1690 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1690—1694 (1973) [Vol. 46, No. 6

Determination of Arsenic(III) by Anodic Stripping Method Using Co-deposition with Copper

Takeshi Kuwabara, Shigetaka Suzuki, and Shun Araki

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

(Received June 10, 1972)

The determination of arsenic(III) by anodic stripping using co-deposition with copper was worked out. A 0.24 M hydrochloric acid containing arsenic(III) and copper(II) was electrolyzed with a rotating platinum electrode (rpm=800) at a constant current. The deposit on the electrode was stripped by linear potential sweep method in 4 M hydrochloric acid. The stripping voltammogram was recorded in the span voltage −0.2—+1.2 volt *vs.* SCE. The stripping voltammogram showed two peaks, at zero volt and 0.5 volt *vs.* SCE. The area of the second peak was proportional to the concentration of arsenic. Linear dynamic range was 1—20 microgram per milliliter. The method was rapid and simple, the time required for analysis being about 35 minutes (electrolysis temperature, 25 °C). X-ray and electron diffractions indicate that the second peak in the stripping voltammogram results from the dissolution of Cu_3As.

Stripping voltammetry was developed to increase the sensitivity of electroanalytical methods. Anodic stripping voltammetry consists of a preliminary concentration or deposition process and a dissolution or stripping (anodic oxidation) process. The deposition step is carried out for a definite time under reproducible conditions, and the stripping process mostly by means of voltammetric scanning. This method has been applied only to elements such as copper or silver, which are easily deposited alone on a working electrode.[1)]

However, it is known that some elements such as arsenic and tellurium, which are hardly deposited alone on a working electrode, have been easily co-deposited with copper on a solid electrode. Some electrogravimetric analyses utilizing co-deposition of two elements have been reported.[2–6)]

We have developed anodic stripping voltammetry for arsenic using co-deposition with copper. Arsenic(III) and copper were first deposited cathodically on a rotating platinum electrode, and the deposit was stripped in another electrolytic cell. The resulting stripping voltammogram showed two peaks. Arsenic was determined from the area of the second peak. Electrolysis conditions both in the stripping and depposition steps were studied, composition of the deposit being also investigated.

Experimental

Apparatus. The apparatus is shown schematically in Fig. 1. A Yanagimoto polarograph Model PA-101 was used as the source of scanning voltage and the recorder in the stripping step. A Yanagimoto controlled potential electrolyzer Model VE-3 was used as the source of constant current. A rotating platinum electrode(RPE) with surface area 0.35 cm² was used as a working electrode. The counter electrode was a platinum plate in the deposition step and a saturated calomel electrode (SCE) in the stripping step.

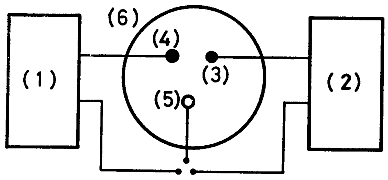

Fig. 1. Schematic diagram of anodic stripping apparatus.
(1) Polarograph; (2) Galvano-stat; (3) Platinum plate electrode; (4) SCE; (5) RPE; (6) Electrolytic cell with sintered glass membrane

Reagents. Standard solution of copper: Pure copper (0.6406 g of four nine purity) was dissolved into concentrated nitric acid (7 ml). After evaporation of the solution to dryness, the residue was dissolved in 10 ml of concentrated hydrochloric acid and then the total volume was made up to 1 l. The concentration of copper was 1.008×10^{-2} M, or 0.6406 mg per ml.

Stadard solution of arsenic: A weighed amount of pure arsenic(III) oxide (0.6605 g) was dissolved in 100 ml of sodium hydroxide solution (0.46%) and acidified with concentrated hydrochloric acid. The total volume was then made up to 500 ml. One ml of this solution contained 1.000 mg of arsenic.

Deionized water was used throughout the experiment. All other reagents were of guaranteed grade.

Results

Stripping Voltammogram of Arsenic. A hydrochloric acid solution of arsenic(III) and copper(II) was electrolyzed with a RPE at a constant current of 100 mA for 30 minutes. The RPE was used as a cathode and a platinum plate as a counter electrode. The deposit on the RPE was stripped in a fresh hydrochloric acid solution by linear potential sweep method, the stripping voltammogram (SV-gram) being recorded. The range of span voltage was −0.2—+1.0 volt *vs.* SCE. The resulting voltammogram is shown in Fig. 2, curve 3, and the SV-gram obtained in the same way in the absence of arsenic, curve 2. No peak appeared in the absence of copper.

Thus, the first peak at 0 volt resulting from stripping of copper and the second peak at +0.5 volt *vs.* SCE indicate the presence of arsenic.

Experimental Conditions in the Stripping Step. The SV-gram showed two peaks resulting from dissolu-

---

1) E. Barendrecht, "Electroanalytical Chemistry," Vol. 2, ed., A. J. Bard, Dekker, New York (1967).

2) S. Torrance, *Analyst*, **63**, 104 (1938).

3) G. Norwitz, *Z. Anal. Chem.*, **131**, 410 (1950).

4) G. Norwitz, *Anal. Chim. Acta*, **5**, 109 (1951).

5) H. Terrey and J. Thabit, *J. Chem. Soc.*, **1957**, 3064.

6) H. Terrey and J. Thabit, *ibid.*, **1958**, 1303.

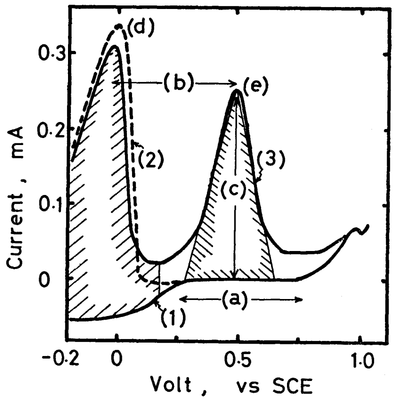

Fig. 2. Anodic stripping voltammogram of arsenic codeposited with copper.
Deposition: Electrolyte (at 25 °C), Curve 1, 2.4×10^{-1} M HCl; Curve 2, 4×10^{-4} M copper in 2.4×10^{-1} M HCl; curve 3, 1.3×10^{-4} M arsenic, 2×10^{-4} M copper in 2.4×10^{-1} M HCl.
Current, 150 mA; Time, 30 min.
Stripping: Scan rate, 0.21 V/min; Span volt. range, $-0.2-+1.2$ V (*vs.* SCE). Electrolyte, 4 M HCl
(a) Zero current range of "background" ($|i|<2\,\mu$A); (b) Distance between two peaks; (c) Peak height of the second peak; (d) First peak; (e) Second peak.

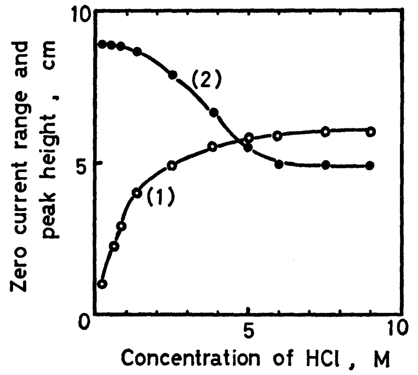

Fig. 3. Effects of concentration of HCl in the stripping step.
Curve 1, Distance of two peaks. Curve 2, Zero current range of background in the stripping step.
Deposition: Electrolyte, 1×10^{-3} M copper, 6.7×10^{-4} M arsenic in 4.8×10^{-1} M HCl at 25 °C Current, 25 mA; time, 5 min
Stripping conditions: Same as Fig. 2.

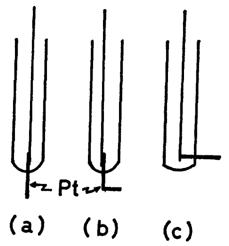

Fig. 4. Types of the rotating platinum electrodes.

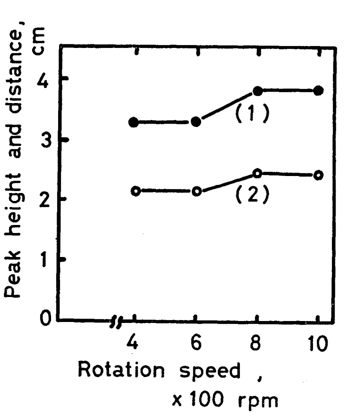

Fig. 5. Effect of the rotation speed of RPE.
Curve 1, Distance between two peaks. Curve 2, Peak height of the second peak.
Experimental conditions: Same as Fig. 3.

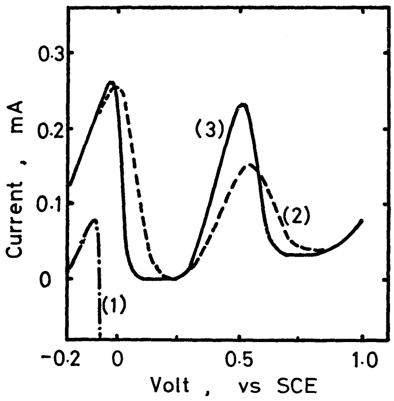

Fig. 6. SV-gram obtained in the cell with or without a membrane.
Curve 1. Cell: without a membrane; Electrolyte: deposition and stripping steps, 0.25 M HCl
Curve 2. Cell: with a membrane; Electrolyte: deposition and stripping steps, 0.25 M HCl
Curve 3. Cell: with a membrane; Electrolyte; deposition step, 0.25 M HCl stripping step, 0.5 M HCl

tion of copper and arsenic. The supporting electrolyte in which two peaks appear in good separation and sensitivity should be chosen. After deposition was over, stripping was carried out in various supporting electrolytes such as sodium sulfate, sodium chloride, perchloric acid and hydrochloric acid, the best SV-gram being obtained in hydrochloric acid solution.

The effect of concentration of hydrochloric acid on the SV-gram was examined under definite conditions in the deposition step. The results are shown in Fig. 3. We see that 3—4 M hydrochloric acid is preferable as regards the extent of the zero current range of the background (Fig. 2) and separation of two peaks in the SV-gram. Subsequent stripping was therefore carried out in 4 M hydrochloric acid.

The rotating platinum electrodes used are shown in Fig. 4. They were rotated at a constant speed by a synchronous motor. Type (a) was preferable to any other electrode because turbulence produced by rotation was less and the current more steady and reproducible. The current depends on the rate of rotation, which also affects reproducibility: the precision deteriorates if the rate of rotation is either too high or low. The rpm 800—1000 was preferable (Fig. 5). The rpm 800 was employed. The RPE was pretreated electrolytically in nitric acid solution by a controlled current of 400 mA. Its polarity was reversed every 5 minutes so that the electrode was in turn the anode, cathode and anode.

The electrolytic deposition was carried out from 0.25 M hydrochloric acid solution of arsenic and copper in a cell without a membrane. After deposition, the deposit was stripped in the same electrolyte. The stripping voltammogram is shown in Fig. 6, curve 1. The curve shows that a reduction current restricted by an oxidant was too large to obtain a SV-gram. The oxidant should be dissolved chlorine generated at the counter electrode during the course of deposition and diffused to the surface of the RPE. Curve 2 was obtained in a cell with a sintered glass membrane by stripping into the same electrolyte as that used in the deposition step. It is seen that the cell should have the membrane to prevent interfering electrode reaction.

Curve 3 was obtained by using 0.25 M HCl as the electrolyte in the deposition step and 0.5 M HCl in the stripping. The cell used had a membrane. The difference between curves 2 and 3 was accounted for by the change of the concentration of HCl in the stripping step. Two peaks appearing in the curve 3 were sharper than those in curve 2. Sharpness of the peak indicates the reversibility of the electrode process. Sharpness changed with the concentration of HCl. The stripping reaction seems to occur accompanied by the formation of a chloro-complex ion.

Experimental Conditions in the Deposition Step. Supporting electrolytes such as sodium sulfate, sodium chloride, perchloric acid and hydrochloric acid were used in the deposition step and the deposit was stripped under definite conditions. Hydrochloric acid was found to be the most suitable electrolyte. Under optimum conditions in the stripping step, the effect of concentration of hydrochloric acid was examined in the deposition bath containing definite amounts of arsenic and copper. Effects of concentration of the acid on the height of the second peak are shown in Fig. 7.

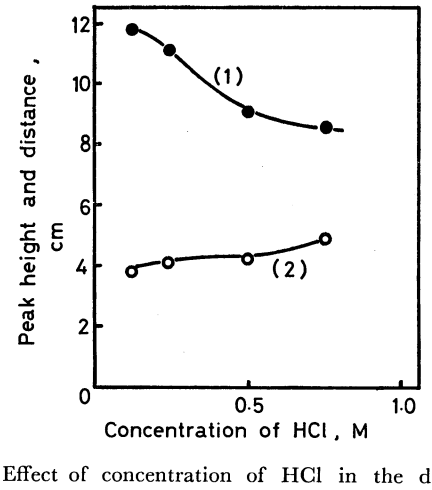

Fig. 7. Effect of concentration of HCl in the deposition step.
Curve 1, peak height; Curve 2, distance between two peaks; Experimental conditions: Same as Fig. 3.

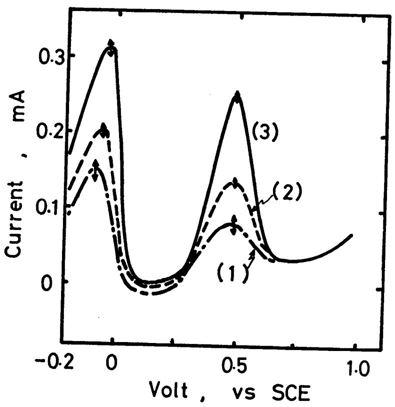

Fig. 8. Effects of deposition current density on peak height. Curve 1, 0.057 A/cm^2; Curve 2, 0.143 A/cm^2; Curve 3, 0.286 A/cm^2. Arrows show ranges of experimental results.

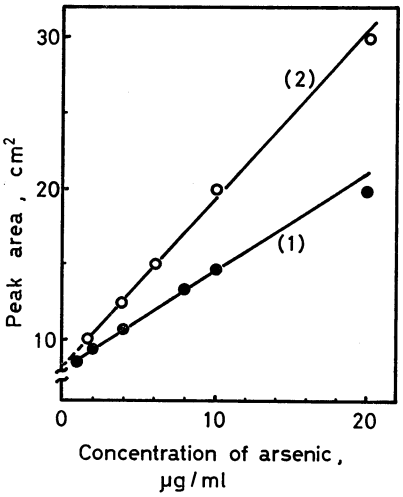

Fig. 9. Analytical curves.
Deposition: Electrolyte, 0.24 M HCl, 2×10^{-4} M Copper; Current, (1) 100 mA, (2) 150 mA
Other experimental conditions: Same as Fig. 2.

Taking into account the height of the second peak and distance between two peaks, 0.2—0.25 M hydrochloric acid solution was found to be preferable for the electrolyte in the deposition step. Hydrochloric acid of 0.24 M was employed. As regards the reproducibility of peak height, the optimum deposition current should be greater than 50 mA (current density 0.14 A/cm^2). The results are shown in Fig. 8. The reproducibility deteriorated when the deposition current exceeded 150 mA. It seems that the current density 0.24—0.4 A/cm^2 is suitable. Current densities 0.28 and 0.42 A/cm^2 (100 and 150 mA, respectively) were employed.

The potential of a working electrode (RPE) was about -1.0 V *vs.* SCE at 100 mA of the deposition current.

Analytical Results. The second peak in SV-gram resulted from the presence of arsenic. A set of 0.24 M hydrochloric acid solutions containing arsenic in concentrations from 10^{-5} M to 2.6×10^{-4} M with copper (2×10^{-4} M) were prepared. Arsenic was co-deposited with copper on RPE at the constant current of 100 or 150 mA for 30 minutes. After deposition, the deposit was stripped into 4 M hydrochloric acid by the linear potential sweep method and the SV-gram was recorded. The areas of the second peaks were calculated through the method of height times width at half height, taking zero current as the the base line (Fig. 2), and were found to be proportional to the amounts of arsenic (Fig. 9). Two analytical curves were obtained for two different deposition current densities. Arsenic was determined in the range $(1—20)\times10^{-6}$ g/ml with a relative deviation less than 10%. Analytical curves did not pass through the zero point because of the capacity current and the graphical method used for measuring the peak areas.

Discussion

Composition of the Deposit. Since it was difficult to obtain the X-ray diffraction pattern of the deposited film on the RPE directly, a platinum sheet (17 mm × 17 mm) was employed as the working electrode instead and the deposition process was carried out with different cathodic current densities, *viz.*, 0.10, 0.16, and 0.28 A/cm^2. The diffraction pattern was obtained with X-ray of CuK_α. It is thought that the phase structure of the deposited film is influenced not only by the cathodic potential but also the rate of cathodic reaction, but that no difference in diffraction pattern is observed with the change of current density. Thus, deposition was carried out with the current density 0.28 A/cm^2 for 25 hr in different solutions as follows:

(1) 2×10^{-4} M copper, 2.67×10^{-4} M arsenic (As, 2.02×10^{-5} g/ml), 0.24 M HCl

(2) 2×10^{-4} M copper, 2.67×10^{-5} M arsenic 0.24 M HCl

However, no difference in diffraction pattern was observed also in this case. Distances between planes, "*d*" values and their relative intensities were calculated from the diffraction patterns. On being compared with data from the ASTM powder data file, the results were found to indicate the presence of Cu_3As and/or Cu_2As in the deposit.

Electron diffraction pattern of the deposit showed that composition of copper arsenide in the deposit was Cu_3As, which was also the most stable in the phase diagram of Cu-As alloys.[7]

Electrode Reaction in the Stripping Step. The deposit on the RPE was first stripped at the constant potential of +0.25 volt *vs.* SCE into 4 M hydrochloric acid. The potential was satisfactory to complete the first anodic oxidation. The copper dissolved in electrolyte was determined by the spectrophotometric method with zinc dibenzyldithiocarbamate.[8] The number of coulombs in the electrode reaction were calculated from total amounts of copper dissolved and the areas under the first peaks.

TABLE 1. AMOUNTS OF COPPER IN THE FIRST PEAK

Amounts of Cu, by colorimetry *W*, (μg)	Peak area (cm^2)	Numbers of coulombs, *Q* (mC)	Valency, *n*[a)]
36.0	39.0	56.2	1.03
35.2	37.8	54.5	1.02
32.8	36.1	52.0	1.04
39.6	42.4	61.0	1.01
39.6	41.5	59.8	1.00

a) $n=QM/WF$, *M*: atomic weight of copper, *F*: Faraday constant.

Deposition: Electrolyte, 1.07×10^{-4} M arsenic in 2×10^{-4} M copper and 0.24 M HCl; Total volume, 10 ml; Current, 10 mA; Time, 28—30 min

Stripping: Scan rate, 0.21 V/min; Span volt. range, −0.2—+1.2 V *vs.* SCE

TABLE 2. AMOUNTS OF COPPER IN THE SECOND PEAK

Amounts of Cu, by colorimetry W_1 (μg)	Peak area (cm^2)	Amounts of Cu as Cu (II) by coulometry W_2 (μg)	W_2/W_1 (%)
21.8	30.2	14.3	65.5
21.0	30.0	14.2	67.6
17.8	24.8	11.8	66.3
11.8	17.0	8.1	68.5
10.8	16.3	7.7	71.0

Deposition: Electrolyte, 2.67×10^{-4} M arsenic in 2×10^{-4} M copper and 0.24 M HCl; Total volume, 10 ml; Current, 150 mA; Time, 25—32 min

Stripping: Conditions same as Table 1.

It was thought that the electrode reaction was oxidation of copper to univalent state(Table 1).

The deposit was thus stripped at the constant potential +0.75 volt *vs.* SCE into a new stripping bath of 4 M hydrochloric acid. This potential corresponded to that of completion of the second anodic oxidation. The total amount of copper dissolved into the electrolyte was determined by the spectrophotometric method and compared with the value calculated from the areas of the second peaks.

Copper was also found in the electrolyte in which the second anodic oxidation occurred, and aresnic was also detected in the electrolyte by Gutzeit's method (Table 2). The number of coulombs under the second peak was equal to two-thirds of the values calculated from oxidizing copper to copper(II) ion and did not coincide with them. The peak potential of the second peak deviated greatly from the half-wave potential in the polarography of arsenic (−0.45, or −0.88 volt) or of copper(II) (+0.03 volt *vs.* SCE) in 1 M HCl. It is considered that the second peak in the SV-gram resulted from dissolution of Cu_3As. The mechanism of the electrode reaction of the second anodic oxidation is not clarified.

Effects of Diverse Ions. The deposition of copper and arsenic was carried out in the presence of several ions by the same procedure employed in the determination of arsenic.

---

7) Hansen, "Constitution of Binary Alloys," 2nd Ed., McGraw-Hill, New York (1958).

8) T. Mukoyama and T. Hasebe, *Bunseki Kagaku*, **20**, 1033 (1971).

Sodium and calcium ions did not interfere in the deposition. We thought that barium would interfere in the deposition with formation of a stable alloy with copper, but no interference was observed. Zinc and nickel, however, had an effect on the area of the second peak in SV-gram.

No effects of foreign anions such as sulfate, nitrate and perchlorate ions were observed.

The authors thank Dr. Y. Tanabe for helpful discussions and suggestions in analysing X-ray and electron diffraction patterns.