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Short communication

Simultaneous determination of copper and lead in seawater using optimised thin-mercury film electrodes in situ plated in thiocyanate media

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Abstract

In the present work the anodic stripping voltammetric (ASV) methodology using a thin mercury film electrode in situ plated in thiocyanate media was re-assessed in order to allow the simultaneous determination of copper and lead in seawater. Under previously suggested conditions [6], i.e. using a concentration of thiocyanate of 5 mM, the ASV peaks of copper and lead overlapped due to the formation of a stable copper(I)–thiocyanate species, limiting the analytical determinations. Therefore, the best value for the thiocyanate concentration was re-evaluated: for 0.05 mM a trade-off between good resolution of the copper and lead peaks and high reproducibility of the mercury film formation/removing processes was achieved. In this media, the ASV peaks for Pb and Cu occurred, separated by 140 mV. Also, the in situ thin mercury film electrode was produced and removed with good repeatability, which was confirmed by the relative standard deviation values for the ASV determinations: 0.5% for Pb and 2.0% for Cu (10 replicate determinations in a solution with metal concentrations 1.5×10^{-8} M for lead and 2.2×10^{-8} M for copper). The optimised methodology was successfully applied to the determination of copper in the presence of lead, in certified seawater (NASS-5).

Keywords: Mercury film electrode; Thiocyanate; Lead; Copper; Anodic stripping voltammetry

1. Introduction

The application of thin mercury film electrodes (TMFEs), in situ or ex situ produced on glassy carbon (CG), to the anodic stripping voltammetric (ASV) quantification of trace heavy metals is widespread [1–6]. Improved sensitivity can be obtained using the in situ plating of mercury, i.e. mercury is deposited simultaneously with the metals of interest, giving a very thin mercury film with a high metal concentration. The common procedures involve plating in an acidified Hg(II) solution. However, poor reproducibility of the mercury deposition is a frequent problem [5]. Fisher and van den Berg proposed an optimised methodology for the determination of lead and cadmium in natural waters, using a thin mercury film produced in situ in the presence of 5 mM thiocyanate at pH 5.6 and accumulating at very negative potentials [6]. They concluded that in the presence of SCN^- the mercury film could be plated reproducibly and fully removed after each scan. The role of thiocyanate, as well as other experimental parameters, namely pH and deposition potential, in the mercury film formation process was examined further in a recent work by Monterroso et al. [4]. Also, the application of TMFEs pre-plated (ex situ) in a 5 mM of thiocyanate solution at pH 3.4 was successfully applied to the determination of lead and copper in acidified seawater without any apparent drawback due to the chloride anion [4].

Our interest focused on the application of the in situ TMFEs optimised by Fisher and van den Berg [6] for lead and cadmium, to the simultaneous determination of copper and lead in seawater. Though, the occurrence of thiocyanate–Cu(I) complexes which are reduced at negative

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potentials at the hanging mercury drop electrode (HMDE) was already documented [7,8]. In certain experimental conditions (relatively high concentrations of SCN^- and of chloride anion) the thiocyanate–Cu(I) reduction peak may overlap with the stripping peak of lead. Hence, in the present work, we have studied the effect of thiocyanate on the ASV stripping peaks of Cu and Pb. Therefore, the optimal concentration of thiocyanate had to be re-evaluated considering the compromise between good resolution of the copper and lead peaks and good reproducibility of the mercury film formation process. The success of this improved methodology is demonstrated by its application to the determination of copper in the presence of lead, in certified seawater (NASS-5).

2. Experimental

2.1. Instrumentation

All the voltammetric experiments were performed with a computer controlled potentiostat (PGSTAT-12 controlled by GPES software from EcoChemie, Netherlands) connected, via an IME-663 module, to an electrode stand (663 VA-Stand, Metrohm, Switzerland). The three-electrode configuration was used comprising a HMDE or a TMFE plated onto a rotating GC disc (1.9 mm diameter, Metrohm) as working electrodes, a GC rod counter electrode and a double junction Ag/AgCl (3 M KCl, saturated AgCl, and 3 M KCl in the bridge) reference electrode. All potentials quoted are relative to this Ag/AgCl reference electrode. All experiments were done at room temperature (approximately 20 °C). A combined glass electrode (Orion 9104SC) connected to a pH meter (Cole Parmer, Model 05669-20) was used for pH measurements.

2.2. Reagents and solutions

Ammonium acetate and ammonium thiocyanate, both from Riedel-de-Haën were of analytical-reagent grade. Sodium chloride (Merck, suprapur) and hydrochloric acid, 37%, (Fluka, trace select) were also used. The stock solution of ammonium acetate (1 M) was cleaned by shaking overnight with a manganese(IV) oxide (Merck) suspension ($9\,mg\,l^{-1}$) followed by filtration through an acid cleaned 0.45 μm cellulose acetate membrane filter (Millipore). Stock solutions of ammonium acetate pH buffer (1 M NH_4Ac/0.5 M HCl) and of thiocyanate 1.0 and 0.01 M were used without further purification. Solutions of metal ions, Hg, Cd, Cu and Pb, were prepared by appropriate dilution of the corresponding 1000 ppm AA-Spectrosol standards (BDH). Certified seawater reference NASS-5 seawater reference was purchased from National Research Council, Canada. Dispensing pipettes (5–50 and 50–200 μl, Proline, Biohit) equipped with disposable tips were used for the appropriate dilutions. Deionised water (18.2 MΩ cm, Milli-Q systems, Millipore-waters) was used for preparing all solutions.

2.3. Procedure

The electrochemical experiments with the HMDE and with the in situ TMFE were carried out in a 20 ml NaCl 0.5 M sample. The pH was adjusted to 4.0 by addition of 200 μl of NH_4Ac/HCl buffer to a cell concentration of 0.01 M and a suitable volume of 0.5 M HCl. Then appropriate amounts of ammonium thiocyanate were added. For the in situ TMFE, the mercury(II) concentration was 0.03 mM in accordance with previous studies [4,6]. All solutions were purged with nitrogen for 5 min before the voltammetric measurements. Three replicate measurements were always performed. The cell concentrations of cadmium(II), lead(II) and copper(II) were in the 10^{-8} M range. In the ASV experiments the deposition step was carried out for 60 s at a deposition potential, E_{dep}, −1.3 V, whilst the electrode (for the TMFE), or the stirring rod (HMDE), was rotated at 1500 rpm. After a 10 s quiescent time, the stripping step was performed from −0.8 to 0 V, using a square-wave (SW) scan: frequency 10 Hz (50 Hz for measurements in the NASS-5 water), amplitude 25 mV and potential step 5 mV. The standard addition method was used for the analytical determinations. In the experiments with the in situ TMFE, each scan was preceded by an electrochemical cleaning step at $E_{cond} = +0.6$ V for at least 15 s, to remove the previous mercury film [4].

The GC electrode was pre-conditioned by polishing, sonication and electrochemical pre-treatment in accordance to published procedures [4]. These polishing and electrochemical pre-treatments were repeated daily. When not in use the GC electrode was stored dry in a clean atmosphere.

3. Results and discussion

Preliminary ASV measurements of cadmium, lead and copper were done using the HMDE in a 20 ml 0.5 M NaCl buffered solution in the presence of 5 mM thiocyanate, the previously suggested concentration for the in situ platting of mercury films [6]. In these experimental conditions the voltammogram presented only two stripping peaks, at approximately −0.61 and −0.42 V (Fig. 1A). The peak at more negative potentials was assigned to cadmium. On the other hand, the stripping peak at −0.42 V increased with the addition of both lead and copper to the cell solution. As depicted from Fig. 1, decreasing the SCN^- concentration originated the progressive deconvolution of the copper peak and, for a thiocyanate concentration of 0.5 mM or lower two separate peaks were clearly seen (Fig. 1B and C). The peak at less negative potentials was assigned to copper, which is stripped back to the solution as a copper(I)–thiocyanate complex [7,8]. In fact, the current intensity of that peak increased with the concentration of copper. Besides, its po-

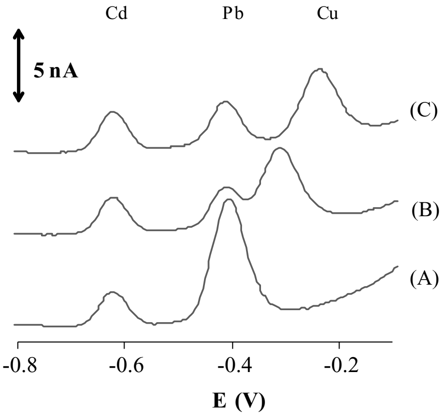

Fig. 1. Effect of thiocyanate on the SW-ASV stripping peak of 20 nM copper in the presence of 50 nM lead and 22 nM cadmium, at the HMDE. (A) NH_4SCN 5 mM, (B) NH_4SCN 0.5 mM and (C) NH_4SCN 0.05 mM. Cell solution: 0.5 M NaCl, in ammonium acetate buffer, pH 4.0. Experimental conditions: deposition at −1.3 V for 60 s, $f = 10$ Hz, $a = 25$ mV, potential step = 5 mV.

Table 1
Peak-to-peak separation, ΔE_p, between the stripping peaks of Cu and Pb at the in situ TMFE, as a function of thiocyanate concentration

[SCN$^-$] (μM)	ΔE_p (mV)
0	175
10	173
20	154
41	146
50	139
77	124
128	89
417	40

Cell solution: 0.5 M NaCl (pH 4.0) containing 0.03 mM Hg(II), 22 nM copper and 15 nM lead. Deposition time was 60 s at −1.3 V.

tential shifted towards less negative values upon decreasing further the concentration of thiocyanate, reaching approximately –0.18 V in the absence of SCN$^-$. The variation of the potential of the copper peak as a function of log[SCN$^-$] was linear, with a slope ranging between 0.071 and 0.053 V per decade for different experiments (correlation coefficients approximately 0.999, $N = 5$). This is in accordance with the predominant formation of a Cu(I)(SCN)^0 species and agrees with previously reported data [7]. The height and potential of the stripping peaks of cadmium and lead remained unaffected by the addition of thiocyanate. Further, no significant changes in the system behaviour were observed by changing pH within the interval 4.0–5.6. The same general behaviour was observed at a TMFE in situ produced in thiocyanate solution and again, using the thiocyanate concentration of 5 mM proposed by Fisher and van den Berg [6], only one single peak occurred for both copper and lead. Therefore, to accomplish the simultaneous determination of copper and lead using a TMFE in situ plated in the presence of SCN$^-$, the optimal concentration of thiocyanate needs re-evaluation. This was done taking into account two main features, i.e. the separation of the copper stripping peak from that of lead (peak-to-peak separation) and the maintenance of a good repeatability in the mercury film formation/removing processes. The best values for the first parameter occurred for SCN$^-$ concentrations lower than 0.08 mM, where the peak-to-peak separation was higher than 124 mV (cf. Table 1). Considering also that thiocyanate must be in excess relative to the mercury ion in the cell solution (which was present at the concentration 0.03 mM), the optimal value for the concentration of thiocyanate was taken as 0.05 mM (for which the peak-to-peak separation was approximately 140 mV). Ten replicate measurements under these proposed conditions afforded good quality results for all metal cations, as depicted from Table 2. The relative standard deviations for the peak currents were all very small, i.e. ≤2.0%, indicating good repeatability of the formation/removing of the mercury film. These low R.S.D. values agree with those reported for the stripping peak of lead using TMFEs produced in thiocyanate media [4]. There were no evidences of erratic current baselines and film degradation upon use. Therefore, reproducible and stable in situ TMFEs can be prepared in the presence of 0.05 mM thiocyanate in moderate acidic solution of NaCl (pH 4.0) at a deposition potential of −1.3 V. In this experimental conditions all three metals, cadmium, lead and copper can be successfully determined with very good resolution.

The accuracy of the optimised methodology was tested by analysing copper in a certified seawater sample, NASS-5 (National Research Council, Canada). This water sample was used without any pre-treatment. The ASV response for copper and lead using the in situ TMFE under the optimised SCN$^-$ concentration 0.05 mM, with 5 min deposition time is shown in Fig. 2A. The determined concentration of copper was 4.48 ± 0.17 nM ($N = 3$), which compares very well with the certified value of 4.67 ± 0.72 nM. The amount of lead was quantified as $(5.4\pm0.1)\times10^{-10}$ M ($N = 3$), which is about 10 times the certified value (40 pM). In spite of our best efforts the blank level of lead in our laboratory could not be lowered any further in order to allow analysis at the pM level. Clean room facilities would certainly be necessary to improve the quality of the work at these very low levels. Nevertheless, the results show that a full discrimination of both Pb and Cu peaks is attainable at the trace levels usually present in seawater [4,6,9]. A further addition of thiocyanate

Table 2
ASV data for 10 successive determinations at in situ TMFEs for 15 nM lead and cadmium and 22 nM copper in a 0.5 M NaCl solution (pH 4.0) containing 0.03 mM Hg(II) and 0.05 mM SCN$^-$

Metal ion	E_p (V)	I_p (nA)[a]	R.S.D. (%)	$W_{1/2}$ (V)[b]
Copper	−0.330	185	2.0	0.057
Lead	−0.469	217	0.5	0.047
Cadmium	−0.678	268	0.7	0.048

Deposition time was 60 s at −1.3 V.

[a] Mean value of the peak current, I_p.

[b] Mean value of the peak width at half height, $W_{1/2}$.

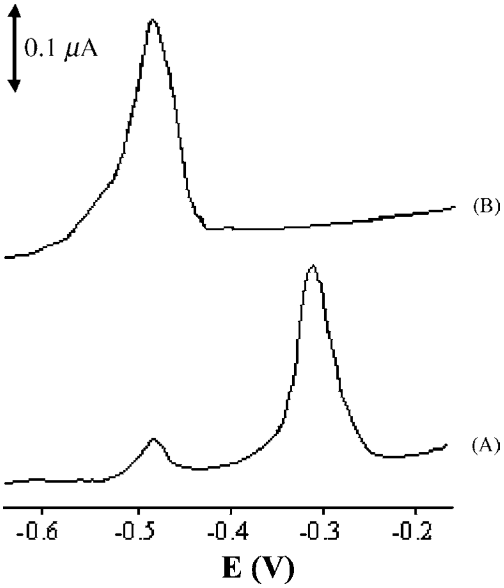

Fig. 2. Square-wave anodic stripping voltammograms for lead and copper in certified seawater sample (NASS-5) using the in situ TMFE in thiocyanate media, containing ammonium acetate buffer (pH 4.0), Hg(II) 0.03 mM and thiocyanate: (A) optimised concentration 0.05 mM and (B) 5.0 mM. Experimental conditions: deposition time 300 s at −1.3 V; $f = 50$ Hz, $a = 25$ mV, potential step =5 mV.

to 5 mM was made (Fig. 2B) confirming the overlapping of both peaks, i.e. the disappearance of the Cu peak with the consequent increase of the height of the peak at more negative potentials.

It may be concluded that the re-optimised ASV methodology using a TMFE plated in situ in buffered acidic Hg(II) solution (pH 4) in the presence of 0.05 mM thiocyanate can be successfully applied to the simultaneous determination of copper and lead in seawater.

Acknowledgements

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