Spectrophotometric Determination of Bismuth with Xylenol Orange

By Hiroshi ONISHI and Nasumi ISHIWATARI

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Xylenol Orange was first proposed by Körbl and Pribil[1] as a metal indicator for the EDTA titration. Cheng recently described photometric methods for the determination of zirconium[2], hafnium[3], and iron[4] using Xylenol Orange. It does not appear, however, that a photometric method for determining bismuth with this reagent has been reported.

The present paper reports the conditions for the spectrophotometric determination of bismuth with Xylenol Orange including the effect of foreign substances. The composition and formation constant of the bismuth complex are also discussed.

Experimental

Apparatus.—Absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1 cm. cells.

Solutions. — L-Ascorbic acid, 10 g. in 100 ml. of water, may be used for several days. A 0.1 g. portion of sodium fluoride was dissolved in 100 ml. of water. A 0.10 g. portion of Xylenol Orange, Dotite XO (Dojindo & Co., Ltd., Kumamoto) was dissolved in 100 ml. of water. This solution can be kept for at least one week. Standard bismuth solution was prepared by dissolving 0.500 g. of pure bismuth metal in a few milliliters of nitric acid, evaporating the solution to dryness on a water bath, dissolving the residue in 1 : 9 nitric acid, and making up to 500 ml. From this stock solution (1.00 mg. Bi per ml.) a working standard solution (e. g., 40 p.p.m. Bi) was prepared by dilution.

Procedure.—Transfer the sample solution (dilute nitric acid solution) containing 10～80 μg. of bismuth to 25 ml. volumetric flask and adjust the nitric acid concentration to make the acidity 0.08～0.12 N after diluting to volume. If the acidity of the sample solution is too high, neutralize excess of acid with sodium hydroxide. Dilute the solution to about 15 ml. with water. Add 1 ml. of ascorbic acid solution and allow to stand at room temperature for about 5 min. Next add 1 ml. of sodium fluoride solution, mix, add 1.0 ml. of Xylenol Orange solution. After diluting to the mark with water and mixing, measure the absorbance of the solution in a 1 cm. cell at 530 mμ. Use the reference solution containing the same amounts of Xylenol Orange and other reagents.

Results and Discussion

The absorption spectra for Xylenol Orange and its bismuth complex are shown in Fig. 1. When a correction is applied for the reagent blank, an absorption peak is found at about 520 mμ. Because the reagent blank against water at 520 mμ is about twice as much as that at 530 mμ, the wavelength of 530 mμ has been adopted for the determination of bismuth.

The effect of nitric acid concentration on the absorbance of bismuth complex is shown in Fig. 2. The absorbances were measured against respective reagent blanks. It is seen that the acidity of 0.08～0.12 N is suitable. Perchloric acid or sulfuric acid also gives the same results as does the nitric acid.

As shown in Fig. 3, a practically constant

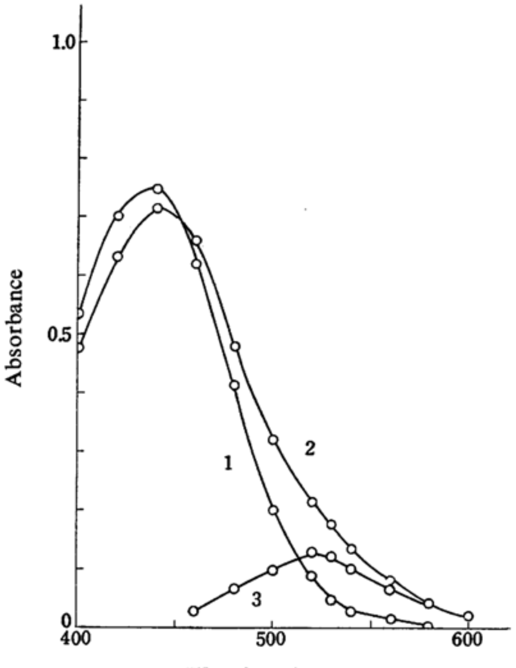

Fig. 1. Absorption spectra ;
1. Xylenol Orange (against water),
2. 1.6 p.p.m. Bi (against water),
3. 1.6 p.p.m. Bi (against reagent blank).

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[1] J. Körbl and R. Pribil, *Chemist-Analyst*, **45**, 102 (1956); J. Körbl, R. Pribil and A. Emr, *Collection Czechoslov. Chem. Communs.*, **22**, 961 (1957).

[2] K. L. Cheng, *Talanta*, **2**, 61 (1959).

[3] K. L. Cheng, ibid., **3**, 81 (1959).

[4] K. L. Cheng, ibid., **3**, 147 (1959).

TABLE I. STABILITY OF COLORED SOLUTION

Time after color development, hr.	Absorbance					
	40 μg. Bi HNO_3 soln.*	80 μg. Bi HNO_3 soln.*	40 μg. Bi HNO_3 soln.	80 μg. Bi HNO_3 soln.	40 μg. Bi $HClO_4$ soln.*	40 μg. B. H_2SO_4 soln.*
About 1/4	—	0.244	0.104	0.207	—	—
1	0.128	0.239	0.104	0.208	0.136	0.123
2	0.128	0.235	0.104	0.207	0.132	0.122
3	0.128	—	0.103	0.207	0.134	0.120
16∼20(Overnight)	0.128	0.212	0.101	0.206	0.135	0.120

* Ascorbic acid and NaF were not added.

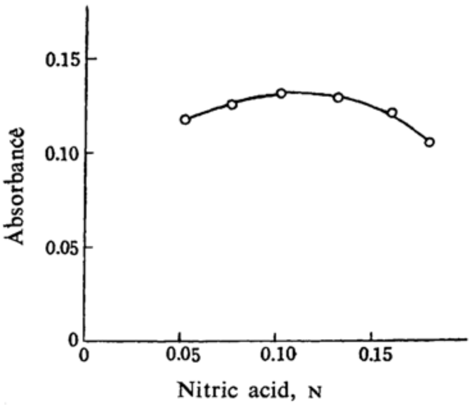

Fig. 2. Effect of nitric acid concentration; 1.6 p.p.m. Bi.

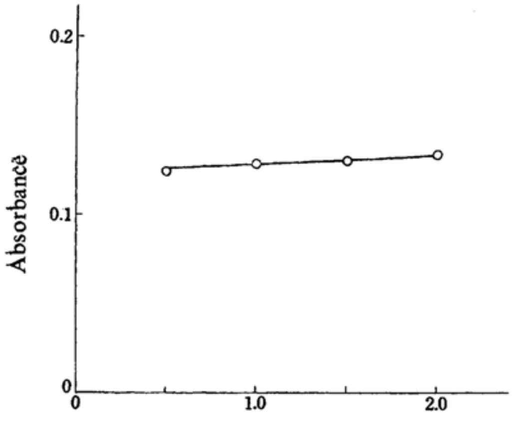

Fig. 3. Effect of Xylenol Orange concentration; 1.6 p.p.m. Bi.

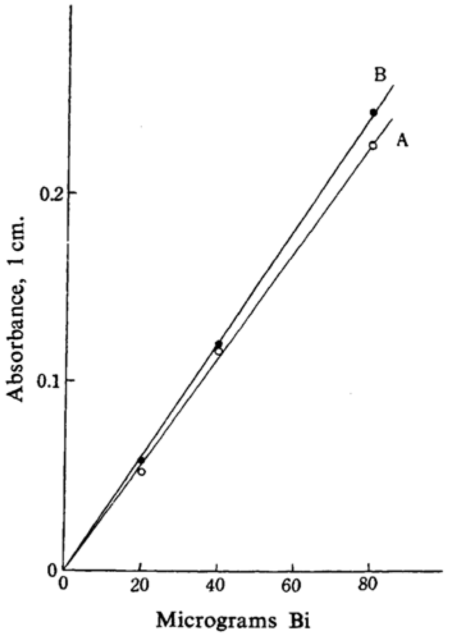

Fig. 4. Absorbance-concentration curve of bismuth;
A. According to the procedure,
B. In the absence of ascorbic acid and NaF.

absorbance is obtained by adding more than 0.5 ml. of 0.1% Xylenol Orange solution (final volume=25 ml.). The absorbances were measured against each reagent blank.

Table I shows the stability of the colored solutions. The absorbances remain constant at room temperature for at least 3 hr.

As shown in Fig. 4, absorbance is proportional to bismuth concentration in the range of 0.4 to at least 3 p.p.m. bismuth (10∼80 μg. Bi). At 530 mμ the molar extinction coefficient of bismuth is 1.6×10^4, or 0.014 μg. Bi/cm² corresponding to $\log I_0/I=0.001$. This sensitivity is comparable to that of the iodide method or the thiourea method[5].

The effects of many elements on the determination of bismuth were studied under the conditions used in the procedure (Table II). Most of the metals were in the form of nitrate. Microgram amounts of zirconium and thorium can be masked by fluoride ion. The interference of iron(III) can be eliminated by reduction with ascorbic acid. The effect of niobium is

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5) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers, Inc., New York (1959), p. 330.

TABLE II. DETERMINATION OF BISMUTH IN THE PRESENCE OF FOREIGN SUBSTANCES
(40.0 μg. of Bi taken in each determination)

Addition	Bi found, μg.
10 mg. K	40
0.2 mg. Cu	39
1 mg. Ag[a)]	40
88 μg. Au[b)]	41
10 mg. Mg	39
10 mg. Ca	39
1 mg. Zn	40
1 mg. Cd	40
2 mg. Hg(II)	41
10 mg. Al	39
0.1 mg. In	41
1 mg. Tl(I)	41
0.1 mg. Ti	39
50 μg. Zr	39
50 μg. Th	42
50 μg. Zr, 50 μg. Th, 1 mg. Fe(III)	37
5 mg. Sn, 5 mg. Sb[c)]	36
10 mg. Pb	40
5 mg. P (as KH_2PO_4)	39
0.1 mg. V (as NH_4VO_3)	40
0.1 mg. Nb[d)]	38
0.1 mg. Ta	37
1 mg. As(III)	40
1 mg. As(V)	40
0.1 mg. Cr (as $K_2Cr_2O_7$)	38
20 μg. Mo (as NH_4 molybdate)	40
0.1 mg. W (as Na_2WO_4)	39
10 mg. U(VI)	40
0.1 mg. Cl (as NaCl)	40
1 mg. Mn(II)	40
1 mg. Fe(III)	39
2 mg. Co	41
2 mg. Ni	41

a) Solution centrifuged after color development.
b) Ascorbic acid not added.
c) Volatilized with $HClO_4$, HBr and HCl.
d) Fumed with $HClO_4$.

removed by fuming with perchloric acid and treating the residue with 2 ml. of hot 1.4 N nitric acid. Apparently niobium is precipitated by this treatment. Absorbance measurements must be made within an hour after color development. (The absorbance increases after that time.) Tin and antimony can be volatilized by treating with perchloric, hydrobromic and hydrochloric acids. Five milligrams each of these elements were evaporated to fumes at about 180°C with 1 ml. of 60% perchloric acid and 2 ml. each of concentrated hydrochloric acid and hydrobromic acid (sp. gr. 1.48). After cooling 2 ml. of hydrobromic acid was again added and the solution was evaporated to dryness. The residue was treated with 2 ml. of 1.4 N nitric acid previous to color development. Silver is precipitated by ascorbic acid, but this can be removed by centrifugation after color development. Molybdenum interferes rather seriously and more than 50 μg. of this element can not be permitted.

The proposed method will probably be applicable to lead-base and tin-base alloys

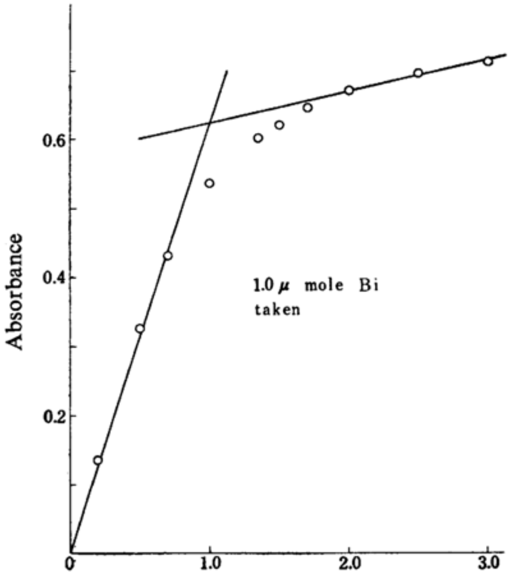

Fig. 5. Mole ratio method.

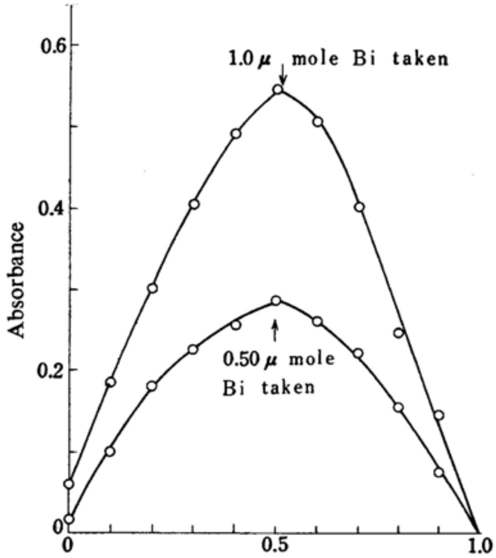

Fig. 6. Method of continuous variation.

after oxychloride precipitation of bismuth⁽⁶⁾.

The composition of the bismuth-Xylenol Orange complex was determined by the mole ratio method and by the method of continuous variation (Job's method). The experiments were carried out at room temperatures ranging from 16° to 20°C. From the results obtained (Figs. 5 and 6), a 1 : 1 complex of bismuth with the reagent is indicated. From the fact that Xylenol Orange is an analogue of EDTA, this composition would be expected. On the basis of the data shown in Fig. 6, the formation constant or stability constant of the complex is calculated to be 1×10^7 by the method described by Majumdar and Chakrabartty[7] and Cheng[8]. This value is greater than that of the iron(III)-Xylenol Orange complex (5×10^5)[4], and is close to that of the zirconium-Xylenol Orange complex (4.0×10^7)[8].

Summary

A method is described for the spectrophotometric determination of 10~80 μg. of bismuth with Xylenol Orange. The error is not likely to exceed ±10 per cent. The molar extinction coefficient of bismuth in 0.1 N nitric acid solution is 1.6×10^4 at 530 mμ. Instead of nitric acid perchloric acid or sulfuric acid may also be used. The interference of small amounts of zirconium, thorium, and iron can be eliminated by masking. Lead and thallium do not interfere with the determination of bismuth. A 1 : 1 complex of bismuth with Xylenol Orange is suggested.

Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken

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[6] B. Bendigo, R. K. Bell and H. A. Bright, *J. Research Natl. Bur. Standards*, **47**, 252 (1951); R. H. Campbell and M. G. Mellon, *Anal. Chem.*, **32**, 54 (1960).

[7] A. K. Majumdar and M. M. Chakrabartty, *Anal. Chim. Acta*, **19**, 372 (1958).

[8] K. L. Cheng, *Talanta*, **2**, 266 (1959).