Studies of Polarography with Organic Solvent Extraction Method.

Part II. Direct Determination of Copper in Mercury.

By

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I. Introduction

The present paper is a part of systematic investigation on the use of the DDTC (diethyldithiocarbamate)-CHCl₃ extraction method in the polarographic analysis. When the DDTC-metal chelate in the chloroform layer is back-extracted with aqueous solution containing an excess of mercuric ions, only free metal ions come into the aqueous layer and DDTC remains in chloroform layer forming stable chelate with mercuric ions. By this method¹⁾, the interference of free DDTC in the polarographic determination of metal ions can be eliminated. Excess of mercuric ions in aqueous solution, however, interferes with the polarographic determination of metal ions. In the previous paper²⁾, the method for removing mercuric ions by precipitating them with hydrazine was applied for the determination of copper.

In the course of search of simpler method to eliminate the interference of the large amounts of mercuric ion, the following method using A.C. polarography was found satisfactory. A.C. polarographic method, as well known, has the advantage over the D.C. method in the point that the interference by the substance reduced at a more positive potential is small. By applying proper SAS's (surface-active substances), which were PAA and agar in this study, to suppress the large maximum in mercuric wave, Hg²⁺ up to $2.0 \times 10^{-2} M$ did not interfere with the determination of Cu²⁺ of concentration down to $2.0 \times 10^{-6} M$ (accuracy of $\pm 4\%$). The details of the experimental results are described in the following.

II. Reagents and Apparatus

II. 1. Reagents.

(1) Copper solution: 0.3204 g of copper (99.95%) was dissolved with 5 ml of concentrated nitric acid and was diluted to 500 ml with redistilled water. The solution was $1.084 \times 10^{-2} M$ in copper ions.

(2) Mercury solution: 20.336 g redistilled mercury was dissolved in 30 ml of concentrated nitric acid and was diluted to 1000 ml with water. The solution was $1.101 \times 10^{-1} M$ in mercuric ions.

(3) Stock solution of base electrolyte: 2 M ammonium acetate + 0.4 M tartaric acid. Both were prepared using reagents of analytical grade.

(4) Maximum suppressor.

a) PAA (Polyacrylamide) solution: PAA solution was prepared by dissolving PAA 75 of American Cyanamide Co. (N.Y.) in 0.4, 0.6 or 1.0% (w/v) concentrations,

b) Agar solution: agar solution in 0.1% or 0.2% (w/v) concentration was prepared using chemical pure product.

II. 2. Apparatus.

(1) Polarograph: for A.C. polarographic measurement, Yanagimoto Polarograph Type 102 was used. Yanagimoto Polaromultiplier Type PM 1 was used with the above instrument to run the square wave polarograms.

(2) D.M.E.: the characteristics of the D.M.E. was $m=0.6817$ mg/sec., $t=4.9$ sec., ($h=59.5$ cm) at -0.08 V *vs.* SCE in 0.5 M $\text{NH}_4\text{OAc}+0.1$ M HTart.

(3) Electrolytic cell: an H-type cell with a D.M.E., mercury pool and SCE was used. Capacitor of $100\ \mu\text{F}$ was inserted between the SCE and the mercury pool. (All the experiment were carried out at $25\pm 0.1^\circ\text{C}$)

III. Experimental

III. 1.1. Behaviour of mercuric ions in 0.5 M $\text{NH}_4\text{OAc}+0.1$ M HTart solution.

For the direct polarographic determination of trace metals in mercury, large amounts of mercuric ions should be dissolved in the supporting electrolyte. It is also desirable that the mercuric ions are soluble in a wide pH range of the solution, because the adjustment of pH is necessary for the determination of various elements. These conditions are fulfilled fairly well in 0.5 M $\text{NH}_4\text{OAc}+0.1$ M HTart, which was used in the back-extraction in the previous work¹⁾.

In this solution, mercuric ions are soluble up to about 1.7×10^{-2} M. When the concentration of mercury ions become greater than 2×10^{-2} M, white or crystalline precipitate begins to form. However, the amount of the precipitate is slight when the concentration of mercuric ion is smaller than 2.5×10^{-2} M. The formation of the precipitate occurs slowly with time. If the concentration of mercuric ion is larger than 3.0×10^{-2} M, the amount of the precipitate increases very much. When the precipitate which was obtained in 5.0×10^{-2} M Hg^{2+} solution was aged at about 90°C , some part of the copper ions was found to coprecipitate with the mercury precipitate. Therefore, in the determination of copper ions, it is necessary to prevent the precipitation of mercuric ions. The author found that the addition of agar was effective to prevent the formation of the precipitate of mercury ions. Mercuric ions in 2.5×10^{-2} , 3.0×10^{-2} and 5.0×10^{-2} M did not form precipitate at least in one hour after their addition, if the solution contained 0.005%, 0.01% and 0.02% agar, respectively. When the concentration of agar was 0.01%, the amount of the precipitate was very small even after 30 hours. Besides this property of agar to prevent the precipitation of mercuric ions, agar was also useful as a suppressor of the polarographic maximum when used together with other surface active substances (see below).

III. 1.2. Maximum of mercury (II) wave in D.C. and A.C. polarogram.

It is well known that A.C. polarography is more useful than D.C. polarography when the solution contains large amounts of substance which is reduced at a more positive potential. For the determination of copper in mercury, therefore, A.C. method is preferable. When the concentration of Hg^{2+} was larger than 4×10^{-3} M, however, the copper wave (peak potential: -0.08 V *vs.* SCE) was masked by that of mercuric ion. In the potential range in which D.C. polarographic maximum is obtained, very large A.C. current flows through the cell and the current comes down to the usual value at the potential at which

maximum disappears. When the concentration of Hg^{2+} ions was increased, the potential region masked was shifted to more negative potentials.

As is shown in Fig. 1, the polarographic maximum of Hg-wave begins to occur at $2.0 \times 10^{-3} M$ of Hg^{2+} ions. At $2.5 \times 10^{-3} M$ of Hg^{2+} ions, the maximum disappears at $+0.19$ V vs, SCE. At $5.0 \times 10^{-3} M$, the maximum comes to about -0.25 V and the determination of the peak height of copper becomes impossible. When the concentration of Hg^{2+} ions is $2.0 \times 10^{-2} M$, the potential region of maximum reaches even to about -0.55 V. At $3.0 \times 10^{-2} M$ Hg^{2+} , there is no potential region measurable before the reduction of the supporting electrolyte. (A.C. polarographic condition: $S = 1.0 \mu\text{C}$, P.C. = $0.3 \mu\text{F}$.)

Fig. 1. Typical maximum wave of Hg^{2+} in $0.5M \text{NH}_4\text{OAc} + 0.1M \text{HTart}$.

- 1) $2.0 \times 10^{-3} M\text{-Hg}^{2+}$, 2) $2.5 \times 10^{-3} M\text{-Hg}^{2+}$, 3) $5.0 \times 10^{-3} M\text{-Hg}^{2+}$,
- 4) $1.0 \times 10^{-2} M\text{-Hg}^{2+}$, 5) $2.0 \times 10^{-2} M\text{-Hg}^{2+}$, 6) $2.5 \times 10^{-2} M\text{-Hg}^{2+}$,
- 7) $3.0 \times 10^{-2} M\text{-Hg}^{2+}$, 8) $5.0 \times 10^{-2} M\text{-Hg}^{2+}$

III. 2.1. Suppression of the maximum of the mercury wave.

As mentioned above, the polarographic maximum due to the mercuric wave makes the measurement of copper wave in A.C. polarography impossible. When the maximum is suppressed by the addition of surface active substance, as expected, the peak of the cop-

per wave appears again and the measurement of copper in mercury becomes possible. Here, it is not necessary to remove the maximum because the peak potential is 0.03V more positive than the potential of copper wave. In this work, PAA and agar were used as the maximum suppressor. The coexistence of PAA and agar was proved to be effective.

However, the higher the concentration of coexistent mercuric ion became, the more the maximum suppressor should be added and the interference owing to the addition of suppressor became larger. This interference was the limiting factor to restrict the upper limit of the coexisting amount of mercuric ion. Namely, two kinds of interference were observed, one of which was the precipitation by adding PAA or the gelatinization by adding agar, which caused an irregular wave shape or lowering of height of copper wave; the other is the swelling of A.C. wave of mercuric ion with PAA or agar (in the following, these waves are designated as PAA + Hg^{2+} wave and agar + Hg^{2+} wave, see Fig. 3). As these interferences increased with the increasing amounts of suppressors for some defined amounts of mercuric ion, the minimum amounts of suppressor should be used. The change in the PAA + Hg^{2+} wave with the increasing concentration of PAA is shown in Fig. 3. As these interferences are increasing with the time, the determination should be made just after adjustment of polarographic solution. The general procedure is as follows. Pipette a stock solution of the base electrolyte into a 20-ml measuring flask, add through small amounts of water, mercuric solution, copper solution and PAA solution, dilute and start to record from +0.05V. On using agar, mercuric solution was added after agar was added.

III. 2.2. The effect of PAA.

In the supporting electrolyte investigated, the maximum of mercuric ion in the concentration of about $1.0 \times 10^{-2} M$ can be completely removed by PAA. For this purpose, PAA of more than 0.3% is necessary. If the concentration of Hg^{2+} ion is larger than $10^{-2} M$, the maximum current cannot be eliminated by the addition of PAA.

As described above, for the determination of copper in mercury it is not always necessary to remove the maximum perfectly. From this point of view, mercuric ions of $2.0 \times 10^{-2} M$ can exist in the solution containing PAA of about 0.10%. When the concentration of PAA becomes larger than 0.10%, white precipitate is formed rapidly. Table 2 shows the influence of PAA on the D.C. and A.C. polarograms of copper in mercury. The height of copper wave in the presence of 0.10% PAA was the same in the absence of mercuric ion as well as in the presence of $2.0 \times 10^{-2} M$ of mercuric ions. The height of copper wave was not influenced by the presence of PAA up to about 0.14%. The copper in $2.5 \times 10^{-2} M \text{Hg}^{2+}$ was not determined due to white precipitate.

Besides the formation of white precipitate, an A.C. polarographic wave is produced just after the copper wave when PAA coexists with mercury ions. But, as this wave is not prominent, the interference in the determination of small amounts of copper and other metals, such as Tl, Pb and Cd, is small.

III. 2.3. The effect of agar*.

Agar in 0.02% concentration can eliminate the polarographic maximum of $5.0 \times 10^{-3} M$ mercury ion. When the concentration of mercuric ion becomes greater than 5.0×10^{-3}

* Agarose³⁾, a non-sulfated polysaccharide constituent of the agar of *Gelidium amansii*, was also tested with regard to its activity as a maximum-suppressor, but the activity was similar to that of agar. The author wishes to express sincere thanks to Prof. S. Hirase for gift of the agarose sample.

M , however, the maximum can not be eliminated even with the greater concentration of agar. In the presence of agar of more than about 0.03%, the solution is gelatinized. Table 1 and 2 show the effect of agar in the determination of copper in mercury. In the solution of $2.0 \times 10^{-2} M$ Hg^{2+} , copper wave could be measured exactly in the presence of 0.025 to 0.03% agar.

Table 1. Effects of PAA or agar on the peak height (μV) and the shape of copper wave in the absence and the presence of Hg^{2+} ions. Cu^{2+} : $10^{-4} M$ in $0.5 M NH_4OAc + 0.1 M HTart$

concn. of PAA (%)	0.00	0.01	0.02	0.04	0.09	0.10	0.12	0.15	0.18	0.20	0.24
concn. of Hg ²⁺											
0	139.5	140.0	139.4	139.2	139.4	139.5	139.2	138.0	137.0	137.0	136.4
1 × 10 ⁻² M	—	139.5 ^{a)}	139.0	139.2	138.5	139.0	139.0	138.0	137.0	136.0	136.0 ^{b)}
2 × 10 ⁻² M	—	—	—	—	139.0	139.0	139.0	136.0	137.0 ^{c)}	135.0 ^{d)}	135.0 ^{e)}
								139.0		138.0	139.0
concn. of agar (%)	0.00	0.005	0.01	0.02	0.025	0.03	0.04	0.05			
concn. of Hg ²⁺											
0	139.5	146.0	147.0	139.0	139.0	138.0	135.0	131.0			
1 × 10 ⁻² M	—	147.0	146.0	138.5	137.0	129.0	128.0	125.5			
2 × 10 ⁻² M	—	—	—	—	—	108.0	107.0	101.0			
2.5 × 10 ⁻² M	—	—	—	—	—	—	101.0	94.5 ^{f)}			

a) slightly irregular shape.

b, c, d, e, f) irregular shape.

Table 2. Effect of PAA or agar concentration on the shift of peak potential (E_p) of maximum wave of Hg^{2+} ion in D.C. and A.C. polarogram.

1) in the presence of $10^{-2} M Hg^{2+}$										
concn. of PAA (%)		0.00	0.02	0.04	0.08	0.10	0.16	0.20	0.30	
E_p	D.C.	-0.47	-0.01	+0.08	+0.11	+0.15	+0.19	a)	b)	
(V. vs. SCE)	A.C.	-0.48	-0.02	+0.18	+0.22	+0.22	+0.22	+0.23	+0.23	
concn. of agar (%)		0.00	0.01	0.02	0.04	0.08	0.10	0.20	0.30	
E_p	D.C.	-0.47	+0.03	+0.06	+0.15	+0.19	+0.20	+0.21	+0.23 ^{c)}	
(V. vs. SCE)	A.C.	-0.48	+0.04	+0.08	+0.21	+0.21	+0.22	+0.22	+0.23	
2) in the presence of $2 \times 10^{-2} M Hg^{2+}$										
concn. of PAA (%)		0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.16	0.20
E_p	D.C.	-0.52	-0.30	-0.22	-0.12	-0.06	-0.02	-0.01	0.00	+0.03
(V. vs. SCE)	A.C.	-0.53	-0.325	-0.23	-0.115	-0.06	-0.025	+0.02	+0.02	+0.025
concn. of agar (%)		0.000	0.005	0.010	0.015	0.020	0.025	0.030	0.060	
E_p	D.C.	-0.52	-0.27	-0.15	-0.12	-0.05	-0.025	-0.01	+0.025	
(V. vs. SCE)	A.C.	-0.53	-0.25	-0.15	-0.135	-0.06	-0.035	-0.015	+0.03	

a) : maximum negligible. b) : maximum disappear. c) : small maximum.

condition D.C. sensitivity = $10 \mu A/mm$ parallel capacitance = $25 \mu F$
A.C. sensitivity = $1.0 \mu V/mm$ parallel capacitance = $0.3 \mu F$

The height of the copper wave in the solution containing 0.01% agar and $10^{-2}M$ Hg^{2+} is the same as that in the solution which does not contain Hg^{2+} ion. The copper wave in the solution containing 0.03 to 0.032% agar and $2.0 \times 10^{-2}M$ to $2.2 \times 10^{-2}M$ Hg^{2+} ions is slightly smaller than that in the solution containing 0.01% agar and $10^{-2}M$ Hg^{2+} ions. The height of the copper wave was not influenced by the addition of agar up to about 0.032%. In the solutions of 0.04% agar + $2.5 \times 10^{-2}M$ Hg^{2+} , the determination of copper was possible but its height was smaller than in the above solutions.

If the solution contains both agar and Hg^{2+} ions, an A.C. wave is observed just as in the case of PAA + Hg^{2+} . The wave of $10^{-2}M$ Hg^{2+} + 0.01% agar was very small, but the amount of agar being 0.02%, the wave became large. This wave is larger than PAA + Hg^{2+} wave.

III. 2.4. Double effect of agar* and PAA.

In the solution containing agar, the precipitation of mercuric ion decreased much as described in III. 1.1.. Therefore, agar is effective in the polarographic determination, if

Fig. 2. Calibration curve of copper in the presence of Hg^{2+} at the various concentrations of agar and PAA (A.C. polarography).

P.C. = 0.3 μF , S. = 1.0 $\mu V/mm$, v.s. SCE-100 μF -Hg pool

* For this study the method in which a polarographic maximum is reduced by lowering the mercury pressure was used. Lowering the mercury reservoir by 7 cm from a standard height made the determination of copper easier because the whole shape of copper wave appeared. When the mercury pressure was decreased, only the height of maximum wave of mercuric ion was reduced fairly in this base electrolyte containing agar, while the wave height of copper on A.C. polarograms was not decreased.

the added amount of agar should be held within 0.01 to 0.02% in order to prevent the gelatinization of the solution. The mixture of PAA and agar was found to be effective in the determination of copper in a larger amount of mercury.

The concentration of mercuric ions, the maximum of which can be eliminated by the mixture of PAA and agar, was as follows: $1.0 \times 10^{-2} M$ in the presence of 0.1% PAA + 0.005 % agar, $1.25 \times 10^{-2} M$ in the presence of 0.2% PAA + 0.04% agar. Copper in $2.5 \times 10^{-2} M$ Hg^{2+} ions can be determined by use of A.C. polarographic method in the presence of 0.1%

Fig. 3. The effect of PAA concentration on the shape of copper wave of $2 \times 10^{-6} M$ Cu^{2+} in $10^{-2} M$ Hg^{2+} in the square wave polarogram.

Recorder Sens. = $0.040 \mu A/mm$, S.W. volt = 20, Amp.

Sens. = 1/2, Gate = 5~8, Time const. = 5.2

Supporting electrolyte : $0.5 M NH_4OAc + 0.1 M HTart$

PAA + 0.02% agar. Copper in $3.0 \times 10^{-2} M$ Hg^{2+} can also be determined in the presence of 0.18% PAA + 0.02% agar.

Thus, the maximum concentration of Hg^{2+} , which is tolerable in the determination of copper, is larger in the solution containing bath PAA and agar than in the solution containing PAA or agar alone.

III. 3.1. Use of the square-wave polarography.

PAA was used as a maximum suppressor, because the wave due to the coexistence of Hg^{2+} with PAA was fairly small. In the presence of 0.1% PAA + $2.0 \times 10^{-2} M$ Hg^{2+} , the height of copper wave was proportional to its concentration as low as $2.0 \times 10^{-6} M$. In the solution containing 0.02% PAA and $1.0 \times 10^{-2} M$ Hg^{2+} , the proportionality holds over the

Fig. 4. Square wave polarogram of copper in mercury.

$4 \times 10^{-6} M$ Cu in $2.0 \times 10^{-2} M$ Hg^{2+}

Recorder Sens. = 0.040 $\mu\text{A}/\text{mm}$

S.W. Volts = 20

Amp. Sens. = 1/2

Gate = 5~9

Time Const. = 4.1

copper concentration as low as $10^{-6} M$. (accuracy of $\pm 4\%$.) Copper wave in $10^{-2} M$ Hg^{2+} had a better shape in the presence of PAA more than 0.02% than that in 0.01% PAA.

Conclusion

By using the A.C. polarography and the square wave polarography, a method for determination of small amounts of copper in mercury was investigated. As the base solution $0.5M$ NH_4OAc + $0.1M$ HTart was used supporting electrolyte. The interference due to the maximum current of mercury was eliminated by the addition of PAA, agar and/or the mixture of PAA and agar. The mixture of agar and PAA was especially effective both in suppressing the maximum and in preventing the precipitation of mercury

ions. This method is useful to determine the other metal elements which are reduced at more negative potential than copper, and can be applied in the polarographic analysis using the extraction method.

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抽出法を用いるポーラログラフ分析法. II.

水銀中の銅の直接定量法

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交流ポーラログラフ法にて高濃度水銀中の金属イオンを直接定量する際, Hg^{2+} によるキレート交換逆抽出法¹⁾に用いた 0.5 M Ammonium acetate + 0.1 M Tartaric acid なる交換液を直ちに支持電解質として定量すれば, 共存 Hg^{2+} の示す拡散電流は妨害せず, 高濃度の Hg^{2+} が示す極大電流が妨害する. この妨害を表面活性剤 PAA および寒天を添加して極大波を抑制することにより除去した.

本報にては比較的正電位側にピーク電位を有する銅

を選び, 銅定量に際しての, PAA および寒天により抑制し得る共存 Hg^{2+} 量の上限界を求めたところ, PAA および寒天おのおの単独では, ほぼ $2 \times 10^{-2}\text{ M}$ Hg^{2+} であり, PAA と寒天を併用すれば, ほぼ $3 \times 10^{-2}\text{ M}$ Hg^{2+} となつた.

ク形波ポーラログラフ法を用いれば, 0.10% PAA にて $2 \times 10^{-2}\text{ M}$ Hg^{2+} 中の $2 \times 10^{-6}\text{ M}$ Cu^{2+} が $\pm 4\%$ の精度で定量できる.