



Short communication

Copper film electrode for anodic stripping voltammetric determination of trace mercury and lead



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ABSTRACT

A novel in-situ prepared copper film electrode (CuFE) for anodic stripping voltammetric measurement of trace levels of Hg(II) and Pb(II) is presented. The optimal electroanalytical performance of the CuFE was achieved in electrolyte solution comprising 0.1 M HCl and 0.4 M NaCl. The CuFE exhibited excellent operation in the presence of dissolved oxygen with calculated LoD of $0.1 \mu\text{g L}^{-1}$ Hg(II) and $0.06 \mu\text{g L}^{-1}$ Pb(II) in combination with 300 s accumulation time, repeatability with RSD of 4.5% for Hg(II) and 0.9% for Pb(II) ($n = 12$), and favourable linear response in the examined concentration range of $10\text{--}100 \mu\text{g L}^{-1}$ ($R^2 = 0.997$) for Hg and $5\text{--}70 \mu\text{g L}^{-1}$ ($R^2 = 0.999$) for Pb after 120 s accumulation. The electrode enabled also simultaneous detection of both investigated metal ions and revealed promising electroanalytical characteristics similar to or in certain cases surpassing those of commonly used gold electrodes.

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1. Introduction

Thin metal-film electrodes are commonly employed in electrochemical stripping analysis due to their appealing operation, simple fabrication and surface regeneration. Mercury film electrodes had been the most widely used metal-film electrodes for stripping analysis [1,2] before the introduction of bismuth [3], lead [4], antimony [5], tin [6] and amalgam [7] film electrodes, usually deposited on a variety of carbon-based substrates, as more environmentally acceptable alternatives. Copper-based electrodes have been mainly used for detecting glucose [8] or carbohydrates in general [9,10], nitrate [11,12], formaldehyde [13], and hydrazine [14] and for electrochemical reduction of CO_2 [15]. These electrodes rarely find their way into electrochemical stripping analysis of metal ions; however, there are some examples showing beneficial characteristics of copper alloys/intermetallics for determination of Se(IV) on Hg–Cu [16], Co(II) on Pb–Cu [17] and Hg(II) on Sb–Cu [18]. Recently, an entirely copper-based disposable sensor was developed for measuring Zn(II) using copper working and counter electrodes in combination with Cu/CuCl₂ reference electrode [19].

In this work we demonstrate the suitability and interesting electroanalytical characteristics of the in-situ prepared copper film electrode (CuFE) for the determination of trace levels of Hg(II) and Pb(II). Mercury exposure causes adverse effects on human health especially brain, kidneys and lungs [20], and can lead to serious medical conditions, such as acrodynia [21] and Minamata disease [22]. Lead poisoning in both its acute and chronic forms causes gastrointestinal, neuromuscular

and neuropathological symptoms [23]. Monitoring and measuring mercury and lead in the environment is therefore of great importance and requires sensitive, reliable and robust analytical techniques and sensors capable of detecting their trace concentration levels. Nowadays, measurements of mercury and lead are performed using sophisticated and expensive analytical techniques, such as atomic absorption spectrometry and in particular inductively coupled plasma-mass spectrometry/optical emission spectroscopy. From this aspect, advanced electroanalytical methods present an attractive alternative, facilitating sensitive and selective direct measurements of both toxic metal ions using relatively simple, portable and inexpensive instrumentation [1]. Gold in its various modifications has been the most commonly employed electrode material for measuring trace Hg(II) in combination with anodic stripping voltammetry [24,25]. On the other hand, Pb(II) is usually determined using various metal film electrodes [2,3,5]; however, there is significant lack of electrode materials capable of simultaneous detection of both actual analytes [26]. Copper is a commonly used material in electronics and can be easily deposited on various conductive surfaces. In addition, it is environmentally friendly, significantly cheaper than gold, and is compatible with numerous microfabrication methods which makes it a potentially suitable candidate for stripping voltammetric platforms and applications.

2. Experimental

Anodic stripping voltammetric (ASV) measurements were carried out using a modular PSTAT10 electrochemical workstation (Autolab, Eco Chemie, Utrecht, The Netherlands) controlled by GPES software. A three-electrode configuration was employed consisting of a copper

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film modified glassy carbon electrode (CuFE) (or a standard Au-disc electrode with $d = 2$ mm, Metrohm), Ag/AgCl/KCl(satd.), and a platinum rod acting as the working, reference and counter electrodes, respectively. During the electrochemical deposition magnetic stirring of approximately 300 rpm was employed.

Standard stock solutions of Cu(II), Pb(II), Au(III) and Hg(II) (1000 mg L^{-1} , atomic absorption standard solutions) were obtained from Merck and diluted as required. A 0.1 M HCl together with 0.4 M NaCl solution was used as the supporting electrolyte if not stated otherwise. All other chemicals were of analytical grade purity. Solutions throughout the work were prepared using Milli-Q water ($R = 18.2 \text{ M}\Omega$) (Millipore). Morphology of the electrodeposited CuFE on the glassy carbon substrate was characterized by scanning field emission electron microscopy (FE-SEM, Zeiss Supra 35 VP).

ASV measurements were conducted using an accumulation potential of -0.8 V for measuring Pb(II) or -0.6 V for measuring both Pb(II) and Hg(II), typically for 120 s, and after an equilibration period of 15 s, the anodic stripping voltammogram was recorded in the quiescent solution by applying a positive-going square-wave potential scan with a frequency of 25 Hz, a potential step of 4 mV and an amplitude of 50 mV. Before each measurement a cleaning step was carried out by keeping the working electrode potential at $+0.4 \text{ V}$ for 30 s.

3. Results and discussion

Since our introductory experiments revealed a promising performance of the in-situ prepared CuFE for measuring low concentration levels of Hg(II) and Pb(II), we further investigated and optimized its electroanalytical characteristics. In fact, mercury was the first metal ion that we tested in combination with CuFE; however, further studies revealed also the suitability of CuFE for detecting Pb(II). Another motivation for studying CuFE for detection of Pb(II) was the lack of metal film electrodes capable of simultaneous measurement of Hg(II) and Pb(II). Fig. 1A shows stripping voltammograms of $30 \mu\text{g L}^{-1}$ Hg(II) and $25 \mu\text{g L}^{-1}$ Pb(II) in test solutions containing 0.5 mg L^{-1} Cu(II) together with the most representative electrolytes (other examined electrolytes were omitted for clarity). It can be seen that electrolyte solutions comprising chloride (Fig. 1A: a, b, c) exhibited two signals for copper oxidation which were strongly dependent on the chloride concentration and pH. Particularly the second, more positive signal of copper, presumably attributed to the oxidation of CuCl to CuCl_2 , was

favourably shifted to more positive potentials when 0.4 M NaCl was added to 0.1 M HCl solution, and at the same time, the signal of Hg(II) was shifted towards more negative potentials. These effects provided significantly improved detection of Hg(II) (Fig. 1Ab) compared to the electrolyte containing solely 0.1 M HCl (Fig. 1Aa), where oxidation signals of Hg(II) and Cu(II) overlapped. A 1.0 M HCl solution (Fig. 1Ac) provided even larger separation between the two copper re-oxidation signals and an enhanced signal of Hg(II), whereas the signal of Pb(II) slightly diminished. On the other hand, a 0.1 M HNO_3 solution (Fig. 1Ad) exhibited unfavourable conditions for detecting Hg(II) together with considerable shifts of Cu(II) and Hg(II) re-oxidation/stripping signals towards more positive potentials, probably due to their preferential direct oxidation to +2 valence state exhibiting relatively high signal of Cu(II), decreased signal of Hg(II), whereas the signal of Pb(II) increased and was shifted towards less negative potentials. It is therefore very important to provide an appropriate concentration of chloride in the measurement solution for simultaneous determination of both metal ions; accordingly, 0.1 M HCl containing 0.4 M NaCl was chosen for further investigations. It has to be also noted that Pb(II), under applied conditions, had negligible effect upon the stripping signal of Hg(II), and vice versa; the only distinction observed were different optimal deposition potentials, i.e. -0.6 V for Hg(II) and -0.8 V for Pb(II).

The electroanalytical performance of the CuFE was compared with two different gold electrodes, i.e. with the standard Au-disc electrode ($d = 2$ mm) and Au-film electrode prepared in-situ on a supporting glassy carbon electrode according to Ref. [24]. The results gathered in Fig. 1B show stripping signals for $40 \mu\text{g L}^{-1}$ of both Hg(II) and Pb(II) after 120 s accumulation at the in-situ prepared CuFE in the electrolyte containing 0.1 M HCl and 0.4 M NaCl (a), at the Au-film electrode in 0.05 M HNO_3 and 0.02 M KCl [24](b), and at the Au-disc electrode in 0.01 M HNO_3 together with 0.01 M NaCl [25] (c). As can be seen there is only a slight difference considering Au-based electrodes, except for higher signal of Pb(II) at the Au-film electrode. On the contrary, the CuFE exhibited well-developed, sharp and high stripping signals for both metal ions at substantially more negative potentials compared to Au-based electrodes, indicating significant difference in accumulation and stripping patterns of the examined electrodes. It is evident that under comparable applied conditions the CuFE exhibited significantly improved signals of both metal ions in terms of peak heights (over 500% increase for both Hg(II) and Pb(II) compared to Au-disc electrode), shape (25% narrower signal half-widths compared to Au-electrodes)

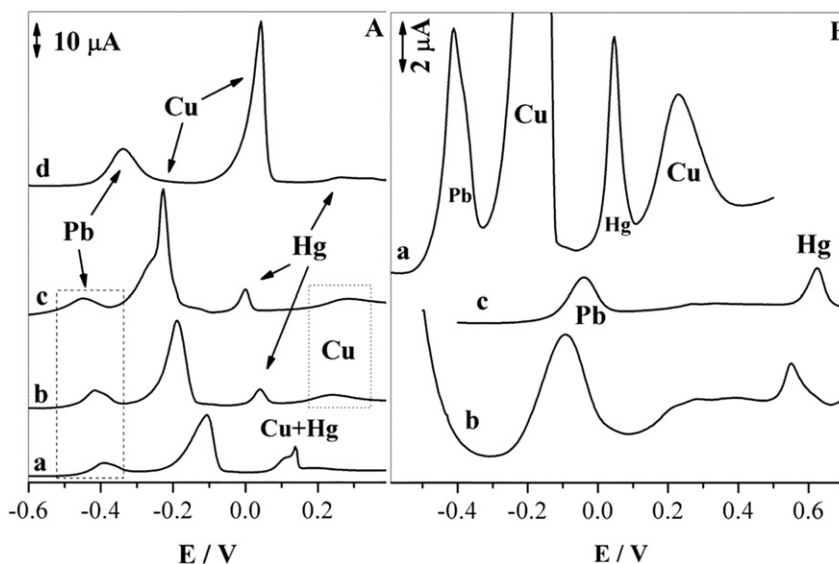


Fig. 1. A: ASV signals of $30 \mu\text{g L}^{-1}$ Hg(II) and $25 \mu\text{g L}^{-1}$ Pb(II) at the in-situ prepared CuFE in solutions containing 0.1 M HCl (a), 0.1 M HCl and 0.4 M NaCl (b), 1.0 M HCl (c), and 0.1 M HNO_3 (d); accumulation potential of -0.6 V for 120 s, equilibration period of 15 s, step potential of 4 mV, frequency of 25 Hz, amplitude of 50 mV, and cleaning step at $+0.4 \text{ V}$ for 30 s. B: ASV signals for $40 \mu\text{g L}^{-1}$ of both Hg(II) and Pb(II) at the in-situ prepared CuFE (a), in-situ prepared Au-film electrode (Ref. [24]) (b) and standard Au-disc electrode (Ref. [25]) (c).

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