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Analytica Chimica Acta 584 (2007) 295–301
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

A solid paraffin-based carbon paste electrode modified with 2-aminothiazole organofunctionalized silica for differential pulse adsorptive stripping analysis of nickel in ethanol fuel

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Received 13 September 2006; received in revised form 21 November 2006; accepted 27 November 2006
Available online 3 December 2006

Abstract

A solid paraffin-based carbon paste electrode modified with 2-aminothiazole organofunctionalized silica (SiAt-SPCPE) was applied to Ni^{2+} determination in commercial ethanol fuel samples. The proposed method comprised four steps: (1) Ni^{2+} preconcentration at open circuit potential directly in the ethanol fuel sample, (2) transference of the electrode to an electrochemical cell containing DMG, (3) differential pulse voltammogram registering and (4) surface regeneration by polishing the electrode. The proposed method combines the high Ni^{2+} adsorption capacity presented by 2-aminothiazole organofunctionalized silica with the electrochemical properties of the $Ni(DMG)_2$ complex, whose electrochemical reduction provides the analytical signal.

All experimental parameters involved in the proposed method were optimized. Using a preconcentration time of 20 min, it was obtained a linear range from 7.5×10^{-9} to 1.0×10^{-6} mol L^{-1} with detection limit of 2.0×10^{-9} mol L^{-1}. Recovery values between 96.5 and 102.4% were obtained for commercial samples spiked with 1.0 μmol L^{-1} Ni^{2+} and the developed electrode was totally stable in ethanolic solutions. The contents of Ni^{2+} found in the commercial samples using the proposed method were compared to those obtained by graphite furnace atomic absorption spectroscopy by using the *F*- and *t*-test. Neither the *F*- nor *t*-values exceeded the critical values at 95% confidence level, confirming that there are not statistical differences between the results obtained by both methods. These results indicate that the developed electrode can be successfully employed to reliable Ni^{2+} determination in commercial ethanol fuel samples without any sample pretreatment or dilution step.

Keywords: Nickel; Ethanol fuel; Solid paraffin-based carbon paste electrodes; Organofunctionalized silica; 2-Aminothiazole; Differential pulse stripping voltammetry

1. Introduction

Ethanol obtained from sugar cane has been used as an automotive fuel in Brazil since the 1970s [1]. This fuel was initially used as an additive in gasoline, which enhances its octane number, replacing the organolead compounds [2,3]. Nowadays, ethanol is used in Brazil predominantly as a transport fuel with both economic and environment benefits [4]. Not only it presents an attractive alternative and renewable biological fuel source, but also allows a significant decrease of CO_2 emission levels in Brazil. For all this, ethanol will surely be a key fuel source worldwide in the very near future.

The determination of metals in ethanol fuel is especially difficult due to their low concentrations and lack of certified reference samples. However, even in low concentrations, metallic species can cause damage to automobile engines [5] and to the environment [6]. The main sources of metal ions are associated to the ethanol production process, storage and transportation [7]. The determination of metals by electrothermal atomic absorption spectroscopy in ethanol fuel is well established [6,8,9] and flame atomic absorption spectroscopy (FAAS) can be used after a preconcentration step [10–12].

Stripping voltammetric techniques have become very popular for metal ions analysis [13,14]. These techniques provide high analytical performance with relatively low instrumental costs and some works have shown that stripping voltammetric techniques can be successfully applied to metal ions determination in ethanol fuel [15–18]. The introduction of a chemical

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doi:10.1016/j.aca.2006.11.069

modifier able to preconcentrate metallic ions at electrode surface either by complexation or electrostatic attraction can lead to more sensitive electroanalytical procedures with lower detection limit values. Silica and organofunctionalized silica with groups containing S, N or O atoms are very efficient materials to promote metal ions preconcentration [19]. These materials have been widely used to preconcentrate metals for subsequent determination by AAS in several kinds of matrices [20–22]. The extremely advantageous silica properties, such as, its high adsorption capacity, chemical stability and the possibility of functionalization with a large variety of functional groups make these materials excellent modifier agents to construct chemically modified electrodes [23,24], which have been widely employed for metal determination in different matrices [25–29].

Carbon paste electrodes (CPEs) are easily modified, since no specific interactions between modifier and electrode surface are necessary, thus this type of electrode has been widely employed in electroanalysis of organic and inorganic compounds [30]. Despite great success in using CPEs in electroanalysis, their use in totally non-aqueous media is limited due to the binder agent dissolution. Several strategies have been used to improve the chemical/mechanical properties of CPEs, all of them replacing mineral oil, the most used binder agent, by another agent capable of producing more rigid composites. Several promising alternative binder agents can be found in literature, such as epoxy [31,32], silicone [33], Teflon® [34], polyurethane [35]. Solid paraffin is another promising binder agent introduced by Petit and Kauffman [36,37], which presents low cost and can be easily handled allowing the electrode preparation in a simple and fast way. Recently, our group has demonstrated that a solid paraffin-based carbon paste electrode modified with 2-aminothiazole organofunctionalized silica (SiAt-SPCPE) is totally stable in ethanolic solutions and it can be successfully employed to Cu^{2+} determination directly in commercial ethanol fuel samples [16].

Most of stripping procedures suggested for electrochemical determination of Ni^{2+} are based on adsorptive stripping voltammetry using complexing agents; this procedure replaces advantageously the usual metal ion reduction/re-oxidation employed in anodic stripping analysis. The main difficulties found in the electrodeposition of Ni^{2+} are its strong tendency to form intermetallic compounds [38] and the fact that irreversible reduction of Ni(II) to Ni(0) requires potentials more negative than −1.1 V versus SCE, potentials in which the H^+ ions are also reduced on different types of carbon [39]. Among the complexing agents used on nickel stripping analysis, dimethylglyoxime (DMG) has been the most widely employed. DMG has been used to prepare chemically modified CPEs [39–41] or in solution, where the $Ni(DMG)_2$ complex is formed and subsequently accumulated onto electrode surface by applying a controlled potential. This last method often employs metallic electrodes, such as mercury [42,43], bismuth [44,45] or lead films [46].

In this context, this work describes the use of SiAt-SPCPEs to Ni^{2+} determination in commercial ethanol fuel samples by differential pulse adsorptive stripping voltammetry using DMG as complexing agent. The proposed method combines the high Ni^{2+} adsorption capacity presented by 2-aminothiazole organofunctionalized silica, which efficiently extracts Ni^{2+} from the ethanolic solutions, with the electrochemical properties of the $Ni(DMG)_2$ complex, whose electrochemical reduction provides the analytical signal. This is a more efficient strategy for Ni^{2+} determination in ethanol fuel in comparison to a DMG-based conventional CPE whose stability is limited to water:ethanol mixtures containing in the maximum 10% of ethanol [41].

2. Experimental

2.1. Reagents

Stock solutions of nickel were prepared by dissolving nickel chloride (Sigma, 99.99%) in analytical purity grade ethanol from Merck. Stock solutions of DMG (J.T. Baker, 99.7%) were prepared by dissolving the complexing agent in analytical purity grade ethanol. Water used to prepare all aqueous solutions was purified via Milli-Q system. Ammonium chloride (Merck) was used to prepare the supporting electrolyte. The pH of supporting electrolyte was adjusted at desired value by adding 2.0 $mol\,L^{-1}$ sodium hydroxide (Merck) or 2.0 $mol\,L^{-1}$ HCl (Merck) solution. Silica gel (Merck) with specific surface area between 486 and 520 $m^2\,g^{-1}$ and average pore diameter of 0.6 nm was utilized to construct both the SiAt-SPCPE and the non-functionalized silica modified solid paraffin-based carbon paste electrode (Si-SPCPE). 2-Aminothiazole (Aldrich) was employed to achieve the silica functionalization. The 2-aminothiazole organofunctionalized silica was synthesized according to the procedure previously described in literature [12]. Spectroscopic carbon powder from Merck was used to obtain the SPCPEs and paraffin from Synth was used as the binder agent. The commercial ethanol fuel samples were acquired from different local gas stations.

2.2. Apparatus

A HANNA Instruments pH-meter model HI 8417 was employed for pH measurements. Differential pulse stripping voltammetry was performed with an AUTOLAB PGSTAT 30 potentiostat coupled to a microcomputer and controlled by GPES 4.9 software. A one-compartment electrochemical cell with a platinum wire auxiliary electrode and an $Ag/AgCl_{sat}$ reference electrode were used in all voltammetric measurements. SiAt-SPCPE was used as working electrode. GFAAS experiments were carried out by using a spectrometer from Varian model Spectra A 640Z containing a Zeeman background corrector and a nickel hollow cathode lamp from Perkin-Elmer. The analytical procedure adopted in GFAAS analysis was the same used by Tartarotti et al. [41].

2.3. Electrode preparation

Unmodified SPCPEs, used for comparison purpose, were prepared by the sluggish addition of carbon powder in melted paraffin in the proportion of 60%:40% (w/w). Modified carbon pastes were prepared by substituting corresponding amounts of the carbon powder by silica or 2-aminothiazole organofunctionalized silica to obtain the desired composition.