

One-step simple method for the determination of palladium using 3-acetyl-2-thiohydantoin as a releasing agent

J Karthikeyan¹, P Parameshwara Naik² & A Nityananda Shetty^{3*}

¹Department of Chemistry, Sathyabama University, Chennai 600 119, India

²Department of Chemistry, Sahyadri Science College, Shimoga 577 203, India

³Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India
Email: nityashreya@rediffmail.com

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A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective masking property of 3-acetyl-2-thiohydantoin (ATH) 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 with standard lead nitrate solution at pH 5-6 (acetic acid – sodium acetate buffer) using xylenol orange as indicator. An excess of a 0.5% solution of ATH 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 0.35–11.00 mg of palladium with relative error of $\pm 0.46\%$ and coefficient of variation not exceeding 0.36%. The effects of diverse ions are studied. The method is used for the determination of palladium in alloys, hydrogenation catalyst and complexes with a fair degree of accuracy.

Keywords: Complexometric methods, Palladium determination, 3-Acetyl-2-thiohydantoin, Masking agent

Palladium and its alloys find extensive application in electronic industry¹, dental alloys², and 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 method⁵ for palladium could not be used for palladium in alloys and mixtures as EDTA is a very unselective reagent. Associated 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 has been found to be very useful in the rapid analysis of palladium in its alloys. The Pd-EDTA complex can be selectively decomposed using the masking agents and the released EDTA can be back titrated. The methods using dimethylglyoxime⁶ and 1,2,3-benzotriazole⁷ as masking agents 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'-dipyridyl method¹⁶. In the recently reported methods, using thioacetamide¹⁷, 2-thiazolinethiol¹⁸ and 2-mercaptopropionic acid¹⁹, metal ions like Hg(II), Tl(III), Sn(IV) shows severe interference. But in the case of 2-mercaptopropionic acid method, the interference of Hg(II), Tl(III) and Sn(IV) can be avoided by using pre-masking these metal ions with suitable reagents. However, some of the reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole²⁰, 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one²¹ require tedious and time consuming preparation methods.

The present investigation describes, the use of 3-acetyl-2-thiohydantoin (ATH) 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 other reported methods is found to be more selective, and there is no interference from Cu(II), Hg(II), Tl(III) and Sn(IV). Comparative accounts of the present method with the reported methods are given in Table 1. The application of the method in the analysis of alloys, 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) 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 dimethylglyoximate method²². Lead nitrate (Merck) solution (0.01 mol L⁻¹) was prepared by dissolving the salt in distilled water and was standardized by the salicylaldoxime method²². EDTA (Merck) solution (0.01 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. 3-Acetyl-2-thiohydantoin (ATH) was prepared and purified by the reported method²³ and used as 0.5% solution in acetone. 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 0.35-11.00 mg of palladium(II) and varying amounts of diverse metal ions, an excess of 0.01 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 in the range 4 to 5 by drop wise addition of dilute sodium hydroxide solution and finally to 5-6 by adding acetic acid-sodium acetate buffer. The surplus EDTA was back titrated (Burette capacity 5 mL, Sensitivity 0.02 mL) with standard lead nitrate solution to a sharp colour change of

Table 1—Comparison of reported methods with the present method

| Reagents | Range (mg) | Precision & accuracy | Remarks | Ref |
|---|------------|--------------------------------|--|----------------|
| Dimethylglyoxime | 2-25 | R.E ≤ ± 1 % | Requires heating to 50°C | 6 |
| 1,2,3-Benzotriazole | 3-24 | R.E ≤ ± 1.1 % | Requires heating at 60°C, Hg(II), Sn(IV) and Mo(VI) interfere. | 7 |
| 1,10-Phenanthroline | 4-18 | R.E ≤ ± 1 % | Many common metal ions including Cu(II) interfere. | 8 |
| Thiourea | 4-40 | R.E ≤ ± 2 % | Cu(II) interferes | 9 |
| Pyridine | 3-30 | R.E ≤ ± 1.33 % | Requires heating to 60°C | 10 |
| Thiosemicarbazide | 1-11 | R.E ≤ ± 0.4 % | Many metal ions including Cu(II) interfere. | 11 |
| Thiocyanate | 3-42 | R.E ≤ ± 1 % | Hg(II), Mn(II), Ir(III) and Sn(IV) interfere. | 12 |
| Hydroxylamine hydrochloride | 0.3-18 | R.E ≤ ± 0.4 % C.V ≤ 0.4 % | Hg(II), Cd(II), Tl(III) and Al(III) interfere. | 13 |
| 3-Mercapto-propane-1,2-diol | 0.5-20 | R.E ≤ ± 0.3 % C.V ≤ 0.36 % | Hg(II), Bi(III), Tl(III) and Sn(IV) interfere. | 14 |
| 2-Mercaptopropionyl glycine | 2-22 | R.E ≤ ± 0.36 % C.V ≤ 0.31 % | Hg(II), Cu(II), Tl(III) and Sn(IV) interfere. | 15 |
| 2,2'-Dipyridyl | 2.5-22 | R.E ≤ ± 0.50 % | Hg(II), Tl(III) and Sn(IV) interfere. | 16 |
| Thioacetamide | 0.5-17 | R.E ≤ ± 0.16 % C.V ≤ 0.26 % | Hg(II), Tl(III) and Sn(IV) interfere. | 17 |
| 2-Thiazolinethiol | 0.5-15 | R.E ≤ ± 0.17 % C.V ≤ 0.33 % | Hg(II), Tl(III) and Sn(IV) interfere. | 18 |
| 2-Mercaptopropionic acid | 0.5-9 | R.E ≤ ± 0.32 % C.V ≤ 0.40 % | Hg(II), Tl(III) and Sn(IV) interfere. | 19 |
| 4-Amino-5-mercapto-3-propyl-1,2,4-triazole | 0.5-5 | R.E ≤ ± 0.4 % | Hg(II), Sn(II), Fe(II), Sb(III) and Al(III) interfere. | 20 |
| 4-Amino-3-mercapto-1,2,4-triazine(4H)-5-one | 0.5-5 | R.E ≤ ± 0.2 % | Hg(II), Tl(III) and Sn(IV) interfere. | 21 |
| 3-Acetyl-2-thiohydantoin | 0.35-11 | R.E ≤ ± 0.46 % C.V ≤ 0.36% | Hg(II) and Cr(III) interfere | Present method |

xylene orange from yellow to red. To this, a freshly prepared 0.5% solution of 3-acetyl-2-thiohydantoin (ATH) 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 lead nitrate solution as before. The second titre value is equivalent to the amount of palladium(II) present in the aliquot.

Analysis of palladium

In alloys

0.1–0.5 g 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 100 mL. The stock solution was standardized gravimetrically by the dimethylglyoximate method²² and complexometrically by thioacetamide method¹⁷. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

In catalysts

A known weight (1.0–2.0 g) of the catalysts 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. The stock solution was standardized gravimetrically by the dimethylglyoximate method²² and complexometrically by thioacetamide method¹⁷. Suitable aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

In complexes

Palladium(II) complexes with dimethylglyoxime, thiosemicarbazide, 1,2,3-benzotriazole and thiocarbonylhydrazide were prepared and purified as per the reported methods^{24,27}. 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 known volume with distilled water. The stock solution was standardized gravimetrically by the dimethylglyoximate method²² and complexometrically by thioacetamide method¹⁷. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

Results and Discussion

3-Acetyl-2-thiohydantoin (ATH) is a polydentate ligand with nitrogen, sulphur and oxygen as donor sites. Thus it may act as bidentate, or polydentate

ligand if required. According to Hard soft acid base theory (HSAB)^{28,29} soft palladium(II) forms strong bond through soft sulphur of mercapto group. Since ATH forms 1:2 complex (Pd: ATH) with Pd(II)³⁰, it is reasonable to expect the bonding of Pd(II) with deprotonated sulphur of thiol group and oxygen of carbonyl group. This results in the formation of a stable chelate. The quantitative release of EDTA from Pd-EDTA complex by ATH indicates that Pd(ATH)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(ATH)₂ complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

It was observed that for instantaneous and quantitative release of EDTA from the Pd(II) – EDTA complex, the amount of ATH 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 the subsequent determinations, the concentration of ATH 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 0.35–11.00 mg were carried out under the optimized experimental conditions. These results are presented in Table 2. The results show that the maximum relative error and coefficient of variation (n=6) of the method not more than ±0.46 and 0.36% respectively. From these results, it is

Table 2—Precision and accuracy in the determination of palladium(II) in palladium chloride solution (n=6)

| Palladium (mg) | | Relative error (%) | Coefficient of variation (%) |
|----------------|-------|--------------------|------------------------------|
| Taken | Found | | |
| 0.36 | 0.36 | 0.00 | 0.00 |
| 0.72 | 0.72 | 0.00 | 0.00 |
| 1.44 | 1.44 | 0.00 | 0.32 |
| 2.16 | 2.15 | -0.46 | 0.22 |
| 2.88 | 2.89 | +0.34 | 0.36 |
| 3.62 | 3.61 | -0.27 | 0.15 |
| 5.78 | 5.77 | -0.17 | 0.14 |
| 7.24 | 7.24 | 0.00 | 0.08 |
| 10.86 | 10.88 | +0.18 | 0.08 |

n = number of average determinations

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 3.62 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 3. However, Hg(II) and Cr(III) interfere severely. The interference of Hg(II) is due to the release of EDTA from its EDTA complex with

Table 3 — Determination of 3.62 mg of palladium in the presence of foreign ions (n = 4)

| Metal ions | Quantity added (mg) | Palladium found (mg) | Relative error (%) |
|----------------------------------|---------------------|----------------------|--------------------|
| Mg(II) | 80 | 3.61 | -0.27 |
| Co(II) | 80 | 3.61 | -0.27 |
| Cu(II) | 80 | 3.62 | 0.00 |
| Ni(II) | 70 | 3.62 | 0.00 |
| Zn(II) | 100 | 3.61 | -0.27 |
| Cd(II) | 100 | 3.62 | 0.00 |
| Pb(II) | 100 | 3.63 | +0.27 |
| Mn(II) | 3 | 3.63 | +0.27 |
| Hg(II)* | 5 | 3.61 | -0.27 |
| As(III) | 50 | 3.61 | -0.27 |
| Tl(III) | 30 | 3.62 | 0.00 |
| Al(III) | 50 | 3.62 | 0.00 |
| Rh(III) | 20 | 3.61 | -0.27 |
| Ru(III) | 15 | 3.61 | -0.27 |
| Au(III) | 5 | 3.62 | 0.00 |
| Fe(III) | 15 | 3.63 | +0.27 |
| Ce(III) | 80 | 3.61 | -0.27 |
| Sb(III) | 30 | 3.61 | -0.27 |
| Pt(IV) | 50 | 3.62 | 0.00 |
| Sn(IV) | 15 | 3.62 | 0.00 |
| Se(IV) | 40 | 3.62 | 0.00 |
| U(VI) | 15 | 3.61 | -0.27 |
| W(VI) | 10 | 3.61 | -0.27 |
| Mo(VI) | 10 | 3.62 | 0.00 |
| F ⁻ | 80 | 3.61 | -0.27 |
| Cl ⁻ | 100 | 3.62 | 0.00 |
| Br ⁻ | 50 | 3.62 | 0.00 |
| I ⁻ | 65 | 3.62 | 0.00 |
| CH ₃ COO ⁻ | 80 | 3.61 | -0.27 |
| Phosphate | 25 | 3.63 | +0.27 |
| Citrate | 30 | 3.62 | 0.00 |
| Sulfate | 50 | 3.62 | 0.00 |
| Nitrate | 70 | 3.63 | +0.27 |
| Tartarate | 80 | 3.62 | 0.00 |
| Oxalate | 50 | 3.62 | 0.00 |
| Bromate | 50 | 3.61 | -0.27 |
| Iodate | 50 | 3.61 | -0.27 |

*Premasked with acetylacetone

positive error 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. Moreover, the interference of Hg(II) can be avoided by pre-masking the metal ion with acetyl acetone.

Applications

In order to explore the practical applications of the proposed method, it was extended for the determination of palladium in alloys, hydrogenation catalysts, complexes and in synthetic mixtures of ions. The experimental results of these analyses are presented in Tables 4-7. It is evident from these

Table 4 — Analysis of palladium alloys (n=5)

| Palladium alloys | Palladium taken (mg) | Palladium found (mg) | Relative error (%) |
|------------------|----------------------|----------------------|--------------------|
| Pd – Rh (90%) | 7.90 | 7.90 | 0.00 |
| Pd – Ni (40%) | 12.00 | 11.98 | -0.16 |

Table 5 — Analysis of palladium catalysts (n = 5)

| Palladium catalyst | Palladium (Certified value) (%) | Palladium found (%) | Relative error (%) |
|------------------------|---------------------------------|---------------------|--------------------|
| Pd – Charcoal catalyst | 5 | 4.98 | -0.40 |
| Pd – Asbestos catalyst | 5 | 5.01 | +0.20 |

Table 6 — Analysis of palladium complexes (n=5)

| Complex | Palladium calculated (%) | Palladium found (%) | Relative error (%) |
|---|--------------------------|---------------------|--------------------|
| Pd(C ₄ H ₇ O ₂ N ₂) ₂ ^a | 31.63 | 31.60 | -0.09 |
| Pd(CH ₅ N ₃ S) ₂ Cl ₂ ^b | 32.50 | 32.43 | -0.21 |
| Pd(C ₆ H ₅ N ₃) ₂ Cl ₂ ^c | 25.61 | 25.60 | -0.03 |
| Pd(CH ₆ N ₄ S) ₂ Cl ₂ ^d | 29.77 | 29.71 | -0.20 |

^aPalladium complex with dimethylglyoximate, ^bthiosemicarbazide, ^c1,2,3-benzotriazole, ^dthiocarbohydrazide

Table 7 — Analysis of palladium in synthetic mixtures of ions (n=5)

| Mixture | Composition (%) | Palladium found (%) | Relative error (%) |
|--------------|----------------------|---------------------|--------------------|
| Pd + Ru | 47.78 + 52.22 | 47.77 | -0.02 |
| Pd + Cu + Au | 3.46 + 94.64 + 1.90 | 3.46 | 0.00 |
| Pd + Cu + Ni | 3.54 + 57.88 + 38.58 | 3.54 | 0.00 |
| Pd + Co + Ni | 4.38 + 23.90 + 71.72 | 4.38 | 0.00 |
| Pd + Pt + Au | 5.58 + 91.38 + 3.04 | 5.58 | 0.00 |
| Pd + Zn + Cu | 18.0 + 42.0 + 40.0 | 17.98 | -0.11 |
| Pd + Co + Cd | 12.0 + 46.0 + 42.0 | 12.01 | +0.08 |
| Pd + Ni + Zn | 20.0 + 55.0 + 25.0 | 19.96 | -0.20 |
| Pd + Bi + Al | 16.0 + 68.0 + 16.0 | 16.02 | +0.12 |

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.

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), Tl(III) and Sn(IV), the method is fairly selective for the rapid analysis of palladium in the presence of these ions.

References

- 1 Barnard C F J & Russell M J H, *Comprehensive Coordination Chemistry*, Vol. 5 (Pergamon Press, Oxford), 1987, 346.
- 2 Ohta M, Hijatsumke K & Yamane M Y, *J Less Com Met*, 65 (1979) 11.
- 3 Loebich O & Raub E, *J Less Com Met*, 30 (1973) 47.
- 4 Gragor N & Henry P M, *J Am Chem Soc*, 102 (1981) 681.
- 5 McNevin W M & Kriege O, *Anal Chem*, 27 (1955) 535.
- 6 Raoot K N & Raoot S, *Indian J Chem*, 12 (1974) 1007.
- 7 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 Shetty Prakash, Khader A M A, Nityananda Shetty A & Gadag R V, *Chim Acta Tur*, 23 (1995) 115.
- 15 Shetty Prakash, 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 (1999) 65.
- 17 Parameshwara P, Karthikeyan J, Nityananda Shetty A & Shetty Prakash, *Annali Di Chimica*, 96 (2006) 125.
- 18 Parameshwara P, Karthikeyan J, Nityananda Shetty A & Shetty Prakash, *Anal Chem – An Indian J*, 2(2) (2006) 73.
- 19 Karthikeyan J, Parameshwara P, Nityananda Shetty A & Shetty Prakash, *Indian J Chem Technol*, 14 (2007) 96.
- 20 Gadiyar H R A, Gadag R V, Gajendragad M R & Sudhaker Nayak H V, *J Indian Chem Soc*, 60 (1983) 889.
- 21 Narayana B & Gajendragad M R, *Curr Sci*, 56 (1987) 1279.
- 22 Vogel A I, *A text book of quantitative Inorganic Analysis*, 3rd edn (Longmann, London), 1968, 511, 128.
- 23 Johnson T B & Nicolet B H, *J Am Chem Soc*, 33 (1973) 1911.
- 24 Shome S C & Das H R, *Anal Chim Acta*, 32 (1965) 400.
- 25 Burns G R, *Inorg Chem*, 7 (1968) 277.
- 26 Mahadevappa B S, Gowda B T & Anand Murthy A S, *Curr Sci*, 45 (1976) 161.
- 27 Mukkanti K, Pandeya K B & Singh R P, *Indian J Chem*, 25A (1986) 277.
- 28 Pearson R G, *Chem Eng News*, 43 (1965) 90.
- 29 Pearson R G, *Chem Brit*, 3 (1967) 103.
- 30 Philippe A, Paule C & Pierre L J, *Trans Met Chem*, 5 (1980) 324.