

MUTUAL INTERFERENCES IN THE DETERMINATION OF Zn(II) AND Cu(II) IN SEAWATER BY ANODIC STRIPPING VOLTAMMETRY

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ABSTRACT

Cu(II) and Zn(II) titration experiments were used to investigate the mutual interference of Zn and Cu in anodic stripping voltammetry (ASV) at the stationary, mercury-coated, glassy carbon electrode. The experiments were conducted on stored seawater with a trace metal concentration range of 10^{-8} – 10^{-7} M. It was found that both Zn(II) and Cu(II) titration curves show a characteristic break point, the position of which is a function of the concentration of the interfering ion.

The mutual interference is attributed to the formation of an intermetallic compound (IC) with a stoichiometric formula ZnCu. The model further assumes that the rate of Zn oxidation off the amalgam is the kinetic-limiting step in the IC dissociation during the stripping cycle of the ASV analysis. Numerical simulation of the titration experiments — using the proposed model and applying experimentally derived parameters — is in good agreement with the experimental results. The model can thus be applied to correct for Zn and Cu interference in ASV.

INTRODUCTION

The mutual interference of Zn(II) and Cu(II) in anodic stripping voltammetry (ASV) was first recognized by Kemula et al. [1]. They attributed this interference to the formation of zinc–copper intermetallic compound (IC) formed in mercury during the deposition step. These compounds were studied earlier by Russell et al. [2] who concluded that at room temperature, the stoichiometric formula of the IC formed in the amalgam is ZnCu. Since then, a number of investigators have attempted to estimate the stoichiometry of these IC and to calculate their solubility or formation constants. A review of several approaches has been presented by Shuman and Woodward [3].

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Although sometimes overlooked, IC formation may severely interfere in the determination of Zn(II) and Cu(II) by ASV when both metals are present in solution [4]. The interference is most pronounced when Zn(II) and Cu(II) are determined simultaneously, but may also be present even when the deposition potential for Cu(II) determination is made positive with respect to Zn(II), due to IC formation by undervoltage deposition of Zn(II) — as indicated below.

Calibration by the standard addition method could be erroneous when applied in the ASV analysis of Zn(II) in the presence of Cu(II) [4]. To overcome this problem, which results from the formation of ZnCu IC, Copeland et al. [4] suggested a procedure in which Ga(III) is added to solution. The Ga(III) binds all the deposited Cu(II) in a Ga—Cu amalgam which has a larger stability constant than Zn—Cu, and hence all the Zn is released from the ZnCu IC. This method, however, is applicable only in acidic solutions with a pH value < 2 [5,6], and therefore not applicable to natural waters unless heavy pH buffering is applied [6].

Recently, Roston et al. [7] described a method for elimination of intermetallic compound interferences. They used a twin electrode to separate physically the interfering ions from a thin layer of the tested solution. The method was shown to be applicable in the ppm concentration range.

Another method for overcoming the problem of Cu(II) interference in Zn(II) determination of ASV is to use a Cu(II) titration procedure [5]. The added copper reduces the Zn(II) stripping peak current ($I_p(\text{Zn})$) and by linear extrapolation to zero $I_p(\text{Zn})$ one can presumably estimate the amount of added Cu(II) required to completely suppress $I_p(\text{Zn})$. This amount plus the one originally presented in solution is equal to the original concentration of Zn(II) if a 1 : 1 IC is assumed. Unfortunately, the titration curve has a characteristic break point [3] and hence simple extrapolation may not be valid.

The calibration curve for $I_p(\text{Cu})$ in seawater, generated by the standard addition method, also shows a characteristic break point, both for deposition potentials which are positive or negative with respect to Zn(II). This was attributed to the formation of metal—organo complexes in seawater [7], but its possible relation to IC formation has not been previously considered.

The purpose of this investigation was to study the problem of Zn and Cu interference in ASV in seawater and to explore possible analytical procedures for eliminating the interference errors. This was accomplished by conducting titration experiments and by deriving a simple IC model to explain the nature and magnitude of the interference. The model was consequently tested by running a numerical simulation on a computer and was then applied to develop an analytical method for simultaneous determination of Zn and Cu in seawater by ASV.

EXPERIMENTAL

Instrumentation

Measurements were made with a Ben-Gurion University (BGU) model EI224 polarographic analyzer developed and built at the Department of Electrical Engineering of BGU. It operates in one of three modes: linear sweep, pulse and

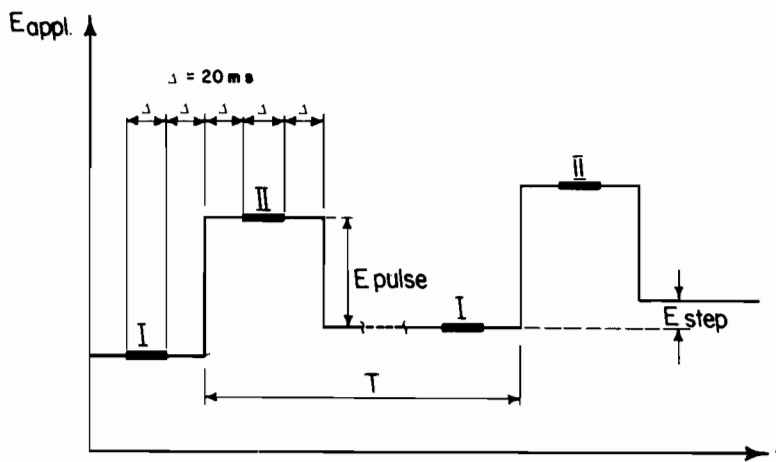


Fig. 1. Pulse shape used during the stripping phase. Current samples are integrated over the periods marked by the heavier lines. The output signal of the polarographic analyzer is proportional to the difference between two integrated currents ($\int_{II} i dt - \int_I i dt$). In the present analysis $E_{step} = 10$ mV; $E_{pulse} = 80$ mV; $T = 640$ ms.

differential pulse mode, and can also use the option of subtractive ASV [9]. The analytical mode used in this study was differential pulse anodic stripping voltammetry (DPASV). In this mode the polarographic analyzer uses a staircase-type waveform on which a pulse is superimposed (Fig. 1).

Electrodes and cell

Measurements were carried out in a 100 ml Teflon beaker fitted with a Teflon cover through which the electrodes and the tube carrying the oxygen purging gas (CO_2) were inserted. The solution was stirred with a Teflon-coated stirring bar.

A radiometer, Type K-401, saturated calomel electrode equipped with a Coleman fiber liquid junction (Perkin Elmer C003-0702) filled with KCl (saturated) served as a reference electrode and a coiled platinum wire was used as an auxiliary electrode. The working electrode was thin mercury film electrode (TMFE) deposited on glassy carbon (GC) 3 mm in diameter (Rignsdorf Werke S-10). A detailed description of the working electrode is presented elsewhere [10].

Reagents and solutions

Gulf of Eilat (Red Sea) seawater was sampled and stored in 15 l PVC containers which had been cleaned with 1 M HNO_3 and rinsed several times with the sampled water. Copper and zinc spiking solutions were prepared from atomic absorption standard solutions (Fisher Scientific Company). Mercury-plating solution was approximately 2×10^{-5} M mercuric nitrate prepared by dissolving the salt (Baker Analyzed Reagent) in seawater. Commercial CO_2 gas, treated with vanadous chloride solution, was used to purge the sample during the entire analysis cycle.

Procedure

The Teflon cover, through which the electrodes were inserted, was transferred to a 100 ml Teflon beaker containing the Hg plating solution and a -1400 mV potential was applied to the working electrode (WE) for 20 min. Plating current was $15.5 \mu\text{A}$ and the volume of the thin film is estimated to be 10^{-6} cm^3 . Following the plating time, the potential was changed to -100 mV for another 3 min to strip any trace metal deposited during plating. The electrodes were then rinsed with twice-distilled water and then placed in the tested solution (stored seawater). The solution was then deaerated for 7 min, after which the ASV cycle was commenced.

The analysis consisted of five steps:

- (1) Application of -1400 mV to the WE in a stirred solution for 90 s.
- (2) Rest period of 30 s to the WE in unstirred solution at a potential of -1400 mV.
- (3) Scanning from -1400 mV to -100 mV ($E_{\text{pulse}} = 80$ mV, $E_{\text{step}} = 10$ mV, $T = 640$ ms) and recording the current.
- (4) Addition of a certain amount of Cu(II) or Zn(II) spike by a micropipette.
- (5) Stripping the WE for 30 s at -100 mV in a stirred solution and starting again from step (1).

In each experiment Cu was added until the Cu : Zn concentration ratio in the solution was > 2 , then Zn was added until the Zn : Cu ratio was > 2 .

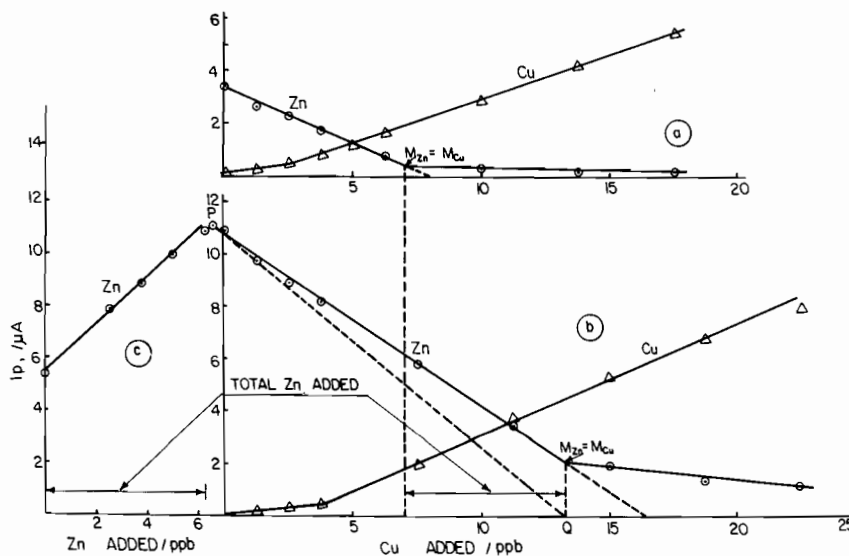


Fig. 2. Cu(II) titration experiments on stored seawater: (a) titration of the original seawater with Cu(II); (b) Cu(II) titration of original seawater spiked with 6.25 ppb of Zn(II); (c) standard addition of Zn(II) to original seawater. This titrated seawater sample was later used as spiked seawater for experiment (b). The Zn(II) concentration as extrapolated from the standard addition (c) is 6.25 ppb, while using the $I_p(\text{Zn})$ curve break point gives Zn(II) concentration of 7.00 ppb. Comparison between the $I_p(\text{Zn})$ break points in (a) and (b) suggests that at the break point $M_{\text{Zn}} = M_{\text{Cu}}$. Note that the $I_p(\text{Cu})$ break point is shifted to the right [compare (a) and (b) for which the initial Zn(II) concentration is higher].

The proposed model for the Zn—Cu IC was simulated on a HP9821A desk calculator equipped with a plotter.

The experiments with ^{65}Zn which are discussed briefly in this work, will be described elsewhere [11].

EXPERIMENTAL RESULTS

The major observations are summarized as follows:

(1) Titration curves of $I_p(\text{Zn})$ and $I_p(\text{Cu})$ as a function of added Cu(II) (Fig. 2a) are composed of two linear segments each with a break point at a given Cu(II) addition. The position of the break points is a function of the initial concentration of Zn(II) in solution (Fig. 2a,b).

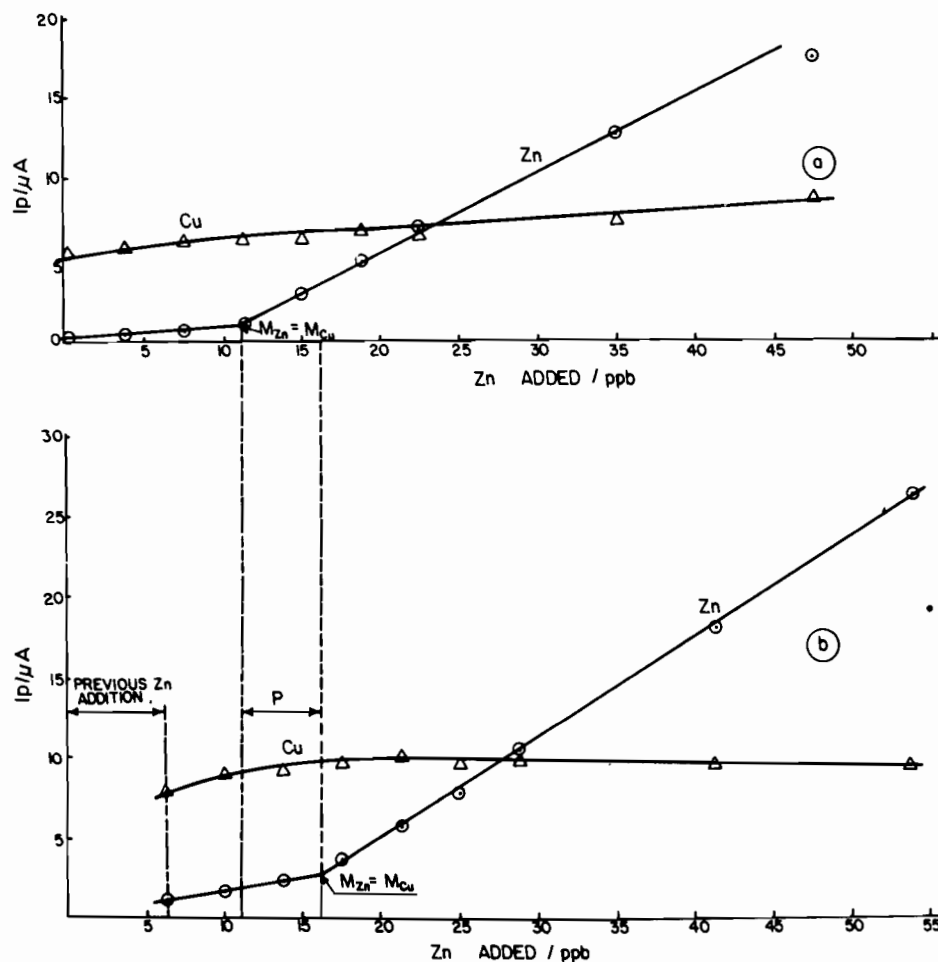


Fig. 3. Titration experiments on stored seawater by addition of Zn(II) to the samples originally spiked with Cu(II): (a) Zn(II) addition to titrated seawater sample of Fig. 2a [$\text{Cu(II)} = 18.00$ ppb]; (b) Zn(II) additions to the seawater of Fig. 2b [$\text{Cu(II)} = 23.00$ ppb]. Note that the segment P , which is the difference between the break points in (a) and (b), is equal to 5.0 ppb, which is also the difference between the Cu(II) concentrations of (a) and (b) ($22.5 - 17.5 = 5.0$).

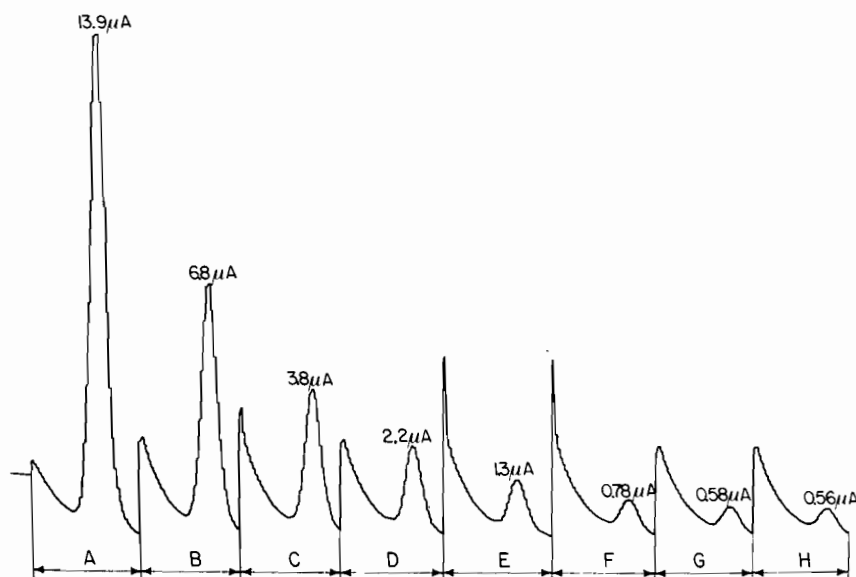


Fig. 4. Eight consecutive stripping scans (A–H) over the Zn(II) peak. Run A was commenced 2 min after deposition at -1400 mV. The stripping steps were run from -1400 mV to -900 mV, at which point the potential was switched again to -1400 mV to start the next scan. As revealed from scans G and H, $0.57 \mu\text{A}$ corresponds to the amount of Zn(II) deposited during the scan. By subtracting $0.57 \mu\text{A}$ from the peak currents of scans B–H one finds that about 50% of the zinc is oxidizing off the electrode during the zinc stripping peak.

(2) The shift in the position of the break point of $I_p(\text{Zn})$ (Fig. 2a,b) between two solutions is equal to the difference in the initial Zn(II) concentration. Hence, at the break point, the Cu(II) concentration (original plus added) is evidently equal to the Zn(II) concentration.

(3) Titration curves of $I_p(\text{Zn})$ as a function of added Zn(II) (Fig. 3) are composed of two linear segments with a break point at a given concentration of added Zn(II). The position of the break point is a function of the concentration of Cu(II) in solution.

(4) The shift in the $I_p(\text{Zn})$ break-point position is equal to the difference in Cu(II) between the solutions (Fig. 3a,b). Hence, at the break point Zn(II) concentration is equal to Cu(II) concentration.

(5) Titration curves of $I_p(\text{Cu})$ as a function of added Zn(II) show slight increase with Zn(II) concentration with no definite break point.

(6) Net removal of Zn from the WE varies during the stripping phase of the analysis. About 50% of the Zn is removed during the -1400 mV to -900 mV portion of the scan (Fig. 4), but only 10% is oxidized between -900 mV and -100 mV (as determined from an experiment similar to Fig. 4).

THE MODEL

The following set of basic and simple assumptions, based on the present experimental results and previously reported data, are used in the development of the model:

(1) Only one zinc—copper IC species, ZnCu is formed and dissociated in the mercury during the ASV at room temperature [2].

(2) The concentration of the ZnCu IC in the amalgam is related to Zn and Cu concentration in the amalgam according to

$$K = c_{\text{ZnCu}}/c_{\text{Zn}}c_{\text{Cu}} \quad (1)$$

where c denotes the concentration of the respective species in the amalgam.

(3) For the present experimental condition, 60% of the Zn oxidizes off the amalgam during the stripping scan between the deposition potential and the Cu(II) peak potential.

(4) The zinc and copper stripping peak currents (I_p) are related to the concentration of Zn, Cu and the IC in the amalgam by the following linear equations:

$$I_p(\text{Zn}) = c'_{\text{Zn}}K_{\text{Zn}} + c'_{\text{ZnCu}}K_{\text{IC,Zn}} \quad (2)$$

$$I_p(\text{Cu}) = c''_{\text{Cu}}K_{\text{Cu}} + c''_{\text{ZnCu}}K_{\text{IC,Zn}} \quad (3)$$

where I_p is the peak current of the metal and the K 's relate the stripping current to amalgam concentrations and are assumed constants for the given experimental conditions. The prime and double prime denote concentrations in the amalgam at the Zn and Cu peaks respectively.

(5) The total amount of Zn and Cu accumulated in the amalgam during the deposition phase of the ASV analysis is linearly proportional to the concentrations of electroactive Zn(II) and Cu(II) in solution [3]. Applying the above assumption to eqns. (1) and (2), for the Zn stripping peak current, one obtains:

$$RK = \frac{c'_{\text{ZnCu}}/R}{(M_{\text{Zn}} - c'_{\text{ZnCu}}/R)(M_{\text{Cu}} - c'_{\text{ZnCu}}/R)} \quad (4)$$

$$I_p(\text{Zn}) = (M_{\text{Zn}} - c'_{\text{ZnCu}}/R)K_{\text{Zn}} + (c'_{\text{ZnCu}}/R)K_{\text{IC,Zn}} \quad (5)$$

where M_{Zn} and M_{Cu} are the concentration of electroactive Zn(II) and Cu(II) in solution respectively, and the proportionality factor R relates c'_{Zn} and c'_{Cu} to M_{Zn} and M_{Cu} respectively. The accumulation factors for Zn and Cu are assumed to be equal since the accumulation factors are identical [3].

(6) Similarly, for the Cu stripping peak currents, eqns. (1) and (3) are rewritten in the form:

$$RK = \frac{c''_{\text{ZnCu}}/R}{(M_{\text{Zn}}(1 - P) - c''_{\text{ZnCu}}/R)(M_{\text{Cu}} - c''_{\text{ZnCu}}/R)} \quad (6)$$

$$I_p(\text{Cu}) = (M_{\text{Cu}} - c''_{\text{ZnCu}}/R)K_{\text{Cu}} + (c''_{\text{ZnCu}}/R)K_{\text{IC,Cu}} \quad (7)$$

where P is the fraction of the Zn oxidized off the amalgam till the potential of the Cu stripping peak current was reached. The value of the stripping peak current constants were derived as follows:

K_{Zn} was derived from the slope of the titration curve of Fig. 2c, for which

$$M_{\text{Zn}} \gg M_{\text{Cu}}.$$

K_{Cu} was derived from the steeper slope of $I_p(\text{Cu})$ in Fig. 2b, for which

$$M_{\text{Cu}} > M_{\text{Zn}}.$$

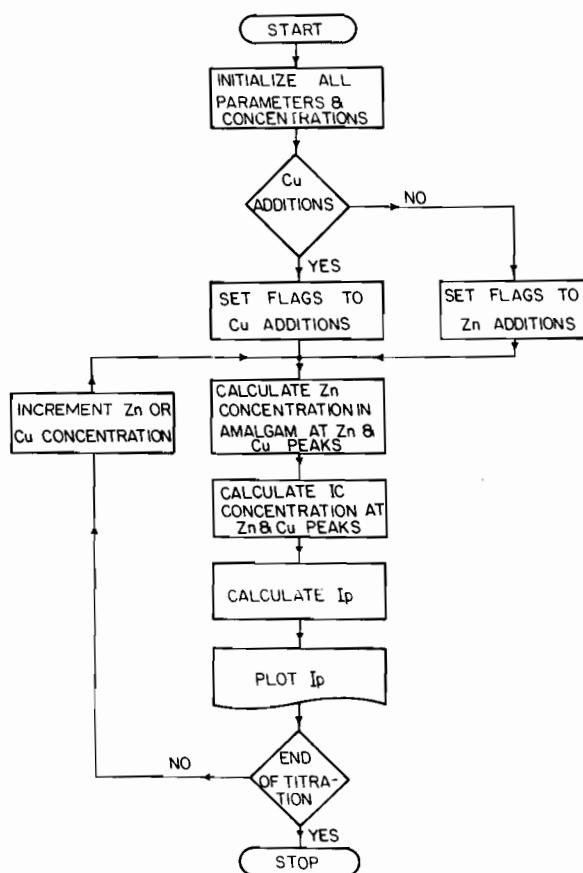


Fig. 5. Flow chart of the computer simulation program.

$K_{IC,Zn}$ was derived from the titration curve of Fig. 2b by assuming that if the IC had not contributed to the Zn stripping current, $I_p(Zn)$ titration line would have been the line PQ. Point P was found by extrapolating the original $I_p(Zn)$ to the left, taking into account the initial amount of 0.5 ppb Cu(II) present in solution. The point Q is the region at which $M_{Zn} = M_{Cu}$ and practically all the Zn is in the form of IC, considering the expected value of the IC formation constant [3,12].

$K_{IC,Cu}$ was derived from the lower segment of the $I_p(Cu)$ titration curve of Fig. 2b, for which $M_{Zn} > M_{Cu}$ and hence practically all the Cu in the amalgam is bound in the IC.

RK was derived by an iterative process during the numerical simulation.

The Zn(II) and Cu(II) titration experiments were simulated numerically by the present model using a computer program that was run on a HP9821 desk calculator, the simulated titration curves being plotted by an auxiliary X-Y plotter. The trial and error procedure (Fig. 5) commenced by guessing the value of RK and then improving the estimate by iteration.

SIMULATION RESULTS AND DISCUSSION

Using the procedures outlined above, the value of the apparent constants were evaluated to be

$$K_{Zn} = 54 \text{ A M}^{-1}; \quad K_{IC,Zn} = 7.7 \text{ A M}^{-1}$$

$$K_{Cu} = 27 \text{ A M}^{-1}; \quad K_{IC,Cu} = 9.0 \text{ A M}^{-1}$$

$$RK = 1.1 \times 10^9 \text{ l M}^{-1}$$

It should be emphasized that the constants are not universal and should be redetermined if any of the experimental parameters are changed.

Comparison of the numerical simulation results to the experimental results for I_p during Cu(II) titration (Fig. 6) reveal a striking similarity between the two curves. In particular, the position of the break points in $I_p(\text{Cu})$ and $I_p(\text{Zn})$ match very well, indicating that the proposed model is sufficient for simulating the characteristic break points. The break point in the $I_p(\text{Zn})$ curve is thus

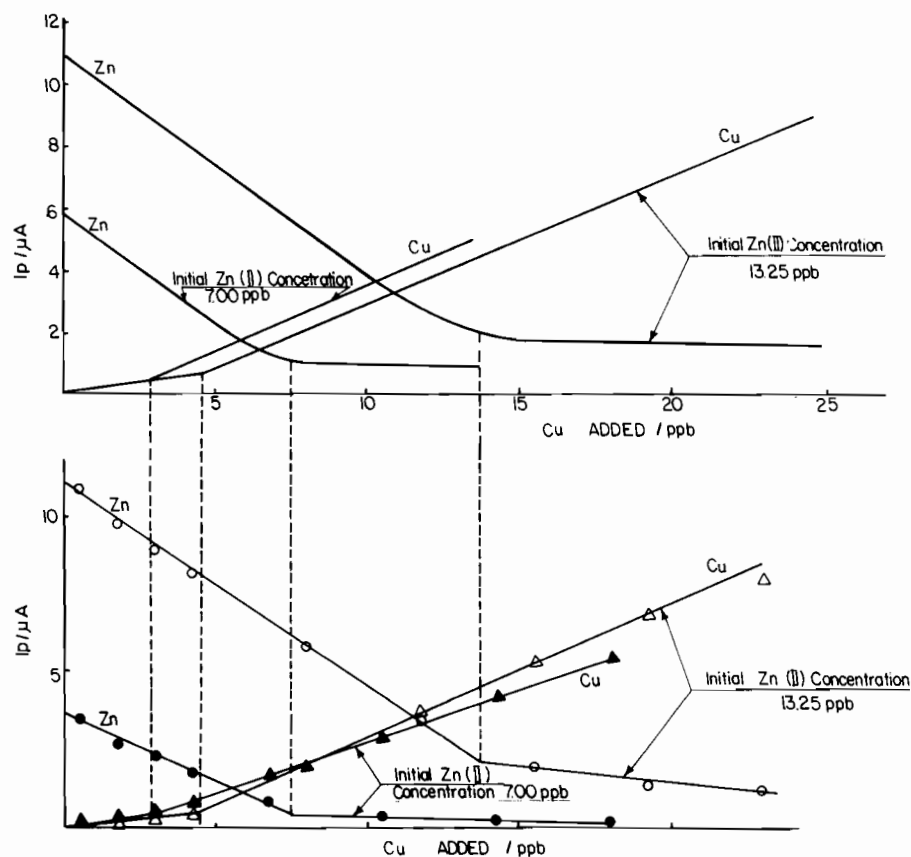


Fig. 6. Comparison between simulation results (a) and the experimental results (b): (a) simulation of Cu(II) titration experiments of Fig. 2; (b) Figs. 2a and 2b superimposed. The experimental results are shifted by +0.5 ppb which is the original Cu(II) concentrations of the stored seawater. Note the good fit between the break points of the experimental results and the model calculation.

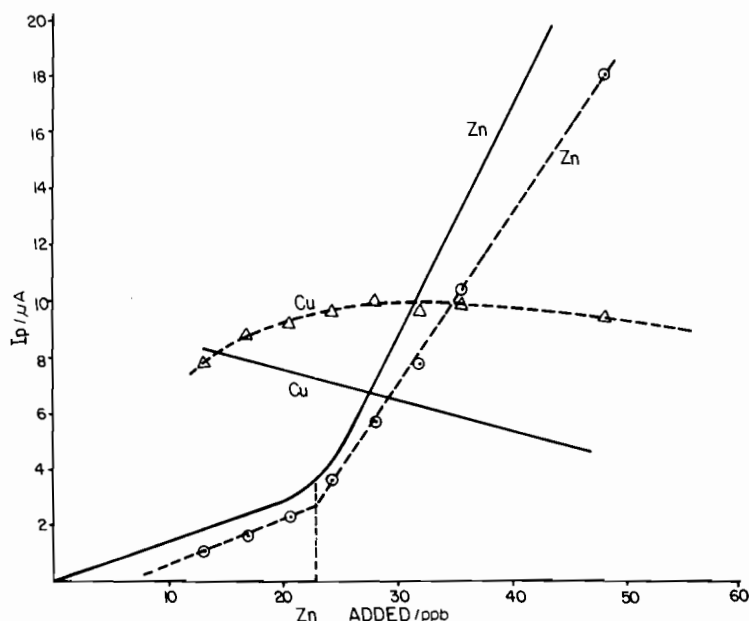


Fig. 7. Comparison between the simulation results and the experimental results of the experiment of Fig. 3b. (Solid line) the simulation results; (dashed line) the experimental results of Fig. 3b, shifted +13.25 ppb which is the initial Zn(II) concentration. The fit between the break points is very good. The discrepancy in the $I_p(\text{Cu})$ curves is explained in the text.

explained as the point at which $M_{\text{Zn}} = M_{\text{Cu}}$. Similarly, the break point in $I_p(\text{Cu})$ is obtained when $0.4 M_{\text{Zn}} = M_{\text{Cu}}$. Assuming that the accumulation factors of Zn(II) and Cu(II) are identical [3] the break point thus represents the equivalence point for Zn and Cu in the amalgam.

Numerical simulation for the Zn titration experiment yields a break point in $I_p(\text{Zn})$ which correlates well with the experimental titration curves (Fig. 7). The break is again reached for the condition $M_{\text{Zn}} = M_{\text{Cu}}$. The model, however, fails to predict the exact shape of the $I_p(\text{Cu})$ titration curves as a function of added Zn (Fig. 7) and the slope of $I_p(\text{Zn})$ in the Cu(II) titration experiments after the equivalence point is reached (Fig. 6a).

These discrepancies probably indicate the formation of higher IC's such as $\text{ZnCu}(\text{CuHg})_n$ which are richer in Cu than in Zn [1,13] and have a smaller stability constant than ZnCu.

Despite these discrepancies which are mostly due to the omission of higher-order IC's from the model, the model clearly indicates the causes of the error in Zn analysis by ASV when a simple standard addition procedure is used for calibration. The magnitude of the error committed will depend on the concentration of Cu(II) in solution (Figs. 2, 3 and 7). This error can be circumvented by applying the fact, verified by the present model, that at the break point of $I_p(\text{Zn})$ in the Cu titration curve and the Zn titration curve, $M_{\text{Zn}} = M_{\text{Cu}}$. The following procedures can thus be adopted for Zn analysis by ASV:

(1) When the original Zn(II) concentration is larger than Cu(II) concentration: titration by Cu(II) until the $I_p(\text{Zn})$ break point is reached. Original Zn(II) concentration is equal to the total amount of Cu(II) in solution (original plus added) (Fig. 2).

(2) When the original Zn(II) concentration is smaller than Cu(II) concentration: titration by Zn(II) until the $I_p(\text{Zn})$ break point is reached. The original Zn(II) is equal to the original Cu(II) concentration less the amount of Zn(II) added to reach the break point (Fig. 3):

In seawater, the concentration of Zn is higher than that of Cu and hence procedure (1) should be adopted. It is evident, however, from the present study that the procedure of Cu(II) titration and extrapolation to zero $I_p(\text{Zn})$ [5] may lead to erroneous results.

Cu(II) can be determined simultaneously with Zn(II) using the same deposition potential and scan, or separately by using a deposition potential positive to $E_p(\text{Zn})$. In the latter case, Zn interference is smaller but not negligible due to undervoltage depositions of Zn(II). This phenomenon was investigated by using ^{65}Zn as a tracer [11]. It was found that about one-third of the Zn deposited at -1400 mV (vs. SCE) will deposit at -900 mV (vs. SCE). For simultaneous determination of Zn and Cu, Zn interference in Cu analysis can be circumvented by using one of the following procedures:

(1) When the original Cu(II) concentration is smaller than Zn(II) concentra-

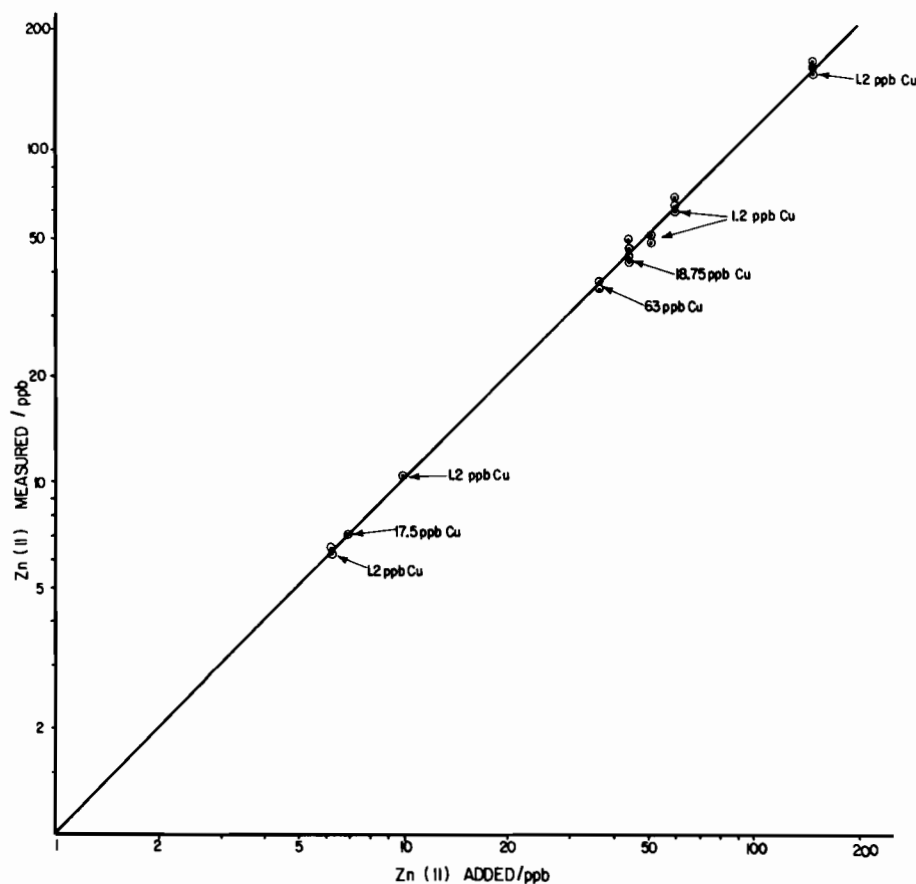


Fig. 8. Experimental results of repeated determination of Zn(II) in stored Gulf of Eilat seawater spiked with Zn(II) and Cu(II). The straight line represents the theoretical 1 : 1 relationship.

tion: standard addition technique is permissible provided that all titration points are below the break point of $I_p(\text{Cu})$.

(2) When the original Cu(II) concentration is larger than Zn(II) concentration: titration by Zn(II) to well below the break point of $I_p(\text{Cu})$ and then calibration by standard addition of Cu(II).

The proposed procedure for the determination of Zn(II) in the presence of Cu(II) was tested on stored Gulf of Eilat seawater. The seawater was first spiked with Cu(II) and Zn(II) and the concentration of Zn(II) was determined following the procedure suggested here. Results of these tests (Fig. 8) seem to support the validity of the proposed method. Maximum deviation of the measured concentration from those expected is $<10\%$ over the range of 6–150 ppb Zn(II) for a wide range of Zn(II) : Cu(II) ratios (Fig. 8).

CONCLUSIONS

The proposed model is sufficient for explaining the break points in $I_p(\text{Zn})$ and $I_p(\text{Cu})$. The break points are attributed to the formation of an IC with the stoichiometry ZnCu .

The discrepancies between the experimental results and model calculation are probably due to formation of Cu-rich IC's (such as Zn_2Cu_5) which were neglected in the model.

The break points of the $I_p(\text{Zn})$ titration curves are equivalence points at which $M_{\text{Cu}} = M_{\text{Zn}}$.

The break point in the $I_p(\text{Cu})$ titration curves represents the case in which the total concentration of Zn and Cu in the amalgam are equal at the stripping peak time. The corresponding relationship in solution is $M_{\text{Cu}} \cong 0.4 M_{\text{Zn}}$ for the present experimental conditions.

Simultaneous determination of Zn and Cu in seawater by ASV is possible provided that the interfering effects are taken into account.

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