The Indirect Determination of Microamounts of Mercury(II) by Means of Dithizone Extraction and AC Polarography

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It was found that dithizone in an aqueous alkaline solution shows sharp AC polarographic peaks; the indirect determination of mercury by means of these peaks was investigated. After the extraction of mercury(II) dithizonate into benzene, the excess dithizone was eliminated. Then the mercuric ion was stripped into the aqueous phase containing the iodide ion. The isolated dithizone in the benzene layer was back-extracted into the alkaline supporting electrolyte solution and the polarogram was recorded. By the present method, up to 30 μg of mercury can be determined.

Dithizone(H_2Dz) is a very sensitive reagent which has been used for the colorimetric determination of many metals. Separation by means of solvent extraction is very easy, useful, and selective. In polarographic determinations of copper, zinc,[1] lead,[2] and cadmium,[3] the metals are extracted as dithizonates into an organic layer, the solvent is evaporated, and the residue is redissolved in water, or the dithizonates are back-extracted from the organic phase into a suitable aqueous solution. Recently Yamashita[4] has reported the interesting polarographic behavior of dithizone and metal dithizonates in a ternary solvent mixture consisting of chloroform, water, and methylcellosolve.

The present authors have now found that dithizone in an aqueous alkaline solution gives sharp peaks in AC polarography, and have investigated the application of these dithizone peaks to the microdetermination of mercury. In the present method, the microamount of mercury is extracted into benzene, and then the excess dithizone in organic layer is back-extracted into an aqueous ammonia solution. Then, dithizone is stripped from the mercury dithizonate by shaking it with an aqueous potassium iodide solution. The dithizone remains in benzene, but the mercury goes into the aqueous phase as an iodo-complex. The electrolysis solution was prepared by shaking the supporting electrolyte solution, consisting of sodium sulfate and sodium hydroxide, with the remaining organic layer, containing the isolated dithizone. The mercury is determined indirectly from the height of the dithizone peak. The fundamental conditions for this method are discussed below.

Experimental

Reagents. 30 mg of dithizone (Wako Chemicals Co., guaranteed reagent) were dissolved in benzene and purified as usual; then the volume was made up to 200 m*l* with benzene. This stock solution was diluted, and the concentration of the dithizone was estimated by the absorbance and the molar absorptivity at 620 mμ.[5]

The standard stock solution of mercury(II) was prepared by dissolving 0.1354 g of mercuric chloride in 100 m*l* of 1 N sulfuric acid and was then diluted when used.

The stripping solution was prepared by dissolving 10 g of potassium hydrogen phthalate and 25 g of potassium iodide in 500 m*l* of distilled water, a few crystals of sodium thiosulfate being added to reduce any trace of the iodine liberated. The solution was then further purified by shaking it with a dithizone-benzene solution in order to remove any heavy metal.

The supporting electrolyte solution was prepared by mixing 250 m*l* of 0.4 M sodium sulfate and an appropriate volume of 1 N sodium hydroxide, and by then making the volume up to 500 m*l* with distilled water.

The other chemicals used were all guaranteed reagents.

Apparatus. AC polarographic measurements were performed by using a Yanagimoto polarograph, type PA-102. The dropping mercury electrode with the following characteristics was used: m=0.526 mg/sec, t=5.57 sec at h=65.0 cm, at an open circuit in the deaerated supporting electrolyte solution.

The absorbances and absorption spectra were measured with a Shimadzu spectrophotometer, type QV-5, by the aid of a 1-cm glass cell. The pH of the solutions was measured with a Hitachi-Horiba glass electrode pH meter, type F-5.

Established Procedure. Take the sample solution up to 50 m*l* containing mercury up to 30 μg that is made about 0.5 N in sulfuric acid. If necessary, add masking reagents. Add 10 m*l* of 1×10^{-4} M dithizone-benzene solution and shake for 1 min. Transfer the organic layer to another separating funnel. Add 10 m*l* of 0.15 N ammonium hydroxide, shake for 15 sec, and discard the aqueous solution. Repeat this operation once again. The excess dithizone is thus removed. Add 10 m*l* of the above-cited stripping solution into a separating funnel, in which the benzene layer containing only mercury dithizonate should remain, and shake for 1 min. Then mercury(II) is transfered into the aqueous solution. Allow the mixture to stand for a while, transfer 5 m*l* of the benzene layer containing the isolated dithizone to another separating funnel containing 5 m*l* of the supporting electrolyte solution (pH=12.5), and shake for 10 sec. Transfer the aqueous solution into a polarographic cell. Record an AC polarogram at 25±0.1°C, after deaeration by passing nitrogen gas through for 5 min.

Results and Discussion

AC Polarogram of Dithizone. Figure 1 shows the AC polarogram of dithizone in a 0.2 M sodium sulfate alkaline solution. Two prominent peaks are observed in the AC polarogram, but the corresponding DC

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[1] G. B. Jones, *Anal. Chim. Acta*, **7**, 578 (1952).

[2] J. Cholak and K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **13**, 583 (1941).

[3] J. Cholak and D. M. Hubbard, *ibid.*, **16**, 333 (1944).

[4] K. Yamashita, *Rev. Polarog.* (Japan), **15**, 65 (1968).

[5] G. Iwantscheff, "Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse," Verlag Chemie, Weinheim (1958), p. 17.

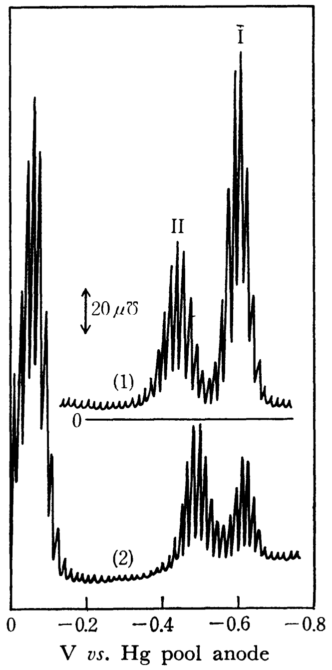

Fig. 1. (1) AC polarogram of 2.0×10^{-5} M dithizonate ion(HDz^-) in a deaerated solution of 0.2 M Na_2SO_4, *ca.* 0.01 M NaOH (pH=12.56) at 25°C.
(2) AC polarogram of 2.0×10^{-5} M dithizonate ion in an air-saturated supporting electrolyte solution.

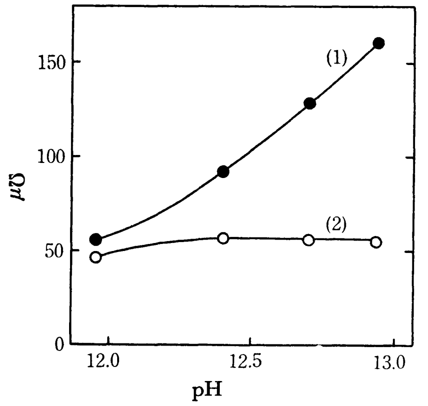

Fig. 2. Effect of pH of the electrolysis solution on the AC peak heights of dithizonate ion.
HDz^-: 1.65×10^{-5} M, 0.2 M Na_2SO_4 (NaOH added), 25°C.
(1) peak I. (2) peak II.

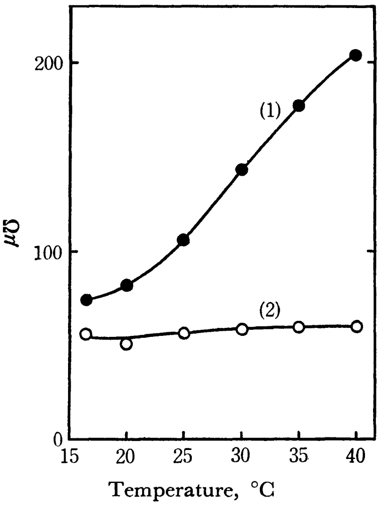

Fig. 3. Effect of temperature on the AC peak heights of dithizonate ion.
HDz^-: 2.22×10^{-5} M, 0.2 M Na_2SO_4 (NaOH added).
pH=12.47 at 19°C.
(1) peak I. (2) peak II.

steps are very ill-defined. Without deaeration, the heights of the two peaks tend to decrease; peak I, appearing at the more negative potential, decreases especially rapidly.

The effect of the pH of the supporting electrolyte solution on the heights of the two peaks is shown in Fig. 2. The height of the peak I increases linearly with the increasing pH, but that of peak II remains constant in the pH region between 12.4 and 12.9.

Figure 3 shows the temperature dependance of the AC peaks. Although the height of peak I increases with the temperature, that of peak II shows an almost constant value. Under the above conditions, the peak I is always higher than peak II. This indicates that the determination of dithizone using peak I is more sensitive; however, the height of peak I is remarkably influenced not only by the pH but also by the temperature. Hence, a little deviation in pH and temperature would cause a significant analytical error. In order to avoid these errors, the present authors employed peak II for the determination of dithizone. The temperature was fixed at 25±0.1°C, and the pH was adjusted to about 12.5. Under the above conditions, the AC peak height shows a linear relationship up to a dithizone concentration of 3×10^{-5} M. In the concentration range higher than the above value, the polarogram becomes ill-defined.

Extraction of Mercury and Elimination of Excess Dithizone. It was first confirmed that 20 μg of mercury(II) in 10 m*l* of 0.5 N in sulfuric acid can be extracted quantitatively by shaking it for only 30 sec with a 4.4×10^{-5} M dithizone-benzene solution.

Now, the method of eliminating the excess dithizone from organic solution will be investigated. When the organic solution is shaken with 10 m*l* of 0.15 N ammonium hydroxide, the free dithizone in the organic solution is back-extracted. In order to eliminate the free dithizone completely, this operation is done once again. 10 m*l* of a 1×10^{-4} M dithizone-benzene solution was found to show no absorbance at 620 mμ after these operations. Milton and Hoskins[6] investigated the mono-color determination method of mercury(II) dithizonate, in which the excess dithizone is removed by shaking with dilute ammonia. According to them, shaking with 0.75 N ammonium hydroxide converts the primary dithizonate, $Hg(HDz)_2$, into the secondary dithizonate, HgDz. When 0.75 N ammonium hydroxide is used in the present study, the longer the shaking time, the greater the decrease in the absorbance at the wavelength of the maximum absorption of mercury (II) dithizonate, $Hg(HDz)_2$. However, the evidence for the formation of the secondary complex has not been found, the shape of the absorption spectrum showing no change. When 0.15 N ammonium hydro-

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[6] R. F. Milton and J. L. Hoskins, *Analyst*, **72**, 6 (1947).

xide is used, neither a change in the absorption spectrum nor a decrease in the absorbance was recognized. It was found that 10 m*l* of a 1×10^{-4} M dithizone-benzene solution can extract 20 μg of mercury quantitatively from 60 m*l* of an aqueous solution.

Stripping of Mercury. In order to isolate the dithizone from the mercury dithizonate, the reversion method proposed by Irving *et al.*[7] was used. That is, the mercuric ion was back-extracted into the acidified iodide solution, presumably as triiodo-mercurate(II).

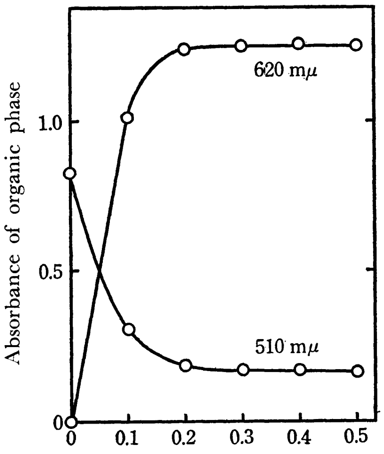

Fig. 4. Effect of the concentration of potassium iodide on the back-extraction of mercury.
$Hg(HDz)_2$ in org. soln.: 1.61×10^{-5} M
pH=3.67 (0.1 M phthalate buffer)
Shaking time: 2 min
$V_{org.} = V_{aq.} = 10$ m*l*

Figure 4 shows the effect of the iodide concentration on the stripping of mercury. 10 m*l* of the organic layer is shaken for 2 min with an equal volume of an iodide solution. The maximum absorbance of dithizone in benzene at 620 mμ shows a constant value when the concentration of potassium iodide is higher than 0.3 M. Also, at 510 mμ, at which dithizone has its minimum absorptivity but mercuric dithizonate shows a high extinction, shaking with a potassium iodide solution higher than 0.3 M results in a constant absorbance. The absorption spectra of these organic layers being the same as that of dithizone in a benzene solution, the existence of the mercury dithizonate in the organic layer may be disregarded.

Thus, it is confirmed that the 0.3 M potassium iodide solution can back-extract mercury quantitatively from an equal volume of a benzene solution of mercury dithizonate. The shaking time of 30 sec is found to be sufficient for the back-extraction under the above conditions. Further, it is found that the ratio of the concentration of the isolated dithizone to that of the mercury taken is two. Hence, the extraction and back-extraction of mercury can be carried out quantitatively. Furthermore, the mercury dithizonate, $Hg(HDz)_2$, is not converted into the secondary complex, HgDz.

Aqueous Solution of Dithizone. The step in which the isolated dithizone is transferred into the supporting electrolyte solution is investigated. A 0.2 M sodium sulfate solution, the pH of which is adjusted with a sodium hydroxide solution, is used as the supporting electrolyte solution. When the pH of the supporting electrolyte solution is higher than 11.5, the dithizone in the benzene layer is back-extracted into the aqueous solution as the dithizonate ion. Irving *et al.*[8] reported the decomposition of dithizone in an aqueous alkaline solution. They stated that dithizone in 1.5 N ammonium hydroxide decomposes at a rate of 20—30%/hr, but in 0.15 N ammonium hydroxide the velocity becomes very slow.

In the present experiment, the dithizonate ion is stable for one hour, at least in 0.2 M sodium sulfate solution, the pH of which is adjusted to 12.52 with sodium hydroxide.

Thus, in this procedure the decomposition of the dithizonate ion can be neglected. It should be further mentioned that the electrolysis solution should be completely free from the iodide ion. Because the iodide ion shows a broad peak as the result of an anodic process, the peak of dithizone is very much disturbed. When a 5-m*l* portion of the isolated dithizone solution is pippeted out to another separating funnel, contamination by the iodide ion is avoided.

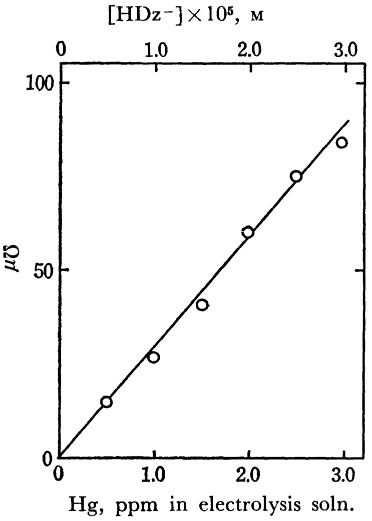

Fig. 5. Calibration curve.

Calibration Curve. The calibration curve obtained according to the above procedure is shown in Fig. 5. Up to 30 μg of mercury the peak height is proportional to the amount of mercury taken. When the determination of 20 μg of mercury was repeated seven times, the relative standard deviation was 4.2%.

For comparison, the same amount of mercury was determined by dithizone spectrophotometric methods. The relative standard deviation of six measurements was 4.6% in the mixed color method and 3.1% in the mono-color method. In the method of the measuring the absorbance of the free dithizone in benzene which is liberated from the mercury(II) dithizonate by stripping mercury(II) with the iodide ion, the relative standard deviation was 2.1%.

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[7] H. Irving, G. Andrew, and E. J. Risdon, *J. Chem. Soc.*, **1949**, 541.

[8] H. Irving, S. J. H. Cooke, S. C. Woodger, and R. J. P. Williams, *ibid.*, **1949**, 1847.

Table 1. Effect of diverse ions
Mercury(II) taken: 20 μg in 20 ml

Interfering ion added	Method of masking	Peak height $\mu\mho$	Peak height, $\mu\mho$, in 95% confidence limits	F_0	t_0
None		58, 62 61, 58 60, 65 63	61.0±2.3		
Ag(I) 2.2 mg	(1)	66 60 67	64.3±9.1	2.22	1.63
Cu(II) 1.3 mg	(2)	63 62 62	62.3±1.3	18.03	0.833

$F(2,6,0.025)=7.26 > F_0=2.22$
$F(6,2,0.025)=39.3 > F_0=18.03$
$t(8,0.025)=2.306 > t_0$

(1) Add 200 mg of NaCl, discard the aqueous layer, shake with 10 ml of 1% NaCl in 0.5 N H_2SO_4.
(2) Add 200 mg of EDTA-2Na salt.

Effect of Diverse Ions. The mercury(II) sample solution is 0.5 N in sulfuric acid, so it is supposed that gold(III), palladium(II), platinum(II), silver(I), and copper(II) are extracted together and that they interfere with the determination of mercury. It is known, however, that these ions are masked with the chloride ion and EDTA.[9] In this work the interferences by silver and copper have been investigated.

The extraction of 20 μg of mercury was investigated; the results are shown in Table 1. When 2.2 mg of silver(I) coexists in 20 ml of the sample solution, it is not masked completely by adding 200 mg of sodium chloride. However, as may be seen in Table 1, the silver(I) ion does not interfere if the benzene extract is shaken once again with 10 ml of a 1% sodium chloride solution in 0.5 N sulfuric acid; further, 1.3 mg of copper(II) is masked completely with EDTA. According to the familiar t-test, no significant difference is found between the means of the peak heights at the 95% significant level.

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 627.