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The Spectrophotometric Determination of Palladium with Chromazurol S*[1]

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A simple spectrophotometric method for the determination of palladium was studied, using chromazurol S as a reagent. Palladium(II), in a slightly acidic or a nearly neutral solution, reacts with chromazurol S to form blue or red complexes, each consisting of one molecule of the reagent and one atom of palladium. The maximum absorption wavelengths of blue and red complexes are respectively 596 mμ and 500 mμ, against the reagent blanks. The color development of the blue complex formed in a slightly acidic medium is more sensitive, therefore, it was applied to the spectrophotometric determination of palladium. Several conditions for the color development were investigated; a calibration curve was made under the optimum conditions; and the influences of coexisting ions were also investigated. The blue complex gives a maximum absorbance at 596 mμ in the pH range from 4.3 to 5.3. About a 2-fold excess of the reagent over the palladium concentration is necessary in order to obtain the maximum color intensity. The color development is almost instantaneous, and the absorbance remains constant for at least 4 hr. The order of the addition of reagents has no effect upon the absorbance. The color system obeys Beer's law over the concentration range up to 70 μg of palladium per 10 m*l*. The molar extinction coefficient at 596 mμ is 18600, which corresponds to a sensitivity index of 0.0058 μg/cm^2 for an absorbance of 0.001. Sulfate, chloride, fluoride, phosphate and acetate ions do not interfere with the color reaction. Thiosulfate ion and polycarboxylate ions such as oxalate, citrate and EDTA *etc.* bleach the color of the complex. Cations such as Sc(III), Y(III), Th(IV), U(VI), Be(II), Al(III) and Cu(II) ions cause an over-estimation of palladium; the interference by these cations except copper, however, could be eliminated by the addition of appropriate amounts of either sodium fluoride or sodium phosphate as masking agent.

Chromazurol S reacts with palladous ion in a weakly acidic or a nearly neutral medium to form blue or red complexes according to the pH value of the solution.

In the present paper are described conditions which permit the spectrophotometric determination of palladium at microgram levels.

Dey *et al.*[1,2] and Horiuchi *et al.*[3] have previously proposed methods for determining palladium, using the colored complex with chromazurol S. Their results differ, however, appreciably from the present results and their procedures for the determination are more complicated.

Several conditions for the color development and the composition of the colored complex were investigated. A calibration curve was made under the optimum condition. The influences of coexisting ions were investigated.

Experimental

Apparatus. Spectrophotometric measurements were made with a Shimadzu model QR-50 spectrophotometer, using 1 cm glass transmission cells. All absorbance measurements were carried out at about 20°C. The pH measurements of the solutions were made with a Hitachi-Horiba model M-4 glass electrode pH meter.

Reagents. *Stock Solution of Palladium.* A palladium stock solution was prepared by dissolving palladous chloride powder of analytical reagent grade in a small amount of 1 N perchloric acid, with heating, and then by diluting with distilled water. The resultant solution was standardized by EDTA titration. A standard working solution was prepared by taking an aliquot of the stock solution and diluting it to the desired concentration.

Chromazurol S Solution. About 1.0×10^{-3} M of a chromazurol S solution was prepared by dissolving Dotite Chromazurol S reagent (Dojindo & Co., Kumamoto) in distilled water and then by filtering off the floating residue.

Buffer Solution. Buffer solutions of various pH values were prepared by mixing 1.0 M hexamethylenetetramine and 1.0 N perchloric acid solutions in different ratios.

Other Reagents. All other reagents were of reagent grade.

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2) S. P. Sangal and A. K. Dey, *J. Indian Chem. Soc.,* **40**, 464 (1963).

3) Y. Horiuchi and H. Nishida, *Bunseki Kagaku* (*Japan Analyst*), **16**, 1018 (1967).

Standard Procedure. Transfer a sample aliquot, containing 10 to 50 μg of palladium, to a 10 m*l* volumetric flask, and then add 0.3 m*l* of a pH 5.0 buffer solution and 1.0 to 1.5 m*l* of a 1.0×10^{-3} M solution of chromazurol S. The solution is diluted to the mark with distilled water, mixed, and allowed to stand for about 1 hr. The absorbance of the solution is measured at 596 mμ by using the reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectrum of the palladium - chromazurol S complex is greatly affected in its shape by pH value of the medium. As described in the following section, however, a spectrum with an absorption maximum at 596 mμ in the pH range between 4.3 and 5.3 was obtained. Figure 1 shows the absorption spectra of chromazurol S and its palladium complex at a pH of 5.0. Chromazurol S is abbreviated as ChS in all figures.

In order to observe the spectral changes cause by varying pH values, a series of solutions containing 32 μg of palladium and 1.0 m*l* of a 1.0×10^{-3} M solution of chromazurol S were prepared at different pH values. The absorption spectrum of each solution was measured against the reagent blank. The results are shown in Fig. 2. In the pH range between 4.3 and 5.3, the maximum absorption wavelength is found at 596 mμ, and the absorption spectra indicate similar shapes. At pH below 4, each peak of the spectrum is shifted toward a longer wavelength; and at pH below 2, a part of the formed complex precipitates. In the pH range between 5.3 and 7.0, the intensity of the absorbance at 596 mμ decreases gradually, in accordance with the increasing pH value of the solution, while an absorption newly appears with a maximum at 500 mμ (curves 7, 6, 5 and 4 in Fig. 2); moreover, these spectra show an isosbestic point at about 545 mμ. It seems that two absorbing species which are in equilibrium with each other have absorption maxima at respectively 596 and 500 mμ. At pH 7.5 or higher, the disappearance of the absorption at 596 mμ is observed, only giving small shoulders. Any absorbance of the complex almost disappears at a pH value of about 8.5.

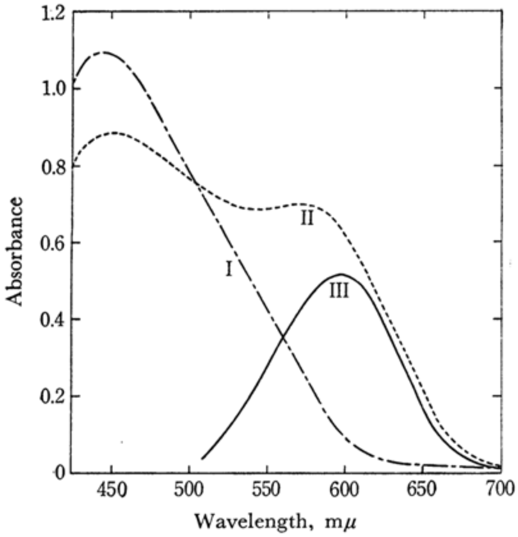


Fig. 1. Absorption spectra of chromazurol S and its palladium complex.
Pd: 3.0×10^{-5} M, ChS: 1.0×10^{-4} M, pH: 5.0
I: ChS *vs.* H_2O, II: Pd-ChS *vs.* H_2O
III: Pd-ChS *vs.* ChS

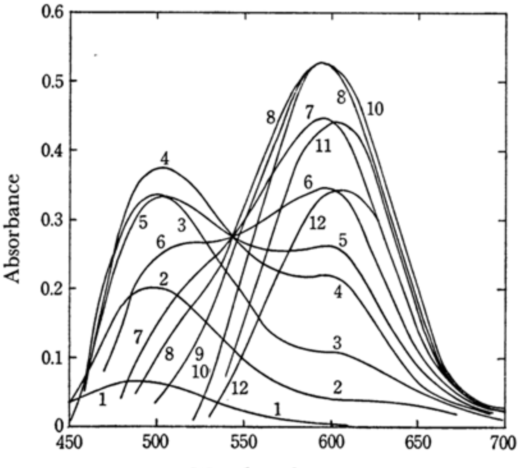


Fig. 2. Absorption spectra of Pd-ChS complex at various pH values.
Pd: 32 μg, ChS: 1.0×10^{-4} M
1: pH 8.2, 2: pH 7.8, 3: pH 7.5, 4: pH 7.1
5: pH 6.9, 6: pH 6.4, 7: pH 5.9, 8: pH 5.3
9: pH 5.0, 10: pH 4.3, 11: pH 3.7, 12: pH 2.7

In the practical spectrophotometric determination of palladium, the complex with absorption maximum at 596 mμ in the pH range between 4.3 and 5.3 was used.

Though the figure is not given, the absorption spectra of solutions containing 0.5 μmol of chromazurol S and palladium added in various amounts up to 5.0×10^{-5} M, show an isosbestic point at about 505 mμ against the water blank at pH 5.0. The occurrence of an isosbestic point indicates that there is only one kind of complex under these conditions.

Effect of pH Value and That of the Amount of the Buffer Solution. The effect of pH on the color development of the palladium complex was studied with solutions varying in pH value from 4 to 8. Figure 3 shows that the maximum and nearly constant absorbance is obtained over the pH range from 4.3 to 5.3.

At a constant pH, the absorbance of the colored solution was measured by varying the amount of the buffer solution. In consequence, the color intensity decreased gradually, by increasing amounts

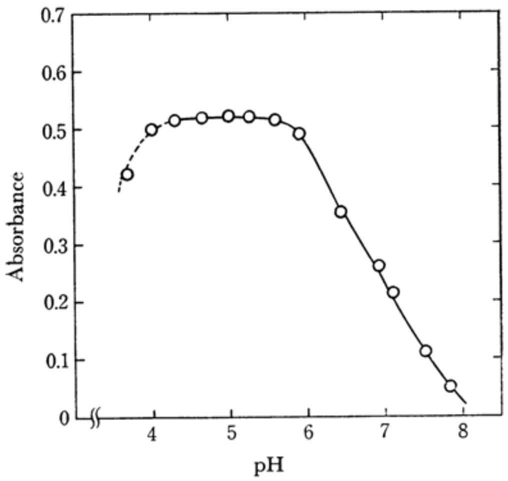
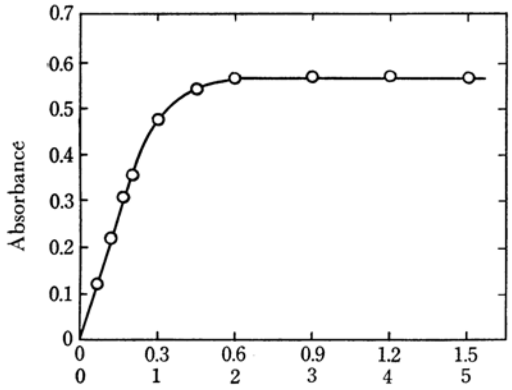


Fig. 3. Effect of pH on color development.
Pd: 3.0×10^{-5} M, ChS: 1.0×10^{-4} M
Wavelength: 596 mμ



Upper scale: 1.0×10^{-3} M ChS, m*l*
Lower scale: Mole ratio, [ChS]/[Pd]

Fig. 4. Effect of addition of chromazurol S.
Pd: 0.3 μmol (32 μg), pH: 5.0
Wavelength: 596 mμ

of the buffer solution. In this series of experiments, therefore, 0.3 m*l* of a 1.0 M buffer solution per 10 m*l* was always used.

Effect of the Addition of Chromazurol S. In order to study the effect of the concentration of chromazurol S, a series of absorbances was measured under various concentrations of chromazurol S, reagent blanks of same concentration being used as the reference. The results are shown in Fig. 4. The maximum absorbance is obtained by adding more than 0.6 m*l* of a 1.0×10^{-3} M chromazurol S solution for 0.3 μmol of palladium. Namely, more than a 2-fold excess of the reagent over the palladium concentration is necessary in order to obtain the maximum color intensity.

Effect of Temperature. The absorbance of colored solution was measured at various temperatures. The absorbance gradually decreases with the rise of temperature, and over 30°C the color intensity decreased remarkably. In this series of experiments, therefore, all absorbance measurements were carried out at about 20°C.

Effect of the Order of Adding Reagents. The varying orders in which the reagents were added had no significant effects on the absorbances.

Color Stability. As is shown in Fig. 5, the absorbance of the resultant solution decreased slowly for the first 30 min. After this period, however, it remained practically constant for at least 4 hr.

Calibration Curve. A calibration curve was made under the optimum conditions of those in the sections above-mentioned. The results are

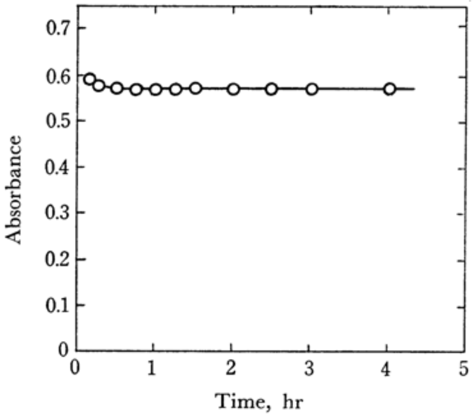


Fig. 5. Color stability.
Pd: 32 μg, ChS: 1.0×10^{-4} M
pH: 5.0, Wavelength: 596 mμ

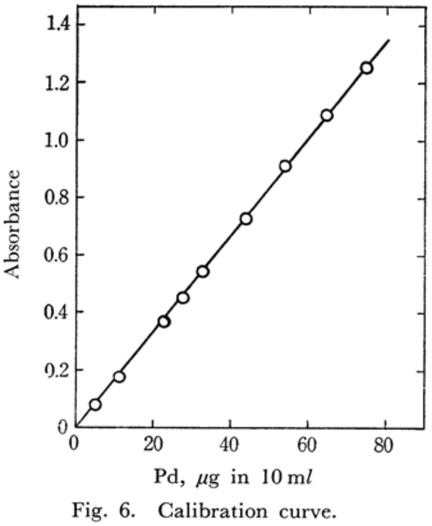


Fig. 6. Calibration curve.
pH: 5.0, Wavelength: 596 mμ

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4) A. Ringbom, *Z. Anal. Chem.*, **115**, 332 (1939).

5) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers Inc., New York (1959), p. 80.

shown in Fig. 6. A linear relationship exists between the absorbance and the palladium concentration over the range investigated. The optimum concentration range was then determined by Ringbom's procedure[4)] and was found to lie between 10 and 50 μg palladium per 10 m*l*. Under the conditions of the spectrophotometric determination, the apparent molar extinction coefficient was found to be 18600. The sensitivity of the reaction as expressed by Sandell's notation[5)] is 0.0058 μg of palladium per cm^2. This value is about 7-folds more sensitive than that of the data of Dey *et al.*[1)]

For the spectrophotometric determination of palladium, several reagents have been used, such as *p*-nitrosodiphenylamine,[6)] *p*-nitrosodimethylaniline,[7)] mercaptoacetic acid,[8)] potassium iodide,[9)] ethylenediaminetetraacetic acid,[10)] 2-nitroso-1-naphthol,[11)] α-furildioxime,[12)] xylenol orange,[13)] 2-hydroxy-5-methylpropiophenone oxime,[14)] and *p*-(mercaptoacetamido)benzenesulfonic acid.[15)] The methods using the above reagents, however, in many cases, required the extraction of the complexes into an organic solvent.

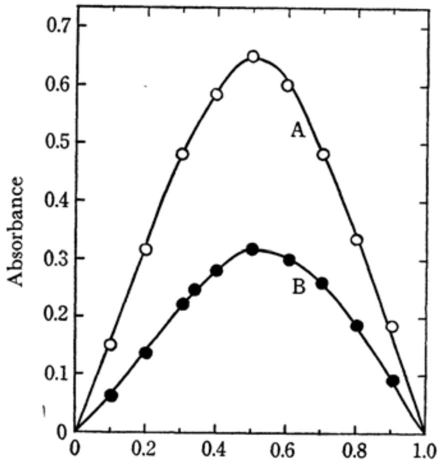

Fig. 7. Continuous variation method.
A: pH, 5.0; Wavelength, 596 mμ; [Pd]+[ChS]=8.0×10^{-5} M
B: pH, 8.0; Wavelength, 500 mμ; [Pd]+[ChS]=1.5×10^{-4} M

The present reagent, chromazurol S, like xylenol orange,[13)] has an advantages as a colorimetric reagent for palladium; that is, no extraction of the complex is required, since a palladium-chromazurol S complex is water soluble. This method is comparable in sensitivity with the 2-nitroso-1-naphthol[11)] and α-furildioxime[12)] methods.

Complex Formation. The combining ratio of palladium and chromazurol S in the complex was studied by the continuous variation method[16)] and by the mole ratio method.[17)] The results are shown in Figs. 7 and 8. Curves A and B in Figs. 7 and 8 show respectively the plots for the complex having a maximum at 596 mμ, which is formed in a weakly acidic medium, and those for the complex having a maximum at 500 mμ, which is formed in a nearly neutral medium. As is shown in these figures, it may be concluded that palladium forms either of two 1 : 1 complexes, one a red complex with its absorption maximum at 500 mμ and the other a blue complex with its absorption maximum at 596 mμ. From the results of these spectrophotometric studies and the appearance of an isosbestic point, which has already been shown in Fig. 2, it is assumed that the two complex ions are charged differently. It is impossible to obtain definite information on the structures of these palladium-chromazurol S complexes on the basis

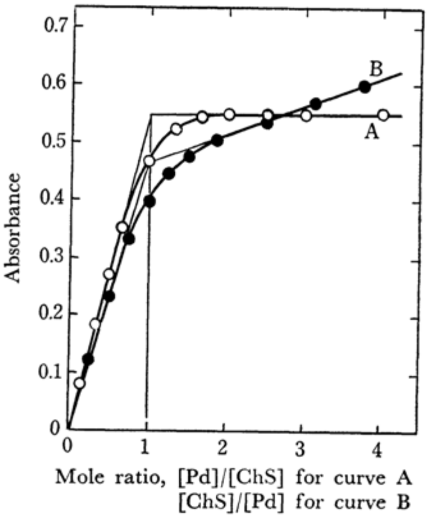

Fig. 8. Mole ratio method.
A: pH, 5.0; Wavelength, 596 mμ; [ChS]=3.0×10^{-5} M
B: pH, 7.8; Wavelength, 500 mμ; [Pd]=8.0×10^{-5} M

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TABLE 1. EFFECT OF DIVERSE IONS ON PALLADIUM DETERMINATION
Palladium taken: 32.0 μg

Ion added, μmol		Palladium found, μg
Sulfate	30	32.3
Chloride	3	32.0
	15	21.5
Fluoride	6	32.1
	15	27.1
Phosphate	1.5	32.2
	3	31.8
	30	30.9
Acetate	3	32.2
	15	26.0
Carbonate	0.3	31.6
	1.5	24.9
Cyanide	0.3	31.9
	1.5	21.1
Pyroborate	0.3	32.0
	1.5	2.5
Thiosulfate	0.03	25.7
	0.1	15.8
Oxalate	0.03	30.0
	0.3	15.0
Citrate	0.03	30.1
	0.3	18.4
EDTA	0.03	26.4
	0.1	14.2
Silver(I)	0.3	32.4
	1.0	29.0
Cadmium(II)	0.3	32.0
	3.0	31.9
Lead(II)	0.3	31.9
	3.0	31.7
Manganese(II)	0.3	32.0
	3.0	31.8
Nickel(II)	0.3	32.7
	3.0	31.7
Barium(II)	0.3	32.2
	3.0	32.0
Strontium(II)	0.3	31.9
	3.0	32.0
Magnesium(II)	0.3	31.8
	3.0	31.8
Zinc(II)	0.3	31.9
	3.0	32.4
Ammonium(I)	0.3	31.8
	3.0	32.2
Cobalt(II)	0.3	31.7
	1.5	31.9
Molybdenum(VI)	0.3	32.1
	1.5	32.4
Calcium(II)	0.3	32.1
	1.5	32.6
Iron(II)	0.15	31.9
	0.3	34.8
Indium(III)	0.03	34.4
	0.3	36.8
Yttrium(III)	0.03	32.9
	0.3	39.6
Thorium(IV)	0.03	32.0
	0.3	47.5
Copper(II)	0.03	34.5
	0.3	47.1
Beryllium(II)	0.03	36.0
	0.3	59.1
Scandium(III)	0.03	38.0
	0.3	70.2
Uranium(VI)	0.03	36.9
	0.15	57.7
Aluminium(III)	0.03	41.3
	0.15	60.0
Tungsten(VI)	0.3	31.2
	1.5	21.0
Mercury(II)	0.3	32.2
	1.5	28.4
Mercury(I)	0.03	32.3
	0.3	27.6
Tin(II)	0.03	31.7
	0.3	27.0
Neodymium(III)	0.03	31.8
	0.15	27.8
Iron(III)	0.03	32.5
	0.15	28.9
Cerium(III)	0.3	32.1
	0.6	ppt.
Bismuth(III)	0.3	31.3
	0.6	ppt.

of the experimental results described in the present paper.

Horiuchi *et al.*[3] have indicated that the optimum pH value range for color development is 5.8 to 6.7 and that complexes of 1 to 1 or 1 to 2 are formed, according to the concentration of the reagent used. It seems that the difference between their results and those obtained here may be attributed to the difference between the experimental conditions used.

Effect of Diverse Ions. In order to test the effect of diverse ions upon the palladium determination, absorbance measurements were made for the solutions containing 32.0 μg of palladium and various amounts of particular ion. The results are summarized in Table 1.

Sulfate, chloride, fluoride, phosphate and acetate ions do not interfere, even when present in considerably large amounts. Such anions as carbonate, cyanide and pyroborate ions do not interfere when their amounts are equivalent with palladium; however, these ions give negative errors at higher concentrations. Thiosulfate, oxalate, citrate and EDTA ions inhibit the color formation of the complex, even when added in very small amounts.

Of the 30 cations tested, Fe(II, III), In(III), Y(III), Th(IV), Cu(II), Be(II), Sc(III), U(VI), Al(III), W(VI), Hg(I, II), Sn(II), Nd(III), Ce(III) and Bi(III) interfere with the palladium determination. Among the above cations, Hg(I), Sn(II), Nd(III) and Fe(III) give negative error,

Table 2. Effect of masking agents on palladium determination

Palladium taken: 32.0 μg
Cation added: each 0.3 μmol

Cation	Palladium found, μg Masking agents added:		
	None	Na_3PO_4 3.0 μmol	NaF 6.0 μmol
In(III)	36.8	32.6	33.9
Y(III)	39.6	31.6	32.3
Th(IV)	47.5	31.3	32.3
Sc(III)	70.2	31.1	30.6
Be(II)	59.1	51.0	31.5
Al(III)	73.1	54.0	31.3
U(VI)	75.9	31.9	39.6
Cu(II)	47.1	42.7	45.5

and 0.6 μmol of Ce(III) and Bi(III) precipitate and interfere under these conditions. However, fluoride and phosphate ions, which probably form more stable complexes with many other metal ions to decompose the corresponding chromazurol S complexes, have almost no influence on the complex formation with palladium and chromazurol S unless large amounts are added. Sodium fluoride and sodium phosphate can, therefore, serve as excellent masking agents to prevent the interference of other metals. The results when used fluoride and phosphate ions as masking agent are shown in Table 2.

As is shown in Table 2, among the coexisting ions which introduce positive error with the determination of palladium, metal cations except copper can be effectively masked by either phosphate or fluoride. Accordingly, it is possible to improve selectivity of chromazurol S reagent for palladium.

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