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Article in *Indian Journal of Chemical Technology* · January 2007

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Quantitative complexometric determination of palladium(II) in its synthetic alloys, complexes and catalysts using 2-mercaptopropionic acid as a selective masking agent

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Received 2 February 2006; revised received 2 July 2006; accepted 10 October 2006

A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective masking property of 2-mercaptopropionic 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 5-5.5 (acetic acid-sodium acetate buffer) using xylenol orange as indicator. An excess of a 0.5% aqueous solution of 2-MPA 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 0.5-17.80 mg of palladium with relative error of $\pm 0.50\%$ and coefficient of variation not exceeding $\pm 0.33\%$. The effects of diverse ions are studied. The method is used for the determination of palladium in its complexes, catalysts and synthetic alloy mixtures.

Keywords: EDTA, 2-Mercaptopropionic acid, Masking agent, Palladium determination

IPC Code: C22B11/00, C01G55/00

Palladium and its alloys find extensive application in electronic industry¹, dental alloys², magnetic materials³ and are also used as hydrogenation catalysts⁴. Considering these excellent and extensive applications of palladium and its compounds, a reliable and rapid method is often essential for the determination of palladium in a single stage.

Existing complexometric methods⁵ for palladium could not be used as EDTA is a very unselective reagent. Alloying metals, along with palladium form strong complex with EDTA, interfering in the method. A complexometric method for the determination of palladium(II) in the presence of diverse metal ion using selective masking agent is very 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. These methods are not rapid as they involve heating and extraction of Pd-reagent complex using chloroform. The 1,10-phenanthroline⁸ method does not work for Pd(II) in the presence of common metal ions. Thiourea⁹ is free from these limitations but interference from copper must be prevented by

lowering the temperature to 8°C during titration. The quantitative release of EDTA by pyridine¹⁰ requires heating of the 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) interfere in thiocyanate method¹², Cd(II) in hydroxylamine hydrochloride method¹³, Bi(III) in 3-mercaptopropane-1,2-diol method¹⁴, 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'-Dipyridyl¹⁶ method. However, some of the reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole¹⁷, 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one¹⁸ require tedious and time-consuming preparation methods.

The present investigation describes 2-mercaptopropionic acid (2-MPA) as a masking agent for the selective and quantitative determination of palladium(II) in the pH range of 5 to 5.5. The effects of foreign ions are studied and the application of the method in the analysis of synthetic mixture of ions, complexes and its catalysts are also reported in this paper.

Experimental Procedure

Reagents

All reagents used were of analytical or chemically pure grade. A stock solution of palladium(II) prepared by dissolving PdCl₂ (supplied by Merck) in minimum amount of concd HCl and diluting to a known volume with distilled water. The stock solution was standardized by the dimethylglyoximate method¹⁹. Zinc sulphate solution (0.01 M) was prepared by dissolving the salt in distilled water and was standardized by the oxinate method¹⁹. EDTA solution (0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water. Freshly prepared (0.5%) aqueous solutions of xylenol orange (indicator) and 2-mercaptopropionic acid (masking agent) (Acros organics, USA) were prepared by dissolving in distilled water. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal chlorides/nitrates/sulphates in distilled water and then making up to a known volume.

Method

To an aliquot of sample solution containing 0.5-17.8 mg of palladium(II) and varying amounts of diverse metal ions, an excess of 0.02 M EDTA was added and the solution was diluted with 25 mL of distilled water. A few drops of xylenol orange indicator were added. The pH of the solution was initially adjusted between 4-5 by dropwise addition of dilute sodium hydroxide solution and finally to 5-5.5 by adding acetic acid-sodium acetate buffer. The surplus EDTA was backtitrated with standard zinc sulphate solution to a sharp colour change of xylenol orange from yellow to red. To this, a freshly prepared 0.5% solution of 2-mercaptopropionic acid 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 palladium complexes

Palladium(II) complexes with some sulphur-donor ligands were prepared and purified as per the reported methods²⁰⁻²³. A known weight (1.0-2.0 g) of the complex was carefully decomposed with aqua regia by evaporating to near dryness. The residue was then cooled, dissolved in minimum amount of 2 N HCl and made up to a known volume with distilled water.

Aliquots of this solution were used for estimation as per the proposed procedure.

Analysis of palladium catalysts

A known weight of the catalysts such as palladium-charcoal and palladium-asbestos (supplied by Merck) was digested with aqua regia to nearly dryness. The residue was treated with 2 N HCl, filtered, if necessary, and made up to a known volume with distilled water. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure

Results and Discussion

Masking property of the reagent

2-mercaptopropionic acid acts as a bidentate ligand and can form a 1:2 complex with palladium(II). According to HSAB theory^{24,25}, palladium(II) forms strong bond through soft sulphur of mercapto group. Therefore, it is reasonable to expect the bonding of Pd(II) with deprotonated sulphur of thiol group and hydroxyl oxygen of carboxyl group, which results in the formation of a stable five membered chelate²⁶. The quantitative release of EDTA from Pd-EDTA complex by 2-MPA indicates that Pd(2-MPA)₂ chelate is more stable than Pd-EDTA complex under the conditions employed. The release of EDTA is quantitative and instantaneous at room temperature itself. The Pd(2-MPA)₂ complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

Effect of 2-MPA concentration

It was observed that for instantaneous and quantitative release of EDTA from the Pd(II)-EDTA complex, the addition of 2-MPA in the molar ratio of 1:2 (M:L) was found to be sufficient. Furthermore, it was noticed that the addition of excess 2-MPA, as much as 10-fold excess over the required molar ratio does not have adverse effect on the results obtained. In all subsequent determinations, the concentration of 2-MPA was maintained at slight excess over the 1:2 (M:L) molar ratio.

Accuracy and precision

In order to check the accuracy and precision of the method, determination of Pd(II) at different concentration levels were carried out under the optimized experimental conditions. These results are presented in Table 1. The results obtained are reproducible and accurate in the concentration range

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

Palladium, mg		Relative error (%)	Standard deviation (mg)	Coefficient of variation (%)
Taken	Found			
0.594	0.591	-0.50	0.002	0.33
1.188	1.188	0.00	0.004	0.33
1.782	1.788	+0.33	0.004	0.22
2.970	2.971	+0.03	0.003	0.10
5.940	5.940	+0.00	0.003	0.05
11.880	11.878	-0.01	0.005	0.04
17.820	17.814	-0.03	0.005	0.02

(n = number of average determinations)

0.5-17 mg of Pd(II), with relative error and coefficient of variation (n = 6) not more than $\pm 0.50\%$ and $\pm 0.33\%$, respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

The effect of various cations and anions on the quantitative determination of Pd(II) was studied by estimating 1.78 mg of Pd(II) in the presence of different metal ions. No interference was observed in the presence of following ions at the amounts in mg shown: Mg(II) (45), Pb(II) (50), Zn(II) (50), Co(II) (20), Ni(II) (40), Cd(II) (20), Mn(II) (5), Fe(III) (10), Al(III), La(III), Y(III) (20), Bi(III) (5), Ce(III) (20), Ti(III) (10), Rh(III) (15), Ru(III) (5), Au(III) (5), Se(IV) (50), Pt(IV) (25), U(VI) (50), acetate(100), chloride(100), sulphate(100), oxalate(100), tartarate (100), phosphate(100). Metal ions such as Hg(II), Cu(II), Tl(III) and Sn(IV) show severe interference with positive error. This is due to the simultaneous release of EDTA from their respective EDTA complexes by the reagent. However, the interference of Hg(II) (up to 10 mg), Tl(III) (up to 12 mg) and Sn(IV) (up to 10 mg) can be avoided by pre-masking the metal ions with acetyl acetone(5 mL), L-histidine(10%, 10-15 mL) and sodium fluoride (5%, 5 to 10 mL) respectively.

Applications

In order to explore the practical application of the proposed method, it was extended for the determination of palladium in its complexes, catalysts and in synthetic mixture of metal ions. The experimental results of these analyses are presented in Tables 2 and 3, respectively. It is evident from these results that the method can be conveniently employed for the rapid analysis of such samples.

Table 2—Determination of palladium(II) in complexes and catalysts (n = 3)

Complex	Palladium calculated (%)	Palladium found (%)	Relative error (%)
Pd(C ₄ H ₇ O ₂ N ₂) ₂ ^a	31.63	31.70	+0.22
Pd(CH ₅ N ₃ S) ₂ Cl ₂ ^b	29.59	29.48	-0.37
Pd(C ₆ H ₅ N ₃) ₂ Cl ₂ ^c	25.60	25.55	-0.19
Pd(CH ₆ N ₄ S) ₂ Cl ₂ ^d	27.31	27.22	-0.33
Pd-charcoal catalyst	5	5.00	0.00
Pd-asbestos catalyst	5	5.02	+0.40

Palladium complex with ^adimethylglyoximate, ^bthiosemicarbazide, ^c1,2,3-benzotriazole, ^dthiocarbohydrazide

Table 3—Determination of palladium(II) in synthetic mixtures of metal ions (n = 3)

Mixture	Composition (%)	Palladium found (%)	Relative error (%)
Pd + Ru	4 + 96	4.01	+0.25
Pd + Zn	4 + 96	4.00	0.00
Pd + Mg	4 + 96	4.00	0.00
Pd + Co + Pb	7 + 18 + 75	7.02	+0.28
Pd + Co + Ni	8 + 46 + 46	7.97	-0.37
Pd + Pt + Au	4 + 48 + 48	4.00	0.00
Pd + Sb + Ni	6 + 31 + 63	6.02	+0.33

Conclusion

The proposed method is simple and rapid as it requires no heating. Reproducible and accurate results are obtained in the determination of 0.5-17 mg of palladium. The masking reagent used forms no precipitate either with Pd(II) or with titrant under the experimental conditions. This facilitates easy detection of a sharp end point. The method tolerates the presence of number of metal ions [including Hg(II), Tl(III) and Sn(IV)] and anions and is useful for the rapid analysis of complexes, catalysts and alloy samples of palladium with a fair degree of accuracy.

References

- Barnard C F J & Russell M J H, *Comprehensive Coordination Chemistry*, Vol. 5 (Pergamon Press, Oxford), 1987, 346.
- Ohta M, Hijatsumke K & Yamane M Y, *J Less Com Met*, 65 (1979) 11.
- Loebich O & Raub E, *J Less Com Met*, 30 (1973) 47.
- Gragor N & Henry P M, *J Am Chem Soc*, 102 (1981) 681.
- McNevin W M & Kriege O, *Analyst Chem*, 27 (1955) 535.
- Raoot K N & Raoot S, *Indian J Chem*, 12 (1974) 1007.
- Raoot K N, Raoot S & Vaidya V G, *Indian J Chem*, 18A (1979) 90.

- 8 Raoot K N & Raoot S, *Indian J Technol*, 18 (1980) 345.
- 9 Raoot K N & Raoot S, *Talanta*, 28 (1981) 327.
- 10 Raoot K N, Raoot S & Lalitha Kumari V, *Analyst*, 107 (1982) 1382.
- 11 Narayana B & Gajendragad M R, *Microchem J*, 36 (1987) 364.
- 12 Raoot K N, Raoot S & Lalitha Kumari V, *Analyst*, 108 (1983) 1148.
- 13 Nityananda Shetty A, Gadag R V & Gajendragad M R, *Indian J Technol*, 27 (1989) 224.
- 14 Prakash Shetty, Khader A M A, Nityananda Shetty A & Gadag R V, *Chim Acta Turc*, 23 (1995) 115.
- 15 Prakash Shetty, Nityananda Shetty A & Gadag R V, *Indian J Chem Technol*, 9 (2002) 127.
- 16 Subrahmanya Bhat K, Narayana B & Nambiar C H R, *Res J Chem Environ*, 3 (3) (1999) 65.
- 17 Gadiyar H R A, Gadag R V, Gajendragad M R & Sudhaker Nayak H V, *J Indian Chem Soc*, 60 (1983) 889.
- 18 Narayana B & Gajendragad M R, *Curr Sci*, 56 (1987) 1279.
- 19 Vogel A I, *A Text Book of Quantitative Inorganic Analysis*, 3rd edn (Longmann, London), 1964.
- 20 Shome S C & Das H R, *Anal Chim Acta*, 32 (1965) 400.
- 21 Burns G R, *Inorg Chem*, 7 (1968) 277.
- 22 Mahadevappa B S, Gowda B T & Anand Murthy A S, *Curr Sci*, 45 (1976) 161.
- 23 Mukkanti K, Pandeya K B & Singh R P, *Indian J Chem*, 25A (1986) 277.
- 24 Pearson R G, *Chem Eng News*, 43 (1965) 90.
- 25 Pearson R G, *Chem Brit*, 3 (1967) 103.
- 26 Srivastava S K, Srivastava P C & Nigam H L, *Curr Sci*, 41 (1972) 601.