The Spectrophotometric Determination of Palladium(II) with Xylenol Orange[1]

By Makoto OTOMO

(Received December 14, 1962)

The preceding works in this series of publications on the spectrophotometric determination of metal cations with xylenol orange have dealt with such metals as rare earths[2], vanadium[3], uranium[4] and aluminum[5], all of which react with this reagent in a slightly acidic medium to give red or reddish-violet chelates. Because of the low selectivity of xylenol orange, for the practical determinations in slightly acidic media it was necessary either to mask interfering ions with an appropriate masking agent or preliminarily to separate these ions from the object ion.

In a strongly acidic solution of perchloric acid, however, this reagent reacts selectively with palladous ions, even in the presence of many other cations, to give a bright-red complex with an absorption maximum at 518 mμ.

This paper chiefly presents a spectrophotometric study of the reaction between palladous ion and xylenol orange in a perchloric acid solution. The formation constant is also calculated from the results of the mole ratio method and those of the method of continuous variations.

Experimental

Reagents and Apparatus. — A stock solution of palladium was prepared by dissolving 1.927 g. of palladous chloride in a small amount of nitric acid and then diluting it with water to one liter. The standardization was carried out volumetrically by EDTA titration[6]. A standard working solution was prepared by taking an aliquot of the stock solution and diluting it to the desired concentration.

A 2×10^{-3} M solution of xylenol orange and a 1 : 1 solution of perchloric acid were prepared.

Stock solutions of diverse cations, which were prepared from reagent grade salts, contained approximately 0.1 μ mol. of the ions per ml.

All absorbance measurements were made at 25$\pm$0.5°C with a Hitachi spectrophotometer, Model EPV-2, using 1 cm. glass cells.

1) Presented at the Tôhoku-Hokkaidô Branch Meeting of The Chemical Society of Japan, Hakodate, July, 1962.
2) K. Tonosaki and M. Otomo, This Bulletin, **35**, 1863 (1962).
3) M. Otomo, ibid., **36**, 137 (1963).
4) M. Otomo, ibid., **36**, 140 (1963).
5) M. Otomo, ibid., **36**, 809 (1963).
6) J. Kinnunen and B. Merikanto, *Chemist-Analyst*, **47**, 11 (1958).

Results and Discussion

The Determination of Palladium.—In a preliminary test, it was shown that a red-colored palladium xylenol orange complex was formed in solutions of nitric, sulfuric and perchloric acids, but no color development was obtained in hydrochloric acid or in a solution containing a large number of chloride ions. In a perchloric acid solution, the complex gave the highest absorbance. Perchloric acid was therefore used in further experiments.

Absorption Spectra.—The absorption spectra of xylenol orange and its palladium complex are shown in Fig. 1. The complex has an

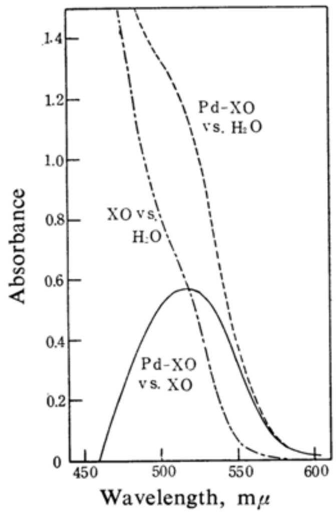

Fig. 1. Absorption spectra of xylenol orange and its palladium complex.
Pd : 57.8 μg. XO : 1.6×10^{-4} M
$HClO_4$: 1.3 N

absorption maximum at 518 mμ. It is of interest to note that the spectrum of xylenol orange has a small shoulder at about 515 mμ and that the position of the absorption peak of the complex is very close to that of the peaks shown by xylenol orange in strongly acidic solutions. For the sake of comparison, the absorption spectra of xylenol orange in sulfuric acid of various concentrations are also shown in Fig. 2.

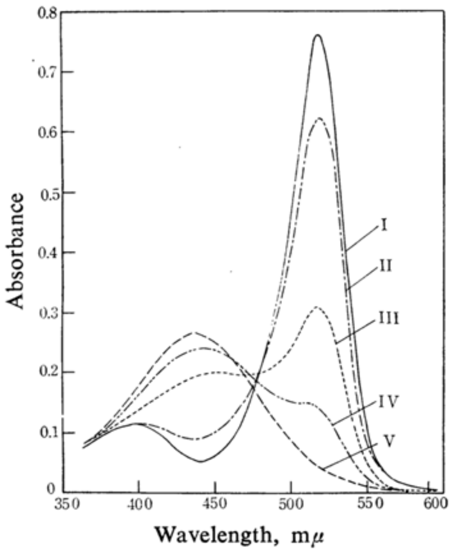

Fig. 2. Absorption spectra of xylenol orange in sulfuric acid of various concentrations.
XO : 2×10^{-5} M
Concentration of sulfuric acid :
I, 21.6 N II, 10.8 N III, 7.2 N
IV, 3.2 N V, 0.7 N

The Effect of the Concentration of Perchloric Acid. — In order to examine the effect of the concentration of perchloric acid, tests were made at varying concentrations of perchloric acid. The maximum and constant absorbance is obtained over the concentration range from 1.1 to 1.7 N in perchloric acid, as is indicated in Fig. 3. Seven to 8 ml. of 1 : 1 perchloric acid in a total volume of 25 ml. is sufficient to maintain the acid concentration within the optimum range.

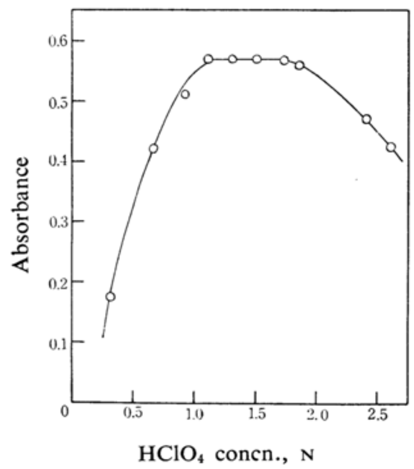

Fig. 3. Effect of concentration of perchloric acid.
Pd : 57.8 μg. XO : 1.6×10^{-4} M
Wavelength : 518 mμ

The Effect of the Concentration of the Reagent. —An excess of xylenol orange must be added, since the absorbance of the complex at 518 mμ is somewhat increased with an increased concentration of the reagent. Two milliliters of a 2×10^{-3} M solution of xylenol orange was found to be a sufficient amount for less than 100 μg. of palladium.

The Effect of Heating Time and the Color Stability. — The maximum color development was reached after about 20 ml. of the sample solution had been kept at boiling temperature for 2 to 3 min. The 20 ml. of solution contained 7 ml. of 1 : 1 perchloric acid and 2 ml. of a 2×10^{-3} M solution of xylenol orange, along with the desired quantity of palladium. After this heating period, the solution was cooled, transferred to a 25 ml. volumetric flask, and diluted to the mark with water. The absorbance of the resultant solution decreased slowly with time for the first 30 min. After this period, however, it remained practically constant for at least 3 hr.

Beer's Law. — Beer's law is obeyed over the concentration range from 0.2 to 4.0 p. p. m. of palladium. The optimum concentration range for the determination of palladium was determined by the method described by Ringbom[7] and was found to be 0.8 to 3.2 p. p. m. The molar extinction coefficient was approximately 26000 at 518 mμ.

Procedure. — To a palladium solution in a 50 ml. Erlenmeyer flask, 7 ml. of 1 : 1 perchloric acid and 2 ml. of a 2×10^{-3} M solution of xylenol orange were added. The volume was made to about 20 ml. with water. After being kept at boiling temperature for 2 to 3 min., the solution was cooled, transferred to a 25 ml. volumetric flask, and diluted to the mark with water. The absorbance of the solution was measured at 518 mμ against the reagent blank. The amount of palladium was then determined from the calibration curve prepared above.

The Effect of Diverse Ions. — The effect of diverse ions on the spectrophotometry was examined. As is shown in Table I, such anions as nitrate, sulfate, oxalate, tartrate and citrate do not interfere, even when as much as 100 μmol. of them are present. However, chloride, nitrilotriacetate and ethylenediaminetetraacetate ions interfere seriously, even when only a small amount is present.

Of the 25 cations which react with xylenol orange in a slightly acidic solution, only zirconium gave a large positive error. However, the interference from less than 200 μg. of zirconium could be effectively removed by

7) A. Ringbom, *Z. anal. Chem.*, **115**, 332 (1938/9).

TABLE I. EFFECT OF ANIONS ON PALLADIUM DETERMINATION

Palladium taken, 57.8 μg.

Anion	Taken, μ mol.	Palladium Found μg.	Palladium Deviation μg.
Cl^-	5	56.6	− 1.2
	20	41.3	−16.5
	100	11.0	−46.8
F^-	10	57.6	− 0.2
	25	56.8	− 1.0
NO_3^-	50	57.5	− 0.3
	100	57.0	− 0.8
SO_4^{2-}	100	57.5	− 0.3
	250	57.8	± 0.0
PO_4^{3-}	10	57.5	− 0.3
	50	56.6	− 1.2
$C_2O_4^{2-}$	10	58.4	+ 0.6
	50	57.8	± 0.0
$C_4H_4O_6^{2-}$	20	58.2	+ 0.4
	50	58.7	+ 0.9
$C_6H_5O_7^{3-}$	10	57.6	− 0.2
	50	58.1	+ 0.3
NTA*	1	57.0	− 0.8
	5	55.9	− 1.9
EDTA**	0.2	45.2	−12.6
	1	16.1	−41.7

* Nitrilotriacetate ion
** Ethylenediaminetetraacetate ion

adding 1 to 2 ml. of a 0.01 M fluoride solution. Accordingly, it is possible to say that, in a strongly acidic solution of perchloric acid, xylenol orange is a highly selective color reagent for palladium.

A Comparison with Other Methods. — Several reagents have been used for the spectrophotometric determinations of palladium. The most sensitive reagents have been found to be *p*-nitrosodiphenylamine and *p*-nitrosodimethylaniline, reported by Yoe and Overholser[8,9]. Thioglycolic acid[10], potassium iodide[11], ethylenediaminetetraacetic acid[12] and nitrilotriacetic acid[13] have been used as colorimetric reagents for palladium by König and Cromell, Fraser et al., McNevin and Kriege and Desideri and Pantani respectively. Niesch[14], Cheng[15], Menis and Rains[16] and, recently, Jacobs et al.[17] have described some new reagents for the determination of palladium. The methods using the above reagents, however, in many cases required the extraction of the palladium complexes into such an organic solvent as chloroform or toluene. A method which can be carried out in an aqueous medium and which is rapid, sensitive, selective and relatively free from interference is more desirable.

The present reagent, xylenol orange, has some advantages as a colorimetric reagent for palladium: No extraction of the complex is required, since a palladium-xylenol orange complexes is water soluble; the acid concentration for the maximum color development can easily be controlled; not many cations besides zirconium interfere; and this method is comparable in sensitivity with the β-nitroso-α-naphthol method[15].

Composition and Formation Constant. — The composition of the palladium-xylenol orange complex was determined by the mole ratio method and also by Job's method of continuous variations. The results are presented graphically in Figs. 4 and 5, from which it is

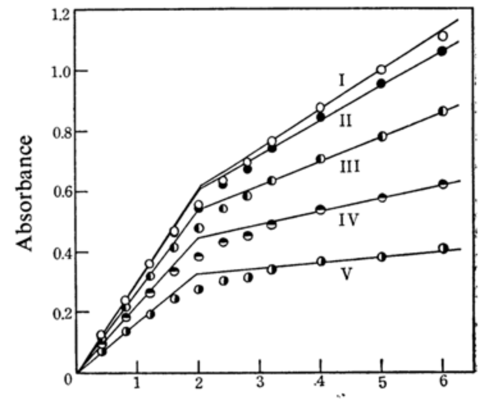

Fig. 4. Mole ratio method.
[Pd] = 2.0×10^{-5} M
Absorbances were measured at:
I, 510 mμ II, 518 mμ III, 530 mμ
IV, 540 mμ V, 550 mμ

evident that only one palladium xylenol orange complex is present and that the mole ratio of xylenol orange to palladium in this complex is 2:1. For the calculation of the formation constant, the absorbance data obtained from the above methods were employed.

Calculation from the Results of the Mole Ratio Method. — Since one part of palladium ions reacts with two parts xylenol orange molecules, the following equilibrium must exist:

$$Pd + 2XO \rightleftarrows Pd(XO)_2$$

$$K = x/(a-x)(b-2x)^2 \qquad (1)$$

8) J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, **61**, 2058 (1939).
9) J. H. Yoe and L. G. Overholser, ibid., **63**, 3224 (1941).
10) O. König and W. R. Crowell, *Mikrochem. ver. Mikrochim. Acta*, **33**, 298 (1948).
11) J. G. Fraser, F. E. Beamish and W. A. E. McBryde, *Anal. Chem.*, **26**, 495 (1954).
12) M. W. McNevin and O. H. Kriege, ibid., **26**, 1768 (1954).
13) P. Desideri and F. Pantani, *Talanta*, **8**, 235 (1961).
14) W. Niesch, *Z. anal. Chem.*, **142**, 30 (1954).
15) K. L. Cheng, *Anal. Chem.*, **26**, 1894 (1954).
16) O. Menis and T. C. Rains, ibid., **27**, 1932 (1955).
17) W. D. Jacobs, C. M. Wheeler and W. H. Waggoner, *Talanta*, **9**, 243 (1962).

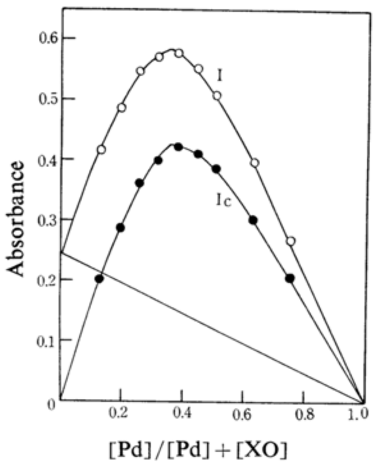

Fig. 5. Method of continuous variations.
[Pd]+[XO]=6.4×10^{-5} M
Wavelength: 518 mμ
I: Uncorrected curve
I_c: Corrected curve

where x is the concentration of the complex at equilibrium, and a and b are the initial concentrations of palladium ion and xylenol orange respectively. In the visible region, the contribution of the palladium ions to the absorbance of the system is negligible. Accordingly, the observed absorbance, D, may be regarded as due to the color of the complex formed and to the free xylenol orange. It is given by:

$$D=\varepsilon_C x+\varepsilon_{XO}(b-2x) \qquad (2)$$

where ε_C and ε_{XO} are the molar extinction coefficients of the complex and xylenol orange respectively. ε_C can be obtained from the equation[18]

$$D'=\varepsilon_C a \qquad (3)$$

where D' is obtained from the absorbance observed by adding xylenol orange in a large excess compared to the concentration of the palladium ions. The values of ε_{XO} and ε_C at various wavelengths are given in Table II. The formation constant, as calculated by combining Eqs. 1, 2 and 3, was found to be

Table II. Values of ε_{XO} and ε_C at various wavelengths

Wavelength, mμ	ε_{XO}	ε_C
510	5280	36240
518	4660	35320
530	3020	30660
540	1520	23560
550	630	16080
560	250	9440

18) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4571 (1957).

1.4×10^{10} (as an average value at the three wavelengths 510, 518 and 530 mμ).

Calculation from the Results Obtained by Job's Method.—Job's method of continuous variation was then employed for the calculation of the formation constant. At the concentration and the wavelengths investigated, the palladous ion has no absorption. Therefore, the color of the system is due to the free xylenol orange and the complex only. Since xylenol orange has a considerable absorption at the wavelengths investigated, corrections were made. The corrected values are also plotted in Fig. 5. The formation constant, K, was then calculated from the curve, based on the relationships described by Harvey and Manning[19]. It was found to be 2.6×10^{10}.

From the above, therefore, K may reasonably be represented as 2×10^{10}. This value is slightly lower than that of the formation constant for the uranium-xylenol orange complex[4], but it is higher than the values for 1:1 complexes between some metal cations and xylenol orange.

Summary

A new, sensitive spectrophotometric method for the determination of palladium(II) by using xylenol orange as a color reagent has been described. The palladium-xylenol orange complex has an absorption maximum at 518 mμ. The effects of the concentration of perchloric acid and of the reagent have been investigated. In addition, various conditions, including the duration of heating, the stability of the color, and the effect of diverse ions, have been investigated. In a solution of perchloric acid (1.1 to 1.7 N), xylenol orange is a highly selective reagent for palladium, although it reacts with a number of metal cations in a slightly acidic or a neutral solution. Beer's law is obeyed in the range from 0.2 to 4.0 p. p. m. of palladium at 518 mμ. The results of Job's method and of the mole ratio method show a complex consisting of two molecules of the reagent to one palladous ion. The formation constant was calculated to be 2×10^{10}.

The author wishes to express his deep thanks to Professor Kôichi Tonosaki for his kind guidance and encouragement throughout this work. He is also grateful to Dr. Kôyô Aida of Tohoku University for his interest.

Department of Chemistry
Faculty of Literature and Science
Hirosaki University
Bunkyo-chô, Hirosaki

19) A. F. Harvey, Jr. and D. L. Manning, ibid., **72**, 4488 (1950).