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Analytical Methods

New voltammetric procedure for determination of thiamine in commercially available juices and pharmaceutical formulation using a lead film electrode

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ABSTRACT

A simple, reliable and reproducible method, based on adsorptive stripping voltammetry (AdSV), for determination of vitamin B_1 (thiamine) in pharmaceutical preparation and food is described in this paper. The in situ plated lead film electrode was used as a working electrode. The lead film was formed and thiamine was accumulated at −1.25 V (vs. Ag/AgCl) on a glassy carbon electrode. Then, the preconcentrated thiamine was reduced by scanning the potential of the electrode from −1.25 to −1.55 V using a square-wave technique. The linear range was from 0.0133 to 0.265 mg L^{-1} for vitamin B_1, with the regression coefficient of 0.999. The detection limit for vitamin B_1 was 0.0053 mg L^{-1} for the accumulation time 120 s. The method developed was applied to the determination of thiamine in certified reference material (BCR-485), pharmaceutical formulation and commercially available juices, and the assay results were satisfactory.

1. Introduction

Thiamine (vitamin B_1) is a biologically and pharmaceutically important compound. It is necessary for carbohydrate metabolism, maintenance of normal neural activity, and prevention and treatment of beriberi disease: pregnant women, infants, adolescents, and especially, elderly people are the groups at risk of hypovitaminosis of vitamin B_1 (Norouzi, Ganjali, Daneshgar, & Mohammadi, 2007). Thiamine is widely distributed in foods, the richest sources being whole grains, pulses, yeast, liver, and milk.

Vitamins might be lost through chemical reactions or by extraction and leaching during the storage and processing of food, which is really the case with water-soluble vitamins. In food samples, the vitamin B_1 may be presented in free (thiamine) and phosphorylated forms, including thiaminmonophosphate (TMP), thiamindiphosphate (TDP) and thiamintriphosphate. Furthermore, it may be bound tightly but non-covalently to proteins. The critical part of the analysis of the vitamin B_1 is extraction usually consists of an acid hydrolysis and an enzymatic treatment necessary to liberate protein- and phosphate-bond thiamine (Jakobsen, 2008; Ndaw, Bergaentzlé, Aoudé-Werner, & Hasselmann, 2000; Tang, Cronin, & Brunton, 2006). Many methods have been developed for the assay of thiamine. Some methods like flow injection analysis (Perez-Ruiz, Martinez-Lozano, Sanz, & Guillen, 2004) high performance liquid chromatography (Chen, Chen, & Yao, 2006; Lebiedzińska, Marszałł, Kuta, & Szefer, 2007; Poongothai, Ilavarasan, & Karrunakaran, 2010), spectrophotometry (Barthus, Mazo, & Poppi, 2007; Ortega-Barrales, Fernandez-de-Cordova, & Molina-Diaz, 1998) and fluorimetry (Vinas, Lopez-Erroz, Cerdan, Campillo, & Hernandez-Cordoba, 2000) are being widely used for quantification of thiamine from different sources. However, the reported methods can cause problems involving the preconcentration and/or separation steps and a high instrumental cost; also these routine techniques have often not been deficiently sensitive.

From the electrochemical point of view, just a few works based on the electrooxidation of vitamin B_1 have been published (Aboul-Kasim, 2000; Jiang & Sun, 2007; Norouzi et al., 2007; Oni, Westbroek, & Nyokong, 2002; Wan, Yang, & Ye, 2002). In these papers the authors exploited voltammetry for the determination of vitamin B_1 in pharmaceutical formulations. However, thiamine is widely distributed in foods, so it is necessary to develop a method for determination of vitamin B_1 not only in pharmaceutical formulations but also in food samples.

Since 2005, a lead film electrode (PbFE) has been proposed for the determination of inorganic ions and organic compounds (Korolczuk, Tyszczuk, & Grabarczyk, 2005). The proposed electrode exhibited interesting characteristics such as: lower toxicity compared to the mercury electrodes, a wide potential window and an ability to operate in a wide range of pH media, simple preparation, good reproducibility and a simple way of electrochemical surface renewal. The aim of this study was to investigate the performance of a lead film electrode for the analysis of vitamin B_1 and to develop a rapid, simple and sensitive method for its determination in pharmaceutical formulations and commercially available juices.

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2. Materials and methods

2.1. Apparatus

All measurements were performed using Autolab analyser made by Eco Chemie, The Netherlands. The conventional voltammetric experiments were carried out using a classical three-electrode quartz cell of volume 10 mL. A glassy carbon electrode of diameter 1 mm was polished daily using 0.3 μm alumina slurry on a Buehler polishing pad. A platinum 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 thiamine was obtained from Fluka and was not further purified. A stock standard solution of thiamine (265 mg L^{-1}) was prepared daily by a dissolving reagent in water. Deionized water was also used for further dilution. The reagents used to study the interference effect were obtained from Sigma–Aldrich. All solutions were prepared in purified water (Millipore quality). The certified reference material, mixed vegetables BCR-485, was obtained from the Institute for Reference Materials and Measurements, Geel, Belgium. Diluted HCl was prepared from Suprapure reagent. Taka-diastase from *Aspergillus oryzae* was obtained from Sigma–Aldrich.

2.3. Procedure of measurements of thiamine at a lead film electrode

About 0.05 mol L^{-1} acetate buffer (pH 5.6) was used as a supporting electrolyte. The concentration of $Pb(NO_3)_2$ added to the electrolyte was 1.25×10^{-4} mol L^{-1}. The electrode was cleaned electrochemically after the preceding measurement by cycling 5-times the potential between −0.53 and 0.5 V with the scan rate of 0.1 V s^{-1}. After cleaning, the potential −1.25 V for 120 s was applied. During this step a metallic lead was plated on a glassy carbon and thiamine was accumulated on the electrode, simultaneously. During all the 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 frequency 100 Hz, while the potential was scanned from −1.25 to −1.55 V. The amplitude was 25 mV. The measurements were carried out from under aerated solutions.

To evaluate the potential effect of foreign species (Ca(II), Mg(II), Zn(II), Al(III), Cd(II), Fe(III), Cu(II), dopamine, ascorbic acid, folic acid, uric acid, glucose, vitamin B_2, vitamin B_6, vitamin B_{12}, and vitamin PP) a systematic study was carried out under the above optimised conditions.

2.4. Sample preparation

Thiamine was extracted from the certified reference material (BCR-485) and commercially available juices by the Jakobsen (2008) method. Before removing the samples for analysis, the materials in the sachet were thoroughly mixed. In a 100 mL conical flasks, 50 mL with 0.1 mol L^{-1} HCl was added to 5 g of the certified reference material and 10 mL of juices. The solutions were autoclaved at 120 °C for 30 min, and then cooled and adjusted to pH 4.0 with sodium acetate. Subsequently, 100 mg taka-diastase was added, and the solutions were incubated at a temperature of 45 °C for 18 h. Then, the solutions were transferred to volumetric flasks and diluted to 100 mL with 0.01 mol L^{-1} HCl. Finally, the solutions were centrifuged for 5 min (4000 rpm) and filtrated with use of 0.45 μm filter. The suitable aliquot of the samples were added to the supporting electrolyte in the voltammetric cell and adsorptive stripping voltammetric measurements at a lead film electrode were carried out under the optimal conditions. The amount of vitamin B_1 present in the certified reference material (mixed vegetables BCR-485) was calculated by the standard addition method.

The pharmaceutical preparation analysed was Vitaminum B compositum tablets produced by Warsaw Pharmaceutical Company, Warsaw, containing 3 mg of vitamin B_1, 5 mg vitamin B_2, 5 mg vitamin B_6 and 5 mg vitamin PP per tablet. The pharmaceuticals were 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 3 mg of vitamin B_1 was dissolved in 20 mL of water by sonication for 30 min. Then the sample was centrifuged for 5 min (4000 rpm) and a suitable aliquot of the sample solution was added to the supporting electrolyte in the voltammetric cell. The amount of vitamin B_1 present in the tablets and juices were calculated by the standard addition method.

3. Results and discussion

In order to identify the general behaviour of vitamin B_1, in the presence and absence of the lead film plated on a glassy carbon electrode, preliminary electrochemical measurements were carried out in the solution containing 0.05 mol L^{-1} acetate buffer (pH 4.6), 0 or 5×10^{-5} mol L^{-1} $Pb(NO_3)_2$ and 0.265 mg L^{-1} thiamine. At the PbFE vitamin B_1 showed the reduction peak at −1.32 V. At the glassy carbon electrode no reduction peak was observed. The above experimental results indicate the advantages of using the lead film as a modifier of a glassy carbon electrode. In the present paper the reduction process of vitamin B_1 was not studied in detail because the main aim of this work was the application of the lead film electrode to the determination of vitamin B_1 in commercially available juices and pharmaceutical formulations.

3.1. Effect of pH of the supporting electrolyte

Before the application of PbFE for a quantitative determination of vitamin B_1, additional optimisation of the pH of the supporting electrolyte and also a characterisation of the working electrode were performed. For determination of organic compounds at the lead film electrode an acetate buffer is usually used as a supporting electrolyte, so $CH_3COONa + CH_3COOH$ was chosen for this study. The measurement of pH dependence of the thiamine sensor was studied over a pH range from 3.5 to 6.1 for a solution containing 0.265 mg L^{-1} of vitamin B_1. The pH was adjusted using 2 mol L^{-1} NaOH or CH_3COOH solution. The data revealed that a peak current of thiamine attached a maximal value at pH equal 5.6 ± 0.1, so this value of pH was chosen for further study.

3.2. Effect of $Pb(NO_3)_2$ concentration

A concentration of $Pb(NO_3)_2$ influences the quality of the lead film formed before each measurement and so the reproducibility of the thiamine signal. It was observed that the presence of the lead film on the glassy carbon support is necessary to obtain the analytical signal for thiamine. The concentration of $Pb(NO_3)_2$ added to the solution was changed from 0 to 1.5×10^{-4} mol L^{-1} and its influence on the thiamine signal added to the solution to concentration 0.265 mg L^{-1} was studied. The results obtained are shown in Fig. 1. When the glassy carbon electrode was modified by the lead film, a reduction peak of thiamine was observed. The thiamine was adsorbed on the lead film but not on the glassy carbon. It was observed that the reduction peak current of the thiamine reached a maximal value and satisfactory reproducibility as the Pb(II)