A New Microdetermination of Bismuth and Mercury by the Extraction of Their Iodides with Organic Solvent

A New Microdetermination of Bismuth and Mercury by the Extraction of Their Iodides with Organic Solvent[*]

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Synopsis

Microdetermination of bismuth and mercury in the range of a few gammas was found to be possible by extraction of the respective iodide complex salts from acid solution with an organic solvent (isoamyl alcohol or mixture of this alcohol and ethyl acetate) and measuring the absorbance of the solvent extract in the ultraviolet region. The absorption maximum of bismuth iodide complex salt was found in the region of 330 mμ, and that of mercury compound in the region of 303 mμ. Optimal conditions for these analytical procedures and effects of coexistent elements were also studied.

I. Introduction

Several reports have already been published[1] regarding the microdetermination of metals by photometry after extraction of organic compound of metals with organic solvent by Sudô in our Laboratory. The present writers studied microdetermination of metals by photometry after extraction of inorganic metallic compounds with organic solvents. First, iodine complex of bismuth was extracted with an organic solvent and its microdetermination was carried out by the utilization of its ultraviolet absorption. It was found that the iodine compounds of mercury was extractable with organic solvents and such an extract, although colorless, was determined by photometry utilizing its ultraviolet absorption.

II. Determination of bismuth

The solution of the iodide complex of bismuth is yellow and can be used for colorimetry but its extraction with organic solvents and the determination from the extract has been reported by Haddock[2] and the method is actually employed. This coloration, however, is very weak and difficult to carry out colorimetry, and so it was thought possible that it might show a strong absorption in the ultraviolet region. It was thereby found that this extract showed a strong absorption band in the region of 330 mμ and the quantitative determination of bismuth by the utilization of this absorption was carried out.

(1) Procedure

Weak nitric acid solution of bismuth nitrate was used as the standard solution

(1) Emiko Sudô, Sci. Rep. RITU. A **72** (1951), 718 ; 817. H. Gotô and Y. Kakita, Ibid., **73** (1952), 339 ; E. Sudô, Sci. Rep. RITU. A **4** (1952), 268, 347 ; H. Gotô, Y. Kakita, Ibid. A **4** (1952), 582 ; 589.

(2) L. A. Haddock, Analyst, **59** (1934), 163.

of bismuth and its concentration was determined by the oxine method (content, Bi 8 γ/ml.).

Bismuth solution was placed in a separating funnel, and 2 ml of 10 per cent potassium iodide solution, 10 ml of 25 per cent sodium hypophosphite solution and 3 ml of 12N sulfuric acid were added to it, and the total volume was brought to 35 ml with water. After shaking thoroughly, to develop the complete coloration of BiI₄, 5 ml of isoamyl alcohol was added and the funnel was shaken vigorously to effect transition of the bismuth compound into the organic solvent layer. After standing for five minutes, the extract was transferred to the 1 cm cell, and the absorbance or transmitance was determined by the Beckman model DU spectrophotometer. Results obtained are shown in Fig. 1.
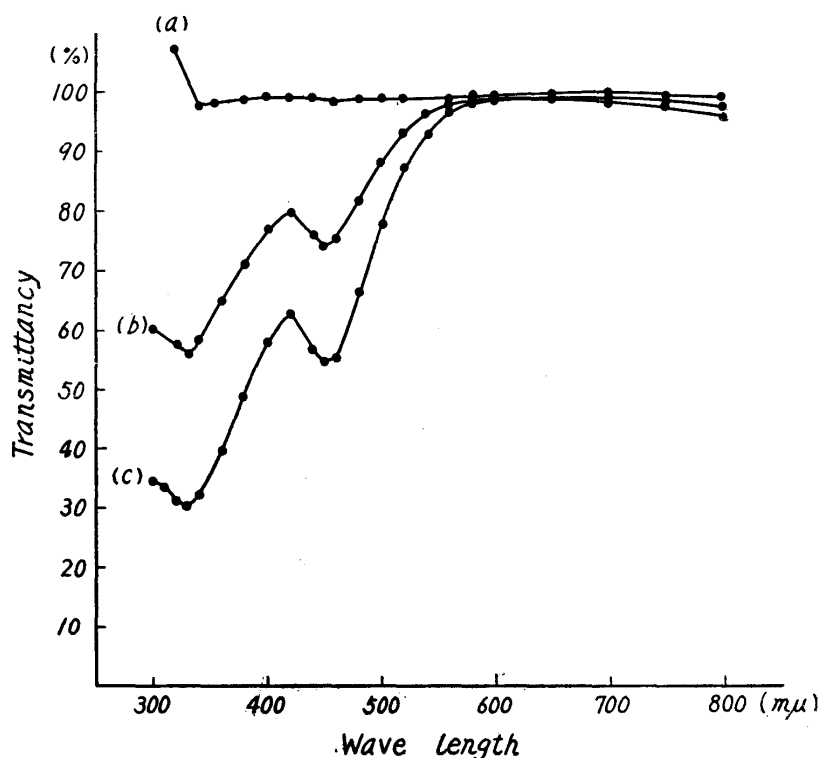

Fig. 1. a : Blank. (isoamylalcohol)
         b : Bi, 20γ.
         c : Bi, 40γ.

As clearly seen from Fig. 1, besides a strong absorption in the region of 450 mμ, there was a far stronger absorption in the region of 330 mμ. By using this region of the maximum absorption, microdetermination became possible and some examinations of this method were carried out.

It was found that the addition of a solvent after standing the colored solution of BiI₄⁻ for some time failed to show any change in the absorption and also that the extraction was complete by one extraction with 5 ml of isoamyl alcohol. The determination of absorption was carried out with the solvent used as the standard in the experiment.

(2) Kinds of solvents

The foregoing isoamyl alcohol served well as the solvent but a mixed solvent of isoamyl alcohol and ethyl acetate (3 : 1) or isoamyl alcohol and amyl acetate (3 : 1) also gave the same absorption curve, the intensity of the absorption being a little stronger than that obtained with isoamyl alcohol alone. However, when the mixture ratio was other than 3 : 1, the absorption of the blank became stronger and so such a mixed solvent was unsuitable for the determination. Amyl acetate

alone did not give a sharp absorption. Bismuth compound could be extracted with carbon tetrachloride, benzene, chloroform, xylene and toluene. Isoamyl alcohol used as the solvent was purified by distillation of the market product.

(3) Effect of the concentration of sulfuric acid

Some tests similar to the above were carried out with 8γ of bismuth and various concentrations of sulfuric acid. The extinctancy was determined at 330 mμ, and the results are shown in Table 1.

A definite absorbance was obtained at 0.8~1.0 N and 1.3~2.0 N sulfuric acid. Above 2.5 N sulfuric acid, the extract became turbid and unsuitable for the determination. Below 0.8 N of sulfuric acid, the absorbance became too small.

Table 1

Concen. of H_2SO_4 (N)	Absorbance	
0.5	0.067	0.068
0.8	0.102	0.103
1.0	0.103	0.104
1.3	0.117	0.118
1.5	0.118	0.120
2.0	0.121	0.122
2.5	0.126	0.129
3.0	0.132	0.134

Table 2

Temperature (°C)	Absorbance	
20	0.099	0.100
25	0.101	0.104
30	0.099	0.101
40	0.103	0.105
50	0.093	0.104

(4) Effect of temperature

The same tests were carried out with 8γ of bismuth and 1N sulfuric acid, and the extinctancy obtained at 330 mμ are shown in Table 2.

These results show that a definite extinctancy can be obtained at 20~40°C while the extract is a turbid above 50°C. Below 20°C, the action of sodium hypophosphite became inefficient. At about 10°C, the result was varied even the amount of sodium hypophosphite was increased and the determination because impossible. It is, therefore, necessary to carry out the procedures at 20~40°C.
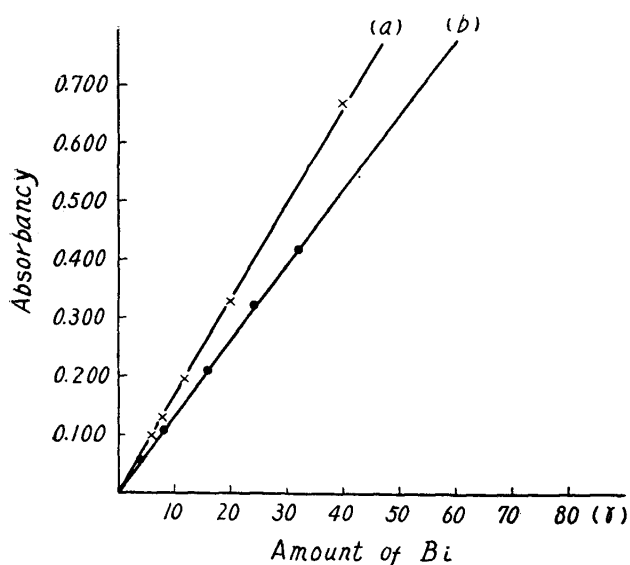

Fig. 2. a : Isoamylalcohol + ethyl acetate
      b : Isoamylalcohol
      Wave length : 330 mμ

(5) Relation between the amount of bismuth and absorbance

The same test was carried out with 1N sulfuric acid solution and with various amounts of bismuth. Absorbance measured at 330 mμ are shown in Fig. 2 and that at 450 mμ in Fig. 3.

The above figures show that the relationship between the amount of bismuth and absorbance is linear and that the quantitative determination of bismuth is possible in a few gammas.

(6) Effect of diverse ions

The effect of diverse ions in the present analytical procedures for

bismuth determination was studied and the maximum amount of ions which does not give any effect is shown in Table 3.

Table 3

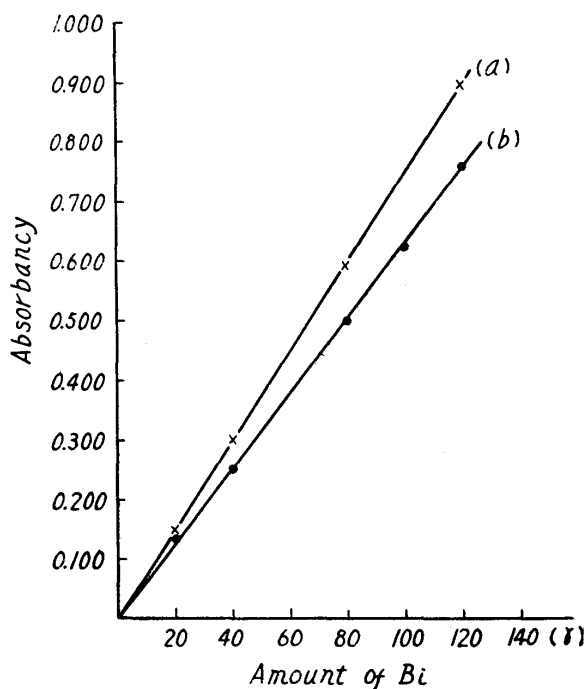| Coexisting ion	Maximum amount ineffective (mg)
Cl^-	3
NO_3^-	9
Fe^{2+}	10
CO	5
Ni	50
Mn	>100
Sn^{2+}	10
ClO_4^-	>100
Zn	3
As^{5+}	>100
As^{3+}	80
Cu^{2+}	5
Ag^+	0.08
Cd	>100
Pb	0.8

Fig. 3. Wave length : 450

III. Determination of mercury

The present writers found that mercury iodide complex could be extracted with isoamyl alcohol from the colorless solution of mercuric iodide dissolved in potassium iodide solution and that this extract showed a strong absorption in the ultraviolet range. Hence, the microdetermination of mercury was studied by utilizing this phenomenon.

(1) Reagent and method

The solution of mercuric chloride used contained $10\,\gamma$ of Hg per ml (concentration determined by electrolysis). Other reagents used were the same as those in the case of bismuth.

A solution of mercuric chloride was placed in a separating funnel, and 3 ml of 1 per cent potassium iodide solution, 10 ml of 10 per cent sodium hypophosphite, and 6 ml of 6N hydrochloric acid were added to it, and the total volume was brought to 35 ml with water (making the concentration of hydrochloric acid approximately 1N). After shaking the mixture, 5 ml of isoamyl alcohol was added, shaken thoroughly and stood for some time, and the transmittance of the extract was determined by the Beckman model DU spectrophotometer. Extract of blank test was used as the standard. The results obtained are shown in Fig. 4.

As shown in Fig. 4, there was no absorption in the visible range but a strong absorption in the ultraviolet range, with the maximum at around 305 mμ. It was found that the extraction was complete with one extraction with 5 ml of isoamyl alcohol.

(2) Kinds of solvents

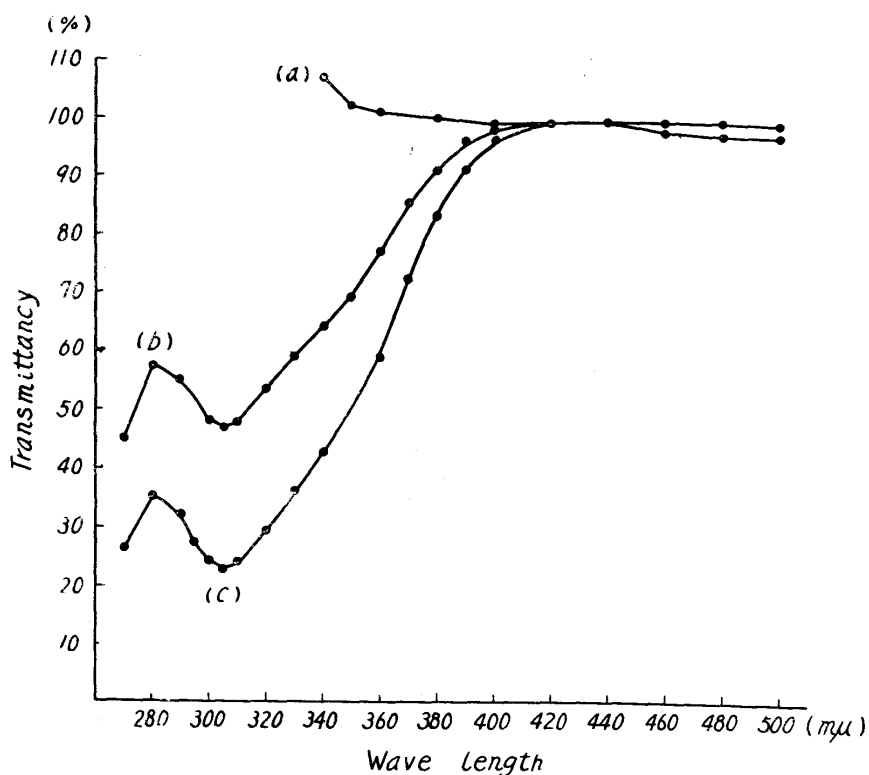As in the case of bismuth, the absorption was slightly stronger with a mixed

Fig. 4. a : Blank (isoamylalcohol)
         b : Hg, 25γ
         c : Hg, 50γ

solvent of isoamyl alcohol and ethyl acetate (3 : 1) than with isoamyl alcohol alone. The extraction could not be effected by using benzene, chloroform, carbon tetrachloride, xylene, and toluene.

(3) Concentration of hydrochloric acid

Extraction was carried out at 20°C with various concentrations of hydrochloric acid and the extinctancy determined at 305 mμ are shown in Table 4.

Table 4

HCl(N) Hg(γ)	0.1	0.3	0.5	1.0	1.3
30	0.331	0.337	0.388	0.386	0.377
50	0.596	0.615	0.636	0.637	0.688
70	0.810	0.860	0.878	0.878	0.940

The determination was possible at 0.5~1.0N hydrochloric acid concentration in which the absorbance became definite. In a weak solution such as 0.3N hydrochloric acid, the absorbance became too small, and the determination values were difficult to be reproducible above 1.3N.

(4) Effect of temperature

Results of tests on the effect of temperature have shown the same tendency as in the case of bismuth, showing the desirability of carrying out the whole procedure at 20~40°C.

(5) Relation between the amount of mercury and absorbance

The same procedure was carried out with various amounts of mercury and the values obtained by the determination of extinction coefficient at 305 mμ are shown in Fig. 5.

These results showed that the precise determination from a few gammas to several ten gammas of mercury was possible by extraction with 5 ml of isoamyl alcohol alone or with a mixture of isoamyl alcohol and ethyl acetate.

(6) Effect of diverse ions

The determination of mercury was carried out exactly in the same manner with 10γ of mercury and the maximum amount of diverse ions which did not affect the determination are shown in Table 5.
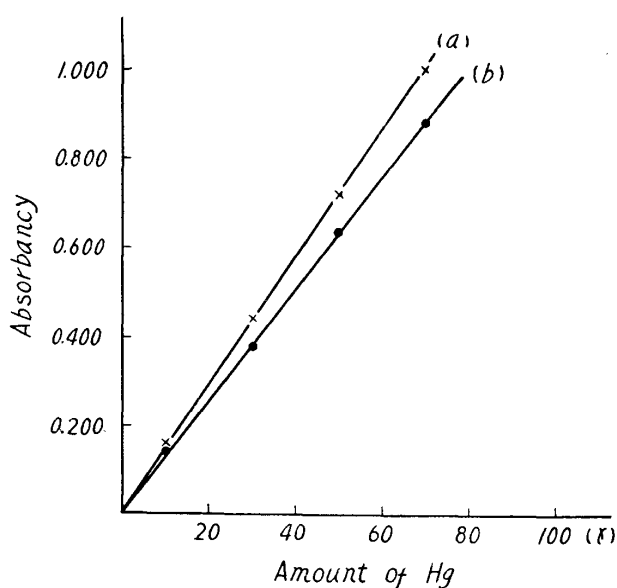

Fig. 5.   a : Isoamyl alcohol + ethyl acetate
b : Isoamyl alcohol
Wave length : 305 mμ

Table 5

Coexistent Ion	Maximum amount ineffective (mg)
SO_4^{2-}	>100
NO_3^-	3
ClO_4^-	>100
Zn	30
Fe^{2+}	5

Ions other than those shown in Table 5 are the same as those shown in the case of bismuth.

Summary

1. A new method for the microdeterminations of bismuth and mercury were studied by photometric measurement in the respective ultraviolet regions of the iodide complex salts of mercury and of bismuth by extraction with organic solvent.

2. Bismuth iodide complex can be extracted from the sulfuric acid solution with isoamyl alcohol and such a solvent shows the maximum absorption in the region of 330 mμ which is much stronger than the absorption maximum in the visible region of 450 mμ, indicating the possibility of determining a few gammas of bismuth.

3. Various conditions of reaction such as temperature, concentration of the acid and others were studied and the optimum conditions were obtained.

4. Iodide complex salt of mercury was extracted from its hydrochloric acid solution with isoamyl alcohol and showed a strong absorption in the ultraviolet region, the maximum being at 305 mμ.

5. By selecting suitable reaction conditions, the determination of a few gammas

of mercury was possible.

6. The effect of diverse elements in the determinations of bismuth and mercury was studied and the maximum allowable amount was determined.