The Rapid Solvent Extraction and Simultaneous Spectrophotometric Determination of Palladium with TTA - Methyl Propyl Ketone

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The chelating agent 2-thenoyltrifluoroacetone (TTA) has been extensively utilised for the extraction, separation and spectrophotometric determination of numerous metals.[1] From a slightly acidic solution palladium(II) gives an orange yellow chelate with TTA which is extractable into methyl propyl ketone (MPK), giving a brilliant orange yellow solution. It appears that MPK exerts a synergestic effect on the extraction of palladium with TTA.

Dimethylglyoxime[2] is commonly used for the solvent extraction separation of palladium in chloroform. 2-Nitroso-1-naphthol in toluene[3] was used for the extraction and colorimetric determination at 370 mμ. In a highly alkaline medium it was extracted with diethyldithiocarbamate.[4] Its complex with dibenzyldithiooxamide[5] was extracted and measured at 450 mμ in order to determine palladium in the presence of platinum. The iodide complex[6] was extracted with tri-*n*-butyl phosphate, whereas the pyridine thiocyanate complex[7] aminoquinoline complexes[8] or chloroiodopyridine complexes[9] were extracted in chloroform and were determined colorimetrically.

In this paper, systematic investigations of the liquid-liquid extraction behaviour of the palladium(II) TTA chelate at different pH's and spectrophotometric studies of it will be described. It will also offer a simple and rapid procedure for the rapid solvent extraction and simultaneous spectrophotometric determination of palladium(II) at the microgram level. (A preliminary note on this work has been published.[10])

Experimental

Apparatus.—Absorbance measurements were carried out with a quartz CΦ4 spectrophotometer, using matched 10-mm. quartz cells, while pH measurements were made with a Cambridge pH meter (Marshal model). Reagents grade chemicals were used. TTA (B. D. H.) solutions in MPK (about 0.15 M) were used. A stock solution of palladium chloride was prepared by dissolving about 0.6334 g. of palladous chloride in one litre of distilled water containing 1 per cent hydrochloric acid. The diluted solution was then prepared by ten-fold dilution and was standardized gravimetrically with dimethyl glyoxime (II). The diluted solution contained 6.334 γ of palladium per millilitre.

General procedure.—An aliquot of the palladous chloride solution (3 ml.), containing 6.334 γ of palladium(II) per millilitre, was adjusted to the desired pH with 0.01 N hydrochloric acid and 0.01 N sodium hydroxide, using a pH meter. For the study of diverse ions, a solution containing the ion under investigation was added prior to the pH

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7) J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, **3**, 324—329 (1960).
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10) A. V. Rangnekar and S. M. Khopkar, *Sci. and Culture*, to be published.

control. The aqueous solution, unless otherwise mentioned, was adjusted to pH ~4.0. Final volume was maintained with water at 25 ml. in each case. It was introduced into a separatory funnel (250 ml.) and shaken for 10 min. with 10 ml. of 0.15 M TTA-MPK. The lower aqueous layer was transferred to a beaker, and the upper MPK layer, to a 10 ml. volumetric flask. The MPK extract was made up exactly to 10 ml. with MPK, and the absorbance was read at 430 mμ against a reagent blank. The amount of palladium extracted was directly obtained from the calibration curve. The aqueous layers at the end of extraction were saved for the pH measurement.

Results and Discussion

Absorption Curve.—The absorption spectrum of a solution of the palladium(II) - TTA complex ($Pd = 1.78 \times 10^{-5}$ M), extracted at pH 4.0, is illustrated in Fig. 1, the reagent blank being used as the reference solution. The spectrum of the reagent blank against MPK was also taken. The orange-yellow palladium(II) chelate solution shows a maximum absorbtion at 415 mμ. Then the curve steadily falls untill the absorbance becomes negligible beyond 500 mμ. The reagent blank itself has a strong absorption up to 400 mμ; this becomes insignificant, compared to the chelate solution, from 420 mμ onward. All the absorbance measurements were performed at 430 mμ. The absorptivity at 430 mμ is $4.2 \times 10^5 \pm 51.4$ (calculated on the basis of the palladium content).

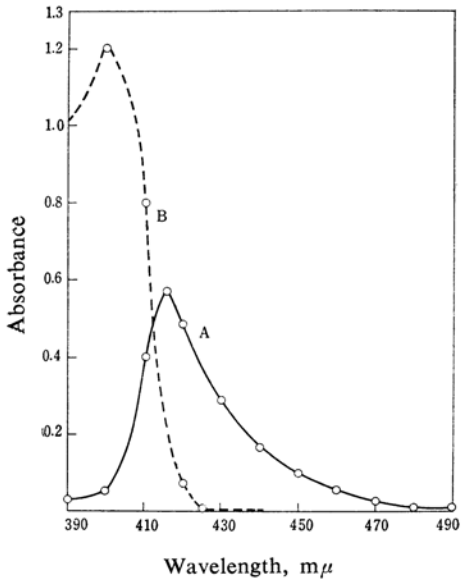

Fig. 1. Absorption spectrum.
A Palladium(II)-TTA chelate in MPK against reagent blank.
Pd(II) 1.78×10^{-5} M at pH 4.0
B Reagent blank against MPK.
TTA 15×10^{-2} M at pH 4.0

The Effect of the pH Value.—The pH range from 0.8 to 6.2 was studied in order to investigate the liquid-liquid extraction behaviour of the palladium(II)-TTA system. At higher pH values the precipitation of palladium hydroxide causes trouble. The distribution ratios, D, were calculated from the extraction curve in a manner described earlier[12] (Fig. 2 and Table I). The extraction starts after pH 1.6 and becomes 100% at pH 4.0. In the pH range from 3.4 to 4.9 extraction occurs to the extent of 80% or more. The extraction curve drops sharply beyond pH 5.0 and terminates at pH 6.0, corresponding to

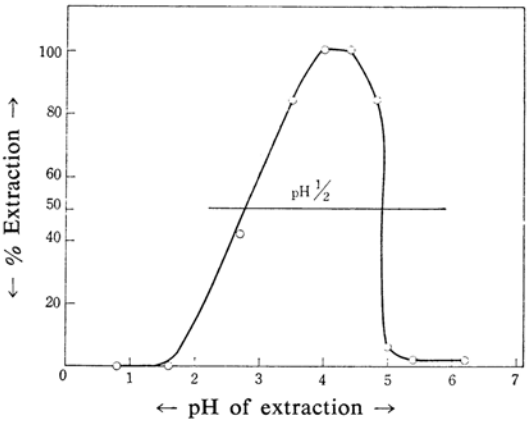

Fig. 2. Extraction of Pd-TTA chelate with MPK as the function pH.

Table I. Distribution ratios of palladium(II)-thenoyl trifluoroacetone between MPK and aqueous solution as a function of pH

pH	% Palladium extraction in MPK	D
0.8	0.0	0.0
1.6	0.0	0.0
2.1	18.4	0.56
2.7	42.1	1.8
3.0	65.7	4.7
3.5	84.2	13.3
3.6	84.2	13.3
4.0	100.0	2500
4.4	100.0	2500
4.6	18.4	0.56
4.8	84.2	13.3
5.0	7.8	0.21
5.4	2.6	0.06
5.8	5.2	0.13
6.2	2.6	0.06

11) A. I. Vogel, "The Text Book of Quantitative Inorganic Analysis," ELBS Series (1960), p. 511.

12) S. M. Khopkar and A. K. De, *Anal. Chem.*, 32, 478 (1960).

zero extraction. The pH for the 50% extraction is 2.8 and 4.9.

Beyond pH 6.2, hydroxide precipitation commences and inhibits the extraction procedure.

Calibration Curve.—Different amounts of palladium(II) were taken and extracted as above at pH 4.0, and the corresponding absorbances were measured against the reagent blank at various wavelengths (420, 430 and 440 mμ) in order to observe the adherence of the coloured system to Beer's law. In each case the solution of palladium(II) was exhaustively extracted for 10 min.; the aqueous phase was always clear and colourless. Table II indicates that the palladium(II)-TTA system closely obeys Beer's law at 430 mμ over the concentration range from 0.60 to 6 γ of palladium per millilitre.

TABLE II. ADHERENCE TO BEER'S LAW

Palladium(II) taken, γ	Absorbance		
	420 mμ	430 mμ	440 mμ
3.16	0.065	0.040	0.025
6.33	0.140	0.095	0.055
9.49	0.210	0.140	0.080
12.66	0.265	0.195	0.105
15.82	0.340	0.240	0.140
18.99	0.410	0.300	0.170
22.15	0.470	0.350	0.190
25.32	0.540	0.400	0.220
28.48	0.610	0.460	0.255

The Stability of the Colour.—The absorbance of the MPK solution of the palladium(II)-TTA complex, prepared according to the general procedure at pH 4.0, was measured at elapsed times of 30 min., 1, 24, 48, 72, 96, 144 and 190 hr. The corresponding absorbances were 0.300, 0.300, 0.300, 0.300, 0.300, 0.310, 0.320 and 0.320 respectively. It is evident that the colour is stable up to 72 hr., at the end of 94 hr. the absorbance increases by about 3%, and after 144 hr. by about 8%. Hence, it is suggested that the colour be measured within 72 hr.

TABLE III. EFFECT OF REAGENT CONCENTRATION

19 γ of palladium(II) after extraction by TTA-MPK at pH 4.0 gives an absorbance of 0.300 ±0.005 in 10 ml. of MPK.

TTA Concn., M	TTA added, ml.	Absorbance at 430 mμ
0.50	10	0.310
0.25	10	0.300
0.15	10	0.300
0.10	10	0.210
0.075	10	0.210
0.050	10	0.200
0.025	10	0.195
0.015	10	0.120
0.15	1	0.150
0.15	2	0.170
0.15	4	0.210
0.15	6	0.220
0.15	8	0.280

Reagent Concentration.—With other factors constant, the concentration of TTA was varied from 0.015 M to 0.5 M. The results in Table III prove that the optimum reagent concentration is 0.15 M. The absorbance is constant, even at such a higher reagent concentration as 0.50 M. With a dilute solution of the reagent, e.g., 0.025 or 0.015 M, the extraction is incomplete.

TABLE IV. DIVERSE IONS

Palladium(II) = 19 γ pH = 4.0

Foreign ion	Added as	Ion concen. mg./ml.	Absorbance at 430 mμ 0.300±0.010
None	—	—	
Pb^{2+}	$Pb(NO_3)_2$	5.0	0.310
Hg^{2+}	$Hg(NO_3)_2 \cdot H_2O$	1.5	0.320
Tl^{+}	Tl_2SO_4	2.0	0.295
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	2.0	1.650
Cd^{2+}	$Cd(NO_3)_2$	5.0	0.295
Sb^{3+}	$Sb_2(SO_4)_3$	5.0	0.310
Bi^{3+}	$Bi_2(CO_3)_3$	1.0	0.290
Sn^{4+}	$SnCl_2$	2.0	0.040
Pt^{4+}	$H_2PtCl_6 \cdot 6H_2O$	2.5	0.310
Fe^{3+}	$Fe(NO_3)_3 \cdot 6H_2O$	2.0	1.350
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	10.0	0.295
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	5.0	0.305
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	2.0	0.400
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	2.0	0.400
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	2.0	0.290
U^{6+}	$UO_2(NO_3)_2 \cdot 6H_2O$	2.5	1.000
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	1.0	0.285
Zr^{4+}	$Zr(NO_3)_4$	2.0	0.295
Ce^{4+}	$Ce_2(SO_4)_3$	2.5	0.800
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	2.5	0.340
Sr^{2+}	$SrCl_2 \cdot 6H_2O$	2.5	0.275
Ba^{2+}	$Ba(NO_3)_2$	2.5	0.275
Mg^{2+}	$MgCl_2 \cdot 6H_2O$	3.0	0.295
Li^{+}	LiCl	1.0	0.320
Ascorbate^{2-}	Ascorbic acid	2.0	0.04
Oxalate^{2-}	Oxalic acid	2.0	0.04
Cit^{3-}	Citric acid	2.0	0.015
$Tart^{3-}$	Tartaric acid	2.0	0.110
PO_4^{3-}	H_3PO_4	2.0	0.295
CH_3COO^{-}	CH_3COOH	2.0	0.305
WO_4^{2-}	Na_2WO_4	1.0	0.285
CN^{-}	KCN	2.0	0.04
SO_4^{2-}	Na_2SO_4	2.0	0.310
CrO_4^{2-}	K_2CrO_4	2.5	0.290
VO_4^{3-}	Na_3VO_4	0.50	0.285
AsO_3^{3-}	Na_3AsO_3	2.0	0.275

Diverse Ions.—The following ions (~2.0—10 mg.) were carried through the procedure, the pH being maintained at about 4.0: Pb^{2+}, Hg^{2+}, Tl^{+}, Cu^{2+}, Cd^{2+}, Sb^{3+}, Bi^{3+}, Sn^{4+}, Pt^{4+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, U^{6+}, Th^{4+}, Zr^{4+}, Ce^{4+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+} Li^{+}, SO_4^{2-}, PO_4^{3-}, WO_4^{2-}, CN^{-}, CH_3COO^{-}, $C_2O_4^{2-}$, CrO_4^{2-}, VO_4^{3-}, AsO_3^{3-}, citrate^{3-}, tartrate^{3-}, ascorbate^{2-}.

The results in Table IV show that about 5—10 mg. of lead(II), thallium(I), cadmium(II), antimony(III), bismuth(III), platinum(IV), aluminum(III), zinc(II), nickel(II), zirconium-(IV), chromate, phosphate, acetate and sulphate do not interfere, whereas copper(II), iron(III), uranium(VI), and cerium(IV) give colour reactions. Palladium can tolerate less than 5 mg. each of mercury(II), thorium(IV), calcium(II), strontium(II), barium(II), magnesium(II), lithium, vanadate, tungstate and arsenite. The ions showing strong interferences are tin(IV), manganese(II), cobalt(II), ascorbate, oxalate, citrate, tartarate and cyanide.

Because palladium(II) is extracted from weakly acidic solutions, metals that yield chelates with TTA under these conditions may be expected to interfere if present in large amounts.

The interferences due to ascorbate, oxalate, citrate, tartarate and cyanide can be easily eliminated by passing them on an anion exchange resin like Dowex 21 K (chloride form). These anions are retained in the resin bed, while palladium(II) passes through. Palladium-(II) may then be extracted as usual with 0.15 M TTA in MPK at pH 4.0.

Recommended Procedure

Take an aqueous solution containing 19 γ of palladium(II) and adjust the pH ~4.0 with a pH meter by using 0.01 N hydrochloric acid and 0.01 N sodium hydroxide. Introduce the solution into a 250 ml. separatory funnel. Shake for 10 min. with 10 ml. of a 0.15 M TTA-MPK solution. Allow the layers to settle; transfer the aqueous layer into a beaker and the MPK layer into a 10 ml. volumetric flask, and measure the absorbance as 430 mμ against the reagent blank. In nine runs with 19 γ of palladium(II), the absorbance found was 0.296 $\pm$0.005. The standard deviation was $\pm$1.2%. Different amounts of palladium(II) were taken and determined by the recommended procedure. The results (Table V) are accurate to within $\pm$1.5%.

TABLE V. ACCURACY OF METHOD

Palladium(II) taken, γ	Absorbance at 430 mμ	Palladium(II) found, γ	% Error
9.5	0.145	9.25	+2.7
12.66	0.195	12.66	0.0
19.00	0.300	19.00	0.0
25.33	0.380	24.0	+5.2
28.50	0.450	28.5	0.0
			Av. $\pm$1.5%

Thus the proposed method is fairly precise, being accurate to within $\pm$1.5%. The total operation for each run requires only 20—25 minutes. As little as 1 γ of palladium(II) can be detected.

Summary

A spectrophotometric method has been developed for the determination of palladium-(II) at microgram levels; the method is based on the colour reaction with 2-thenoyltrifluoro-acetone (TTA) in methyl propyl ketone (MPK). The bright orange-yellow-coloured palladium(II) - TTA chelate solution follows Beer's law at 430 mμ over the 0.6—6.0 γ range of palladium(II) per millilitre. At pH values from 3.4 to 4.9, about 80% or more of palladium(II) is removed from an aqueous solution of TTA-MPK in a single extraction. The coloured system is stable for 72 hr. It can tolerate lead(II), thallium(I), cadmium(II), antimony(III), bismuth(III), platinum(IV), aluminium(III), zinc(II), nickel(II), zirconium-(IV), phosphate, chromate, acetate and sulphate, whereas tin(IV), manganese(II), cobalt(II), ascorbate, oxalate, citrate, tartarate and cyanide seriously interfere. Mercury(II), thorium(IV), calcium(II), strontium(II), barium(II), magnesium(II), vanadate and tungstate are moderately tolerated. The method is accurate and reproducible to within $\pm$1.5%, and it offers a simple procedure for the simultaneous extraction and spectrophotometric determination of palladium(II).

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