

Determination of trace aluminium by adsorptive stripping voltammetry on a preplated bismuth-film electrode in the presence of cupferron

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Abstract

This work reports the use of adsorptive stripping voltammetry (AdSV) for the determination of aluminium on a rotating-disc bismuth-film electrode (BiFE). Al(III) ions in the non-deoxygenated sample were complexed with cupferron and the complex was accumulated by adsorption on the surface of the preplated BiFE. The stripping step was carried out by using a square-wave (SW) potential-time voltammetric excitation signal. The experimental variables as well as potential interferences were investigated and the figures of merit of the method were established. Using the selected conditions, the 3σ limit of detection for aluminium was $0.5 \mu\text{g l}^{-1}$ at a preconcentration time of 240 s and the relative standard deviation was 4.2% at the $5 \mu\text{g l}^{-1}$ level for a preconcentration time of 120 s ($n=8$). The accuracy of the method was established by analysing water and metallurgical samples.

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1. Introduction

Aluminium is a metal with considerable biological, environmental and industrial significance and, hence, sensitive, selective and precise methods are required for its determination in various matrices. The utility of direct voltammetric approaches for the determination of aluminium is limited by the very negative reduction potential of the Al(III) cation which is very close to the reduction potential of hydrogen, potassium, sodium and barium [1]. In order to shift the reduction potential of aluminium to more positive potentials, complexation with di-*o*-hydroxyazo dyes has been employed prior to the polarographic determination of aluminium [2]. An alternative indirect electrochemical strategy for the determination of aluminium is to monitor the change (reduction) in the voltammetric response of an electroactive ligand that forms a complex with aluminium [3]. By far the most sensitive electrochemical approaches are those based on accumulation of aluminium on the electrode

prior to electrochemical detection. The most common variant of this methodology, adsorptive stripping voltammetry (AdSV), involves complexation of the metal with a surface-active ligand followed by adsorptive preconcentration of the complex on the electrode under conditions of enhanced mass-transfer. Glassy carbon electrodes have been used for the accumulation of aluminium as its 8-hydroxyquinoline [4] or tetramethylammonium chloride [5] complexes. Another accumulation scheme with similar benefits in terms of sensitivity relies on immobilising aluminium-specific ligands on solid electrodes, resulting in chemically modified electrodes (CMEs). Glassy carbon, sol-gel or screen-printed electrodes chemically modified with alizarin or pyrocatechol violet have been reported [6–8]. The use of mercury electrodes in AdSV imparts a significant improvement in sensitivity. The commonest mercury electrode is the hanging-mercury drop electrode (HMDE) in conjunction with which various complexing agents have been investigated and applied in AdSV of aluminium, including Palatine Chrome Black 6BN, Chromazurol S and Eriochrome Black T [9], Solochrome Violet RS [10], Arsenazo III [11], 1,2-dihydroxy-anthraquinone-3-sulphonic acid (DASA) [1], cupferron [12], calmagite [13],

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morin [14] and alizarin [15]. The mercury-film electrode (MFE), prepared by electroplating a thin “film” of mercury on a solid support, has also been reported in conjunction with cupferron [16]. Recently, the bismuth-film electrode (BiFE), prepared by electroplating a thin layer of bismuth on a solid electrode, has been proposed for anodic stripping voltammetry (ASV) and has been shown to offer comparable performance to the MFE [17–19]. Over the last 2 years, a few selected applications of AdSV on the BiFE have also been reported with promising results [20–23]. The main drawback of the BiFE, as opposed to mercury electrodes, is the more negative oxidation potential of bismuth that limits the anodic range of the BiFE; the typical anodic limit of a BiFE at pH 4.5 is -0.25 V while it could be as negative as -0.55 V in strongly alkaline media [24]. As many adsorbates accumulate and reduce at potentials in the range of 0 to -0.6 V, the BiFE is not as universally applicable as mercury electrodes in AdSV. This is the main reason for which the reported applications of AdSV on the BiFE involve species with rather negative accumulation and redox potentials (e.g. complexes of Ni and Co with dimethylglyoxime [20], of Cr with DTPA [21] and of Cr and uranium with cupferron [22,23]). Despite this limitation, it has been shown that the BiFE is more tolerant to the presence of dissolved oxygen than the MFE [20,22]. This fact, combined with the low toxicity of bismuth, offers great scope for the preparation of sensors based on BiFEs.

In this work, we have investigated the utility of the BiFE for the determination of aluminium by AdSV in the presence of cupferron. Previous investigations on the HMDE have highlighted the advantages of using cupferron as a ligand for aluminium determination (since it offers high sensitivity, fast complexation kinetics, reduced interferences from co-existing metals and satisfactory chemical stability) [12,16]. All the parameters associated with the determination were investigated and the developed AdSV method was applied to water and metallurgical samples.

2. Experimental

2.1. Instrumentation

Voltammetric measurements were performed with a home-made potentiostat interfaced to a PC through a 6025E PCI multi-purpose interface card (National Instruments, Austin, TX). The experimental sequence was fully automated and controlled by the PC using a control application developed in LabVIEW 5.1 (National Instruments) as reported previously [25].

The voltammetric cell was a standard 50 ml glass vial (Metrohm, Switzerland) equipped with an Ag/AgCl reference electrode and a Pt counter electrode. An electrode rotator (Metrohm 628-10) or a magnetic stirrer was used during the preconcentration and cleaning steps.

The glassy carbon (GC) working electrode (3 mm in diameter) was from Metrohm. Before use, the electrode was pol-

ished with a water slurry of $0.3 \mu\text{m}$ Al_2O_3 and rinsed with ethanol and water. A carbon paste (CP) electrode was prepared by mixing thoroughly 1.5 g of graphite powder with 1.2 ml of Nujol and filling a syringe-type holder with the resulting paste; the diameter of the active surface was 5 mm. A smooth surface was formed by gently rubbing the electrode on a clean filter paper. The impregnated graphite (IG) electrode (6 mm in diameter) was donated by M. Halama (University of Cosice, Slovakia) and was polished by rubbing on a clean filter paper before use.

2.2. Reagents and glassware

All the chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany). De-ionised water was used throughout. Working solutions of aluminium and other metals were prepared from 1000 mg l^{-1} atomic absorption standard solutions after appropriate dilution with de-ionised water. The stock supporting electrolytes were 1 mol l^{-1} ammonia buffer (pH 9.2), 1 mol l^{-1} acetate buffer (pH 4.5), 1 mol l^{-1} KCl, 0.01 mol l^{-1} EDTA and 0.2 mol l^{-1} PIPES buffer (pH 7). A 0.1 mol l^{-1} solution of cupferron was prepared by dissolving the appropriate amount of the solid compound in de-ionised water. The bismuth and mercury plating solutions were 100 mg l^{-1} Bi(III) or Hg(II) in acetate buffer (1 mol l^{-1} in total acetate species, pH 4.5). A 1000 mg l^{-1} stock solution of Triton X-100 (BDH, Poole, England) was prepared in water.

2.3. Procedure

2.3.1. Preparation of the samples

The manganese bronze sample was purchased from Hoepfner Gebr. (Hamburg, Germany) and the dowmetal sample from Thorn Smith (Michigan, USA); their certified aluminium content was 8.03 and 2.90% (w/w), respectively. 0.2 g of the sample was dissolved in 5 ml of 6 mol l^{-1} HNO_3 under mild heating and this solution was diluted to 1 l. For the voltammetric analysis, $10 \mu\text{l}$ of the sample, 1.0 ml of 1 mol l^{-1} KCl, 1.0 ml of 0.2 mol l^{-1} PIPES buffer and 18.0 ml of de-ionised water were placed in the cell and the determination was carried out as described in the following section.

The tap water sample was collected from taps in our laboratory while the mineral water sample was purchased from a local store. Analysis was carried out after filtering the sample through a $0.22 \mu\text{m}$ PTFE filter in order to determine the labile aluminium fraction. For the voltammetric analysis, 5.0 ml of water sample, 1.0 ml of 1 mol l^{-1} KCl, 1.0 ml of 0.2 mol l^{-1} PIPES buffer and 13.0 ml of de-ionised water were placed in the cell and the determination was carried out as described in the following section.

2.3.2. Determination of Al(III)

The bismuth or the mercury films were preplated from the 100 mg l^{-1} Bi(III) or Hg(II) solutions, respectively, for 4 min on the working electrode at -1.0 V. The electrodes

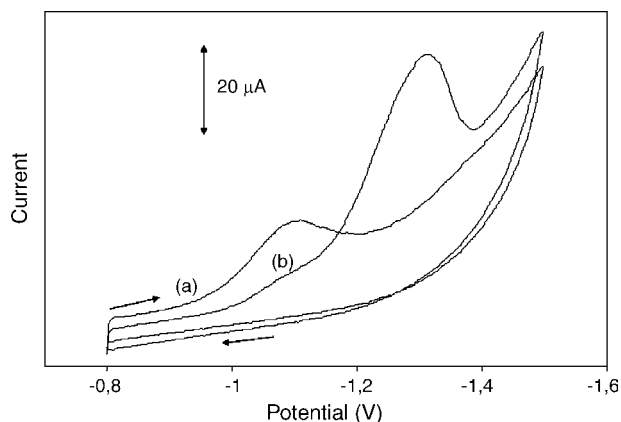


Fig. 1. Cyclic voltammograms in a solution containing (a) $0 \mu\text{g l}^{-1}$ and (b) $15 \mu\text{g l}^{-1}$ of Al(III) after preconcentration for 60 s on a preplated BiFE in the presence of 0.04 mol l^{-1} cupferron; deposition potential: -0.8 V ; supporting electrolyte: 0.01 mol l^{-1} PIPES/ 0.05 mol l^{-1} KCl; potential scan rate: 100 mV s^{-1} ; electrode rotation speed: 500 rpm.

were immersed into the sample solution (20.0 ml), the sample was spiked with the required volume of cupferron solution (to give the desired final cupferron concentration) and the preconcentration was carried out at the selected preconcentration potential under stirring or rotation of the electrode. After accumulation, the solution was left to equilibrate for 10 s and a cathodic SW scan to a final potential of -1.45 V was applied on the working electrode while the voltammogram was recorded. After the scan, the bismuth film was cleaned of the remaining adsorbed complexes by keeping the potential of the electrode at -1.45 V for 10 s under rotation or stirring. After the cleaning step, standard additions of aluminium were made as required and the measurement procedure repeated on the same bismuth or mercury film. After a series of measurements the bismuth or mercury film was removed by wiping the electrode with a wet tissue.

3. Results and discussion

Two successive cyclic voltammogram (in the range -0.8 to -1.5 V) of a solution containing cupferron after preconcentration at -0.8 V on a BiFE in the presence and absence of Al(III) are shown in Fig. 1. In the absence of Al(III), a small cathodic peak was obtained at -1.11 V (Fig. 1(a)); this peak was attributed to the reduction of the free cupferron ligand in agreement with earlier studies on the HMDE [26] and the MFE [16]. In the presence of Al(III), the cathodic scan revealed a much more prominent peak at -1.31 V arising from the reduction of Al(III) in its complex with cupferron (Fig. 1(b)) while the peak at -1.11 V due to the reduction of free cupferron was significantly reduced in height and was hardly discernible. No peaks were observed in the anodic scan suggesting that the reduction of the complex was an irreversible process. Irreversibility of the reduction process was also implied by the shift of peak potentials to more negative

values upon increasing the scan rate. Fast desorption of the complex from the electrode surface was indicated by lower peaks obtained in successive scans that immediately followed the first scan (not shown). Indeed, it was found that holding the electrode potential at -1.45 V for 10 s was enough to ensure efficient cleaning of the electrode surface before initiating the next adsorption/stripping cycle. This cleaning step allowed the same bismuth film to be used for a series of experiments (e.g. a number of accumulation/stripping/cleaning cycles in a standard additions experiment).

Three substrates (glassy carbon, impregnated graphite and carbon paste) were compared for the determination of aluminium under identical conditions. The highest peak and flattest baseline was obtained on the glassy carbon electrode which was selected for subsequent experiments although carbon paste also produced a satisfactory response and could be used as an alternative substrate.

The bismuth film plating time effectively controlled the thickness of the bismuth film. The effect of the bismuth plating time was investigated in the range 30–480 s. The aluminium peak increased with increasing bismuth deposition time up to 240 s and remained almost constant at higher deposition times and, additionally, the width of the peak increased at higher deposition times. So, a bismuth deposition time of 240 s was found to offer the best combination between sensitivity and peak sharpness.

Earlier studies of the determination of aluminium with cupferron on mercury electrodes have utilised a PIPES buffer at pH 7 [12,16] but no study in other media was carried out. On the BiFE, a small peak for the Al(III)–cupferron complex was obtained at -1.03 V in acidic medium (0.1 mol l^{-1} acetate buffer, pH 4.5) but the sensitivity was low. No aluminium stripping peak was obtained on the BiFE in alkaline medium (0.1 mol l^{-1} ammonia buffer, pH 9.2). In earlier studies of adsorption of the Al(III)–cupferron complex on mercury electrodes, the PIPES buffer concentration was variable (ranging from 10^{-3} to 0.05 mol l^{-1}) [12,16]. It was found that the concentration of the PIPES buffer did affect both the aluminium stripping peak shape and peak height on the BiFE. The lowest concentration of the buffer ($10^{-3} \text{ mol l}^{-1}$) proved unsuitable, presumably due to the low conductivity of the solution. On the other hand, higher concentration of the PIPES buffer (0.05 mol l^{-1}) produced wide aluminium stripping peaks. Therefore, in order to achieve high conductivity at an intermediate PIPES concentration ($\sim 0.01 \text{ mol l}^{-1}$), KCl at different concentrations (ranging from 0.025 to 0.2 mol l^{-1}) was also added to the solution. The effect of the PIPES and KCl concentrations is illustrated in Fig. 2 and the results dictated the use of a mixed 0.01 mol l^{-1} PIPES/ 0.05 mol l^{-1} KCl solution.

The effect of dissolved oxygen was studied by performing AdSV analysis in a solution containing Al(III) on both a BiFE and an MFE with and without solution deoxygenation by purging with nitrogen (Fig. 3). As demonstrated in Fig. 3(a), on the BiFE the aluminium stripping peak in the presence of oxygen was 70% of the peak height in the deoxy-

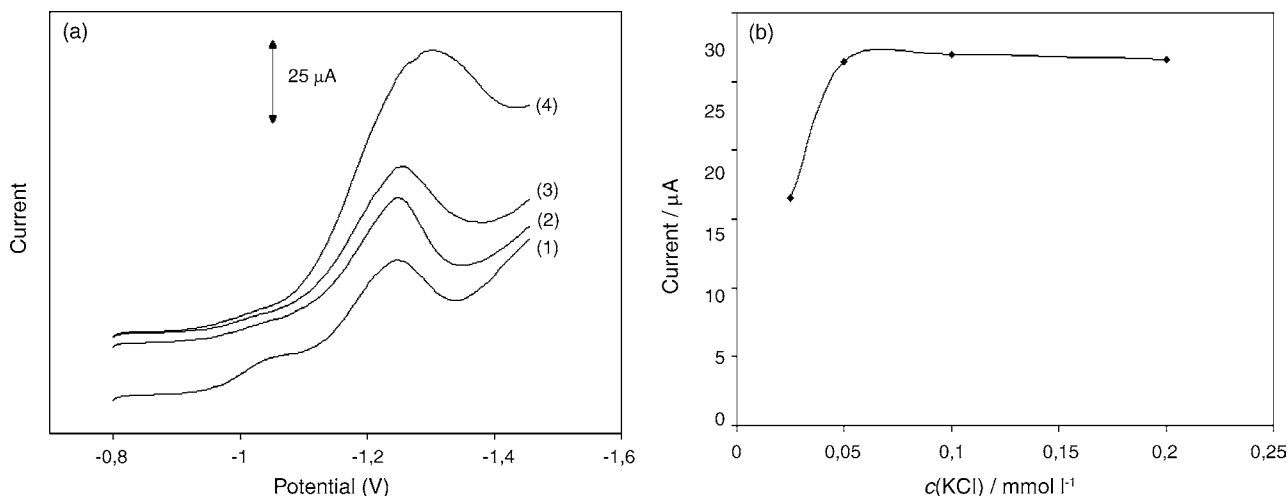


Fig. 2. The effect of: (a) the PIPES concentration ((1) 0.005; (2) 0.01; (3) 0.02; (4) 0.05 mol l⁻¹); (b) the KCl concentration on the AdSV response in a solution containing 5 μg l⁻¹ of Al(III) after preconcentration for 120 s on a BiFE; SW frequency: 25 Hz; pulse height: 40 mV; scan increment: 8 mV; cupferron: 0.06 mol l⁻¹; other conditions as in Fig. 1.

generated solution. On the contrary, on the MFE the aluminium stripping peak in the unpurged solution was only 30% of the peak height in the purged solution (Fig. 3(b)). In addition, the absolute stripping peak height was higher on the BiFE compared to the MFE but, on the other hand, the background current was higher on the BiFE. The improved performance of the BiFE in unpurged solutions was a significant advantage since the time-consuming deoxygenation step was obsolete. Thus, for the rest of this work, direct measurements of samples without solution purging was adopted.

The effect of the cupferron concentration on the Al peak was investigated in the range 0.01–0.14 mmol l⁻¹ and is illustrated in Fig. 4. At low cupferron concentrations, the aluminium peak height increased with increasing ligand concentration and reached a maximum for cupferron concentrations

in the region 0.03–0.05 mmol l⁻¹. At cupferron concentrations higher than 0.06 mmol l⁻¹, the aluminium peak height started to decrease and became wider and this phenomenon was attributed to the competition of the free ligand for free adsorption sites on the electrode surface. The assumption of competitive adsorption was supported by the observation that, as the cupferron concentration was increased, the reduction peak of free cupferron at -1.1 V became more prominent. Thus, a cupferron concentration of 0.04 mmol l⁻¹ was selected.

The effect of the preconcentration potential on the aluminium peak height was studied in the range -0.3 to -1.1 V. The peak height was completely suppressed at -0.3 V presumably owing to the reduction of the bismuth coating itself. The peak height remained essentially constant in the range

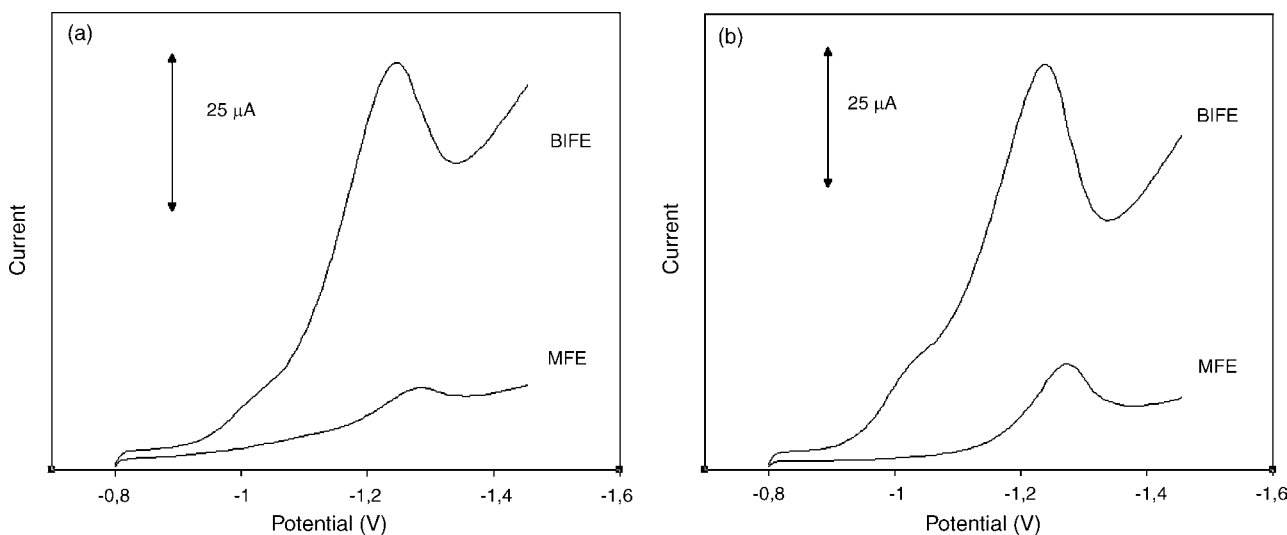


Fig. 3. SW voltammograms in a solution containing 5 μg l⁻¹ of Al(III) after preconcentration for 120 s on an MFE and a BiFE: (a) before deoxygenation and (b) after deoxygenation; conditions as in Fig. 2.

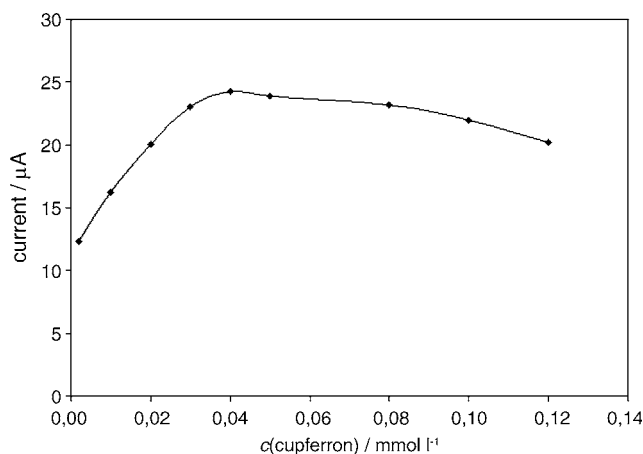


Fig. 4. The effect of the cupferron concentration on the AdSV response in a solution containing $5 \mu\text{g l}^{-1}$ of Al(III) after preconcentration on a BiFE for 120 s; conditions as in Fig. 2.

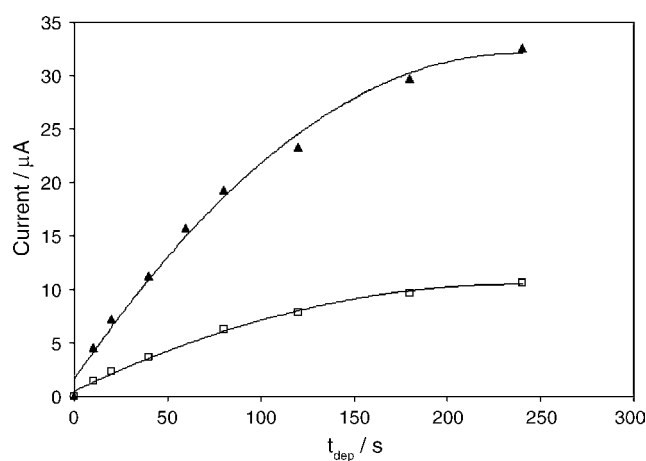


Fig. 5. Effect of the preconcentration time on the aluminium peak height in a solution containing: (▲) $1 \mu\text{g l}^{-1}$; (□) $4 \mu\text{g l}^{-1}$ of Al(III) after preconcentration on a BiFE; conditions as in Fig. 2.

–0.4 to –1.0 V, indicating a potential independent adsorption efficiency. However, at preconcentration potentials more negative than –1.1 V, the peak height was suppressed since the complex was immediately reduced upon adsorption.

For an adsorption step controlled by mass-transport of the adsorbate, it has been shown that the surface concentration of the adsorbate species (and consequently the peak current) will increase with increasing preconcentration time until the saturation surface concentration is gradually reached [27]. The effect of the preconcentration time on the aluminium stripping peak height was studied in the range 0–520 in solutions containing 1 and $4 \mu\text{g l}^{-1}$ of Al(III) as illustrated in Fig. 5. The peak current increased initially almost linearly with increasing deposition time while at higher deposition times the plots started to level-off as the equilibrium surface concentration of the adsorbed complexes was approached. As expected, the peak current corresponding to the saturation surface concentration was lower at the lower aluminium concentration.

The SW parameters investigated were the frequency, the pulse height and the scan increment. The effect of the frequency and the scan increment were studied in the range 12.5–100 Hz and 1–16 mV, respectively. The aluminium peak height increased with increasing SW frequency and scan increment due to the increase in the effective scan rate. At frequencies higher than 50 Hz the background slope deteriorated and this was attributed to the shorter pulse widths associated with higher frequencies. Increase in the effective scan rate (caused by an increase in either the frequency or the scan increment) resulted in a shift of the peak potentials to the negative direction. The effect of the pulse height was examined in the range 10–80 mV. The aluminium peak height increased with increasing pulse height and, at the same time, the peak potential was shifted to the positive direction and the background current increased. The best compromise between sensitivity, background and peak width was achieved with the following conditions: frequency, 25 Hz; increment, 8 mV; pulse height, 40 mV.

Linearity was dependent on the concentration range and preconcentration time. For preconcentration times of 240, 120 and 60 s, the linear concentration ranges were 0.5–5, 1–10 and 2–20 $\mu\text{g l}^{-1}$ and the analytical sensitivities were, 9, 5.7 and $3.3 \mu\text{A}/\mu\text{g l}^{-1}$, respectively. The limit of detection was $0.5 \mu\text{g l}^{-1}$ Al(III) at the 3σ level (for 240 s accumulation time) and the relative standard deviation was 4.2% at the $5 \mu\text{g l}^{-1}$ level with 120 s of preconcentration ($n=8$).

Surfactants and metal cations present in most real samples are the more serious interferences in stripping analysis. Triton X-100, which was used as a “model” surfactant, did not affect the analysis at concentrations up to 4mg l^{-1} but at higher concentrations interfered by causing distortion of the aluminium peak. Metal ions can interfere with the measurement by complexing with cupferron or by producing reduction peaks that overlap with, or even completely suppress, the aluminium peak. A number of metal ions that could potentially interfere were examined; Pb(II), Hg(II), Cu(II), Fe(II), Cd(II), Ti(IV), Ca(II) and Mn(II) added at a 10-fold mass concentration excess over Al(III) did not interfere (the criterion for interference was a $\pm 8\%$ error in the peak height

Table 1
Results for the determination of aluminium in different samples

Sample	Al found (AdSV) ^a	Al found (AAS) ^a	Al reference content
Water samples ($\mu\text{g l}^{-1}$)			
Tap water	14 ± 1	15 ± 2	–
Mineral water	ND ^b	ND ^b	–
Metal samples (Al % (w/w))			
Dowmetal	3.0 ± 0.3	3.1 ± 0.3	2.90
Bronze	7.8 ± 0.8	^c	8.03

^a Mean of three determinations.

^b Not detected.

^c Quantification not possible due to serious interference by Cu.

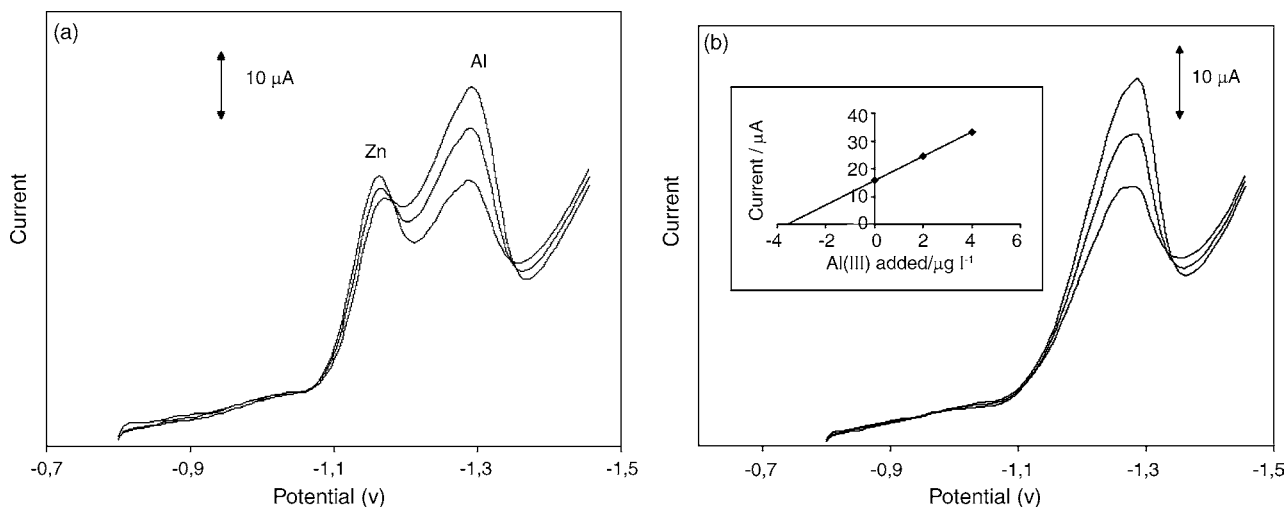


Fig. 6. SW voltammogram for the determination of aluminium by the method of standard additions in a tap water sample after preconcentration for 120 s on a BiFE: (a) without EDTA; (b) after addition of $4 \times 10^{-5} \text{ mol l}^{-1}$ EDTA. From below: sample and two successive standard additions of $2 \mu\text{g l}^{-1}$ Al(III); conditions as in Fig. 2.

of a solution containing $5 \mu\text{g l}^{-1}$ of Al(III). Zn(II) at a 10-fold mass concentration excess over Al(III) interfered with the determination by producing a diffusion-controlled peak at -1.18 V which appeared as a shoulder on the anodic side of the aluminium peak. However, this interference was easily alleviated by addition of EDTA that completely suppressed the zinc peak but did not affect the aluminium peak. Cr(III) produced a stripping peak at -0.95 V which was well separated from the aluminium peak. U(VI) was the only serious interference by producing a stripping peak at -1.21 V which severely overlapped with the aluminium peak.

The accuracy of the method was assessed by determining aluminium in manganese bronze and dowmetal samples as well in tap water and mineral water samples. The results are shown in Table 1. For both the metal samples, the initially digested sample was extensively diluted and no interference from matrix components was observed. A series of voltammograms after standard additions for the determination of aluminium in tap water is illustrated in Fig. 6(a). A large, diffusion-controlled interfering peak due to reduction of Zn(II) cations appeared on the anodic side of the aluminium peak in agreement with the interference study conducted previously. However, as shown in Fig. 6(b), the addition of EDTA completely suppressed the zinc peak and allowed convenient quantification of aluminium.

As a conclusion, the proposed voltammetric method utilising a BiFE has been shown to offer an alternative to mercury electrodes for the determination of aluminium. Indeed, the main attraction of the BiFE over various mercury-based electrodes is the negligible toxicity of bismuth. In addition, the BiFE presents greater tolerance to dissolved oxygen than the MFE. As demonstrated in the present work, the higher background current exhibited by the BiFE close to the aluminium peak (due to the more pronounced hydrogen evolution) is accompanied by higher analytical sensitivity compared to

the MFE; as a result, the limits of detection with the two electrodes are similar [16].

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