

Determination of palladium using 2-thiobarbituric acid as a releasing agent

J Karthikeyan^a, P Parameshwara^a, A Nityananda Shetty^{a*} & Prakash Shetty^b

^aDepartment of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India

^bDepartment of Chemistry, Manipal Institute of Technology, Manipal 576 119, India
Email: nityashreya@rediffmail.com

Received 19 March 2007; revised 20 November 2007

A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective masking property of 2-thiobarbituric acid towards palladium(II). In the presence of diverse metal ions, palladium(II) is complexed with excess of EDTA and the surplus EDTA is backtitrated with standard zinc sulphate solution at pH 5-6 (acetic acid-sodium acetate buffer) using xylenol orange as indicator. An excess of a 0.3% solution of 2-TBA is then added to displace EDTA from Pd(II)-EDTA complex. The released EDTA is titrated with the same standard zinc sulphate solution as before. Reproducible and accurate results are obtained in the concentration range 1.30-20.00 mg of palladium with relative error of 0.50% and coefficient of variation not exceeding 0.45%. The effects of diverse ions are studied. The method is used for the determination of palladium in alloys, hydrogenation catalysts and complexes.

Keywords: Complexometric method, Palladium determination, 2-Thiobarbituric acid

Palladium and its alloys find extensive application in electronic industry¹, dental alloys², magnetic materials³, and are also used as hydrogenation catalysts⁴. Considering these extensive applications of palladium and its compounds, a reliable and rapid method is often essential for the determination of palladium in a single stage. The commonly recommended complexometric method⁵ for palladium is not reliable in many cases because EDTA is an unselective reagent. Alloying metals, present with palladium form strong complexes with EDTA, interfering in the determination of palladium. A complexometric method for the determination of palladium(II) in the presence of diverse metal ions using selective masking agent has been found to be useful in the rapid analysis of palladium in its alloys. The Pd-EDTA complex can be selectively decomposed using demasking agents such as dimethylglyoxime⁶ and 1,2,3-benzotriazole⁷. However, these methods are not rapid as they involve heating and extraction of Pd-reagent complex using chloroform. Similarly, 1,10-phenanthroline⁸ method is not reliable for Pd(II) determination in the presence of common metal ions. Though thiourea⁹ is free from these limitations, interference from copper requires the lowering of temperature to 8°C during titration, whereas the quantitative release of EDTA by pyridine¹⁰ requires heating of solution to 60°C for

10 min. Metal ions such as Cu(II), Al(III) and Bi(III) interfere in thiosemicarbazide¹¹ method. In most of the methods, metal ions such as Hg(II), Tl(III) and Sn(IV) interfere. Ir(III) interferes in thiocyanate method¹², Cd(II) in hydroxylamine hydrochloride method¹³, Bi(III) in 3-mercaptopropane-1,2-diol method¹⁴ and Cu(II) in 2-mercaptopropionyl glycine method¹⁵. The metal ions like Cu(II), Mn(II), Cd(II), Ni(II), Co(II) and Au(III) interfere in 2,2' prime -Dipyridyl method¹⁶. In the recently reported thioacetamide¹⁷ and 2-thiazolinethiol¹⁸ methods, metal ions like Hg(II), Tl(III), Sn(IV) show severe interference. Some of the reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole¹⁹ and 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one²⁰ require tedious and time-consuming preparation methods.

Present investigation describes, the use of 2-thiobarbituric acid (2-TBA) as a masking agent for the selective and quantitative determination of palladium (II) in the pH range of 5 to 6. The proposed method when compared with similar other reported methods is found to be more selective, as there is no interference from Cu(II), Hg(II) and Sn(IV). Moreover, most of the metal ions does not show any interference, and the application of the method in the analysis of alloys, complexes and its catalysts are reported in this paper.

Experimental Procedure

Reagents

All reagents used were of analytical or chemically pure grade. A stock solution of palladium(II) was prepared by dissolving PdCl₂ (Merck) in minimum amount of conc. HCl and diluting to a known volume with distilled water. The stock solution was standardized by the dimethylglyoximate method²¹. Zinc sulphate (Merck) solution (0.01 mol L⁻¹) was prepared by dissolving the salt in distilled water and standardized by the oxinate method²¹. EDTA (Merck) solution (0.02 mol L⁻¹) was prepared by dissolving the disodium salt of EDTA in distilled water. A freshly prepared (0.5%) aqueous solution of xylenol orange (Rankem) was used as indicator. 2-Thiobarbituric acid (0.3%) (Spectrochem, India) solution was prepared by dissolving 0.3 g of 2-TBA in 100 mL of (1:1) acetone-water mixture. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal chlorides/ nitrates/sulphates in distilled water or with suitable acids and then making up to a known volume.

Method

To an aliquot of the sample solution containing 1.30-20.00 mg of palladium(II) and varying amounts of diverse metal ions, an excess of 0.02 mol L⁻¹ EDTA was added and the solution was diluted with 25 mL of distilled water. The pH of the solution was initially adjusted between 4 to 5 by dropwise addition of dilute sodium hydroxide solution and finally to 5-6 by adding acetic acid-sodium acetate buffer. The surplus EDTA was backtitrated (Burette capacity 5 mL, accuracy 0.02 mL) with standard zinc sulphate solution to a sharp colour change of xylenol orange from yellow to red. To this, a freshly prepared 0.3% solution of 2-TBA was added in required amount. The contents were mixed well and allowed to stand for 5 min in order to ensure the quantitative release of EDTA. The liberated EDTA was then titrated with the standard zinc sulphate solution as before. The second titre value is equivalent to the amount of palladium(II) present in the aliquot.

Analysis of the palladium alloys

The alloy sample (0.1-0.5 g) was carefully decomposed with aqua regia by evaporating to near dryness. The residue was then cooled, dissolved in minimum amount of dilute HCl and made up to 100 mL. Then the stock solution was standardized²¹. Aliquots of this solution were used for the estimation of palladium as per the proposed method.

Analysis of the palladium catalysts

A known weight (1.0-2.0 g) of the catalysts such as palladium-charcoal and palladium-asbestos (Merck) was digested with aqua regia to nearly dryness. The residue was treated with dilute HCl, filtered, wherever necessary, and made up to a known volume with distilled water. The stock solution was standardized gravimetrically²¹. Suitable aliquots of this solution were used for the estimation of palladium as per the proposed method.

Analysis of palladium complexes

Palladium(II) complexes with dimethylglyoxime, thiosemicarbazide, and 1,2,3-benzotriazole, thio-carbohydrazide were prepared and purified²²⁻²⁵. A known weight of the complex was carefully decomposed with aqua regia by evaporating to near dryness. The residue was then cooled, dissolved in minimum amount of dilute HCl and made up to a known volume with distilled water. The stock solution was standardized²⁰. Aliquots of this solution were used for the estimation of palladium as per the proposed method.

Results and Discussion

Masking property of the reagent

2-Thiobarbituric acid acts as a bidentate ligand and can form a 1:2 complex with palladium(II). According to hard-soft acid-base theory (HSAB)^{26,27}, soft palladium(II) forms strong bond through soft sulphur of mercapto group. It has been reported that 2-TBA forms a 1:2 complex with palladium(II)^{28,29}, with deprotonated sulphur of thiol group and oxygen of hydroxyl group, which results in the formation of a stable six-membered chelate. The quantitative release of EDTA from Pd-EDTA complex by 2-TBA indicates that Pd(2-TBA)₂ chelate is more stable than Pd-EDTA complex under the conditions employed²⁸. The release of EDTA is quantitative and instantaneous at room temperature itself. The Pd(2-TBA)₂ complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

Effect of reagent concentration

It was observed that for instantaneous and quantitative release of EDTA from the Pd(II)-EDTA complex, the amount of 2-TBA required was in the molar ratio of 1:2 (M:L). Further, it was noticed that the addition of excess reagent, as much as 20-fold excess over the required molar ratio, had no adverse

effect on the results obtained. In all subsequent determinations, the concentration of 2-TBA was maintained at slight excess over the 1:2 (M: L) molar ratio.

Accuracy and precision

Determination of palladium in the concentration range 1.30-20.00 mg were carried out under the optimized experimental conditions. The results show that the maximum relative error and coefficient of variation (n=6) of the method is not more than 0.50 and 0.45% respectively (Table 1). From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

In order to ascertain the possible interference of the diverse ions, palladium determination was carried out with an aliquot containing 3.34 mg of Pd(II) in the presence of various metal ions and anions. No interference was observed for the ions at the amounts shown in Table 2. However, Hg(II), Tl(III), Cr(III) and Sn(IV) interfere severely. The interference of Hg(II), Tl(III) and Sn(IV) is due to the release of EDTA from their respective EDTA complexes on the addition of the reagent. The interference of Cr(III) is mainly due to the deep purple colour of its EDTA complex, which makes the detection of the end point rather difficult. The interferences of Hg(II) and Sn(IV) can be avoided by pre-masking the metal ions with acetyl acetone and sodium fluoride respectively.

Applications

In order to explore the practical application of the proposed method, it was extended for the determination of palladium in alloys, hydrogenation catalysts, complexes and in synthetic mixture of ions. The experimental results of these analyses are

Table 1 — Precision and accuracy in the determination of palladium(II) in palladium chloride solution (n=6)

Palladium (mg)		Relative error (%)	Standard deviation	Coefficient of variation (%)
Taken	Found			
1.33	1.33	0.00	0.006	0.45
2.00	2.01	+0.50	0.008	0.40
3.33	3.34	+0.30	0.010	0.30
6.67	6.69	+0.30	0.020	0.29
10.01	9.98	-0.30	0.020	0.20
13.35	13.31	-0.30	0.010	0.07
16.69	16.67	-0.12	0.010	0.06
20.03	20.02	-0.05	0.020	0.09

presented in Tables 3 and 4. It is evident from these results that the method can be conveniently employed in the analysis of palladium in alloys, complexes, catalysts and in synthetic mixtures of ions with fair degree of accuracy.

Table 2 — Determination of 3.34 mg of palladium in the presence of foreign ions (n=4)

Metal ions	Quantity added (mg)	Palladium found (mg)	Relative Error (%)
Mg(II)	80	3.33	-0.30
Co(II)	80	3.34	0.00
Cu(II)	80	3.33	-0.30
Ni(II)	70	3.33	-0.30
Zn(II)	100	3.34	0.00
Cd(II)	100	3.33	-0.30
Pb(II)	100	3.34	0.00
Hg(II)*	5	3.33	-0.30
As(III)	50	3.34	0.00
Al(III)	50	3.34	0.00
Rh(III)	20	3.34	0.00
Ru(III)	5	3.34	0.00
Au(III)	5	3.33	-0.30
Fe(III)	15	3.33	-0.30
Ce(III)	80	3.33	-0.30
Sb(III)	30	3.33	-0.30
Pt(IV)	50	3.34	0.00
Sn(IV)**	15	3.33	-0.30
Se(IV)	40	3.34	0.00
U(VI)	15	3.34	0.00
W(VI)	10	3.33	-0.30
Mo(VI)	10	3.33	-0.30
Cl ⁻	100	3.34	0.00
Br ⁻	50	3.34	0.00
CH ₃ COO ⁻	80	3.34	0.00
Phosphate	25	3.33	-0.30
Citrate	30	3.34	0.00
Tartarate	80	3.34	0.00
Oxalate	50	3.34	0.00
Bromate	50	3.33	-0.30
Iodate	50	3.34	0.00

*Premasked with acetyl acetone.

**Premasked with sodium fluoride

Table 3 — Analysis of palladium alloys, catalysts and complexes (n=5)

Palladium sample	Palladium present (%)	Palladium found (%)	Relative error (%)
Pd-Rh (90%) alloy	10.00	10.03	+ 0.30
Pd-Ni (40%) alloy	60.00	59.92	- 0.13
Pd-Charcoal catalyst	5	5.01	+0.20
Pd-Asbestos catalyst	5	4.98	-0.40
Pd(C ₄ H ₇ O ₂ N ₂) ₂ ^a	31.63	31.70	+0.22
Pd(CH ₃ N ₃ S) ₂ Cl ₂ ^b	32.50	32.38	-0.36
Pd(C ₆ H ₅ N ₃) ₂ Cl ₂ ^c	25.61	25.56	-0.19
Pd(CH ₆ N ₄ S) ₂ Cl ₂ ^d	29.77	29.70	-0.23
Palladium complex with dimethylglyoximate ^a , Thiosemicarbazide ^b , 1,2,3-benzotriazole ^c , thiocarbonylhydrazide ^d .			

Table 4—Determination of palladium in synthetic mixtures of ions (n=5)

Mixture	Composition (%)	Palladium found (%)	Relative error (%)
Pd + Ru	47.78 + 52.22	47.74	-0.08
Pd + Cu + Au	3.46 + 94.64 + 1.90	3.46	0.00
Pd + Cu + Ni	3.54 + 57.88 + 38.58	3.53	-0.28
Pd + Co + Ni	4.38 + 23.90 + 71.72	4.37	-0.23
Pd + Pt + Au	5.58 + 91.38 + 3.04	5.58	0.00

Conclusion

The proposed method is simple and rapid, as it does not require any adjustment of pH after the addition of the reagent or heating for the quantitative release of EDTA from the Pd-EDTA complex. The absence of any precipitate during the titration facilitates easy detection of a sharp end point. Since, many metal ions do not show interference including Cu(II), Hg(II) and Sn(IV), the method is fairly selective for the rapid analysis of palladium in the presence of these ions.

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