Spectrophotometric Determination of Palladium with Eriochrome Cyanine R

Tsunenobu Shigematsu, Masakazu Matsui* and Katsuya Uesugi**

A new spectrophotometric method for the determination of palladium was studied, using eriochrome cyanine R as a reagent. Palladium reacts very sensitively with eriochrome cyanine R in the presence of tetradecyldimethylbenzylammonium chloride (TDBA) to form a colored complex. The palladium complex in the presence of TDBA gives the higher order complex with its absorption maximum shifted to longer wavelengths. The complex shows maximum absorbance at the pH range from 4.0 to 5.6; Beer's law is obeyed over the range from 0.1 to 1.2 ppm of palladium at 620 nm. The molar absorptivity is 99,000 and the sensitivity is 0.0011 μg of palladium per cm^2, corresponding $\log I_o/I = 0.001$. The mole ratio of palladium and reagent in the complex is estimated to be 1 : 3 in the presence of TDBA. Copper(II) and iron(III) interfere with the determination of palladium when sodium fluoride is used as a masking agent. This method is the most sensitive among the methods using some triphenylmethane dyes, which have structures similar to this reagent.

INTRODUCTION

In spectrophotometric studies of various triphenylmethane dyes as reagents, it has been found that eriochrome cyanine R (Sodium-2″-sulfo-4′-hydroxy-3,3′-dimethylfuchsone–5,5′-dicarboxylate; Color Index 43820) gives a very sensitive color reaction with palladium in a slightly acidic medium. This dye has been used as a spectrophotometric reagent for aluminum,[1~3] beryllium,[4] iron(III),[3] and scandium.[5] Recently, the high sensitive methods of spectrophotometric determination based on the complex-formation on the micelle surface formed in the presence of quaternary ammonium salts have been suggested.[3,6~8] Kohara *et al.*[8] have defined the behavior of some organic ligands in the solutions containing micelle ions.

This paper describes a spectrophotometric method for the determination of palladium using eriochrome cyanine R and a quaternary ammonium salt. Several conditions under which microgram amounts of palladium can be determined, the influences of coexisting ions and the composition of the complex will be discussed. Under the optimum conditions described below, eriochrome cyanine R is a more sensitive reagent for palladium than pontachrome azure blue B[9] and its analogues, which are similar in structure to the proposed reagent.

EXPERIMENTAL

Apparatus and Reagents

Absorbance measurements were made with a Hitachi Perkin-Elmer 139 UV-VIS

* 重松 恒信, 松井 正和: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

** 上杉 勝弥: Laboratory of Chemistry, Himeji Institute of Technology, Himeji, Hyogo.

spectrophotometer using 1.00-cm matched quartz cells. The pH measurements were carried out with a Hitachi-Horiba glass electrode pH meter, model M-5.

The stock solution of palladium were prepared by dissolving palladium chloride in distilled water, and then adding small amounts of hydrochloric acid. The palladium content of this stock solution was standardized gravimetrically by the dimethylglyoxime method.[10] The working solutions containing 10 μg of palladium per ml was prepared by appropriate dilution of the stock solution. Eriochrome cyanine R used was supplied by E. Merck AG (pro analysi) and the aqueous 0.1% (w/v) solution of it was prepared. The aqueous 0.5% (w/v) solution of tetradecyldimethylbenzyl ammonium chloride (abbreviated as TDBA) was prepared by dissolving Dotite zephiramine (Dojindo Co., Ltd., Research Laboratories). The buffer solution of pH 5.4 was prepared by mixing a 0.1 M potassium dihydrogenphosphate solution and a 0.1 M disodium hydrogenphosphate solution. The other organic dyes, eriochrome brilliant violet B[11] (C. I. 43570, Geigy Co., Inc.,), chromazurol S (C. I. 43825, Dojindo Co., Ltd., Research Laboratories), pontachrome azure blue B[9] (C. I. 43830, E. I. du Pont de Nemours and Co., Inc.,), chromal blue G[12] (C. I. 43835, Geigy Co., Ltd.,) and eriochrome azurol G[13] (C. I. 43855, Tokyo Kasei Kogyo Co., Ltd.,) were used. All other chemicals used were reagent grade quality.

Reagent 40 ppm
1 : Pd 0.8 ppm, TDBA 400 ppm
2 : Pd 1.2 ppm, without TDBA
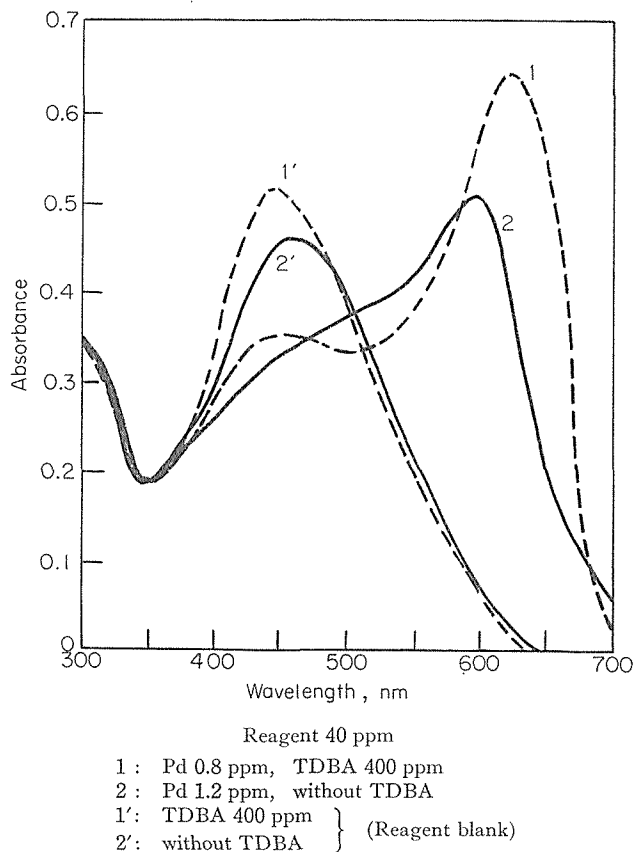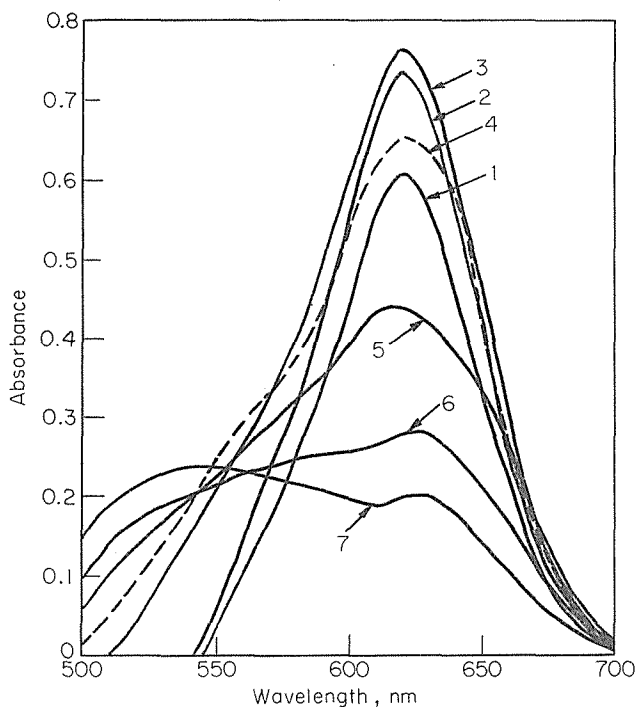1′: TDBA 400 ppm   }
2′: without TDBA   } (Reagent blank)

Fig. 1. Absorption spectra of eriochrome cyanine R and its palladium complex at pH 5.4

Standard Procedure

Transfer a sample aliquot containing 2–30 μg of palladium to a 25-ml volumetric flask. Add 2.0 ml of a 0.1% eriochrome cyanine R solution, 5 ml of a pH 5.4 phosphate buffer solution, add 2 ml of a 0.5% TDBA solution. If the pH of the resulting solution is not between 4.0 and 5.6, it may be prenutralized with hydrochloric acid or sodium hydroxide solution. The solution is diluted to the mark with distilled water and mixed. After 10 minutes, measure the absorbance at 620 nm against a reference solution containing the same amounts of reagents.

RESULTS AND DISCUSSION

The absorption spectra of eriochrome cyanine R and its palladium complex are shown in Fig. 1. The solutions were adjusted to pH 5.4 with the phosphate buffer solution. In the presence of TDBA, the maximum absorption of the palladium complex is found at 620 nm, at which point the reagent does not absorb appreciably. The presence of quaternary ammonium salts had the expected effect of intensifying the color of palladium complex, and causing a bathochromic shift in the wavelength of maximum absorbance; in the presence of TDBA, the absorbance of the palladium complex shows a marked

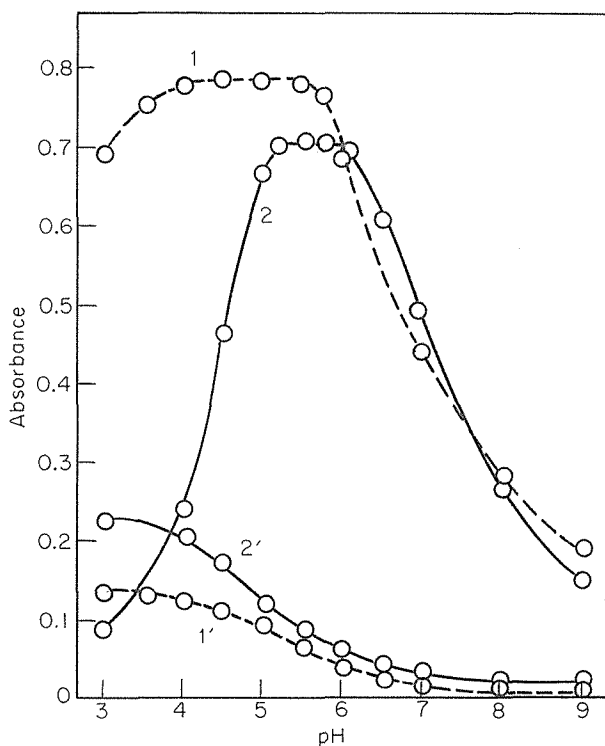Reagent 80 ppm, Palladium 0.8 ppm, TDBA 400 ppm

pH: (1) 2.5, (2) 3.5, (3) 5.0, (4) 6.0,
(5) 7.0, (6) 8.0, (7) 9.0

Fig. 2. Absorption spectra of palladium complex at various pH values.

increase and the position of the maximum absorption of it shifts about 15 nm toward a longer wavelength.

In order to observe the spectral changes on varying pH values, absorption curves for the palladium complex were prepared at different pH values; the results are shown in Fig. 2. The curves in Fig. 2 were obtained by measuring the absorbance of colored solutions containing 0.8 ppm of palladium, 80 ppm of eriochrome cyanine R, and 400 ppm of TDBA at various pH values against a reagent blank containing the same amount of reagents. The maximum absorption of the palladium complex occurs at 620 nm below pH 7.0. Above pH 9.0, two absorbance maxima occur, one at 550 nm and one at 630 nm. The curves obtained between pH 6.0 and 8.5 have a shoulder at about 550 nm.

The effect of pH on the color development of palladium complex was examined by measuring the absorbance of a colored solution. The results are shown in Fig. 3, from which it can be seen that maximum absorbance can be obtained in the pH range from 5.2 to 5.8, in the presence of TDBA, however, the absorbance is almost constant in wider range toward the lower pH value (pH 4.0–5.6). A phosphate buffer solution, pH 5.4, was found to be satisfactory and the volume of the buffer used found to have no effect on the

1 : Reagent 80 ppm, Pd 0.8 ppm, TDBA 400 ppm
2 : Reagent 200 ppm, Pd 1.1 ppm
1′: Reagent 80 ppm, TDBA 400 ppm (Reagent blank)
2′: Reagent 200 ppm (Reagent blank)
     Wavelength: 1,1′ 620 nm, 2,2′ 605 nm

Fig. 3. Effect of pH on color development.

absorbance of a 0.4-ppm palladium solution over the range from 2 to 10 ml per 25 ml of solutions.

The effect of changes in the concentration of eriochrome cyanine R on the absorbance of palladium complex at pH 5.4 was determined by measuring the absorbance on the solutions kept constant concentration of palladium and varying amounts of the reagent. Figure 4 shows that the absorbance is increased by an increase in the reagent concentration, in the presence of TDBA, however, the absorbance is almost constant by adding more than 1 ml of a 0.1% eriochrome cyanine R solution for 0.4 ppm of palladium. The optimum
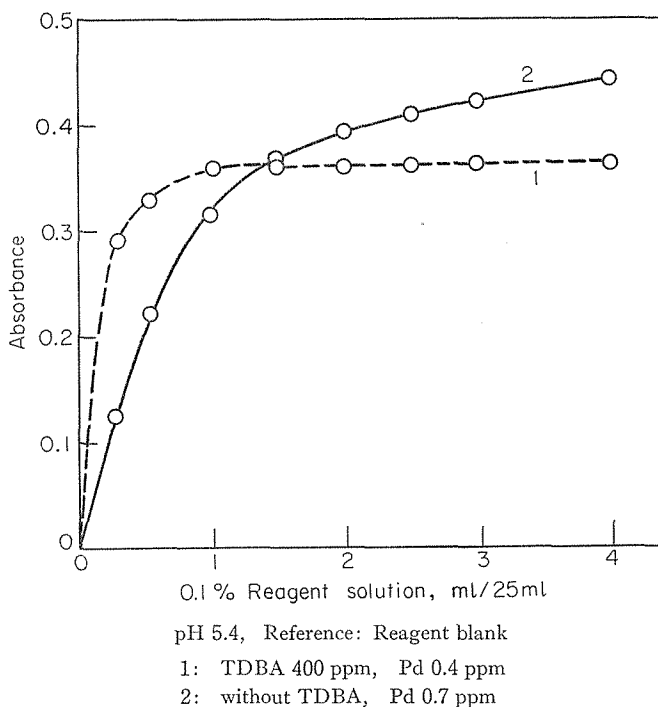

0.1% Reagent solution, ml/25ml

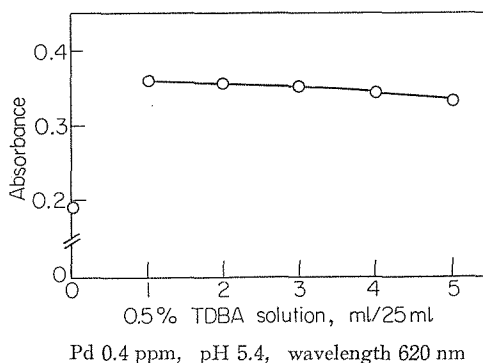pH 5.4,   Reference: Reagent blank
1:   TDBA 400 ppm,   Pd 0.4 ppm
2:   without TDBA,   Pd 0.7 ppm

Fig. 4.   Effect of reagent concentration.

0.5% TDBA solution, ml/25ml

Pd 0.4 ppm,   pH 5.4,   wavelength 620 nm

Fig. 5.   Effect of TDBA concentration.

1: In the presence of TDBA
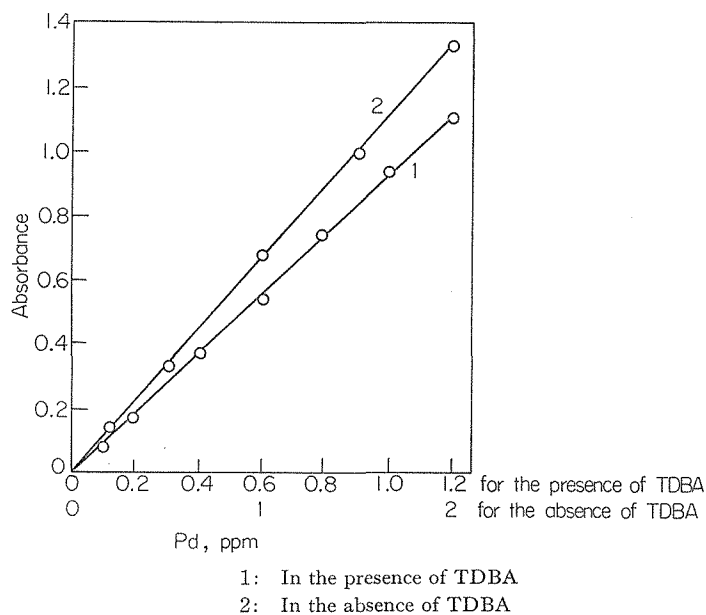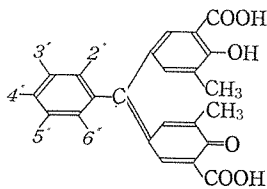2: In the absence of TDBA

Fig. 6. Calibration curves.

Table I. Spectrophotometric Determination of Palladium with Some Triphenylmethane Dyes

Sequence	Substituents	Name	Color Index
1	2″-chloro, 4″-diethylamino	Eriochrome brilliant violet B	43570
2	2″, 6″-dichloro, 5″-sulfo	Chromazurol S	43825
3	2″, 5″, 6″-trichloro	Eriochrome azurol G	43855
4	2″, 6″-dichloro	Pontachrome azure blue B	43830
5	2″-chloro, 4″-nitro	Chromal blue G	43835
6	2″-sulfo	Eriochrome cyanine R	43820

Sequence	λ_{max}	Range for adherence to Beer's law (ppm)	Molar absorptivity ($\times 10^4$)	Sensitivity ($\times 10^{-3}$ $\mu g/cm^2$)	*pH range	Reagent concentration (ppm)
1	600	0.2–2.0	2.86	3.7	7–8	80
2	620	0.2–3.0	3.6	3.0	5.2–5.7	200
3	630	0.1–2.0	4.78	2.2	5.2–6.0	200
4	605	0.2–2.0	4.79	2.2	5.2–5.7	200
5	635	0.1–1.6	5.15	2.1	4.6–5.6	200
6	605	0.2–2.0	6.8	1.6	5.2–5.8	200

In the absence of TDBA
* Adjusted with a phosphate buffer solution

amount of the reagent was 2.0 ml of a 0.1% reagent solution in a final volume of 25 ml, which sufficed for less than 1.2 ppm of palladium.   This concentration represents a 13.3– fold molar excess of reagent over the maximum concentration of palladium determined under the given conditions.

The effect of variable amounts of TDBA on the color development was examined by measuring the absorbance at 620 nm on the solutions containing constant concentrations of palladium and eriochrome cyanine R.   The results are shown in Fig. 5.   The absorbance of palladium complex at 620 nm gradually decreases at more than 200 ppm of TDBA concentration.

The absorbance of the palladium complex did not attain its constant value instantly; it decreased very slightly during the first 10 minutes after preparation of the colored solutions, then it remained constant for about an hour.   It was necessary, therefore, to allow at least 10 minutes for obtaining constant absorbance values.

The effect of the temperature on the color development was examined by measuring

Table II.   Effect of Diverse Ions on the Determination of Palladium.

(Palladium taken:15.0 μg)

| Ion	Added (μg)	Pd found (μg)
Beryllium(II)	10	>50
Copper(II)	30	21.1
Iron(III)	50	15.2
	100	17.6
Aluminum(III)	15	16.7
	50	18.2
Scandium(III)	100	14.9
Yttrium(III)	100	14.8
Lanthanum(III)	100	14.9
Cerium(III)	100	14.7
Neodymium(III)	100	15.1
Gadolinium(III)	100	15.0
Dysprosium(III)	100	15.0
Erbium(III)	100	14.9
Ruthenium(III)	250	15.2
Rhodium(III)	250	15.5
Osmium(III)	250	15.3
Gold(III)	250	15.2
Platinum(IV)	250	14.6
Manganese(II)	100	15.0
Nickel(II)	100	15.2
Cobalt(II)	100	15.4
Zinc(II)	100	15.0
Uranium(VI)	100	14.7
Molybdenum(VI)	100	15.1
Fluoride	10000	15.0
Sulfate	1000	15.2
Chloride	1000	14.9
Phosphate	1000	15.3
Acetate	1000	14.8
Nitrate	1000	14.7

the absorbance of colored solutions kept for 20 minutes at various temperatures. The absorbance did not change over the temperature range of 10 to 40°C. Above 40°C, the absorbance gradually decreased with rise of temperature. Hence, normal temperature changes in the laboratory seem to introduce no error.

A calibration curve was made under the optimum conditions mentioned above. As shown in Fig. 6, the absorbance is proportional to the palladium concentration in the range of 0.1 to at least 1.2 ppm of palladium (2–30 μg per 25 ml). At 620 nm the apparent molar absorptivity is 9.9×10^4. The spectrophotometric sensitivity is estimated to be 1.1×10^{-3} μg palladium per cm^2, corresponding to log $I_0/I = 0.001$.

In the absence of TDBA, 5 ml of a 0.1% eriochrome cyanine R solution and 5 ml of a 0.1 M phosphate buffer solution (pH 5.4) should be added in a final volume of 25 ml for less than 2.0 ppm of palladium. Beer's law is obeyed up to at least 2.0 ppm of palladium; at 605 nm the apparent molar absorptivity is 6.8×10^4 and the spectrophotometric sensitivity is 1.6×10^{-3} μg of palladium per cm^2.

Many organic reagents which are very sensitive to palladium have been used for the spectrophotometric determination: 2,2'-Dipyridylketoxime,[14] N,N'-bis-(2-sulfoethyl)–dithio-oxamide,[15] N,N'-bis-(3-dimethylaminopropyl)-dithio-oxamide,[16] 4-(2-Thiazolazo)–1-naphthol,[17] α-Furildioxime,[18] Didodecyldithio-oxamide,[19] 2,1,3-Benzoselenadiazole,[20] Xylenol orange,[21] and 3-Hydroxy-1-p-sulfonatophenyl-3-phenyltriazine.[22] The sensitivity of the proposed method is much greater than that of the methods using these reagents.[9] The proposed method is compared with methods using some triphenylmethane dyes, similar in structure to eriochrome cyanine R in Table I. It can be seen that proposed method is the most sensitive for palladium.

The precision of the method was tested by measuring the absorbance of 10 samples containing 0.4 ppm of palladium developed by the standard procedure. The mean
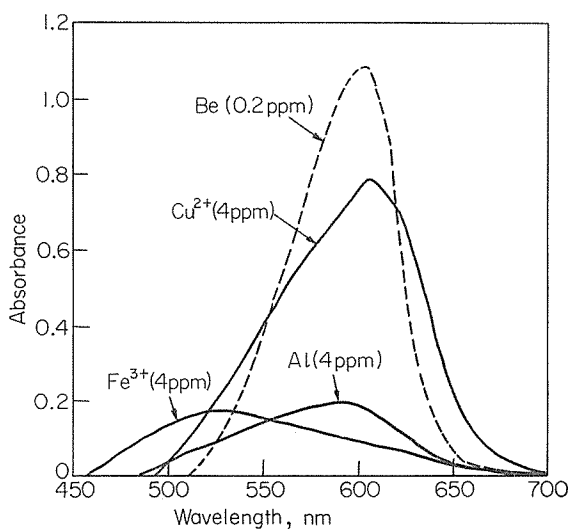
Reagent 80 ppm, TDBA 400 ppm, pH 5.4 (phosphate buffer)

Fig. 7. Absorption spectra of Cu(II), Be(II), Fe(III) and
Al(III)-Eriochrome cyanine R complex at 5.4.

absorbance was 0.372, with a standard deviation of 0.003 absorbance unit or 0.8%.

The effect of diverse ions on the determination of palladium was examined under the conditions of the standard procedure. The diverse ions were added, individually, to solutions containing 15 μg of palladium. The results are summarised in Table II, from which it can be concluded that some diverse ions, especially beryllium, copper (II), aluminum, and iron (III), interfered seriously. These cations also form colored complexes with eriochrome cyanine R under the present experimental conditions (Fig. 7). The maximum absorption of the beryllium and copper(II) complexes are at 605 nm, that of aluminum complex appears at slightly a shorter wavelength, and that of iron(III) complex is shifted toward a shorter wavelength. Chloride, sulfate, nitrate, phosphate and fluoride

Table III. Effect of Fluoride as a Masking Agent

Ion added	μg	Pd found, μg	Error, %
Aluminum(III)	100	14.9	− 0.7
	250	14.8	− 1.3
Iron(III)	100	15.0	± 0
	250	17.6	+17.3
Beryllium(II)	100	15.0	± 0
	250	15.2	+ 1.3
Copper(II)	30	16.5	+10.0
	50	22.1	+47.3

Palladium taken: 15.0 μg   Fluoride added: 5 ml of 0.1 M NaF solution
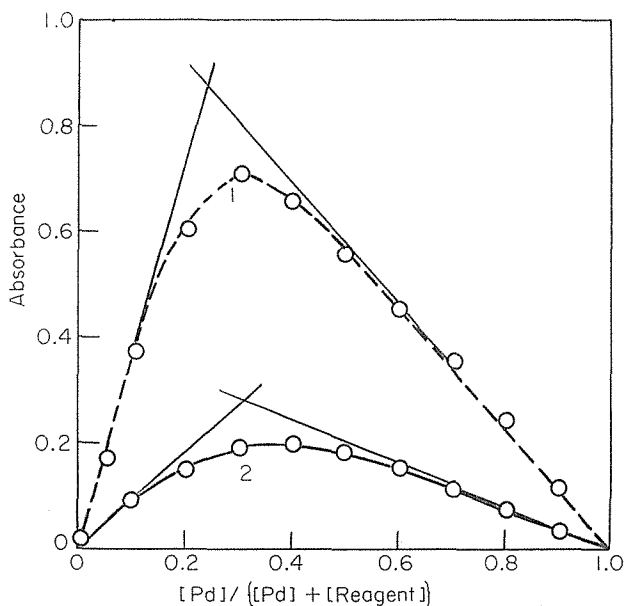
pH 5.4, $[Pd]+[Reagent]=4.40\times10^{-5}$ M

1: TDBA 400 ppm, wavelength 620 nm
2: without TDBA, wavelength 605 nm

Fig. 8. Continuous variation method.

pH 5.4, [Reagent] $= 2.20 \times 10^{-5}$ M

1: TDBA 400 ppm, wavelength 620 nm
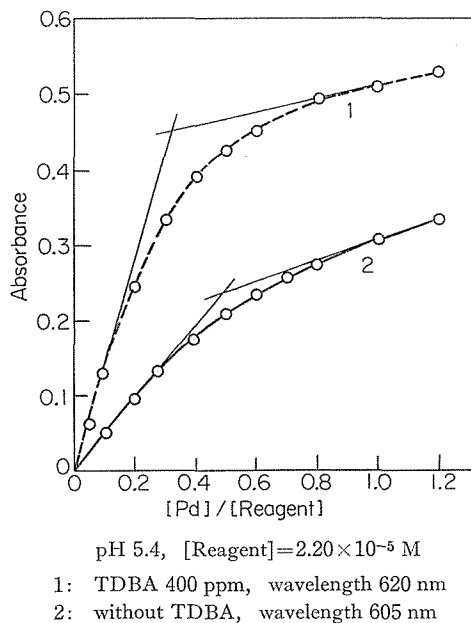2: without TDBA, wavelength 605 nm

Fig. 9. Mole ratio method.

do not interfere, but cyanide and EDTA prevent the formation of the palladium complex.

Fluoride was investigated as a masking agent of the more seriously offending ions. As shown in Table III, aluminum, beryllium, and iron(III) of less than 100 μg can be effectively masked by fluoride and can be tolerated without further separation. However, the interference by copper(II) and iron(III) of more than 150 μg can not be eliminated by the addition of fluoride. Therefore, these ions must be separated completely with suitable procedures.

The method of continuous variations was applied using a series of solutions which was prepared from equimolar concentration of palladium and eriochrome cyanine R. The color was developed and measured in the usual way. A plot of absorbance against mole fraction of palladium is shown in Fig. 8, which indicates that a 1-to-2 complex and a 1–to-3 complex are formed between palladium and eriochrome cyanine R, in the absence, and in the presence of TDBA, respectively. These results were confirmed by the mole ratio method (Fig. 9).

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