Journal of Electroanalytical Chemistry 731 (2014) 49–52

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Determination of Fe(III) in wine samples using a ruthenium oxide hexacyanoferrate modified microelectrode

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ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 23 July 2014
Accepted 1 August 2014
Available online 19 August 2014

Keywords:
Fe(III)
Modified microelectrode
Amperometry
Fe(III) speciation
Wine

ABSTRACT

The electrocatalytic reduction of Fe(III) was investigated using a carbon fibre microelectrode modified with a ruthenium oxide hexacyanoferrate film (RuOHCF/CFM). At surfaces containing this chemical modifier, Fe(III) is electrocatalytically reduced at 0.0 V without interference from Fe(II), hence allowing the speciation of Fe(III). A linear relationship between the cathodic current and concentration of Fe(III) was obtained by amperometry in the range 10–210 μmol L^{-1} with detection and quantification limits of 0.22 ($S/N = 3$) and 0.74 ($S/N = 10$) μmol L^{-1}, respectively. The described amperometric method was successfully applied for the determination of Fe(III) in different wine samples.

1. Introduction

Iron is an abundant element in the earth's crust and plays an important role in environmental, industrial, human and biological systems, and as such, is of key interest for analytical studies [1]. For essential elements like iron, speciation methods are needed because their bioavailability and metabolism are strongly dependent on the oxidation state of the chemical species. Many analytical methods have been developed to determine iron; these include flow injection analysis [2], chemiluminescence [3], mass spectrometry (ICP-MS) [4] and chromatography [5]. Spectrophotometric methods [6,7] have been widely used, however, they are relatively expensive for use in ultra trace determination of metal ions and can suffer from interferences. Moreover, methods involving colour measurement are less convenient because they are based on derivatisation of the analyte to produce a coloured compound, which is time-consuming. On the other hand, amperometric sensors for Fe(III) present several advantages based on low detection limits, large dynamic concentration range, good selectivity, rapid response time and inherent miniaturization and portability. However, these features depend on the use of mediators capable of recognising selectively the analyte in complex samples. Under the analytical point of view, the use of chemically modified electrodes coupled to electrochemical methods has presented a considerable increase in the last years. In this context, several works on literature have reported electrochemical detection of iron in aqueous medium using a broad spectrum of chemically modified electrodes with different organic and inorganic compounds [8–14].

The use of metal-hexacyanoferrates complexes in electroanalytical chemistry has been continuously investigated in the last years because these materials are easily immobilized onto bare electrode surfaces and show good properties for the reduction process of different analytes [15–21]. We have recently reported that glassy carbon electrodes coated with an electrodeposited film of ruthenium(III) oxide hexacyanoferrate (RuOHCF) present good electrocatalytic features for electrodic processes involving 20-deoxyguanosine [22], ascorbate [23,24] and hydrogen peroxide [25]. Transition-metal hexacyanoferrates consist of polynuclear mixed-valence compounds with open, zeolite-like structure, and have been used as electrocatalytic reaction mediators because of their excellent electron-transfer features [26]. However, no reports have been found in the literature on the Fe(III) determination using a RuOHCF electrochemical sensor.

The use of microelectrodes has some advantages, such as the possibility of carrying out the experiment in low-volume samples and the miniaturization of the apparatus. In addition, since one of the dimensions of a microelectrode is smaller than the thickness of the Nernst diffusion layer, an efficient mass transport to the electrode surface is achieved, resulting in a steady state response in a very short time [27–31]. Accordingly, the aim of this work was to develop a ruthenium oxide hexacyanoferrate modified microelectrode for determination of Fe(III) in wine samples using amperometry.

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http://dx.doi.org/10.1016/j.jelechem.2014.08.004
1572-6657/

2. Experimental

2.1. Chemicals and materials and samples

All solid reagents were of analytical grade and were used without further purification. The solutions were prepared by dissolving the reagents in deionized water processed through a water purification system (Nanopure Infinity, Barnstead). Potassium ferricyanide, potassium chloride, sodium chloride and ferric chloride were obtained from Merck (Darmstadt, Germany) and $RuCl_3{\cdot}xH_2O$ was obtained from Alfa Aesar (Massachusetts, USA). Wine samples were acquired in a local supermarket and were diluted in supporting electrolyte (0.5 mol L^{-1} KCl + 0.05 mol L^{-1} HCl solution) prior to analysis.

2.2. Electrodes and instrumentation

An Autolab PGSTAT 30 (Eco Chemie) bipotentiostat with data acquisition software made available by the manufacturer (GPES 4.8 version) was used for electrochemical measurements. A homemade Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrodes, respectively. The working electrode was a carbon fibre microelectrode (CFM).

2.3. CFM fabrication

A carbon fibre was connected to a Ni/Cr wire with silver paste (Joint Metal Comércio Ltda, São Paulo, Brazil) and inserted into a pipette whose tip was insulated with epoxy resin. The microelectrode was left to dry for about 3 h, and then its surface was polished with sandpaper and alumina (1 μm, Alfa Aesar, Massachusetts, USA), followed by copious washing with distilled water. The radius of the microelectrode was determined by measuring the limiting diffusion current in a $K_3Fe(CN)_6$ solution of known concentration using KCl as the supporting electrolyte and the value was found to be 14.5 μm.

2.4. Modification of the electrode surface

Prior to the electrodeposition of the RuOHCF film, the surface of the CFM was polished with alumina suspension on a microcloth polishing pad, rinsed with water and sonicated for five minutes in distilled water. The electrodeposition of the ruthenium oxide hexacyanoferrate film onto the surface of CFM was performed by repetitive sweeping at the potential limits of −0.5 and 1.3 V at 100 mV s^{-1} in a 0.5 mol L^{-1} KCl + 0.05 mol L^{-1} HCl + 1 mmol L^{-1} $K_3Fe(CN)_6$ + 1 mmol L^{-1} $RuCl_3$ solution. The stability of the modified microelectrode was established by recording cyclic voltammograms with the modified microelectrode in a 0.5 mol L^{-1} KCl + 0.05 mol L^{-1} HCl supporting electrolyte solution at the same potential limits.

3. Results and discussion

3.1. Electrodeposition of a RuOHCF film onto the CFM

The electrodeposition of the ruthenium oxide hexacyanoferrate film was carried out by repetitive potential cycles in a 0.5 mol L^{-1} KCl, 0.05 mol L^{-1} HCl, 1 mmol L^{-1} $K_3Fe(CN)_6$ and 1 mmol L^{-1} $RuCl_3$ solution. Voltammograms obtained during this experiment are shown in Fig. 1 and the continuous current increase demonstrates the accumulation of the RuOHCF film onto the microelectrode surface. Redox activity of ruthenium oxide hexacyanoferrate films is mainly based on electron-transfer processes involving the Ru(II)/Ru(III) and Ru(III)/Ru(IV) couples, as reported in the literature [32,33].

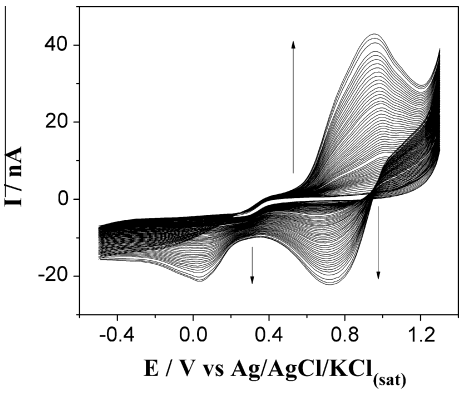

Fig. 1. Cyclic voltammograms recorded during the modification of the surface of a carbon fibre microelectrode in a 0.5 mol L^{-1} KCl, 0.05 mol L^{-1} HCl, 1 mmol L^{-1} $K_3Fe(CN)_6$ and 1 mmol L^{-1} $RuCl_3$ solution. Vertical arrows indicate changes in voltammograms during the experiment. Scan rate: 100 mV s^{-1}.

3.2. Fe(III) reduction at the RuOHCF/CFM

The electrocatalytic property of RuOHCF films towards the cathodic reduction of Fe(III) can be demonstrated by analysing voltammograms recorded with the a bare and a modified microelectrode (Fig. 2). Curve (a) shows that no significant response for Fe(III) is noticed when the experiment was performed with a bare electrode. In the supporting electrolyte solution (curve b) a current signal due to the Ru(II/III) redox process is observed, whereas after the addition of Fe(III), the current associated with the cathodic process increases due to the electrocatalytic reduction of Fe(III) in the presence of Ru(II/III) centres (see Scheme 1). Concomitant with the increase in the cathodic current, a decrease in the anodic current is noticed due to the consumption of the reduced ruthenium species by Fe(III) (Fig. 2c–d). These results confirm that the RuOHCF film is able to mediate the reduction of Fe(III), which allows low-potential amperometric measurements that are less susceptible to interferences from other species.

In order to evaluate the influence of Fe(II) on the sensor response, an additional voltammogram was recorded after addition of Fe(II) (curve e, Fig. 2). It is clearly seen that Fe(II) is not electroactive in the presence of the RuOHCF film, hence allowing the

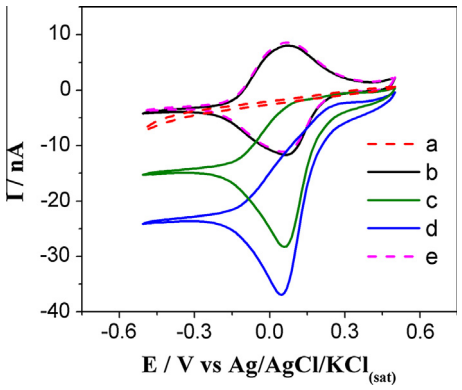

Fig. 2. Cyclic voltammograms recorded in a 0.5 mol L^{-1} KCl + 0.05 mol L^{-1} HCl solution before (b) and after (a, c and d) addition of Fe(III) (final concentration 1 (a and c) and 2 (d) mmol L^{-1}) by using a bare carbon fibre microelectrode (a) and a RuOHCF/CFM sensor (b–e). Influence of Fe(II) on the voltammetric profile after addition of 2 mmol L^{-1} Fe(II) (final concentration) (e). Scan rate = 50 mV s^{-1}.