Spectrophotometric Determination of Palladium and Bismuth(III) with Semimethylxylenol Blue

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Procedures are described for the spectrophotometric determination of palladium and bismuth(III) with Semimethylxylenol Blue (SMXB). SMXB reacts with palladium and bismuth(III) to form reddish-violet 1:1 complexes. The optimum pH ranges for the color development are pH 1.0—1.7 for palladium and pH 1.0—1.4 for bismuth(III). The absorption maxima of the colored solutions lie at 565—568 nm and at 568—570 nm, respectively. Beer's law is obeyed over the range of 0.4—3.2 μg cm^{-3} of palladium and 0.4—4.0 μg cm^{-3} of bismuth(III), and the sensitivities of the determinations are 4.0×10^{-3} μg Pd cm^{-2} and 6.1×10^{-3} μg Bi cm^{-2} for 0.001 of absorbance. For the palladium determination, gallium, tin(IV), bismuth(III), scandium, zirconium, and iron(III) interfere, but tin(IV), scandium, zirconium, and iron(III) can be masked by the addition of fluoride. For the bismuth(III) determination, gallium, tin(IV), scandium, zirconium, and iron(III) interfere, but the effect of iron(III) is eliminated by the addition of L-ascorbic acid, and tin(IV) and scandium can be masked by fluoride. A consecutive determination of palladium and bismuth(III) by the difference of the rates of color developments for their complexes was also studied.

Semimethylxylenol Blue (SMXB) is obtained as one of the products in the synthesis of Methylxylenol Blue. In the previous papers, we described photometric methods for the determination of thorium,[1] iron(III),[2] aluminium,[2] zirconium,[3] and gallium[4] using SMXB. In this work, we examined the usefulness of this reagent as the spectrophotometric reagent for palladium and bismuth(III), and observed that SMXB was a suitable reagent for these elements in respect to sensitivity and selectivity. Comparing the present methods for palladium and bismuth(III) with other methods which use reagents with structures similar to that of SMXB, for bismuth(III), SMXB is less sensitive than Semixylenol Orange,[5] but more sensitive than Xylenol Orange,[5,6] Methylxylenol Blue,[7,8] and Methylthymol Blue.[9] For palladium, this reagent has nearly the same sensitivity as Xylenol Orange.[10] As for the selectivity, the present methods are nearly as specific as the methods using the above reagents.[5-10] In the proposed methods, the color development for the bismuth(III) complex is rapid at room temperature, but that for the palladium complex is very slow, especially in the presence of chloride. Thus, utilizing the difference of the rates of color developments, 20—80 μg of palladium and 20—120 μg of bismuth(III) could be determined consecutively from the solution containing both elements. This paper describes the fundamental conditions for the spectrophotometric determination of palladium and bismuth(III), and for the consecutive determination of the two elements.

Experimental

Reagents. *Standard Palladium Solution*: A solution containing about 1 mg cm^{-3} of palladium was prepared by dissolving guaranteed reagent grade palladium chloride in 1.5 mol dm^{-3} nitric acid. The solution was standardized by the complexometric back titration with a standard solution of thorium using Xylenol Orange as an indicator. This solution was diluted as required.

Standard Bismuth(III) Solution: A solution containing about 1 mg cm^{-3} of bismuth(III) was prepared by dissolving guaranteed reagent grade bismuth(III) nitrate in 2 mol dm^{-3} nitric acid. The solution was standardized by the complexometric titration using Xylenol Orange as an indicator. This solution was diluted as required.

SMXB Solution: A 0.05% SMXB solution was prepared by dissolving in distilled water a weighed amount of the SMXB which had been synthesized by the Mannich condensation and purified by means of cellulose column chromatography.[1,2]

1 mol dm^{-3} nitric acid and 1 mol dm^{-3} aqueous ammonia was used for pH adjustments.

All the other reagents used were of guaranteed reagent grade.

Apparatus. A Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells was used for the absorbance measurements, and a Hitachi-Horiba model M-5 glass electrode pH meter for the pH measurements.

Recommended Procedures. *Determination of Palladium*: A sample solution containing 10—80 μg of palladium is taken into a 50 cm^3 Erlenmeyer's flask, and adequate amounts of 1 mol dm^{-3} nitric acid and 3 cm^3 of 0.05% SMXB solution are added. Then, the total volume is made about 20 cm^3 with water. After being kept for 5 min in a boiling water bath, the solution is cooled with running water, transferred to a 25 cm^3 volumetric flask, and diluted to the mark with water (the final pH:1.1). The absorbance is measured at 568 nm against the reagent blank.

Determination of Bismuth(III): A sample solution containing 10—100 μg of bismuth(III) is transferred to a 25 cm^3 volumetric flask. Then, adequate amounts of 1 mol dm^{-3} nitric acid and 3 cm^3 of 0.05% SMXB solution are added. After increasing the volume to 25 cm^3 (the final pH:1.1), the absorbance is measured at 568 nm against the reagent blank.

Consecutive Determination of Palladium and Bismuth(III): The sample solution containing 20—80 μg of palladium and 20—120 μg of bismuth(III) is divided equally. In one solution, the absorbance of bismuth(III) complex is measured by the recommended procedure for bismuth(III), by adding 3 mg of chloride before the addition of the SMXB solution. In this case, the measurements must be done within 4 min after color development. From this absorbance, bismuth(III) is determined by using calibration curve III in Fig. 3. In the other, the total absorbance of the palladium and bismuth(III) complexes is measured by the recommended procedure for palladium, by adding 3 mg of chloride before the addition of the SMXB solution. Then, palladium is determined by subtracting the absorbance due to bismuth(III) from the total absorbance and using calibration curve

II in Fig. 3.

Result and Discussion

Absorption Curves. Figure 1 shows the absorption curves of palladium and bismuth(III) complexes obtained by the recommended procedures. The absorption maxima of the colored solutions of the complexes are at 565—568 nm and at 568—570 nm, respectively.

The Effect of pH. The effect of pH on the color development of the complexes was examined. As shown in Fig. 2, the ranges in which the maximum and nearly constant absorbance was obtained were pH 1.0—1.7 for palladium and pH 1.0—1.4 for bismuth(III). When sulfuric acid, perchloric acid and hydrochloric acid were used instead of nitric acid for the pH adjustment on the palladium determination, sulfuric acid and perchloric acid gave nearly the same results as nitric acid, while hydrochloric acid reduced the absorbance. In the bismuth(III) determination, all of these acids gave almost the same results.

The Effect of the Reagent Concentration. Various amounts of 0.05% SMXB solution were added to a solution containing 40 μg of palladium or 50 μg of bismuth(III). The maximum and reasonably constant absorbances were obtained by adding from 1.5 to 7 cm^3 of SMXB solution for each element.

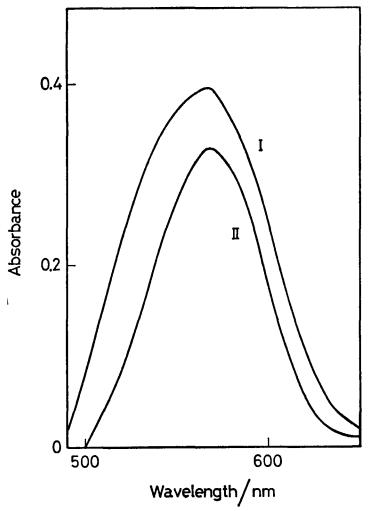

Fig. 1. Absorption curves.
0.05% SMXB: 3 cm^3, pH: 1.1, reference: reagent blank, I: Pd 40 μg/25 cm^3, II: Bi(III) 50 μg/25 cm^3.

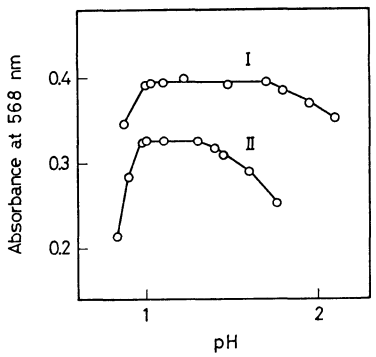

Fig. 2. Effect of pH.
0.05% SMXB: 3 cm^3, reference: reagent blank, I: Pd 40 μg/25 cm^3, II: Bi(III) 50 μg/25 cm^3.

The Stability of the Color. The color development for the palladium complex is very slow at room temperature. However, heating in a boiling water bath hastened the color development and the maximum absorbance was obtained within a few minutes. Heating for 5 min in a boiling water bath, therefore, was adopted in further experiments. On the other hand, the full color development for bismuth(III) complex occurred immediately after the reagent was added, and the color intensity was independent of heating for at least 20 min in a boiling water bath.

The color of the both complexes, once developed, was very stable, and the absorbances remained constant for at least 3 h.

Calibration Curves. The calibration curves for palladium and bismuth(III) which were prepared by the recommended procedures are shown in Fig. 3. Linear relationships between absorbance and concentration held over the range of 0.4—3.2 μg cm^{-3} of palladium and 0.4—4.0 μg cm^{-3} of bismuth(III); the molar absorptivities calculated from the curves were 2.64×10^4 and 3.43×10^4, respectively. The relative standard deviations for five replicate determinations were 1.4% for 40 μg of palladium and 1.2% for 50 μg of bismuth(III). In Fig. 3, the calibration curve for palladium in the presence of 3 mg of chloride is also shown. In this case, the absorbance decreased about 10% compared with that in the absence of chloride, but Beer's law was obeyed over the range of 0.4—3.2 μg cm^{-3} of palladium.

The Effect of Diverse Ions. Table 1 shows the effect of diverse ions on the determination of 40 μg of palladium and 50 μg of bismuth(III). Palladium could be determined within 5% errors in the presence of 1 mg each of 20 cations such as alkali metals, alkaline earth metals, lead, zinc, lanthanoids, manganese(II), cobalt, and nickel, and in the presence of 10 mg each of 6 anions such as fluoride, oxalate, citrate, *etc.*

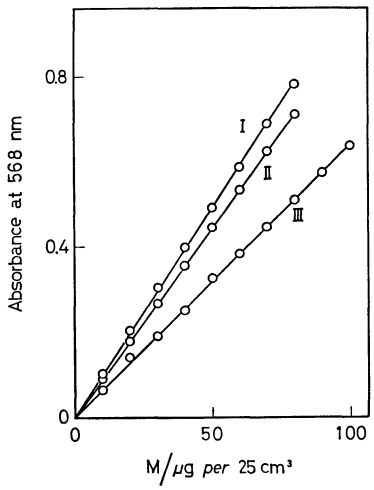

Fig. 3. Calibration curves.
0.05% SMXB: 3 cm^3, pH: 1.1, reference: reagent blank, M—I, II: Pd, III: Bi(III), II: 3 mg of chloride was added.

TABLE 1. EFFECTS OF DIVERSE IONS

Ion	A		B	
	Amount added (mg)	Pd found (μg)	Amount added (mg)	Bi(III) found (μg)
Li^+	1	39.8	1	51.5
K^+	1	40.6	1	49.6
Be^{2+}	1	41.0	1	51.2
Mg^{2+}	1	40.0	1	50.9
Ca^{2+}	1	40.0	1	49.0
Sr^{2+}	1	40.9	1	48.9
Ba^{2+}	1	40.3	1	50.0
Al^{3+}	0.04	40.2	1	49.6
Al^{3+}	1[a]	40.8	—	—
Ga^{3+}	0.04	74.2	0.05	51.4
In^{3+}	0.5	38.4	0.1	51.2
Sn^{4+}	0.04	45.6	0.05	83.0
Sn^{4+}	1[a]	39.8	0.05[b]	51.8
Pb^{2+}	1	40.9	1	50.0
As(V)	0.5	41.1	1	51.6
Bi^{3+}	0.04	65.1	—	—
Cu^{2+}	0.04	40.2	0.05	50.5
Zn^{2+}	1	40.9	1	50.0
Cd^{2+}	1	40.8	1	49.6
Hg^{2+}	1	40.0	1	49.6
Sc^{3+}	0.04	47.1	0.05	97.7
Sc^{3+}	0.5[a]	40.0	0.5[b]	52.0
Y^{3+}	1	39.8	1	50.0
La^{3+}	1	39.2	1	48.5
Ce^{3+}	1	40.3	1	49.1
Zr^{4+}	0.04	129.7	0.01	101.0
Zr^{4+}	1[a]	40.3	—	—
Th^{4+}	0.04	41.1	0.05	89.7
Th^{4+}	1[a]	41.4	0.5[b]	51.6
V(V)	0.1	38.8	0.1	50.0
Cr^{3+}	1	41.5	1	50.3
Mo(VI)	0.04	40.0	0.05	51.0
W(VI)	1	40.8	0.1	50.4
UO_2^{2+}	1	40.0	1	48.9
Mn^{2+}	1	38.9	1	49.1
Fe^{3+}	0.04	97.8	0.01	83.3
Fe^{3+}	0.04[a]	40.0	1[c]	50.5
Co^{2+}	1	40.0	1	50.0
Ni^{2+}	1	40.6	1	48.5
Rh^{3+}	1	39.4	1	48.9
Pd^{2+}	—	—	0.05[d]	51.5
Pt(IV)	1	41.1	1	49.6
F^-	10	38.9	1	49.0
Cl^-	1	39.0	10	48.9
PO_4^{3-}	10	40.2	10	51.3
SO_4^{2-}	10	40.0	10	48.3
Oxalate	10	39.8	0.05	49.0
Tartrate	10	40.8	10	51.5
Citrate	10	40.0	10	51.0

A: Effect on palladium determination (40 μg of palladium was taken). B: Effect on bismuth(III) determination (50 μg of bismuth(III) was taken). a) 10 mg of fluoride was added. b) 1 mg of fluoride was added. c) 3 cm^3 of 4% L-ascorbic acid solution was added. d) Absorbance was measured immediately after color development.

Gallium, tin(IV), bismuth(III), scandium, zirconium, and iron(III) interfered with the determination, but tin(IV), scandium, zirconium, and iron(III) could be masked by the addition of fluoride. For the bismuth(III) determination, interfering ions such as tin(IV) and scandium, could be masked by fluoride and the effect of iron(III) is eliminated by ascorbic acid. Gallium and zirconium, however, interfered seriously.

Consecutive Determination of Palladium and Bismuth(III). The color development for the palladium complex is slow at room temperature. The speed of this reaction becomes slower by the addition of chloride, and as a result, no color development occurs for about 3 min immediately after preparation of the color system. After that, the color development occurs gradually, but the increase of the absorbance in the next 5 min is only about 4% of the absorbance which is obtained when the color develops fully. So, if the absorbance is measured within 4 min after preparation of the color system, the absorbance from palladium complex is negligible. The order of the addition of chloride is important, and if chloride is added after the addition of the SMXB solution, it has no effect on the rate of color development. On the other hand, the color formation of the bismuth(III)

TABLE 2. CONSECUTIVE DETERMINATION OF PALLADIUM AND BISMUTH(III)

Taken (μg)		Found (μg)	
Pd	Bi(III)	Pd	Bi(III)
10	10	9.3	10.2
10	60	9.2	59.5
30	30	30.3	30.8
40	10	41.0	10.9
40	50	40.9	49.9
40	60	40.9	61.2

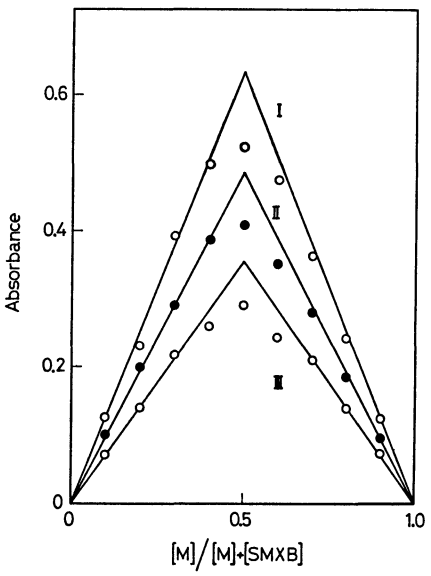

Fig. 4. Continuous variation method.
pH: 1.1, [M]+[SMXB] (mol dm^{-3})—I, III: 5.64×10^{-5}, II: 3.23×10^{-5}, M—I, III: Pd, II: Bi(III), wavelength(nm)—I, II: 568, III: 520.

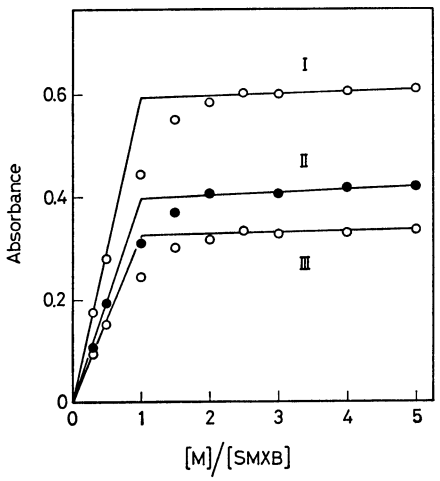

Fig. 5. Mole ratio method.
pH: 1.1, [M] (mol dm^{-3})—I, III: 2.26×10^{-5}, II: 1.34×10^{-5}, M—I, III: Pd, II: Bi(III), wavelength (nm)—I, II: 568, III: 520.

complex is rapid, and the maximum absorbance is obtained instantaneously. Utilizing these facts, the fundamental conditions for the consecutive determination of the two elements have been examined. As shown in Table 2, satisfactory results of the determinations were obtained with the solution containing 20—80 μg of palladium and 20—120 μg of bismuth(III).

The Composition of the Complexes. As shown in Figs. 4 and 5, the continuous variation and the mole ratio methods indicated that both palladium and bismuth(III) formed the 1:1 complexes with SMXB.

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