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On the suppression of zinc–copper interactions in square wave anodic stripping voltammetry in flowing solution by addition of gallium ions

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Abstract

The problems arising from the formation of copper–zinc intermetallic compounds in square wave anodic stripping voltammetry at wall-jet mercury thin-film electrodes in continuous flow systems have been investigated. These effects are reduced to zero by spiking the analyte solution with gallium ions and ensuring a sufficiently low value of pH, either by using acetate buffer or acidifying the generally-used sodium perchlorate electrolyte. Advantages of this approach are assessed, as are the benefits of stopping solution flow during the determination step of each experiment.

Keywords: Anodic stripping voltammetry; Wall-jet electrode; Square wave voltammetry; Copper; Zinc; Gallium; Trace metals

1. Introduction

Anodic stripping voltammetry is a very convenient method for determining trace concentrations of a number of heavy metal ions in solution, including copper and zinc [1,2]. Although copper ions can be reduced to the zero oxidation state in the preconcentration step at potentials of the order of −0.6 V vs. SCE, for zinc a potential around −1.3 V vs. SCE is necessary, which means that mercury electrodes have to be employed. Difficulties arise in the simultaneous measurement of the concentrations of copper and zinc in solutions containing both ions: copper–zinc intermetallic compounds of varying composition are formed in the mercury phase [3,4] which are reoxidised at a potential close to that of copper itself. This problem is more evident when employing mercury thin film electrodes (MTFE's) rather than hanging or static mercury drop electrodes, owing to the higher concentration of dissolved metal in mercury thin films [5].

A number of approaches have been suggested to eliminate the formation of copper–zinc compounds in various types of experimental systems and for different voltammetric waveforms in the determination step: potential step, linear scan and differential pulse, as described below. Square wave voltammetry, which offers the advantages of no (or, at least, very much reduced) necessity

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of sample deoxygenation and of increased scan rate has not been investigated at electrodes in flowing solution in this context.

A first strategy involves determinations in a twin-electrode thin-layer cell. By judicious choice of applied potentials, the exhaustive deposition of copper on one electrode is followed by the deposition of zinc on the second electrode; there is thus physical separation between the constituents [6].

A second strategy employs a two-part experiment involving anodic stripping voltammetry with collection, exemplified by quantition at a wall-jet ring-disc mercury thin film electrode using a potential step to strip the deposited metals from the disc and which are then collected at the ring in the determination step [7]. In the first, copper is preconcentrated by deposition at a potential of −0.6 V and quantified through redissolution and collection. Following this, copper and zinc are both deposited at −1.3 V followed by quantition of the sum of the concentrations. Subtraction of the two signals lead to the zinc ion concentration.

In a third strategy, a copper complexing agent is added (cyanide or Triton X-100) enabling the determination of zinc without interference from copper [8]. Copper is determined by preconcentration at a less negative potential.

A fourth strategy consists of using the standard addition method and analysing the results through chemometrics in such a way that interference effects are corrected for [9]. Whilst the compensation can theoretically be 100%, in practice accurate elimination of interferences requires the detailed knowledge of the stoichiometry of the intermetallic compounds formed and their relative concentrations. In [9], good results were obtained, but only for concentrations of the order of 5 μg dm^{-3} ($\sim 8\times10^{-8}$ mol dm^{-3}).

Finally, one can add an element in cationic form to solution which, on being reduced in the preconcentration step, forms a more stable intermetallic compound than that between the two elements in question [10–12]. In the case of copper and zinc at a mercury electrode, the element of choice is usually gallium which preferentially interacts with copper, e.g. [11].

The objective of this work was to investigate the suppression of Cu–Zn interferences in square wave anodic stripping voltammetry (SWASV) at a wall-jet electrode mercury thin-film electrode in a continuous flow system. Particular advantages of this electrode system are no build-up of products of electrode reactions, no reagent depletion and direct applicability to on-line monitoring. The SWASV of lead and cadmium at a wall-jet electrode has already been studied and leads to practical detection limits in the nanomolar range [13]. The effect of the addition of gallium and its concentration was investigated, and the merits of this approach assessed.

2. Experimental

Experiments were performed using a computer-controlled PSTAT10 Autolab potentiostat (Eco-Chemie, Utrecht, Netherlands). A wall-jet cell (Oxford Electrodes) contained a glassy carbon working electrode of diameter 3.0 mm, which was polished prior to mercury film formation with diamond spray (Kemet International) down to 1 μm particle size on a polishing cloth. The nozzle-electrode separation was maintained at 3.0 mm in all experiments and the nozzle diameter was 0.345 mm. A platinum tube in the cell exit served as counter electrode and the Ag/AgCl (3.0 M KCl) reference electrode compartment was separated from the main body of the cell by a porous glass frit.

The continuous flow system consisted of a Gilson Miniplus 3-way peristaltic pump (flow rate regulated between 0.035 and 0.045 cm) together with a 3 m length of PTFE tubing and a partially filled glass ball for pulse damping.

All reagents were of analytical grade and solutions were made with Millipore Milli-Q ultrapure water, resistivity >18 MΩ cm. Microlitre volumes of stock solutions of Cu, Zn and Ga (10^{-3} M) were added to electrolyte solution (0.10 M sodium perchlorate or 0.10 M acetate buffer) using Gilson micropipettes immediately before analysis and after appropriate dilution. The mercury thin film was formed under continuous flow conditions from a solution containing 10^{-4} M Hg^{2+} in 0.1 M $NaClO_4$ supporting electrolyte. All experiments were conducted at room temperature (22°C–23°C).

3. Results and discussion

Typical square wave voltammograms for the SWASV of copper and zinc separately and in a mixture at a wall-jet mercury thin film electrode without addition of gallium ions are shown in Fig. 1. The shapes of the SW responses for the metal ions separately in Fig. 1(a) show some hydrodynamic effects on peak shapes. Nevertheless, the half-width of the copper peak shows it conforms closely to a reversible oxidation reaction (peak half-width= 90.5 mV in stationary solution for small square wave amplitude [14]) whereas that of zinc shows slower electrode kinetics. It is easily verified for the mixture of the two ions as shown in Fig. 1b that the height of the zinc peak is diminished, the half-width remaining at ~95 mV, and that of the "copper" peak increased in the mixture, as is its width from 45 to 65 mV, due to the formation of copper–zinc intermetallic compounds and their oxidation at a potential similar to that of copper.

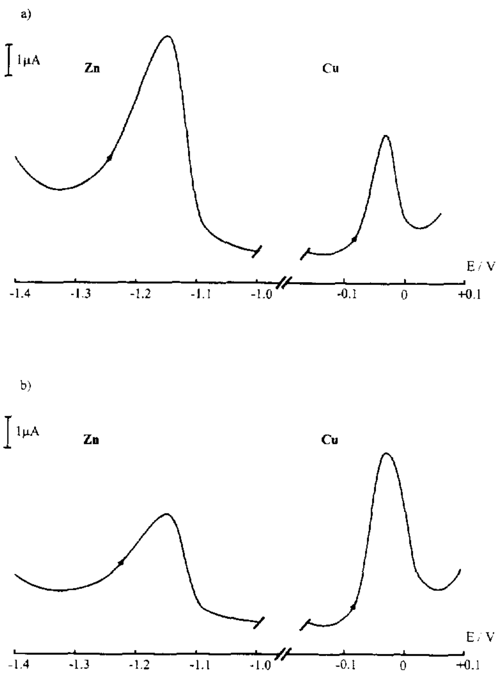

Fig. 1. SWASV of Cu and Zn at wall-jet MTFE's (a) separately and (b) as a mixture. $[Cu^{2+}]=[Zn^{2+}]=5\times10^{-8}$ mol dm^{-3}; $[Hg^{2+}]=10^{-4}$ mol dm^{-3}; 0.10 M $NaClO_4$, $V_f=0.035$ cm^3 s^{-1}; oxygen not removed. $E_{dep}=-1.4$ V, $t_{dep}=120$ s; SW parameters: $f=100$ Hz, $h=30$ mV, scan increment=2 mV.

For the two ions analysed separately, linear dependences on deposition time, t_{dep} (for deposition of copper at −0.5 or −1.1 V and of zinc at −1.3 V), square wave amplitude, h, and frequency, f, were observed and good detection limits and sensitivities obtained. Better in situ mercury film formation was found at −1.1 V which reflected itself in a 20% greater sensitivity for copper than using −0.5 V deposition potential; nevertheless, good calibration curves were obtained for both deposition potentials. Calibration curves under optimised conditions of $E_{dep}=1.4$ V, $t_{dep}=120$ s; $f=100$ Hz, $h=30$ mV and $V_f=0.035$ cm^3 s^{-1} have slopes of 0.122 ± 0.001 A $mmol^{-1}$ dm^3 ($r=0.99987$) and 0.309 ± 0.001 A $mmol^{-1}$ dm^3 ($r=0.99995$) for copper and zinc with zero concentration intercepts (0.040 ± 0.077 and 0.015 ± 0.079 μA, respectively). Theoretical detection limits based on three times the standard deviation are $\sim2\times10^{-11}$ mol dm^{-3} although the practical detection limit is ~1 nmol dm^{-3}; the linear range extends up to 1 μmol dm^{-3}.

In mixtures, there was a tendency for the appearance of a wide peak between −800 and −200 mV in perchlorate supporting electrolyte, which can compromise the determination of the height of the copper peak at low concentration, besides negatively affecting lead and cadmium quantification in mixtures of all four elements. Note that in the experimental conditions used for cadmium and lead only, [13], deposition preconcentration was done at less negative potentials (−1.0 V) and the peak did not appear. It was found that this wave could be removed by partially deoxygenating the solution and/or stopping solution flow during the reoxidation step, suggesting that this wave is due to dissolved oxygen in solution. Of these two methods for removing the peak, it is simpler and sufficient to stop solution flow by diverting the solution through a second channel on a temporary basis, which can be accomplished by an automatically operated valve. Fig. 2 shows the effect of stopping the peristaltic pump on the peak current of this wave. 20 s after stopping the pump, when the solution flow has reached zero, the wave completely disappears. All further results presented below used this mode in the determinations.

Fig. 3 illustrates the effects of copper–zinc interactions on performing SWASV on analyte solutions containing both copper and zinc ions using data

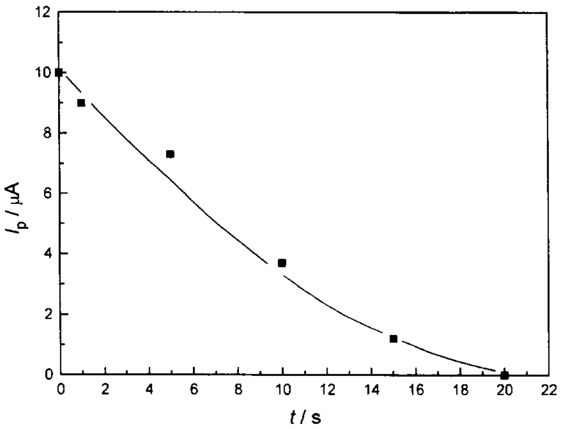

Fig. 2. Peak current intensities, I_p of wave centred at −0.5 V as function of time, t, during which solution flow was stopped after accumulation and before the square wave scan. Other conditions as Fig. 1.

obtained from experiments giving peaks like those shown in Fig. 1(b). Fig. 3(a) is a plot showing the depression of the peak current corresponding to zinc at −1.1 V on increasing the concentration of copper ions; at a 1 : 1 ratio, I_p is reduced to one half and to 20% at a 1 : 2 zinc : copper ratio. In Fig. 3(b), a twin plot for the "copper peak" at −0.1 V with and without zinc ions in solution, shows the corresponding inverse behaviour: in the presence of zinc ions, the copper signal is not only increased but the linearity also becomes less good. The purpose of the addition of Ga was to eliminate these dependences and enable peaks such as those illustrated in Fig. 1(a) to be registered.

An SW voltammogram for the oxidation of preconcentrated gallium is shown in Fig. 4. In fact, in 0.1 M $NaClO_4$ electrolyte a high concentration of Ga^{3+}, $\sim 10^{-4}$ M, was necessary to obtain any signal, which at first sight suggests the cause may be linked to the low solubility of gallium in mercury. However, this deduction is at variance with previously published work where gallium signals were registered at submicromolar concentrations using linear scan voltammetry, e.g. [11]. Thus, the same electrolyte as in [11], 0.1 M acetate buffer, pH 4.75, was tested. A gallium signal at submicromolar concentrations was then easily obtained as illustrated in Fig. 4; the position of this signal does not interfere with determinations of lead or cadmium by SWASV at the wall-jet electrode in continuous flow [13].

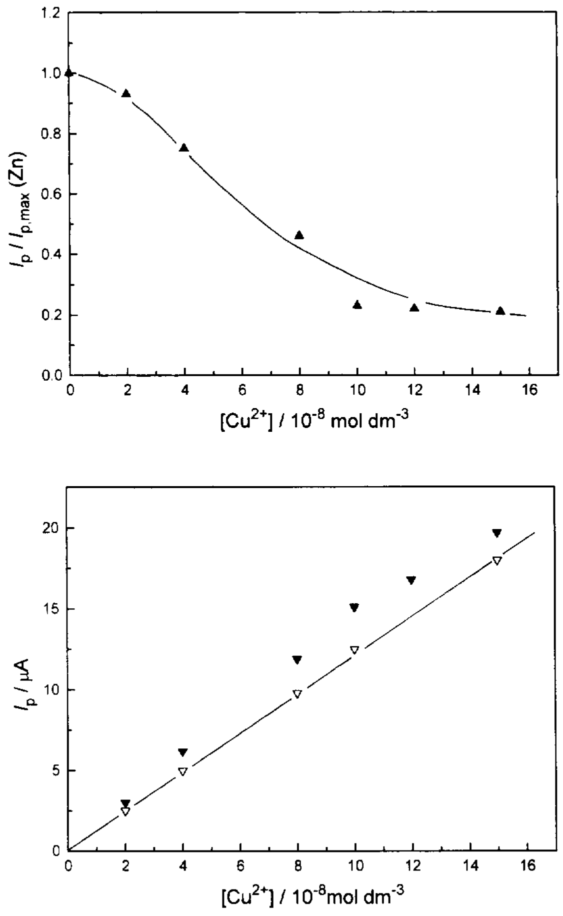

Fig. 3. Effect of intermetallic compound formation on analysis of mixtures of Cu and Zn by SWASV. $E_{dep}=-1.4$ V, $t_{dep}=120$ s. (a) Depression of I_p (Zn) caused by addition of Cu^{2+} to the analyte solution, $[Zn^{2+}]=8\times10^{-8}$ mol dm^{-3}. (b) Plot showing I_p(Cu) in the absence (▽) and in the presence (▼) of 8.0×10^{-8} mol dm^{-3} zinc ions in solution. The solid line is the line of best fit in the absence of Zn.

Consequently, acetate buffer medium was employed for determinations of zinc in the presence of copper after spiking with gallium ions. The lack of influence of increasing concentrations of copper ion in bulk solution in depressing the zinc signal under these conditions is shown in Fig. 5(top).

To test the hypothesis that differences in experiments with gallium ions carried out in sodium perchlorate and in acetate buffer were due to pH effects, sodium perchlorate electrolyte, acidified with nitric acid to pH 3.0, was employed. This led to

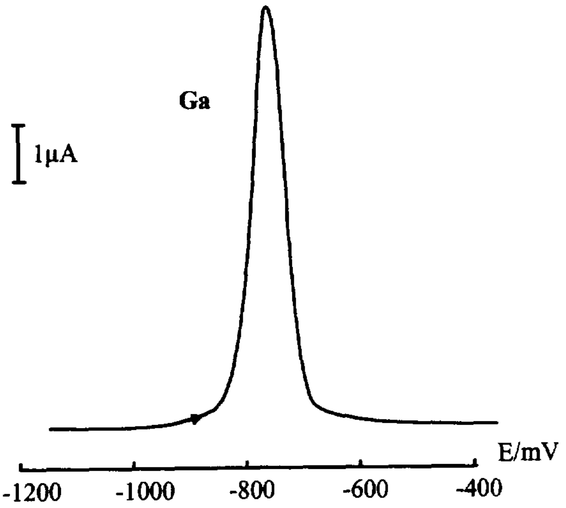

Fig. 4. Typical voltammogram for SWASV from a solution of Ga^{3+} (1.0×10^{-6}mol dm^{-3}) in 0.1 M acetate buffer electrolyte, pH 4.75. Other SWASV conditions as Fig. 1.

identical results to those in acetate buffer as seen in Fig. 5(bottom). It was found that a simple, efficient procedure was to spike the perchlorate electrolyte with acidified gallium ion solution, acidified in such a way that the final pH would be 3.0.

Calibration curves constructed from experimental data in the concentration range 5–200 nmol dm^{-3} are linear under these conditions and lead to peak currents for zinc which are equal with and without the presence of copper. For experimental conditions as described earlier (E_{dep}=−1.4 V, t_{dep}=120 s, f=100 Hz, h=30 mV and V^f = 0.035 cm calibration plots lead to a slope of 0.346±0.002 A mmol^{-1} dm^3=0.99993), intercept 0.150±0.157 μA, and 0.348±0.002 A mmol^{-1} dm^3=0.99991), intercept 0.090±0.183 μA, respectively. Theoretical detection limits are once more ~2×10^{-11} mol dm^{-3}.

Thus, the strategy in mixtures, which applies equally well to mixtures of copper, zinc, lead and cadmium can be either of:

- A two-part experiment in which cadmium, lead and copper are measured after deposition at −0.9 V. Addition of acidified gallium solution and deposition at −1.4 V leads to the zinc concentration.
- A two-part experiment in which copper is determined first and separately following deposition at −0.5 V. After spiking with acidified gallium, deposition at −1.4 V leads to concentrations of zinc, cadmium and lead.

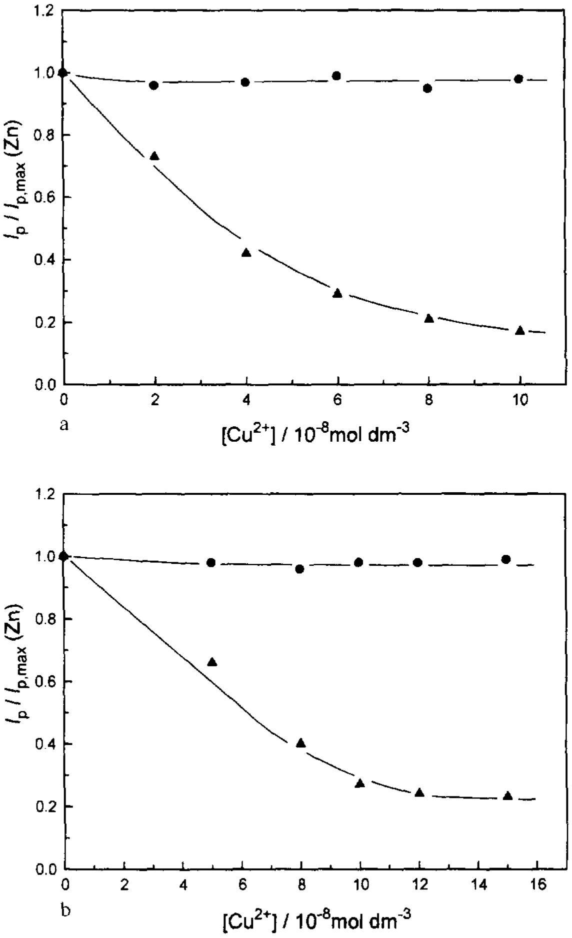

Fig. 5. Plots showing the influence of Ga^{3+} on the height of the Zn peak in SWASV as a function of [Cu^{+2}] (▼) without Ga^{3+} (●) with 4×10^{-5} mol dm^{-3} Ga^{3+}. Condition as Fig. 1. (top) In 0.1 M acetate buffer electrolyte, pH 4.75, [Zn^{2+}]=8.0×10^{-8} mol dm^{-3}. (bottom) In acidified 0.1 M sodium perchlorate electrolyte, pH 3.0, [Zn^{2+}]=4.0×10^{-8} mol dm^{-3}.

Both of these methods give equally good results and can be adapted for standard addition. They are simple to carry out and show practical advantages relative to the other strategies outlined in the introduction, namely physical separation, use of a double electrode, addition of a complexing agent or chemometric evaluation.

An example where the methodology was applied was a subterranean water which led to the following results in g dm (ppb) using the standard addition method, with % recovery in brackets: Zn, 43.1±0.2 (103); Cu, 25.2±0.1 (98); Pb, 7.5±0.1 (98); Cd, not detected (<0.2) in good agreement with those determined by AAS with electrothermal atomization. These levels obtained by SWASV correspond to the following molar concentrations in μmol dm^{-3}: Zn, 0.66; Cu, 0.397; Pb, 0.036, which are well above the detection limits of the technique. The results of the analysis of a number of waters will be the subject of a separate publication [15].

4. Conclusions

It has been shown that adaptation of current ASV procedures through spiking with a solution of acidified gallium ions permits the analysis of mixtures of copper and zinc, together with lead and cadmium, in perchlorate electrolyte in flowing solution at wall-jet mercury thin film electrodes by SWASV. In order to improve the background current after deposition at -1.4 V in the zone of potential corresponding to lead and cadmium it is recommended that the rate of solution flow be reduced after the accumulation step and before determination. In this way highly selective and sensitive responses can be obtained with practical detection limits in the nanomolar range.

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