

## MINIMIZATION OF COPPER-ZINC INTERACTIONS IN TRACE ELECTROANALYSIS IN FLOWING SOLUTION

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### ABSTRACT

The square wave anodic stripping voltammetry of copper and zinc mixtures at wall-jet mercury thin film electrodes in continuous flow was investigated with the aim of minimizing interferences which appear in solutions containing the two cations due to Cu-Zn intermetallic compound formation in the mercury phase. The addition of gallium ions led to the preferential formation of Ga-Cu intermetallics making the determination of zinc possible. Best results were obtained in acetate buffer or acidified sodium perchlorate electrolyte at pH~3. It was shown that the method is applicable to the analysis of waters in flowing solution.

### INTRODUCTION

With the increasingly widespread application of electroanalytical methods for the determination of copper and zinc in solution matrices and the necessity for on-line monitoring in flow systems [1], simple, efficient, rapid response methods for determining mixtures of these metal ions, which often occur together in nature, are necessary. In order to attain the required practical sub-ppb detection limits, using anodic stripping voltammetry (ASV), mercury electrodes have to be employed, owing to the rather negative deposition potential of  $\sim -1.3\text{V}$  vs. Ag/AgCl (3.0M KCl) for zinc. Mercury-soluble copper-zinc intermetallics are formed during the preconcentration deposition step [2]. Stripping leads to a Cu-Zn stripping peak almost coincident with the copper peak ( $\sim -0.05\text{V}$ ) and a reduction of the height of the zinc peak ( $-1.15\text{V}$ ). Effective ways of

circumventing this problem have to involve the removal of one or other of the components from the solution or the mercury film or, alternatively, the avoidance of copper-zinc intermetallic formation. Most previous work on interference removal has involved linear scan or differential pulse potential programs in the ASV stripping step, e.g. [3]. In these cases the solution is deoxygenated. One of the benefits of square wave anodic stripping voltammetry (SWASV) is the possibility of carrying out the whole experiment in the presence of oxygen, thus reducing the experimental time.

In this work, SWASV of copper and zinc mixtures at wall-jet mercury thin-film electrodes (MTFE) in continuous flow has been investigated.

### EXPERIMENTAL

The wall-jet cell contained a glassy carbon disc electrode, diameter 0.3 cm, a platinum tube counter electrode in the cell outlet and a Ag/AgCl (3.0M KCl) reference electrode in a separate compartment. Experiments were carried out with a PSTAT10 Autolab, Eco-Chemie, Netherlands. Flow rates used were in the range 0.035 to 0.045 cm<sup>3</sup> s<sup>-1</sup>. Solutions were prepared from analytical grade reagents with ultrapure water (Millipore, Milli-Q, resistivity >18 MΩ cm). Experiments were conducted at room temperature (22-23°C), deoxygenation not being necessary.

### RESULTS AND DISCUSSION

Preliminary experiments demonstrated that copper and zinc in separate solutions can be determined by SWASV down to nanomolar levels using co-deposition of mercury from 10<sup>-4</sup>M Hg<sup>2+</sup> in 0.1M sodium perchlorate electrolyte. The deposition potential used for copper was -0.6V and for zinc was -1.4V.

In mixtures of copper and zinc ions the zinc peak in SWASV diminished and that of copper increased in height and also in width, since the intermetallic compound formed strips at a potential close to that of copper, see Fig.1. The results of a quantitative study at the wall-jet electrode using a constant concentration of zinc and increasing concentrations of copper are shown in Table 1.

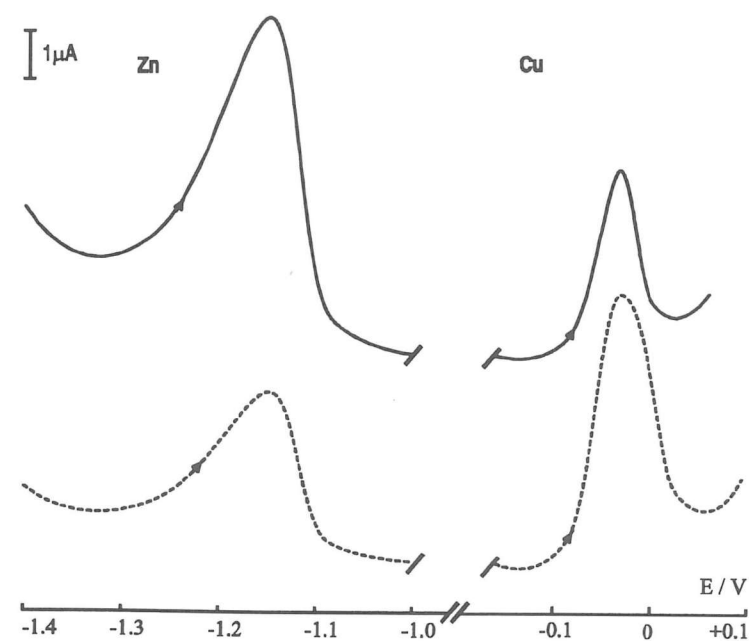


Fig.1 SWASV at wall-jet MTFE of Zn and Cu (—) separately and (----) in mixture: [Cu<sup>2+</sup>] = [Zn<sup>2+</sup>] = 5 × 10<sup>-8</sup> mol dm<sup>-3</sup>; [Hg<sup>2+</sup>] = 10<sup>-4</sup> mol dm<sup>-3</sup>; 0.1M NaClO<sub>4</sub>, V<sub>f</sub> = 0.035 cm<sup>3</sup> s<sup>-1</sup>. E<sub>dep</sub> = -1.4V, t<sub>dep</sub> = 120s. SW parameters: f = 100Hz, h = 30mV, scan increment = 2mV.

Table 1 Values of peak current, I<sub>p</sub>, for zinc after addition of increasing quantities of copper; SWASV conditions as in Fig.1. Values correspond to the average of 5 determinations with standard deviation ≤ 0.2.

[Zn <sup>2+</sup> ] × 10 <sup>8</sup> /mol dm <sup>-3</sup>	[Cu <sup>2+</sup> ] × 10 <sup>8</sup> /mol dm <sup>-3</sup>	I <sub>p</sub> (Zn)/μA	ΔI <sub>p</sub> (Zn)/%
8.0	0.0	24.3	-
8.0	2.0	22.5	-7.3
8.0	4.0	18.3	-24.8
8.0	8.0	11.2	-53.9
8.0	10.0	5.7	-76.7
8.0	12.0	5.4	-77.7
8.0	15.0	5.2	-78.7

In order to eliminate the formation of copper-zinc intermetallic compounds, gallium ions were added since gallium-copper intermetallics are formed preferentially, thus permitting the determination of zinc without interference. It was found that good results could not be obtained in sodium perchlorate electrolyte, whereas in acetate buffer at pH 4.5, excellent, reproducible results were obtained. This suggested the acidification of the sodium perchlorate electrolyte to pH 3, in which equally good results for copper and zinc were obtained, with no decrease in the zinc peak height due to the presence of copper, Table 2.

A two part experimental protocol was developed: selective deposition of copper alone at -0.6V, leading directly to the copper ion concentration, followed by spiking with 5 $\mu$ M gallium ions and deposition at -1.4V, measuring the zinc peak to give the zinc ion concentration. In this way low concentrations with a practical detection limit of 2 nmol dm<sup>-3</sup> can be measured, below levels found in nature.

Table 2 Peak current,  $I_p$ , for SWASV of zinc in analyte solutions containing zinc only and containing zinc and copper ions in equal concentration with 5 $\mu$ M Ga<sup>3+</sup>. Electrolyte 0.1M NaClO<sub>4</sub> acidified to pH3 with nitric acid. SWASV conditions as Fig.1. Values correspond to the average of 5 determinations with standard deviation  $\leq$  0.2.

[Zn <sup>2+</sup> ] $\times 10^8$ /mol dm <sup>-3</sup>	$I_p$ (Zn)/ $\mu$ A	$I_p$ (Zn)/ $\mu$ A in mixture spiked with Ga
2.0	7.1	7.2
4.0	14.0	13.3
6.0	21.9	21.6
8.0	27.7	27.8
10.0	35.1	34.9

In order to show the application of the methodology various waters were analysed for their content in zinc, copper, lead and cadmium, validated by AAS with electrothermal atomization. As an example, a sample from a public water supply led to the following results in  $\mu$ g dm<sup>-3</sup> using the standard addition method, with % recovery in brackets: Zn - 14.1 $\pm$ 0.1 (102); Cu - 4.0 $\pm$ 0.1 (103); Pb - 13.8 $\pm$ 0.1 (103); Cd <0.2 (below detection limit).

## CONCLUSIONS

The addition of gallium ions to solutions containing both copper and zinc ions permits their determination at wall jet mercury thin film electrodes by SWASV without solution deoxygenation. Excellent results are obtained with practical detection limits of the order of 2 nmol dm<sup>-3</sup> in acidified sodium perchlorate electrolyte, which allows the simultaneous quantification of zinc, copper, lead and cadmium ions.

## ACKNOWLEDGEMENT

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