



April 2006

Volume 2 Issue 2

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 2(2), 2006 [73-77]

Quantitative Complexometric Determination Of Palladium(II) Using 2-Thiazoline Thiol As A Selective Masking Agent



Nityananda A. Shetty
Department of Chemistry, National Institute
of Technology Karnataka, Surathkal,
Srinivasnagar-575 025, Karnataka (INDIA)
Fax: 0824-2474033
E-mail: nityashreya@rediffmail.com

Received: 23rd November, 2005

Accepted: 30th December, 2005

Web Publication Date : 5th April, 2006



P. Parameshwara¹, J. Karthikeyan¹, Prakash Shetty²

¹Department of Chemistry, National Institute of Technology Karnataka,
Surathkal, Srinivasnagar – 575 025, Karnataka (INDIA)

²Department of Chemistry, Manipal Institute of Technology,
Manipal-576 119, Karnataka (INDIA)

ABSTRACT

A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective masking property of 2-thiazoline thiol 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 2-thiazoline thiol 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 $\pm 0.17\%$ and coefficient of variation not exceeding 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.

© 2006 Trade Science Inc. - INDIA

KEYWORDS

Complexometric methods;
EDTA-titrations;
Masking agent;
Pd(II) determination;
2-Thiazoline thiol.

INTRODUCTION

Palladium and its alloys find extensive applications in electronic industry^[1], dental alloys^[2], magnetic materials^[3] and are also used as hydrogenation catalysts^[4]. Considering these excellent and exten-

sive applications of palladium and its compounds, a reliable and rapid method is often essential for the determination of palladium in a single stage.

Direct complexometric methods^[5] for palladium can not be used as EDTA is a very unselective reagent. Alloying metals, along with palladium form

Full Paper

strong complexes with EDTA, interfering in the method. The direct complexometric method for the determination of palladium(II) has mostly dealt with its pure solution or in the presence of platinum group metals which do not normally form complexes with EDTA. Determination of palladium(II) in the presence of diverse metal ions using selective masking agent is very useful in the rapid analysis of palladium in the presence of other metal ions. 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 10 min. Many metals interfere in thiosemicarbazide^[11] method. Other reported reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole^[12], thiocyanate^[13], thiosulphate^[14], 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one^[15], hydroxylamine hydrochloride^[16], N-(2-pyridyl)thiourea^[17], DL-methionine^[18] and 3-mercaptopropane-1,2-diol^[19], 2-mercaptopyrionyl glycine^[20] etc. were found to be reliable besides being convenient. However, some of the reagents require tedious and time-consuming preparation methods.

The present investigation describes, 2-thiazoline thiol 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 mixture of ions, catalysts and palladium complexes are also reported in this paper.

EXPERIMENTAL

Reagents

All reagents used were of analytical or chemically pure grade.

Palladium(II) chloride solution: Prepared by dissolving a known amount of PdCl₂ in minimum amount of conc. hydrochloric acid and making up

to a known volume with distilled water. The stock solution was standardised gravimetrically by dimethylglyoximate method^[21].

Lead nitrate solution (0.01M): Prepared by dissolving a known amount of lead nitrate in minimum amount of water and making up to a known volume with distilled water and standardizing gravimetrically by the chromate method^[21].

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

Xylenol orange indicator – A freshly prepared 0.5% aqueous solution of the indicator was used.

2-Thiazoline thiol solution – Used as a freshly prepared 0.2% aqueous solution

Preparation of Foreign ions – Solutions of various metal ions were prepared by dissolving the appropriate metal salts in water or 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 4-5 by the drop wise 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 2-thiazoline thiol 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 palladium complexes

Palladium(II) complexes with dimethylglyoxime, thiosemicarbazide, 1,2,3-benzotriazole, thiocarbonylhydrazide and catalysts such as palladium on asbestos and activated charcoal were prepared and purified as per the reported methods^[22-25]. A known weight of the complex and catalysts were carefully decom-

posed 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

2-Thiazoline thiol(TT) can act as a ligand through sulphur of the mercapto group. According to HSAB theory^[26,27] soft palladium(II) forms strong bond through soft sulphur of mercapto group. Therefore, it is reasonable to expect the bonding of Pd(II) through the sulphur atom. The quantitative release of EDTA from Pd-EDTA complex by TT indicates that Pd-TT 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-TT 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 TT 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 TT was main-

TABLE 1: Precision and accuracy in the determination of Palladium (II) (n=6)

Palladium, mg		Relative error (%)	Standard deviation (mg)	Coefficient of variation (%)
Taken	Found			
0.590	0.590	0.00	0.001	0.17
1.770	1.770	0.00	0.002	0.17
2.360	2.363	+0.12	0.008	0.34
2.950	2.953	+0.10	0.008	0.27
4.720	4.716	-0.08	0.012	0.25
5.900	5.910	+0.17	0.014	0.24
8.850	8.842	-0.09	0.013	0.15
11.800	11.790	-0.08	0.013	0.11
14.750	14.776	+0.17	0.024	0.16

tained 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

TABLE 2: Determination of palladium (II) in presence of diverse ions (2.95mg)

Diverse ions	Concentration (mg)	Palladium found* (mg)	Relative error (%)
Pb(II)	200	2.95	0.00
Zn(II)	100	2.95	0.00
Ba(II)	100	2.94	-0.33
Cd(II)	20	2.96	+0.33
Co(II)	20	2.95	0.00
Mg(II)	10	2.94	-0.33
Ni(II)	10	2.94	-0.33
Cu(II)	5	2.96	+0.33
Mn(II)	5	2.95	0.00
La(III)	80	2.95	0.00
Y(III)	80	2.95	0.00
As(III)	60	2.94	-0.33
Bi(III)	60	2.94	-0.33
Rh(III)	25	2.96	+0.33
Ce(III)	10	2.95	0.00
Ti(III)	10	2.96	+0.33
Ru(III)	5	2.95	0.00
Al(III)	5	2.95	0.00
Se(IV)	80	2.96	+0.33
Sb(IV)	50	2.95	0.00
Pt(IV)	40	2.94	-0.33
Sn(IV) [£]	5	2.95	0.00
W(VI)	60	2.94	-0.33
U(VI)	50	2.95	0.00
Sulphate	150	2.95	0.00
Borate	120	2.94	-0.33
Tartarate	100	2.95	0.00
Oxalate	100	2.95	0.00
Acetate	100	2.94	-0.33
Chloride	80	2.94	-0.33
Citrate	80	2.96	+0.33
Nitrate	80	2.95	0.00

[£] Premasked with sodium fluoride

Full Paper

TABLE 3: Analysis of palladium complexes (n=3)

Complex	Palladium (%)		Relative error (%)
	calculated	found	
Pd(C ₄ H ₇ O ₂ N ₂) ₂ ^a	31.63	31.69	+0.19
Pd(CH ₃ N ₃ S) ₂ Cl ₂ ^b	29.59	29.51	-0.27
Pd(C ₆ H ₅ N ₃) ₂ Cl ₂ ^c	25.60	25.54	-0.23
Pd(CH ₆ N ₄ S) ₂ Cl ₂ ^d	27.31	27.25	-0.22
Palladium- Asbestos catalyst	4.98	4.97	-0.20
Palladium-Charcoal catalyst	5.02	5.04	+0.40

^aPalladium complex with dimethylglyoxime

^bPalladium complex with thiosemicarbazide

^cPalladium complex with 1,2,3-benzotriazole

^dPalladium complex with thiocarbohydrazide

that the maximum relative error and coefficient of variation (n=6) of the method are $\pm 0.17\%$ and 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 3.05 mg of Pd(II) in the presence of different metal ions. The results pertaining to the non interfering ions listed in TABLE 2. Metal ions like Tl(III), Cr(III) and Sn(IV) interfere severely with positive error. The interference of Cr(III) is due to the deep purple colour of its EDTA complex, which makes the detection of the end point rather difficult. In the case of Sn(IV), interference can be avoided by pre-masking the metal ions with sodium fluoride as a secondary masking agent.

Applications

In order to explore the practical application of the proposed method, it was extended for the determination of palladium in its complexes, in catalysts and in synthetic mixture of metal ions. The experimental results of these analyses are presented in TABLE 2 and 4 respectively. It is evident from these results that the method can be conveniently employed in the analysis of palladium in its complexes, catalysts and alloys with fair degree of accuracy.

TABLE 4: Determination of palladium(II) in synthetic mixtures of metal ions (n=3)

Mixture	Composition (%)	Palladium found (%)	Relative error (%)
Pd + Pb + Ba	3.2 + 48.4 + 48.4	3.21	+0.31
Pd + Pb + Sb	3.8 + 60.1 + 36.1	3.79	-0.26
Pd + Zn + La	3.5 + 53.6 + 42.9	3.49	-0.28
Pd + Pb + As	3.8 + 48.1 + 48.1	3.81	+0.26
Pd + Sb + Y	5.0 + 47.5 + 47.5	5.01	+0.19
Pd + Zn + Y	4.4 + 54.6 + 41.0	4.39	-0.23

CONCLUSIONS

The proposed method is simple and rapid, as it requires no heating for the quantitative release of EDTA from 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, the method is fairly selective for the rapid analysis of palladium in its complexes, catalysts and in synthetic mixtures of ions. Moreover as it does not require any adjustment of pH after the addition of the reagent.

REFERENCES

- [1] C.F.J.Barnard, M.J.H.Russell; 'Comprehensive Coordination Chemistry', Pergamon Press, Oxford, **5**, 346 (1987).
- [2] M.Ohta, K.Hijatsumke, M.Y.Yamane; J.Less.Com. Met., **65**, 11 (1979).
- [3] O.Loebich, E.Raub; J.Less.Com.Met., **30**, 47 (1973).
- [4] N.Gragor, P.M.Henry; J.Am.Chem.Soc., **102**, 681 (1981).
- [5] W.M.McNevin, O.Kriege; Analyst Chem., **27**, 535 (1955).
- [6] K.N.Raoot, S.Raoot; Indian J.Chem., **12**, 1007 (1974).
- [7] K.N.Raoot, S.Raoot, V.G.Vaidya; Indian J.Chem., **18A**, 90 (1979).
- [8] K.N.Raoot, Sarasota; Indian J.Technol., **18**, 345 (1980).
- [9] K.N.Raoot, S.Raoot; Talanta, **28**, 327 (1981).
- [10] K.N.Raoot, S.Raoot, V.Lalitha Kumari; Analyst, **107**, 1382 (1982).
- [11] B.Narayana, M.R.Gajendragad; Microchem.J., **36**, 364 (1987).
- [12] H.R.A.Gadiyar, R.V.Gadag, M.R.Gajendragad, H.V.

Full Paper

- Sudhaker Nayak; J.Indian Chem.Soc., **60**, 889 (1983).
- [13] K.N.Raoot, S.Raoot, V.Lalitha Kumari; Analyst, **108**, 1148 (1983).
- [14] K.N.Raoot, S.Raoot; Talanta, **33**, 544 (1986).
- [15] B.Narayana, M.R.Gajendragad; Curr.Sci., **56**, 1279 (1987).
- [16] A.Nityananda Shetty, R.V.Gadag, M.R.Gajendragad; Indian J.Technol., **27**, 224 (1989).
- [17] A.Nityananda Shetty, R.V.Gadag, M.R.Gajendragad; Rev.Roum.Chem., **38**, 1305 (1993).
- [18] B.M.Rao, B.Narayana; Analyst, **119**, 2217 (1994).
- [19] Prakash Shetty, A.M.A.Khader, A.Nityananda Shetty, R.V.Gadag; Chim.Acta Tur., **23**, 115 (1995).
- [20] Prakash Shetty, A.Nityananda Shetty, R.V.Gadag; Indian J.Chem.Tech., **9**, 127 (2002).
- [21] A.I.Vogel; 'A Text Book of Quantitative Inorganic Analysis', 3rd edn., Longmann, London, 511, 128 (1964).
- [22] S.C.Shome, H.R.Das; Anal.Chim.Acta., **32**, 400 (1965).
- [23] G.R.Burns; Inorg.Chem., **7**, 277 (1968).
- [24] B.S.Mahadevappa, B.T.Gowda, A.S.Anand Murthy; Curr.Sci., **45**, 161 (1976).
- [25] K.Mukkanti, K.B.Pandeya, R.P.Singh; Indian J.Chem., **25A**, 277 (1986).
- [26] R.G.Pearson; Chem.Engg.News, **43**, 90 (1965).
- [27] R.G.Pearson; Chem.Britt., **3**, 103 (1967).