

Studies on the Controlled Potential Electrolysis. (IX)

Electrolytic Separation of Copper from Bismuth by the Use of Ethylenediaminetetraacetic Acid*

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Lustrous electrolytic deposit of copper is obtained quantitatively by the use of EDTA. The deposition potentials of copper and bismuth at a rotating platinum electrode and the half-wave potentials of them at a dropping mercury electrode from their EDTA solutions of various pH values have been measured. The conditions for electrolytic separation of copper from bismuth were tested and the following procedure proved to give good results. About 130~140 ml. of the sample solution adjusted to pH 3.1, which contains 2~3 times as much the amount of EDTA as that of copper plus bismuth in molar ratio, 1 g. of ammonium nitrate and 1.5 g. of hydroxylamine hydrochloride, are electrolyzed at 60~70°C, keeping the cathode potential at -0.41 V *vs.* S. C. E. automatically. The results indicated that copper can be quantitatively electrolyzed in the presence of bismuth less than 1.2 g. and that in the presence of 1.3 g. of bismuth a trifle error of $+0.5\sim0.6$ mg. is involved.

INTRODUCTION

Although disodium salt of ethylenediaminetetraacetic acid (EDTA) has been used very widely in analytical chemistry, it is scarcely used in electrolytic gravimetry¹⁾. The authors applied this reagent to the electrolytic analysis of copper, and could obtain a good deposit of it.

The electrolytic separation of copper from bismuth, which is rather difficult, was performed by J. J. Lingane, S. L. Jones²⁾, and by authors³⁾, using tartrate. EDTA forms the blue complex with copper which is stable between pH 4.75 and 6.50. Its absorption maximum lies between 720 and 730 m μ , and this complex can be used for the colorimetric determination of copper⁴⁾. Bismuth also forms the stable complex with EDTA at low pH⁵⁾. After studying the deposition potentials of these two metals from their EDTA solutions at various pH values, the authors examined the electrolytic determination of copper in the presence of much bismuth, using the automatically-controlled cathode potential technique, and obtained far better results than those in the previous methods^{2),3)}.

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EXPERIMENTALS

I. Samples and Reagents

Copper. The stock solution was prepared by dissolving pure copper sulfate in water and acidifying with sulfuric acid. The concentration of it was determined by electrolysis of the ammoniacal solution or the EDTA complex solution described below.

Bismuth. The stock solution was prepared by dissolving pure bismuth nitrate in dilute nitric acid, adding about twice as much the amount of EDTA as that of bismuth in molar ratio to prevent hydrolysis, and adjusting the pH to an appropriate value (3~7) with aqueous sodium hydroxide and ammonia. The stock solution was also prepared by dissolving metallic bismuth in nitric acid and diluting it with water. The concentration of bismuth was gravimetrically determined by the usual method as the oxide and by electrolysis of the EDTA complex solution.

EDTA. One-tenth M and 0.2 M solutions were prepared by dissolving "ETA" of the Kanto Chemicals Co., or "Dotite" of the Dojindo Co., in water.

Hydroxylamine hydrochloride. Reagent, made by Merck, was used.

Ammonium nitrate. Forty % solution was prepared by dissolving pure chemicals in water. One ml of the solution contains 0.4g of ammonium nitrate.

II. Apparatus

A 200 ml. beaker was used as an electrolysis cell, and the platinum electrodes made in accordance with JIS (Japanese Industrial Standard) were used as anode and cathode. In some cases, a platinum gauze electrode (a cylindrical form of 3.5 cm. in diameter and 5 cm. in height) was used as cathode. A spiral anode was placed in the middle of the cylindrical cathode. The solution was stirred thoroughly with a motor-driven stirring rod placed in this spiral form of the anode. A saturated calomel electrode (S. C. E.) was used as a reference electrode to control the cathode potential, and the tip of the saturated potassium chloride solution of the electrode was placed just outside the cathode. As an apparatus for the automatic control of the potential, an automatic balancing instrument using electronic servo-mechanism was used, the sensitivity of which is ± 5 mV⁶⁾, and a Beckman H2 type glass electrode pH meter was used for adjusting the pH of the solution.

III. Electrolysis of Copper when it is present alone. (Constant Bath Voltage Method)

Copper forms the complex with EDTA as described above. Table 1 shows the results of electrolyses of copper, varying the molar ratio of copper to

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EDTA under various conditions. The total volume of the electrolytic solution was 130~140 ml. and the pH of the solution was adjusted with aqueous ammonia and sulfuric acid. In some cases, it contained 2.5~5 ml. of 40 % ammonium nitrate solution.

Table 1.

Cu taken, mg.	Cu : EDTA Molar Ratio	NH ₂ OH · HCl, g.	pH	Bath Voltage, V	Temperature °C	Cu		Remarks
						Found, mg.	Error, mg.	
62.8	1 : 5	—	7.5	13~18	Room Temp. →45	63.1	+0.3	Rather loose, * blackish deposit.
"	"	—	8.3	9~10	40~50	63.0	+0.2	" *
"	"	—	7.6	10~13	40~55	63.1	+0.3	"
"	"	—	6.0	8~10	Room Temp. →60	62.6	-0.2	" *
"	"	—	6.1	7~7.5	Room Temp. ~a little higher	63.0	+0.2	" *
"	"	1.0	5.9	5~6	Room Temp.	62.8	0	Glistening black* color, and does not come off by touching.
"	"	"	"	4~4.3	40~55	62.8	0	Lustrous, beautiful deposit. *
"	1 : 3	"	5.7	3.5~3.6	50~59	63.0	+0.2	"
"	"	"	"	4.9~5.0	52~58	62.9	+0.1	"
"	"	"	"	3.5~3.7	50~55	62.8	0	"
"	"	"	"	"	53~56	62.8	0	"
"	"	"	"	"	55~58	62.8	0	"
"	"	"	3.0	"	60~63	62.8	0	"
"	"	"	2.9	3.5~3.8	55~63	62.6	-0.2	" **
"	"	"	5.6	"	65~70	62.7	-0.1	"
"	"	"	6.1	0.7~0.8	55~60	62.7	-0.1	"

* In the absence of ammonium nitrate.

** Only sodium hydroxide was used for adjusting the pH.

*** When the bath voltage was made 3.5V in the beginning of electrolysis, the cathode potential was about -0.7V *vs.* S. C. E. and so electrolysis was undertaken at the cathode potential of -0.7V at first and then at -0.8V *vs.* S. C. E.

As is seen in Table 1, good agreements were obtained in the amount of copper, and the deposition became much better by adding hydroxylamine hydrochloride and raising the temperature above 50°C. It seems that the formation of this lustrous deposit is of great advantage. The higher the pH, the longer is the time of electrolysis, and there is no effect of pH on the amount of copper deposit. Raising the temperature is also useful for shortening the time of electrolysis. In the experiments of Table 1, the time for complete electrolysis was 15~60 minutes.

IV. Electrolytic Separation of Copper from Bismuth (Controlled Cathode Potential Method)

(A) On the deposition potentials and the half-wave potentials.

(a) At first the deposition potentials (*vs.* S. C. E.) of the two metals from their EDTA complex solutions at a rotating platinum electrode were measured respectively, as shown in Table 2. For these measurements, the solutions of essentially the same composition as that used in the actual electrolysis were used (see the Note in the Table).

Table 2.

Cu			Bi			EDTA Itself		
pH	Temperature, °C	-V	pH	Temperature, °C	-V	pH	Temperature, °C	-V*
2.48	57~50	0.30	2.48	57~50	0.62	2.48	57~51	0.82
"	57~50	0.34	"	57~50	0.68	"	50~46	0.83
3.06	60~58	0.36	3.05	57~53	0.70	3.03	45~41	0.82
"	58~55	0.36	"	53~50	0.70	"	52~47	0.83
4.06	40~38	0.52	4.06	51~47	0.74	4.08	49~45	0.79
"	52~49	0.48	"	47~43	0.75	"	45~42	0.81
5.48	61~55	0.56	5.49	59~55	0.80	5.45	57~51	0.82
"	55~50	0.59	"	54~49	0.80	"	50~46	0.83
6.51	60~53	0.69	6.51	59~55	0.80	6.51	55~49	0.84
"	53~50	0.68	"	55~51	0.80	"	48~45	0.83

* Potential at which an abrupt increase of current takes place.

Note. All the sample solutions (ca. 130-140 ml.) contain 30 ml. of 0.1 M EDTA (free acid deposits out at pH 2.8 or lower), 1g. of ammonium nitrate and 1g. of hydroxylamine hydrochloride, besides 63.3 mg. of copper in the copper solution and 41.3 mg. of bismuth in the bismuth solution are contained respectively.

An H-type electrolytic cell was used here. The dissolved oxygen was thoroughly removed from the solution by passing purified hydrogen gas through it, and measurements were made under the passage of hydrogen on the surface of the solution. V-i curves were recorded automatically with a pen-recording polarograph, and the potentials (tangent potentials) are shown in Table 2.

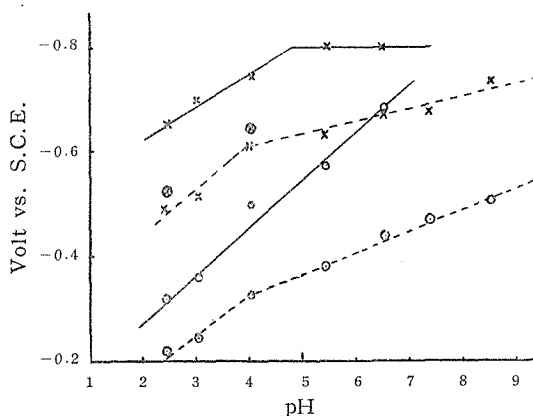


Fig. 1. Relation between deposition potential or half-wave potential and pH.
 ---x--- Bi on Pt; -⊗- Bi on Cu; ---○--- $E_{1/2}$ -Bi; -○- Cu on Pt; ---○--- $E_{1/2}$ -Cu.

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In the case of bismuth, the increase of current is very abrupt, and it is easy to find the deposition potential, but it is somewhat difficult in the case of copper. Although the value of deposition potential of bismuth gradually becomes more positive with the increase of pH, that of copper becomes more positive very quickly (Fig. 1). Then same measurements about bismuth were made using a rotating copper plated platinum electrode, the results of which are shown in Table 3. In this case, the value of deposition potential of bismuth shifted by about 0.1 V toward positive. Therefore, it may be said that bismuth deposits more easily on the copper electrode than on the platinum electrode.

Table 3.

pH	2.46			4.06	
Temperature, °C	57~55	54~50	48~46	59~56	53~51
-V (vs. S. C. E.)	0.52	0.52	0.54	0.65	0.63

Table 4.

pH	Half-wave potential, -V(vs. S. C. E.)		Remarks
	Cu	Bi	
2.42	0.22 0.22	0.49 0.49	Maximum of copper appears. (Free acid deposits.)
3.03	0.24 0.25	0.51 0.52	
4.03	0.33 0.33	0.61 0.61	
5.42	0.38 0.38	0.63 0.63	
6.58	0.44 0.44	0.67 0.67	
7.40	0.47 0.47	0.67 0.68	
8.55	0.51? 0.50?	0.73? 0.74?	Waves of two metals lie very closely and it is difficult to discern.
9.60	?	?	Waves of two metals do not separate at all.

(b) The polarograms were recorded at room temperature using a dropping mercury electrode and an H-type cell, and the half-wave potentials of copper and bismuth were determined. The results are shown in Table 4 and Fig. 1. The components of the solutions were $1.5 \times 10^{-3}N$ with respect to copper and to bismuth, 0.023 M with respect to EDTA, 1 g of ammonium nitrate per 130 ml., and 1.5 g. of hydroxylamine hydrochloride per 130 ml, and no maximum suppressor was used⁷⁾. Typical examples of polarograms are shown

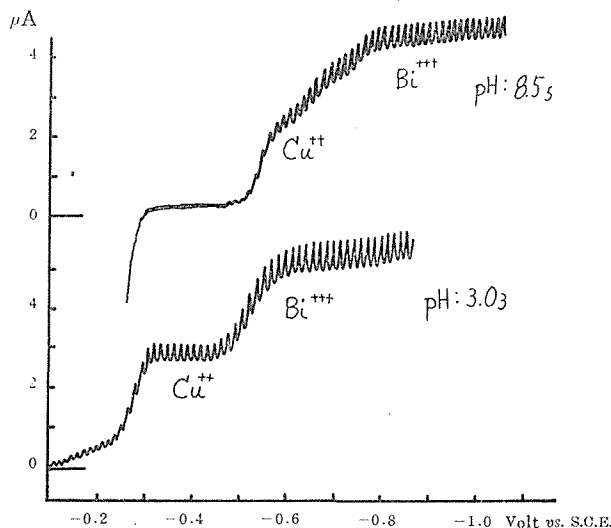


Fig. 2. Typical examples of polarograms of copper and bismuth.

in Fig. 2.

(c) In the polarographic method, the applied potential is raised at fairly high speed, and so, especially in the case of the platinum electrode, it seems that the condition is not the same as that of the actual electrolysis. Therefore, in order to set the condition (see "Preparation of the electrolytic solution" and "Operation of electrolysis" in the following section (B)), the bath voltage was set at a certain value for some time, and the cathode potential and the current were read, and then the bath voltage was raised a little and after setting for some time, the cathode potential and the corresponding current were read. Repeating these treatments, the currents were plotted against the cathode potentials and the range of potential in which an abrupt jump of current occurs in the current-voltage curve was sought. As regards copper, the estimation was undertaken for the solution containing both copper and bismuth. In the case of bismuth, the estimation was made at the copper-plated platinum cathode. When copper is electrodeposited onto the platinum cathode, the current increases gradually as the electrolysis proceeds, it reaches the maximum value and then decreases. From this fact, it seems that copper deposits more easily onto the copper surface than onto the platinum surface. The same effect is also recognized in the case of the deposition of bismuth onto the copper-plated cathode. The results are shown in Table 5.

From the data described above, it is expected that their separation will be difficult at pH below ca. 2.5 and will be possible at pH above 3 at properly controlled cathode potential. This was proved experimentally as described below. It is also anticipated that the separation will become impossible at pH 8~9, but as for the higher pH, the time required for the complete electro-

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Table 5.

Cu		Bi		Cu		Bi	
pH	-V(vs. S. C. E. *)	pH	-V(vs. S. C. E. *)	pH	-V(vs. S. C. E. *)	pH	-V(vs. S. C. E. *)
2.48	0.3~0.4	2.46	The current rised gradually above 0.4 and jumps up above 0.5. ^a	5.48	0.3~0.4	5.50	0.50~0.60 ^a
				3.07		Not adjusted after elect- rolysis	0.50~0.60 ^b
2.90	//	Not ad- justed after elect- rolysis	0.50~0.60 ^a	3.46	0.3~0.4	3.54	0.50~0.65 ^b
3.47	//	3.51	// ^a	3.96	0.3~0.4 (The current does not rise so abruptly.)	4.00	0.60~0.70 ^b
3.97	//	3.96	// ^a				
4.50	//	4.50	// ^a				
4.96	//	4.96	// ^a				

* The range of potential in which an abrupt jump of current occurs.

Notes. ^a Hydroxylamine hydrochloride was used as a depolarizer.

^b Hydrazine hydrochloride was used as a depolarizer.

lysis becomes so long that no further experiments were made.

(B) Operation of separating copper from bismuth.

Preparation of the electrolytic solution. A definite volume of EDTA solution was added to the solution containing the definite quantity of copper and bismuth, and to this solution 2.5 ml. of ammonium nitrate solution (as supporting electrolyte) and 1.5 g of hydroxylamine hydrochloride were added,

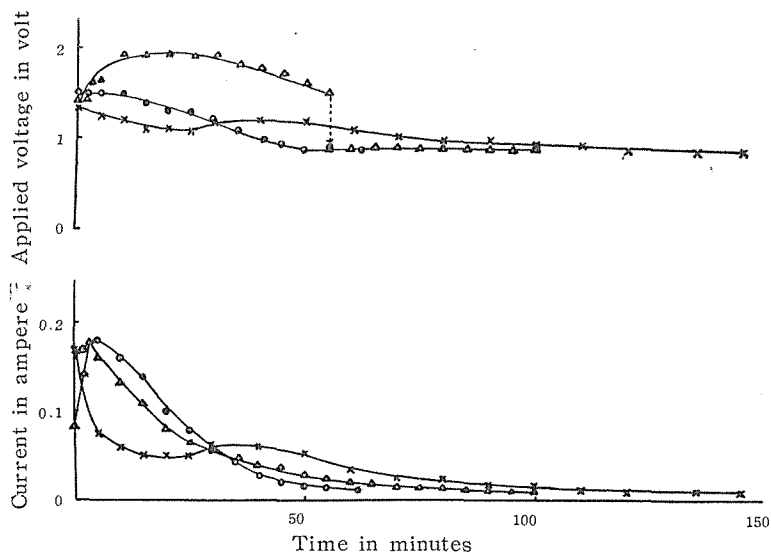


Fig. 3. Typical voltage-time and current-time diagrams. In experiment No. 42, the temperature rose suddenly between 30 and 50 minutes after electrolysis began.

—○—Exp. No. 28 ; —△—Exp. No. 41 ; —×—Exp. No. 42.

then this was diluted to 130 ml. with water, and its pH was adjusted to the definite value (about 3.1 is the optimum value) with aqueous ammonia and sulfuric acid, and its final volume was about 140 ml.

Operation of electrolysis. After heating the beaker containing the electrolytic solution described above on the heating plate of the apparatus and homogenizing the temperature of the solution by stirring it thoroughly (if foams attach on the surfaces of electrodes, electrodes are taken out of the solution and immediately they are immersed into the solution), the potentiostat is adjusted to the definite voltage and then the solution is electrolyzed. The current and the bath voltage were measured during the electrolysis and current-time and bath voltage-time diagrams were made. Typical examples are given in Fig. 3. The temperature of the electrolytic solution is maintained at 60~70°C. The time of electrolysis can be shortened at a higher temperature. The solution is electrolyzed until the blue color of copper-EDTA complex disappears and the small constant residual current value continues. (The larger the EDTA concentration, the smaller was the residual current value, and it ranged from 6 mA to 13 mA.) After the electrolysis, the electrodes are taken out of the solution, washing the cathode with distilled water, and the cathode is washed thoroughly with distilled water, then with alcohol or acetone, dried at about 90°C for 3~5 minutes and weighed as usual.

(a) On the amount of EDTA. The experimental data, changing the molar ratios of the sum of copper and bismuth to EDTA, are shown in Table 6. The results indicate that EDTA acts not only as a complex-forming agent but also as a buffering agent in a sense and prevents the decrease of pH. It is also seen that the amount of EDTA required is more than 1.3 times as many moles as that of copper plus bismuth, but in these experiments, about 2~3 times moles of EDTA were used.

Table 6.

Experi- ment No.	Cu taken, mg.	Bi taken, mg.	Cu+Bi:EDTA molar ratio	pH*	Cathode potential, -V(vs. S.C.E.)	Tempe- rature, °C	Time, min.	Cu	
								Found, mg.	Error, mg.
9	63.5	40.5	1:3	3.47(2.75)	0.41~0.44	61~63	60	63.5	0
15	"	"	1:2	3.46(2.72)	0.44	60~63	35	63.7	+ 0.2
14	"	"	1:1	3.47(2.30)	"	61.5~63	45	71.3	+ 7.8
42	63.3	711.0	1:1.6	3.10(2.69)	0.41	63~66	135	63.5	+0.2**
41	"	474.0	1:1.5	3.16(2.80)	"	60~64	95	63.4	+ 0.1
45	"	355.5	1:1.3	3.17(2.48)	"	60.5~62	90	63.5	+ 0.2
43	"	237.0	1:1.1	3.15(2.49)	"	64~67	45	64.4	+ 1.1
44	"	118.5	1:0.8	3.11(2.34)	"	58~67.5	35	76.6	+13.3**

* In parentheses, pH values after electrolyses are shown, as well as in the following tables.

** The copper-plated platinum cathode was used.

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Table 7.

Experi- ment No.	Cu taken, mg.	Bi taken, mg.	Cu+Bi:EDTA molar ratio	pH	Cathode potential, -V(<i>vs.</i> S. C. E.)	Tempe- rature, °C	Time, min.	Cu	
								Found, mg.	Error, mg.
65	63.3	10.8	1:5	3.11(2.62)	0.46	64~65	50	65.8	+ 2.5
5	63.5	40.0	1:3	3.08	0.52	63~64		The deposit became black.	
4	“	36.0	“	3.00	0.46	59~63.5	45	64.6	+ 1.1
7	“	40.5	“	3.06	0.44	61~63.5	60	63.6	+ 0.1
63	63.3	10.8	1:2	3.10(2.57)	0.46	65~67	40	64.8	+ 1.5
64	“	“	“	3.10(2.58)	0.44	65~67.5	45	63.4	+ 0.1

Table 8*.

Experi- ment No.	Cu taken, mg.	Bi taken, mg.	Cu+Bi: EDTA molar ratio	pH	Tempe- rature, °C	Time, min.	Cu	
							Found, mg.	Error, mg.
23	63.5	40.5	1:2.8	2.48(2.46)	63~65	40	74.1	+10.6
11	“	“	1:3	3.97(2.80)	61~65.5	55	63.5	0
16	“	“	“	4.50(3.40)	60.5~62.5	60	63.7	+ 0.2
17	“	“	1:2.8	4.96(3.12)	63~64	50	63.7	+ 0.2
21	“	“	“	5.48(2.98)	62~64	140	63.5	0

* See also, Tables 6 and 7. Cathode potential was kept at -0.44V (*vs.* S. C. E.) in all experiments in this table.

(b) On the cathode potential during electrolysis (*vs.* S. C. E.)

The results are shown in Table 7. For the quantity of bismuth as shown in Table 7, that is, 40.5 mg. of bismuth in 140 ml of solution, a potential of -0.44 V is sufficient for separating copper, but when the potential is lowered to -0.46 V, the separation becomes incomplete in the presence of only 10 mg. of bismuth (even when 5 equivalents of EDTA are present).

(c) On the pH value of the electrolytic solution. The results are shown in Table 8. The separation is impossible at pH 2.48, but is possible at pH above 3. At pH 5.4, that is, the region in which copper-EDTA complex is stable, very long time is required for carrying out a complete electrolysis, and therefore it is best to adjust the pH of the solution to about 3.1.

(d) On the anodic depolarizer. In all experiments in this paper, hydro-

Table 9*.

Experi- ment No.	Cu taken, mg.	Bi taken, mg.	pH	Cathode potential, -V(<i>vs.</i> S. C. E.)	Tempe- rature, °C	Time, min.	Cu	
							Found, mg.	Error, mg.
8	63.5	40.5	3.07	0.44	62~64.5	75	63.5	0
10	“	“	3.46(2.82)	“	62~63.5	110	63.3	- 0.2
12	“	“	3.96(3.38)	0.44~0.52	61~65	175	64.1	+ 0.6
13	“	“	3.51	0.48	62~63	50	64.5	+ 1.0

* The molar ratio of EDTA to the copper plus bismuth is 3:1.

xylamine hydrochloride was used, but in Table 9, 1.5 g. of hydrazine hydrochloride was used as a depolarizer. Other constituents of the solution are the same as in other experiments. As is obvious from Table 9, it cannot be recognized that hydrazine hydrochloride is superior to hydroxylamine hydrochloride. Lustrous deposits are also obtained in this case. The current efficiencies are over 90 % in the case of hydrazine hydrochloride and 70~90 % (average, 80.2 %) in the case of hydroxylamine hydrochloride, respectively. The high current efficiency is a point of advantage of hydrazine hydrochloride, but it takes so long time for complete electrolysis that hydroxylamine hydrochloride was used. As indicated by Lingane and Jones²¹, when hydroxylamine hydrochloride was used as a depolarizer, the anode potential sometimes dropped suddenly and so bath voltage also dropped during the electrolysis. However, in the electrolysis at room temperature, hydrazine hydrochloride has more ability as a depolarizer than hydroxylamine hydrochloride⁸¹. The effect will be reported later.

(e) On the permissible quantity of bismuth. The results of experiments in which the amounts of bismuth were increased in the presence of a certain amount of copper are shown in Table 10.

Table 10*.

Experiment No.	Cu taken, mg.	Bi taken, mg.	pH	Cathode potential, -V(<i>vs.</i> S. C. E.)	Temperature, °C	Time, min.	Cu	
							Found, mg.	Error, mg.
27	63.5	60.8	3.04(2.66)	0.44	62~65	55	65.5	+ 2.0
24	"	"	3.61(3.18)	"	61~62	55	63.6	+ 0.1
20	"	81.0	2.99	"	57.5~60	40	67.3	+ 3.8
18	"	"	3.54(2.68)	"	62.5~64.5	37	64.8	+ 1.3
22	"	"	3.03(2.68)	"	61.5~63	45	64.5	+ 1.0
19	"	121.5	3.59(2.70)	"	62.5~63.5	35	65.4	+ 1.9

* The molar ratio of EDTA to the copper plus bismuth is 3 : 1.

At the cathode potential of -0.44 V (*vs.* S. C. E.), the separation of copper from less than 40.5 mg. of bismuth is possible, but that from 60.8 mg. of bismuth is incomplete at pH 3. At pH 3.6, although the separation from 60.8 mg. of bismuth becomes possible, that from more than 81.0 mg. bismuth is impossible. And so, keeping the cathode potential at -0.41 V (*vs.* S. C. E.), the electrolyses were undertaken, and the results are shown in Table 11.

It is clear that copper can be quantitatively separated from less than 1.2 g of bismuth per 140 ml. of solution and in the presence of 1.3 g. of bismuth the positive error of 0.5~0.6 mg. is involved in the deposition of copper. (But this error is only 1/2600 of the amount of bismuth coexisted.)

(f) When the total amounts of copper and bismuth are kept almost constant. Keeping the total amounts of them almost constant (about 0.35 g.) and

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Table 11*.

Experiment No.	Cu taken, mg.	Bi taken, mg.	Cu+Bi : EDTA molar ratio	pH	Temperature, °C	Time, min.	Cu	
							Found, mg.	Error, mg.
25	63.5	81.0	1 : 3	3.53(2.75)	61.5~65	115	63.4	- 0.1
26	"	"	"	3.07(2.63)	64~65.5	70	63.5	0
28	63.3	"	"	3.11(2.60)	61~64	55	63.3	0
29	"	121.5	"	3.15(2.60)	62~65.5	65	63.3	0
30	"	162.0	"	3.13(2.61)	63~65.5	50	63.4	+ 0.1
32	"	186.9	"	3.17(2.60)	63.5~67.5	80	63.2	- 0.1
31	"	208.1	"	3.13(2.58)	64.5~65.5	55	63.5	+ 0.2
33	"	249.2	"	3.10(2.70)	62.5~64	70	63.3	0
34	"	311.5	"	3.06(2.70)	62.5~63.5	90	63.4	+ 0.1
35	"	373.8	"	3.19(2.73)	60~64	75	63.3	0
36	"	436.1	"	3.10(2.70)	56.5~66	105	63.5	+ 0.2
37	"	498.4	"	3.18	65.5~69	65	63.3	0
38	"	568.8	"	3.19(2.76)	64~67	130	63.2	- 0.1
39	"	616.2	"	3.13(2.78)	61~68	255	63.4	+ 0.1
47	"	948.0	1 : 1.7	3.17	61~67.5	170	63.6	+ 0.3**
52	"	1082.0	1 : 2	3.11(2.84)	67.5~69	125	63.5	+ 0.2
57	"	"	"	3.12(2.90)	63.5~68	110	63.5	+ 0.2
59	"	1190.2	"	3.13	63~67.5	120	63.3	0
61	"	"	"	3.10(2.90)	63~66	160	63.3	0
55	"	1298.4	1 : 1.7	3.11(2.82)	66.5~70	150	63.9	+ 0.6
60	"	"	"	3.12	60~70	180	63.8	+ 0.5

* See also Table 6.

** The copper-plated platinum cathode was used.

changing the relative amount of copper to bismuth, the electrolyses were undertaken; the results are shown in Table 12. In this case, the bismuth solution obtained by dissolving the metal in nitric acid was used. The molar ratio of EDTA to the copper plus bismuth was 2 : 1, and the cathode potential was kept at -0.41 V (*vs.* S. C. E.).

Table 12.

Experiment No.	Cu taken, mg.	Bi taken, mg.	pH	Temperature, °C	Time, min.	Cu	
						Found, mg.	Error, mg.
46	126.6	237.0	3.18(2.78)	61~66.5	95	126.5	- 0.1
53	189.9	161.7	3.20(2.60)	66~70	95	190.1	+ 0.2
49	253.2	107.8	3.17(2.78)	64.5~67.5	120	253.5	+ 0.3
48	316.5	47.4	3.10	64~67.5	190	316.6	+ 0.1
54	316.5	53.9	3.12(2.82)	69.5~72	190	316.5	0

It is clear from these results that copper can be quantitatively separated from bismuth.

(C) Comparison of this method with others.

On comparing this method with other methods of separation using tart-rate, the following points deserve mention.

- i) The permissible amount of bismuth coexisted is much larger.
- ii) Even when the large amount of bismuth is present, all electrolyses can be carried out by keeping the cathode potential at -0.41 V (*vs.* S. C. E.). If the amount of bismuth is less than 40 mg the cathode potential can be lowered to -0.44 V.
- iii) As to the pH value of the electrolytic solution, it is sufficient to be higher than 3, and it is unnecessary to adjust it so precisely as other methods.
- iv) As to temperature, it is also unnecessary to limit it so precisely.
- v) Both hydroxylamine and hydrazine hydrochlorides can be effectively used as a depolarizer.
- vi) The electrodeposited copper is very lustrous.
- vii) The quantity of EDTA, acting as a complex-former, must be more than 1.3 times as many moles as that of the sum of bismuth and copper, but it is unnecessary to measure it out so accurately.
- viii) It is also unnecessary to add other buffering agents particularly.
- ix) The blue color of copper-EDTA complex can be utilized as the indicator in electrolysis.

The effects of coexistent ions besides bismuth and the separation by the usual electrolysis at room temperature will be reported later.

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REFERENCES

- (1) J. A. Dean and S. A. Reynolds, *Anal. Chim. Acta*, **11**, 390 (1954).
- (2) J. J. Lingane and S. L. Jones, *Anal. Chem.*, **23**, 1798 (1951).
- (3) M. Ishibashi and T. Fujinaga, *Japan Analyst*, **2**, 342 (1953).
- (4) W. Nielsch and G. Böltz, *Z. anal. Chem.*, **143**, 1 (1954).
- (5) R. Přibil and B. Matyska, *Chem. listy*, **44**, 305 (1950) [*C. A.*, **45**, 3756, (1951)].
K. Ter Haar and J. Bazen, *Anal. Chim. Acta*, **10**, 108 (1954).
- (6) M. Ishibashi and T. Fujinaga, *This Bulletin*, **33**, 103, (1955).
- (7) R. L. Pecsok, *Anal. Chem.*, **25** 561 (1953).
- (8) A. J. Lindsey and H. J. S. Sand, *Analyst*, **60**, 739 (1935).