  Bull. Chem. Soc. Jpn., 64, 3075—3078 (1991)

Spectrophotometric Determination of Palladium Using 2-(2-Hydroxyimino-1-oxoethyl)thiophene

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(Received February 28, 1991)

A highly sensitive and selective method for the determination of palladium in trace amounts is developed by complexation of Pd(II) with 2-(2-hydroxyimino-1-oxoethyl)thiophene (INAT) at pH 2.8—6.5, adjusted with diluted acetic acid. The colored species is quantitatively extracted into chloroform, whose absorbance is measured at 425 nm. The method is free from the interference of a large number of elements of great analytical importance. The usefulness of the method is further tested by analyzing different samples and the results obtained are quite satisfactory.

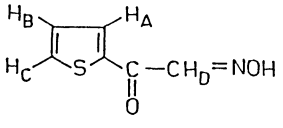
Though a number of methods using organic reagents[1-4] have been developed for the spectrophotometric determination of palladium, but most of them suffer from disadvantages[3,4] particularly due to the serious interferences from several elements of interest and poor sensitivities. Complexes potentially useful for the solvent extraction of palladium are those formed with 8-quinolinethiol[5,6] and thiocyanate.[7] There are also methods available where complexes are formed with hydroxyimino-substituted ketones[8-11] and some of their derivatives.[12] The efficiency of these extractions as separatory methods in the presence of other platinum and associated base metals has received relatively little attention. In many instances, the problem of coextraction has been related to the degree of interference with the colorimetric measurements. Taking into account all these factors, modern analytical techniques for the determination of trace amount of noble metals are growing in demand to the extent that one can deal effectively with a few μg of metals so as to achieve very acceptable results.

Consequently, it has been found while working that Pd(II), in microgram amounts, forms a yellow complex with 2-(2-hydroxyimino-1-oxoethyl)thiophene [(2-[α-(hydroxyimino)acetyl]thiophene, abbrev. to INAT] in diluted acid solutions (pH 2.8—6.5) which is extractable into chloroform whose absorbance is measured at 425 nm, where the absorbance of the reagent blank is minimal.

Experimental

Reagents. A stock solution of palladium containing 1 mg Pd ml^{-1} is prepared by dissolving an accurately weighed amount of $PdCl_2$ (Johnson Metthey & Co,, London) in a minimum volume of hydrochloric acid and is standardized gravimetrically.[13] Stock solutions with lower concentrations of the metal ion at the μg ml^{-1} level are prepared by suitable dilutions therefrom.

Preparation of 2-(2-Hydroxyimino-1-oxoethyl)thiophene:



Sodium metal (1.15 g) is dissolved in 23 ml absolute ethanol and to the solution 6.7 ml of isopentyl nitrite are added slowly under cooling and stirring at the same time. This is followed by the addition of 5.4 ml of 2-acetylthiophene. The mixture is kept overnight at 0 °C. The brown sodium salt thus obtained is washed well with diethyl ether and dried in air. It is then dissolved in ice-water and neutralized with glacial acetic acid. The creamish solid is filtered, dried and crystallized from ethanol, (70% yield): Mp 115 °C; IR (Nujol) 3186 (ν_{O-H}, intramolecular hydrogen bonding), 1592 ($\nu_{C=O}$, intramolecular hydrogen bonding) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.00—7.18 (1H, m, H_B), 7.65 (1H, d, $J_{C,B}$=5.4 Hz, H_C), 7.89 (1H, s, H_D), 8.03 (1H, d, $J_{A,B}$=3.6 Hz, H_A); Found: C, 46.23; H, 3.13; N, 8.95%. Calcd for $C_6H_5NO_2S$: C, 46.45; H, 3.22; N, 9.03%. 0.1% solution of INAT in ethanol is used.

Buffer solution is prepared with sodium acetate–acetic acid (1 mol dm^{-3}).

Sample solutions are obtained by mixing the solutions of palladium(II) and other metal ions in a suitable proportion as shown in Table 2.

Pd-Charcoal Catalyst (Aldrich 20, 568-0): A weighed amount of the sample is brought into solution by heating with HCl and HNO_3 (3 : 1). Charcoal is filtered off from the solution and the excess of HNO_3 is decomposed completely by evaporating it to dryness. The residue is treated with water and diluted HCl and processed for the determination of palladium as described below in the procedure.

Procedure for the Determination of Palladium. To the sample solution containing 50 μg Pd(II) and/or other ions in a 100 ml separatory funnel, add 1 ml of the 0.1% INAT, 5 ml of buffer solution and the volume is made to 20 ml with distilled water (pH 4.75—4.78). The contents are gently mixed and equilibrated once with an equal volume of chloroform for one min. The two phases are allowed to separate. The organic phase is filtered through a Whatman's filter paper (No. 41) into a 25 ml volumetric flask which is then filled upto the mark with the pure chloroform. The absorbance of the yellow complex is measured at 425 nm against reagent blank on UV-visible 140-02 spectrophotometer (Shimadzu, Japan) using 1 cm cells and the amount of the metal ion is determined from the standard curve obtained by plotting different concentrations of Pd(II) and the corresponding absorbance values.

Results and Discussion

The extractability of the palladium(II)–INAT complex is affected by the kind of acid. The extractability

Table 1. Effect of Various Parameters on the Absorbance of Palladium–INAT Complex

pH[a]	2.10	2.5	2.8—6.5	7.5	8.6	9.6	10.1	10.65
Absorbance	0.595	0.605	0.63	0.605	0.595	0.58	0.56	0.52
2-(2-hydroxyimino-1-oxoethyl) thiophene[b] (ml)	0.0	0.1	0.2	0.3	0.4	0.5	0.7—5.0	
Absorbance	0.002	0.375	0.585	0.61	0.62	0.625	0.63	
Equilibration time[c] (sec)	5	10	20	30	45	60—240		
Absorbance	0.61	0.62	0.625	0.63	0.63	0.63		

a) Conditions: Pd(II)=50 μg, INAT (0.1%)=1 ml, aqueous volume=solvent volume=20 ml, solvent=chloroform, equilibration time=1 min, number of extractions=1, pH=variable. b) Conditions: pH=4.75—4.78; other conditions are the same as in (a) except variation in the INAT content. c) Conditions: INAT (0.1%)=1 ml; other conditions are the same as in (b) except the variation in equilibration time.

Table 2. Analysis of Different Samples by the Proposed Method

Sr. No.	Composition of sample: Matrix[a]	Pd(II) added	Pd(II) found
		μg	μg
1.	Pt(4), Rh(5)	45	45.0
2.	Pt(0.6), Rh(0.5), Ru(0.5), Os(0.7)	28	28.0
3.	Pt(5), Rh(4), Ru(3), Os(3)	65	65.0
4.	W(5), Mo(5), V(4)	20	20.0
5.	U(5), Ni(4), Mn(6)	40	39.5
6.	Cu(5), Co(5), Fe(4)	10	10.0
7.	Zn(4), Hg(5), Cd(6)	30	30.0
8.	Cr(4), Ce(2), Zr(2)	35	34.5
9.	Ti(4), Se(4), Be(5)	55	54.0
10.	Re(5), Ag(2)	15	15.0
11.	Ca(5), Ba(3), Sr(4)	60	61.0
12.	Bi(2), Sb(1), As(2)	17	16.0
13.	[Ag(0.053)][b]	80	80.0
14.	[Pt(0.05), Ni(0.15), V(0.025)][b]	50	50.0
15.	[Ru(0.004), Rh(0.001)][b]	100	100.0
16.	[Pt(2.85)][b]	90	90.0
17.	[Pt(0.071), Ni(0.0034)][b]	25	25.0
18.	Pd–charcoal catalyst (50 mg) Aldrich 20, 568-0	5%[c]	4.8%

a) Figure in brackets indicates the amount of the metal ion in mg. b) Sample Nos. 13, 14, 15, 16, and 17 are analogous to palladium–silver, palau, jewellery alloys, cooperite, and braggite ores, respectively. c) Reported value.

at constant acidity decreases in the following order $CH_3COOH > H_2SO_4 > HNO_3 > HClO_4 > H_3PO_4 > HCl$. Therefore, acetic acid is preferred for adjustment of pH of the solution.

The effect of various parameters namely, pH, reagent concentration and equilibration time on the absorbance of Pd(II) complex is depicted in Table 1. It is evident from the study of these variables, that for getting optimal absorbance for 50 μg Pd, pH 2.8—6.50, 0.7—5.0 ml (0.1% INAT in ethanol), 0.5—5 min shaking time are the necessary conditions to transfer quantitatively the colored species into chloroform, whose λ_{max} lies at 425 nm. The absorbance shows a downward trend if 1,2-dichloroethane, ethyl acetate, benzene, toluene, carbon tetrachloride, dichloromethane, and 1-pentanol, respectively, are used as extractant in place of chloroform.

Effect of Diverse Ion. Under the optimum conditions as given in the procedure, Os(VIII), Re(VII), Mo(VI), W(VI), Cr(III,VI), V(V), Ce(IV), Ti(IV), Se(IV), Pt(IV), Rh(III), As(III), Fe(II,III), Ni(II), Cu(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II), Be(II), Sr(II), Ba(II), Ca(II), Ag(I), each 1 mg ml^{-1}; in 20 ml aqueous volume, do not show any absorbance and hence are noninterfering.

Chloride (150), sulfate (400), nitrate (500), phosphate (100), acetate (100), citrate (150), tartrate (200), fluoride (75), oxalate (10), added initially to the aqueous phase, do not affect the absorbance of the Pd(II)–INAT complex. The figure in parentheses indicates the amount of sodium salt of the anion in milligram.

Spectral Studies and Stoichiometry of the Complex. The spectrum of the Pd(II)–INAT complex shows absorption maxima at 425 nm. Beer's law is obeyed in the range 0—4 μg Pd ml^{-1} with molar absorptivity of 3.27×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity is 0.003 μg Pd cm^{-2}. The ratio of metal to INAT in the extracted species is determined by Job's method of continuous variations[14] as modified by Vosburgh and Cooper[15] by taking equimolar solutions (1.8793×10^{-4} M, 1 M=1 mol dm^{-3}) of both Pd and INAT at three different wavelengths, namely, 400, 425, and 450 nm. The sharp break in the three curves obtained indicates that metal and INAT are present in the ratio of 1 : 2 in the complex. This is further confirmed by mole ratio method.[16]

Back Extraction. The metal ion of the Pd(II)–INAT complex in the organic phase can be easily stripped by shaking the organic phase with an equal volume of 0.5 M HCl.

Applications. The proposed method for the

Table 3. Comparison of the Proposed Method with the Existing Methods for Palladium Determination

Sr. No.	Aqueous conditions	Extractant λ_{max}	i) Beer's law range ii) Molar absorptivity iii) Sandell's sensitivity	Interfering ions	Comments	Reference
1.	10—100 μg Pd, 1 ml 2.5 M Perchloric acid, 10 ml *N,N*-dimethylformamide, 1 ml 0.1% (w/v) 3-nitroso-2,6-pyridinediol (in 9:1 water: *N,N*-dimethylformamide), heating for 20 min, in 25 ml volume	— 430 nm	i) 0.8—3.5 ppm of Pd ii) 2.6×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.004 μg Pd cm^{-2}	Pt(IV), Ru(III) and Fe(III).	Tolerates only lower amounts of other ions of analytical interest.	17
2.	1—200 μg Pd, 2 ml 5 M acetic acid, in 10 ml volume	1% ethyl-2-(hydroxyimino)acetoacetate in $CHCl_3$ (10 ml), 400 nm	i) 0.1—20 μg Pd ml^{-1} ii) 9460 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.011 μg Pd cm^{-2}	I^-, SCN^-, CN^-, EDTA, tartrate, citrate, oxalate, $S_2O_3^{2-}$, SO_3^{2-}, Cl^- interfere if not eliminated.	Requires different masking agents to check interference of several anions.	18
3.	Upto 50 μg Pd, 0.5 ml KI (0.1 M), 0.1 ml Hexadecyltrimethylammonium bromide (0.1 M), Pot. hydrogenphosphate–NaOH buffer (pH 6), in 10 ml volume	$CHCl_3$ (10 ml), 340 nm	i) upto 5 ppm of Pd ii) 2.038×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.0052 μg Pd cm^{-2}	Pt(IV), Hg(II), Ag(I), SCN^-, SO_3^{2-}.	Behavior of Os(VIII), Rh(III), Ir(IV), Ru(III), not known.	19
4.	Palladium, 2-hydroxy-4-methoxy-5-chlorochalcone oxime at pH 2.5	Isobutyl alcohol, 380 nm	i) 1.4×10^{-5}—1.95×10^{-5} M (1.5—2.0 μg Pd ml^{-1}) ii) 0.73×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.0145 μg Pd cm^{-2}	Au(III), Cr(III), Zr(IV), EDTA.	Since only C.A. is available, detailed information about the work could not be obtained.	4
5.	42 μg Pd, 3 ml of 1 M HCl, in 10 ml volume	1×10^{-3} M 2-Thiazolecarbaldehyde 2-quinolylhydrazone in C_6H_6 (10 ml), 625 nm	i) upto 4.2 μg Pd ml^{-1} ii) 1.93×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.0055 μg Pd cm^{-2}	I^-, SCN^-, EDTA, Hg(II), Au(III), Re(VII), Ir(III), W(VI); low tolerance limits for Hg(II), Au(III), Re(VII), Ir(III), W(VI) which give yellow insoluble precipitates.	Pt(II) forms blue complex, behavior of Os(VIII), Rh(III), Ru(III) are not studied.	20
6.	50 μg Pd, 1 ml 0.1% INAT in ethanol, 5 ml buffer solution (Sodium acetate–acetic acid) pH (4.75—4.78), in 20 ml volume (PROPOSED METHOD)	$CHCl_3$ (20 ml), 425 nm	i) 0—4 μg Pd ml^{-1} ii) 3.27×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ iii) 0.003 μg Pd cm^{-2}	26 Cations and 9 anions do not show any effect on the absorbance of Pd complex.	High sensitivity and selectivity, good tolerance limits, easy back extraction of the metal ion from the solvent.	(PROPOSED METHOD)

microdetermination of palladium is highly accurate and is free from the interference of a large number of elements especially the other platinum metals. The results are quite reproducible with a standard deviation of ±0.002. It compares favorably with the existing methods in terms of its sensitivity and selectivity (Table 3). Moreover, the recovery of Pd(II) from the organic solvent can be easily effected by simple back extraction. The validity of the method is further tested by analyzing satisfactorily several samples of varying complexity (Table 2).

Our sincere thanks are due to the Chairman, Department of Chemistry, Kurukshetra University, Kurukshetra for providing laboratory facilities and to UGC, New Delhi for financial support to one of us (AKC).

References

1) Y. P. Chang and N. Zhou, *Talanta,* **33**, 939 (1986).
2) G. Hernandez, R. Rodriguez, J. A. Silva, E. Chacon, and R. Mocelo, *Rev. Cubana Quim.,* **3**, 41 (1987).
3) D. Rao, K. H. Reddy, and D. V. Reddy, *Indian J. Chem., Sect. A,* **26**, 363 (1987).
4) B. K. Deshmukh and M. G. Awari, *Chem. Anal. (Warsaw),* **32**, 369 (1987).
5) J. Bankovskis and A. Ievins, *Zh. Anal. Khim.,* **13**, 507 (1958).
6) G. G. Lystsova, *Zavod. Lab.,* **28**, 543 (1962).
7) E. S. Prsheval'skii, V. I. Shlenskaya, and L. F. Maternykh, Ser. Fiz.-Mat.-i Estestven. Nauk No. 4, 71 (1954), *Chem. Abstr.,* **49**,96 (1955).
8) B. J. Desai and V. M. Shinde, *Fresenius' Z. Anal. Chem.,* **298**, 158 (1979).
9) U. B. Talwar and B. C. Haldar, *Anal. Chem.,* **38**, 1929 (1966).
10) B. J. Desai and V. M. Shinde, *Fresenius' Z. Anal. Chem.,* **295**, 412 (1979).
11) U. B. Talwar and B. C. Haldar, *Anal. Chim. Acta,* **39**, 264 (1967).
12) S. K. Majumdar, P. Chattopadhyay, and P. K. Paria, *J. Indian Chem. Soc.,* **62**, 544 (1985).
13) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 4th ed, Longman, London (1978), p. 474.
14) P. Job, *Ann. Chem.,* **9**, 113 (1928).
15) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.,* **63**, 437 (1941).
16) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.,* **16**, 111 (1944).
17) C. W. McDonald and J. H. Bedenbaugh, *Mikrochim. Acta,* **1970**, 474.
18) M. R. Patil and B. C. Haldar, *J. Indian Chem. Soc.,* **50**, 569 (1973).
19) T. K. Thokdar, P. K. Paria, and S. K. Majumdar, *Indian J. Chem., Sect. A,* **28**, 443 (1989).
20) T. Nakagawa, K. Doi, and M. Otomo, *Analyst,* **110**, 387 (1985).