the manufacturer and with those obtained by a reported method (the recovery was 101% with R.S.D. of 2.8%, $n = 5$) [22]. On the basis of these results it can be stated that the proposed procedure can be applied to rapid and sensitive determination of rutin in its pharmaceutical formulations.

4. Conclusions

The proposed voltammetric procedure of the rutin determination is based on its adsorptive accumulation at an in situ plated lead film electrode and then its oxidation. The electrochemical sensitivity of rutin at the proposed electrode improved significantly compared with the rutin response at a GCE. In addition, the proposed electrode exhibited a distinct advantage of simple preparation, good reproducibility and electrochemical surface renewal. The measurements were performed in undeaerated solutions. Under the optimised conditions, the proposed procedure offers a lower detection limit for the rutin analysis than other modified electrodes. The proposed procedure was successfully applied to the direct determination of rutin in the tablets.

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