

Short communication

Resolving the copper interference effect on the stripping chronopotentiometric response of lead(II) obtained at bismuth film screen-printed electrode

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Abstract

As copper(II) is a common ion in a variety of analytical samples, its effect on the stripping response of lead(II) at bismuth film screen-printed carbon electrode (BFSPCE) was investigated. The study was conducted using a screen-printed three-electrode system (working, counter and reference electrodes), with the carbon-working electrode plated in situ with bismuth film. Copper present at significant concentration level in samples was found to affect the sensitivity of the electrode by reducing the constant current stripping chronopotentiometric (CCSCP) response of lead(II). Recovery of the lead stripping response at the BFSPCE in the presence of copper was obtained when 0.1 mM ferricyanide was added to the test solution. The ferricyanide added circumvents the detrimental effect of copper(II) by selectively masking the copper ions by forming a complex. The analytical utility of the procedure is illustrated by the stripping chronopotentiometric determinations of lead(II) in soil extracts.

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1. Introduction

Due to the increasing demand for metal detection in soil, environmental companies and pollution monitoring agencies have expressed the need for de-centralised monitoring equipments that can produce reliable results in field conditions. To carry out heavy metal ions analysis in the field a simple and cheap sensing device, which is portable, accurate, precise and can highlight ‘hotspots’ and facilitate more rapid decision-making for remediation of polluted sites is needed. Electrochemical methods satisfy this need, with their low power demands lending itself to the design of portable field-based instruments [1–8].

In addition to this, the advent of screen-printing (thick-film) technology has made it possible to fabricate inexpensive disposable electrodes in large volumes [5,6,8–13,16], which can be used with these electrochemical instruments.

Numerous electrochemical procedures involving the coupling of electrochemical techniques (ASV and PSA) with disposable screen-printed electrodes have been reported for the detection of heavy metals [5–18]. Although, these procedures offer the desired sensitivity in most cases, observation made from an earlier work [7] where the presence of significant amounts of copper ions in samples resulted in the suppression of the lead stripping response obtained on bismuth film screen-printed carbon electrode (BFSPCE) and hence the concentrations of lead(II) in soil samples, shows that the accuracy of determinations can be adversely affected by the interaction among metal ions co-deposited onto the electrode surface.

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Hence, the quantification of lead in the presence of significant levels of copper provides a particularly challenging analytical problem [7,8,18,19]. A number of studies [8,19–26] have focused on the elimination of this interference since copper is a common ion in a variety of analytical samples [7,8,19,22,24,25]. Typical approaches include the addition of a chelating agent [4,8,19,20] or a third element [21], applying a CSV method incorporating a boron-doped diamond electrode and power-ultrasound [22], the use of chemically modified electrodes [23,24], the selective removal by means of ion-exchange [25] and the use of a copper electrode [26] to force total lead-copper amalgamation.

This paper presents another approach simply based on the addition of a complexing agent to mask the interfering effect of copper on the stripping response of lead(II) at a bismuth film electrode. To achieve this using a screen-printed three-electrode system (working, counter and reference electrodes) with the carbon-working electrode plated in situ with bismuth film, ferricyanide was used as the masking agent. The bismuth film electrode was used due to its low toxicity compared to mercury electrode [7,16,27] and because the layer of bismuth film on the electrode surface dramatically improves the sensitivity of lead stripping response [7,16]. The adequacy of the masking agent in suppressing the effect of copper on the stripping response of lead was also verified with the analysis of acetic acid and aqua-regia extracted soil samples obtained by solid-liquid extraction. The acetic acid extract is based on the first step of the sequential extraction protocol proposed by the European Community Bureau of Reference (BCR, now known as the Standards, Measurements and Testing Programme) [28,29] while the aqua-regia extract is the procedure used for obtaining the total content of heavy metals in soil samples.

2. Experimental

2.1. Chemicals and solutions

All chemicals were of analytical reagent grade and used as received. Hydrochloric acid (HCl), nitric acid (HNO₃) and potassium ferricyanide were obtained from BDH Ltd. (Poole, England) while ammonium acetate was obtained from Merck (Darmstadt, Germany). The lead(II), copper(II) and bismuth(III) atomic absorption standard solutions (1000 mg l⁻¹ in 5 wt.% nitric acid) were obtained from Aldrich (Gillingham, Dorset, UK). Working solutions were prepared by the dilution of standard solution with deionised water and supporting electrolyte to the appropriate concentration. The supporting electrolyte used in the experiments was either 0.1 M HCl solution or a mixed solution of 0.5 M ammonium acetate + 0.1 M HCl (pH 4.6).

2.2. Soil sample preparation

Soil samples collected from a contaminated mine area in Spain were extracted with acetic acid and aqua-regia. The treatment (extraction process) applied to the soil samples using conventional methods are detailed below:

Step 1. A portion (1 g) of soil sample was placed in a 65 ml stoppered extraction tube with 40 ml of 0.11 M acetic acid (pH 2.85) added and shaken for 16 h in a rotary rack shaker. Then the mixture was centrifuged for phase separation and the aqueous phase filtered with filters of 0.22 µm pore size (Millex[®]-GS, Millipore Corporation, Bedford MA).

Step 2. A portion (0.25 g) of the solid sample from step 1 was placed in a microwave vessel and 9 ml of aqua-regia (6 ml concentrated HCl, 2 ml concentrated HNO₃ and 1 ml water) were added and then left closed for 10 h to predigest before microwave treatment. After that, total digestion proceeded by first ramping to 200 °C for 4 min and then maintaining for 6 min using pressure between 160 and 180 psi. The vessel was cooled down to room temperature before opening and the remaining solution brought up to 100 ml final volume. The solution was filtered with Millipore filters of 0.22 µm pore size.

The extracts from the two steps were kept refrigerated at 4 °C prior to the analyses being carried out.

2.3. Electrode fabrication

Screen-printed electrodes (SPEs) were mass-produced in-house by a multi-stage screen-printing process using a DEK 248 machine (DEK, Weymouth, UK) and screens with appropriate stencil designs (100 per screen) fabricated by DEK Precision Screen Division. The fabrication process has been described elsewhere [6,7].

2.4. Procedure

A hand-held, battery-powered PalmSens potentiostat/galvanostat (Palm Instruments BV, The Netherlands), interfaced to a Compaq iPAQ pocket PC and a computer-controlled Autolab PGSTAT-10 Electrochemical Analyser with general-purpose electrochemical software operating system GPES version 4.8 (Eco Chemie, Utrecht, The Netherlands) were used for electrochemical measurements. The screen-printed electrode strips were connected to the potentiostat/galvanostat with a specially adapted electrical edge connector from Maplin (Milton Keynes, UK). Studies were carried out by placing a 100 µl sample drop on the three-electrode strip. Each electrochemical measurements were carried out in triplicates with a new electrode strip in non-deaerated and unstirred solution. Stripping chronopotentiometric measurements were carried out by depositing bismuth(III) ions with the target metal ion (lead). A deposition

potential of -0.9 V (versus screen-printed Ag/AgCl reference electrode) was applied to pre-concentrate the analyte. After the deposition period (120 s), a constant current ($1 \mu\text{A}$) was applied to strip the pre-concentrated analyte until a limit of -0.2 V (versus screen-printed Ag/AgCl reference electrode). The background signal for the supporting electrolyte was also measured in the same manner.

The concentrations for lead(II) in the acetic acid and aqua-regia extracts of soils were quantified by the use of standard addition method. CCSCP measurements were conducted by diluting the soils extracts with deionised water and supporting electrolyte. The diluted acetic acid and aqua-regia extracted soil samples were analysed by spiking with appropriate concentrations of standard lead(II) solution. An inductively coupled plasma–mass spectrometer (ICP–MS—model PQ EX-CELL VG ELEMENTAL) was used to verify the results obtained.

3. Results and discussion

3.1. CCSCP—effect of co-existing copper(II) ions

The fact that analytical results obtained with electrochemical stripping techniques can be affected by the potential in-

teraction between metals that have been co-deposited onto the electrode surface, the selectivity of CCSCP measurements at BFSPCE was investigated by examining the interfering effect of copper on the stripping response of lead(II).

The effect of different concentrations of copper(II) (50 – $2000 \mu\text{g l}^{-1}$) on the stripping peak responses of lead(II) (50 – $300 \mu\text{g l}^{-1}$) was evaluated and the result is presented in Table 1. As the concentration ratio of copper to lead increased, the stripping chronopotentiometric response for the oxidation of electrodeposited lead was suppressed at the BFSPCE and this clearly negates the benefit of the bismuth film electrode as the metallic film on the screen-printed carbon surface increases the sensitivity of lead stripping response compared to that obtainable on bare electrode surface [7,16]. The suppression of the lead stripping response by copper is probably due to the competition between electrodeposited bismuth and copper for surface sites on the electrode [27] as well as the formation of an intermetallic compound between copper and lead [7,8,17–19,21–23,26]. Wang et al. [27] suggested that lead does not compete with bismuth for the surface site but rather form a binary alloy with bismuth.

Table 1

Effect of copper on lead response at different concentration ratios on bismuth film screen-printed carbon electrode (BFSPCE)

Ratio Pb:Cu ($\mu\text{g l}^{-1}$)	Signal change (%)
1:0.3	–14
1:0.5	–36
1:1	–45
1:2	–47
1:2.5	–60
1:5	–77
1:20	–87
1:40	–100

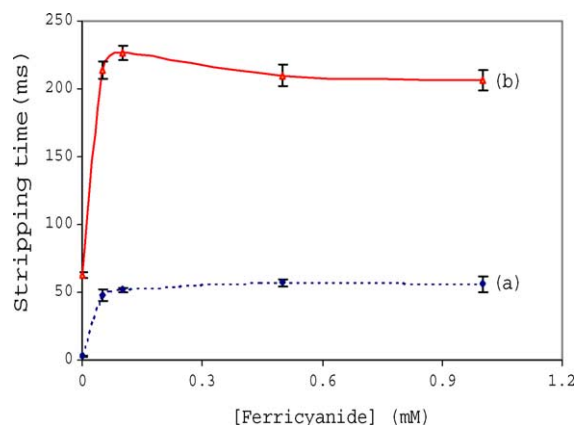


Fig. 1. Variation of (a) $60 \mu\text{g l}^{-1}$, (b) $200 \mu\text{g l}^{-1}$ lead(II) responses in the presence of copper ($2000 \mu\text{g l}^{-1}$) as a function of the ferricyanide concentration. Electrolyte = 0.1 M HCl, deposition potential = -0.9 V, $\text{Bi}^{3+} = 500 \mu\text{g l}^{-1}$, deposition time = 120 s, constant current = $1 \mu\text{A}$.

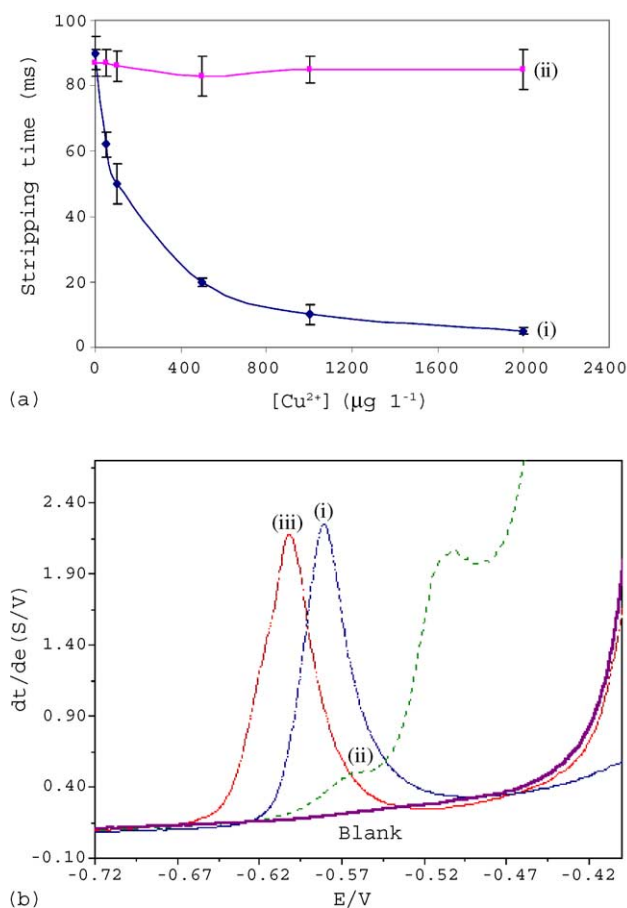


Fig. 2. (a) Plot showing the effect of copper on the stripping response of lead(II) at BFSPCE (i) without ferricyanide added and (ii) with ferricyanide added. (b) Stripping chronopotentiograms of $100 \mu\text{g l}^{-1}$ lead(II) in the presence of (i) $0 \mu\text{g l}^{-1}$ copper(II), (ii) $2000 \mu\text{g l}^{-1}$ copper(II) and (iii) $2000 \mu\text{g l}^{-1}$ copper(II) + 0.1 mM ferricyanide. Base curve: blank response for 0.1 M HCl electrolyte. Other experimental conditions are as in Fig. 1.

Table 2

Results data for lead(II) determination on BFSPCE showing the benefit of adding 0.1 mM ferricyanide to the acetic acid extract of soil samples (mean \pm S.D.)

Sample	Dilution factor ($\times 39$)	Reference method ($\mu\text{g l}^{-1}$)	CCSCP–BFSPCE (without ferricyanide) ($\mu\text{g l}^{-1}$)	CCSCP–BFSPCE (with ferricyanide) ($\mu\text{g l}^{-1}$)	Copper reference value ($\mu\text{g l}^{-1}$)
A1	10	127 ± 4	33 ± 2	109 ± 5	520
A2	50	124 ± 4	27 ± 1	111 ± 7	760
A3	5	56 ± 2	nd	49 ± 2	496
A4	25	126 ± 1.5	86 ± 5	130 ± 4	50
A5	20	77 ± 1.4	43 ± 2.5	62 ± 4	13
A6	2.5	58 ± 1.3	nd	55 ± 2	398
A7	10	70 ± 0.8	nd	62 ± 3	14
A8	5	71 ± 1.5	nd	77 ± 5	71

nd = not detected; BFSPCE = bismuth film screen-printed carbon electrode; CCSCP = constant current stripping chronopotentiometry; electrolyte = 0.5 M ammonium acetate + 0.1 M HCl.

3.2. Eliminating the copper interference

To successfully circumvent the detrimental effect of copper(II), the selective masking of copper was carried out using ferricyanide. The concentration of ferricyanide added was determined by studying the effect of copper ($2000 \mu\text{g l}^{-1}$) on lead(II) (60 and $200 \mu\text{g l}^{-1}$) solutions (Fig. 1). A concentration of 0.1 mM of ferricyanide was found to be appropriate for suppressing the copper interference. As can be seen from the graphical plot in Fig. 2a, the adverse effect of various concentrations of copper(II) on the stripping response of $100 \mu\text{g l}^{-1}$ lead(II) was eliminated when 0.1 mM ferricyanide was added to the test solution. The stripping chronopotentiograms in Fig. 2b also illustrates this benefit with the lead-stripping peak suppressed in the presence of copper, recovering and revealing a peak response similar to that obtained in the absence of copper. Examinations of both the electrolyte solutions of 0.1 M HCl and 0.5 M ammonium acetate + 0.1 M HCl (pH 4.6) for trace lead and copper, revealed no extrinsic contamination by impurities present in the analytical reagent.

Although other authors [19,20] have used ferrocyanide and cyanide ions as masking agent for copper, in this work we have gone further by applying another similar reagent, ferricyanide, which is less toxic compared to cyanide, to neutralise the action of copper on an electrode surface like BFSPCE, which has a different nature and structure to that of bare carbon electrodes and mercury film electrodes.

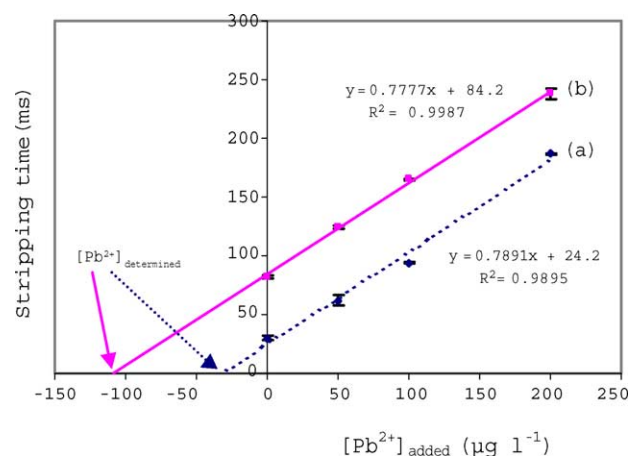


Fig. 3. Typical standard addition plots showing the benefit of eliminating the interference of copper on the determination of lead(II) in soil sample at BFSPCE. (a) No ferricyanide added, (b) ferricyanide added. Electrolyte = 0.5 M ammonium acetate + 0.1 M HCl, other experimental conditions as in Fig. 1.

3.3. Application to soil extract samples

As interference from copper(II) can undermine the utilisation of BFSPCE for analysing lead(II) in certain matrices where copper present is significant, the practicality of ferricyanide as a masking agent for suppressing the copper interference effect at BFSPCE was examined. Tables 2 and 3 show the results obtained by adding 0.1 mM

Table 3

Concentration data for lead(II) determination on BFSPCE showing the benefit of adding 0.1 mM ferricyanide to the aqua regia extract of soil samples (mean \pm S.D.)

Sample	Dilution factor ($\times 390$)	Reference method ($\mu\text{g l}^{-1}$)	CCSCP–BFSPCE (without ferricyanide) ($\mu\text{g l}^{-1}$)	CCSCP–BFSPCE (with ferricyanide) ($\mu\text{g l}^{-1}$)	Copper reference value ($\mu\text{g l}^{-1}$)
B1	500	59 ± 0.1	17 ± 1.2	48 ± 3	9
B2	500	73 ± 0.4	22 ± 2	62 ± 3	21
B3	500	102 ± 0.1	30 ± 2	96 ± 7	20
B4	500	103 ± 0.1	36 ± 2	98 ± 6	16
B5	25	97 ± 0.9	nd	86 ± 4	74
B6	10	82 ± 1.8	nd	74 ± 5	71
B7	50	56 ± 0.9	16 ± 2.3	58 ± 4	26
B8	50	63 ± 1	19 ± 2	69 ± 3	29
B9	10	66 ± 1	24 ± 1.6	50 ± 4	54

nd = not detected; BFSPCE = bismuth film screen-printed carbon electrode; CCSCP = constant current stripping chronopotentiometry; electrolyte = 0.5 M ammonium acetate + 0.1 M HCl.

ferricyanide to the different soil sample extract solutions. The concentration data obtained, closer to the reference values generated with ICP–MS illustrate the benefit of using ferricyanide when analysing the different sample extracts. The standard addition plots shown in Fig. 3 also illustrate this benefit with the methodology involving the addition of ferricyanide, having a higher intercept value than one without the addition of ferricyanide. This aids the deduction of the right amount of lead(II) in the soil extracts.

4. Conclusion

To eliminate the detrimental effect of copper(II) on lead(II), excess amount of ferricyanide was used to complex the copper(II). Complete recovery of the lead stripping response in the presence of copper was obtained when 0.1 mM ferricyanide was added to the test solution. The concentration data obtained by adding 0.1 mM ferricyanide to the different sample extract solutions is closer to the ICP–MS results, illustrating the benefit of masking the copper present when analysing the different sample extracts.

The results obtained within this investigation, has gone a long way in providing a relatively accurate and precise screening device for lead determination in extracted soil samples. The electrode configuration and it being a single-use electrode, makes it in combination with the detection technique, CCSCP, a convenient screening tool for lead at contaminated sites.

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