# DETERMINATION OF PALLADIUM(II) IN ALLOYS, CATALYST AND COMPLEXES USING 1-PROPANETHİOL AS A RELEASİNG REAGENT

P. Parameshwara[*], J. Karthikeyan[*], A. Nityananda Shetty[*] and Prakash Shetty [**]

Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India
Department of Chemistry, Manipal Institute of Technology, Manipal 576 119, India

**Abstract:** A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective masking property of 1-propanethiol towards palladium(II). In the presence of diverse metal ions, palladium(II) is complexed with excess of EDTA and the surplus EDTA is back titrated at pH 5-5.5(acetic acid-sodium acetate buffer) with standard lead nitrate solution using xylenol orange as indicator. An excess of a 0.2% aqueous solution of 1-propanethiol is then added to displace EDTA from Pd(II)-EDTA complex. The released EDTA is titrated with the same standard lead nitrate solution as before. Reproducible and accurate results are obtained in the concentration range 0.5mg -15.30mg of palladium with relative error of ±0.41% and coefficient of variation not exceeding 0.27%. The effect of diverse ions are studied. The method is used for the determination of palladium in alloys, complexes and catalysts.

## INTRODUCTION

Palladium and its alloys find extensive application in electronic industry[1], dental alloys[2], magnetic materials[3] and are also used as hydrogenation catalysts[4].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 methods[5] for palladium can not be used as EDTA is a very unselective reagent.

Alloying metals, along with palladium form strong complexes with EDTA, interfering in the method. A complexmetric 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 complexes and alloys. The Pd-EDTA complex can be selectively decomposed using demasking agents such as dimethylglyoxime[6] and 1,2,3-benzotriazole[7]. These methods are not rapid as they involve heating and extraction of Pd-reagent

complex using chloroform. The 1,10-phenanthroline[8] method does not work for Pd(II) in the presence of common metal ions. Thiourea [9] is free from these limitations. The quantitative release of EDTA by pyridine[10] requires heating of the solution to 60°C for 10min. Metal ions such as Cu(II), Al(III) and Bi(III) interfere in the thiosemicarbazide[11] method. In most of the method, metal ions such as Hg(II), Tl(III) and Sn(IV) interfere, Ir(III) interfere in thiocyanate method[12], Cd(II) in hydroxylamine hydrochloride method[13], Bi(III) in 3-mercaptopropane-1,2-diol method[14], Cu(II) in 2-mercaptopropionyl glycine method[15]. The metal ions like Cu(II), Mn(II), Cd(II), Ni(II),Co(II) and Au(III) interfere in 2,2'-Dipyridyl method[16]. In the recent reported reagent thioacetamide[17], metal ions such as Hg(II), Tl(III) and Sn(IV) shows severe interference. However, some of the reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole[18], 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one[19], require tedious and time-consuming preparation methods.

The present investigation describes, 1-propanethiol (PT) as a masking agent for the selective and quantitative determination of palladium(II) in the pH range of 5 to 5.5. The proposed method when compared with other reported methods is found to be more selective, there is no interference from Cu(II), Hg(II), Tl(III) 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 also reported in this paper.

## EXPERIMENTAL

### Reagents

All reagents used were of analytical or chemically pure grade.

Palladium chloride solution was prepared by dissolving known amount of palladium chloride in minimum amount of conc. hydrochloric acid and making up to a known volume with distilled water. The stock solution was standardized gravimetrically by dimethylglyoxime method[20].

Lead nitrate solution (0.01M) was prepared from an analytical grade sample, and was standardizing gravimetrically by the chromate method[20].

EDTA solution (~ 0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water.

Freshly prepared 0.5% aqueous solution of the xylenol orange indicator was used.

1-Propanethiol (PT) was used as a 0.2% solution in distilled water.

Solutions of various metal ions were prepared by dissolving the appropriate metal salts in distilled water or with suitable acids.

### Procedure

To an aliquot of sample solution containing 0.6-15.25 mg of palladium(II) and varying amounts of diverse metal ions, an excess of 0.02M EDTA was added and the solution was diluted with 25ml of distilled water. The pH of the solution was initially adjusted between 4 and 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 back titrated with standard lead nitrate solution to a sharp color change of xylenol orange from yellow to red. To this, a freshly prepared 0.2% solution of 1-propanethiol was added in required amount. The contents were mixed well and allowed to stand for 5 minutes in order to ensure the quantitative release of EDTA. The liberated EDTA was then titrated with the standard lead nitrate solution as before. The second titre value is equivalent to the amount of palladium(II) present in the aliquot.

### Analysis of the Palladium alloys

Dissolve 0.1-0.5g of the alloy sample 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 100 mL standard flask. Then the stock solution was standardized by the dimethylglyoximate method[20]. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

### Analysis of the 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 dilute 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

### Analysis Of Palladium Complexes

Palladium(II) complexes with dimethylglyoxime, thiosemicarbazide, 1,2,3-benzotriazole, thiocarbohydrazide were prepared and purified as per

the reported methods[21-24]. 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 2N HCl and made up to a known volume with distilled water. Aliquots of this solution were used for estimation as per the proposed procedure.

## RESULTS AND DISCUSSION

### Masking property of the reagent

1-Propanethiol can act as a monodentate ligand through sulphur of the mercapto group. According to HSAB theory[25,26] soft palladium(II) forms strong bond through soft sulphur of mercapto group. Therefore, Pd(II) forms strong bond through soft sulphur of thiol group. The quantitative release of EDTA from Pd-EDTA complex by PT indicates that Pd-PT complex 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-PT 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 PT 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 our subsequent determinations, the concentration of PT 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 palladium in the concentration range 0.6-15.25mg were carried out under the optimized experimental conditions. These results are presented in Table 1. The results show that the maximum relative error and coefficient of variation (n=6) of the method are ±0.41% and 0.27% 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 3.05 mg of Pd(II) in the presence of different metal ions. The results pertaining to the non interfering ions are listed in Table 2. Metal ions like Hg(II), Tl(III), Cr(III) and Sn(IV) shows severe interference with positive error. However the interference of Hg(II) (up to 20mg), Tl(III) (15mg) and Sn(IV) (5mg) can be avoided by premasking these metal ions with acetyl acetone (5ml), hydrazine sulphate (5% $N_2H_4.H_2SO_4$, 10ml), and Sodium fluoride (sat. solution NaF, 10ml) respectively. The interference of Cr(III) is due to the deep purple color of its EDTA complex, which makes the detection of the end point rather difficult.

### Applications

In order to explore the practical application of the proposed method, it was extended for the determination of palladium in its alloys, catalysts and complexes. The experimental results of these analyses are presented in Table 3, 4, 5 and 6 respectively. It is evident from these results that the method can be conveniently employed in the analysis of palladium in its complexes and alloys with fair degree of accuracy.

### Conclusions

The proposed method is simple and rapid, as it requires no heating for the quantitative release of EDTA. The absence of any precipitate during the titration facilitates easy detection of a sharp end point. Since, many metal ions do not show interference, the method is fairly selective for the rapid analysis of palladium. Even the interference of the interfering ions can be eliminated by using secondary masking agents. The proposed procedure does not require any adjustment of pH after the addition of the reagent.

**Table 1:** Precision and accuracy in the determination of Palladium(II)

| Palladium, mg | | Relative error (%) | Standard deviation(mg) | Coefficient of variation(%) |
|---|---|---|---|---|
| Taken | Found[*] | | | |
| 0.61 | 0.61 | 0.00 | 0.001 | 0.16 |
| 1.83 | 1.83 | 0.00 | 0.005 | 0.27 |
| 3.05 | 3.04 | +0.32 | 0.008 | 0.26 |
| 4.88 | 4.87 | -0.20 | 0.011 | 0.23 |
| 6 10 | 6.12 | +0.32 | 0.015 | 0.24 |
| 9.15 | 9.13 | -0.22 | 0 017 | 0.19 |
| 12.20 | 12.23 | +0.24 | 0.023 | 0.19 |
| 15.25 | 15.22 | -0.19 | 0.025 | 0.16 |

[*]Average of six determinations

**Table 2:** Determination of palladium(II) in presence of diverse ions (3.05mg)

| Diverse ions | Concentration (mg) | Palladium found [°] (mg) | Relative error (%) |
|---|---|---|---|
| Pb(II) | 150 | 3.05 | 0.00 |
| Zn(II) | 100 | 3.05 | 0.00 |
| Ba(II) | 60 | 3.04 | -0.32 |
| Cd(II) | 25 | 3.06 | +0 32 |
| Co(II) | 20 | 3.05 | 0 00 |
| Hg(II) ♦ | 20 | 3.05 | 0.00 |
| Mg(II) | 15 | 3.04 | -0.32 |
| Ni(II) | 15 | 3.04 | -0.32 |
| Cu(II) | 05 | 3.06 | +0.32 |
| Mn(II) | 05 | 3.05 | 0.00 |
| As(III) | 60 | 3.05 | 0.00 |
| La(III) | 50 | 3.05 | 0.00 |
| Y(III) | 50 | 3.04 | -0.32 |
| Tl(III)* | 15 | 3.05 | 0.00 |
| Ce(III) | 10 | 3.04 | -0.32 |
| Ti(III) | 10 | 3.06 | +0.32 |
| Ru(III) | 10 | 3.05 | 0.00 |
| Al(III) | 05 | 3.06 | +0.32 |
| Bi(III) | 05 | 3.05 | 0.00 |
| Se(IV) | 80 | 3.05 | 0.00 |
| Sn(IV) ♦ | 05 | 3.05 | 0.00 |
| Sb(IV) | 05 | 3.06 | +0.32 |
| U(VI) | 50 | 3.05 | 0.00 |
| Oxalate | 210 | 3.04 | -0.32 |
| Acetate | 200 | 3.04 | -0.32 |
| Chloride | 180 | 3.05 | 0 00 |
| Sulphate | 180 | 3.05 | 0.00 |
| Tartatate | 150 | 3.04 | -0.32 |
| Bromide | 60 | 3.05 | 0.00 |

[°]Average of four determinations
♦ Premasked with Acetyl acetone
* Premasked with hydrazine hydrate
♦ Premasked with sodium fluoride

**Table 3:** Determination of Palladium in alloys

| Palladium alloys | Palladium taken (mg) | Palladium found[*] (mg) | Relative error (%) |
|---|---|---|---|
| Pd – Rh (90 %) | 10.00 | 9.96 | - 0.40 |
| Pd – Ni (40 %) | 12.00 | 11 95 | - 0.41 |

[*]Average of four determinations

**Table 4:** Determination of Palladium in catalysts

| Palladium alloys | Palladium taken (%) | Palladium found[*] (%) | Relative error (%) |
|---|---|---|---|
| Palladium- Asbestos catalyst | 5.00 | 4.99 | -0.20 |
| Palladium-Charcoal catalyst | 5.00 | 5.00 | 0.00 |

[*]Average of four determinations

**Table 5:** Analysis of palladium complexes

| Complex | Palladium calculated (%) | Palladium found[(*)] (%) | Relative error (%) |
|---|---|---|---|
| $Pd(C_4H_7O_2N_2)_2$[a] | 31.63 | 31.70 | +0.22 |
| $Pd(CH_5N_3S)_2Cl_2$[b] | 29.59 | 29.48 | -0.37 |
| $Pd(C_6H_5N_3)_2Cl_2$[c] | 25.60 | 25.55 | -0.19 |
| $Pd(CH_6N_4S)_2Cl_2$[d] | 27.31 | 27.22 | -0.33 |

[(*)]Average of four determinations

[a] *Palladium complex with dimethylglyoxime*

[b] *Palladium complex with thiosemicarbazide.*

[c]Palladium complex with 1,2,3-benzotriazole

[d]Palladium complex with thiocarbohydrazide.

**Table 6:** Determination of palladium(II) in synthetic mixtures of metal ions

| Mixture | Composition (%) | Palladium found[(*)] (%) | Relative error (%) |
|---|---|---|---|
| Pd + Pb + Se | 3.0 + 58.2 + 38.8 | 3.01 | +0.33 |
| Pd + Zn + Se | 3.3 + 53.7 + 43.0 | 3.31 | +0.30 |
| Pd + Zn + Pb | 2.7 + 53.0 + 44.3 | 2.71 | +0.37 |
| Pd + Pb + As | 4.2 + 68.4 + 27.4 | 4.19 | -0.24 |
| Pd + Zn + Ba | 3.3 + 53.7 + 43.0 | 3.29 | -0.30 |
| Pd + Ba + As | 4.9 + 63.4 + 31.7 | 4.91 | +0.20 |

[(*)]Average of four determinations

## REFERENCES

1. C.F.J.Barnard & M.J.H.Russell, *Comprehensive coordination chemistry*, Vol-5, (Pergamon press, Oxford) 1987, p.346.

2. M.Ohta, K. Hijatsumke & M. Y. Yamane, *J. Less Com. met.*, **65** (1979) 11.

3. O.Loebich & E. Raub, *J. Less Com. Met.*, **30** (1973) 47.

4. N.Gragor & P. M. J.Henry, *Am. Chem. Soc.*, **102** (1981) 681.

5. W. M. McNevin & O.Kriege, *Analyst Chem.*, **27** (1955) 535.

6. K. N.Raoot & S.Raoot, *Indian J. Chem.*, **12** (1974) 1007.

7. K. N.Raoot, S.Raoot & V. G.Vaidya, *Indian J. Chem.*, **18A** (1979) 90.

8. K. N.Raoot & Sarasota, *Indian J. Technol.*, **18** (1980) 345.

9. K. N.Raoot & S.Raoot, *Talanta*, **28** (1981) 327.

10. K. N.Raoot & S.Raoot, V.Lalitha Kumari, *Analyst*, **107** (1982) 1382.

11. B.Narayana & M. R.Gajendragad, *Microchem. J.*, **36** (1987) 364.

12. K. N.Raoot, S.Raoot & V.Lalitha Kumari, *Analyst*, **108** (1983) 1148.

13. A.Nityananda Shetty, R. V.Gadag & M. R. Gajendragad, *Indian J. Technol.*, **27** (1989) 224.

14. Prakash Shetty, A. M. A. Khader, A.Nityananda Shetty & R. V.Gadag, *Chim. Acta Tur.*, **23** (1995) 115.

15. Prakash Shetty, A.Nityananda Shetty & R. V.Gadag, *Indian J. Chem. Tech.*, **9** (2002) 127.

16. K.Subrahmanya Bhat, B.Narayana & C.H.R..Nambiar, *Res J. of Chem. and Environ.*, **3** (1999) 65.

17. P.Parameshwara, J.Karthikeyan, A.Nityananda Shetty & Prakash Shetty, *Annali Di Chimica*, **96**(2006) 125.

18. A.Nityananda Shetty, R. V.Gadag & M. R.Gajendragad, *Rev. Roum. Chem.*, **38** (1993) 1305.

19. H.R.A.Gadiyar, R.V.Gadag, M.R.Gajendragad & H.V.Sudhakar Nayak, *J. Indian Chem. Soc.*, **60**(1983) 889.

20. A. I. Vogel, *A text book of quantitative Inorganic Analysis*, 3rd edn., (Longmann, London) 1964, p.511, 128.

21. S. C. Shome & H. R. Das, *Anal. Chim. Acta*, **32**(1965) 400.

22. G. R.Burns, *Inorg. Chem.*, **7** (1968) 277.

23. B. S. Mahadevappa, B. T.Gowda & A. S. Anand Murthy, *Curr. Sci.*, **45** (1976) 161.

24. K. Mukkanti, K. B.Pandeya & R. P.Singh, *Indian J. Chem.*, **25A** (1986) 277.

25. R. G. Pearson, *Chem. Engg.* News, **43** (1965) 90.

26. R. G. Pearson, *Chem. Britt.*, **3**, (1967) 103.