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Complexometric determination of palladium(II) using ethanethiol as a selective masking agent

J Karthikeyan[a], P Parameshwara[a], A Nityananda Shetty[a*] & Prakash Shetty[b]

[a] Department of Chemistry, National Institute of Technology Karnataka, Surathkal 575 025, India

[b]Department of Chemistry, Manipal Institute of Technology, Karnataka Manipal 576 104, India

Email: nityashreya@rediffmail.com

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A complexometric method based on the selective masking property of ethanethiol towards palladium(II) is proposed. In presence of diverse metal ions, palladium(II) is complexed with excess EDTA and the surplus EDTA is backtitrated with standard zinc sulphate solution at *p*H 5-5.5 (acetic acid-sodium acetate buffer) using xylenol orange as indicator. An excess of a 0.1% aqueous solution of ethanethiol 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 of 0.5-14.26 mg of palladium with relative error of ±0.40% and coefficient of variation not exceeding ±0.34%. The effect of diverse ions is studied. The method has been used for the determination of palladium in its complexes, catalysts and synthetic alloy mixtures.

Keywords: Complexometry, Masking reagent, EDTA titration, Ethanethiol, Palladium determination

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

Existing direct complexometric method[5] for palladium cannot be used to determine palladium in presence of other ions as EDTA is a very unselective reagent. Alloying metals like Cu(II), Ru(III) and Pt(IV) etc. along with palladium form strong complexes with EDTA and interfere in the method. Therefore a complexometric method for the determination of palladium(II) in the presence of diverse metal ions using selective masking agent is very useful in the rapid analysis of palladium 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 10 min. Many metals interfere in the 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], 3-mercapto-propane-1,2-diol[19], 2-mercaptopropionyl glycine[20], thioacetamide[21], 2-thiazolinethiol[22] 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 ethanethiol as a masking agent for the selective and quantitative determination of palladium(II) in the *p*H range of 5 to 5.5. The effect of foreign ions is studied and the application of the method in the analysis of mixture of ions and palladium complexes is also reported.

Experimental Procedure

Materials

All reagents used were of analytical or chemically pure grade. A stock solution of palladium(II) prepared

by dissolving calculated amount of $PdCl_2$ (Merck) in minimum amount of conc. HCl and diluting to a known volume with distilled water. The stock solution was standardized by dimethylglyoximate method[23]. Zinc sulphate solution (0.01 M) prepared by dissolving the salt in distilled water was standardized by the oxinate method[23]. EDTA solution (0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water. Freshly prepared (0.5%) aqueous solution of xylenol orange was used as indicator. Ethanethiol (0.1%) (masking agent) (Acros Organics, USA) solution was prepared by dissolving the reagent in distilled water. Solutions of various metal ions were prepared by dissolving required amounts of the metal chlorides/nitrates/sulphates in distilled water.

Method

To an aliquot (5 mL) of sample solution containing 0.5-14.26 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 *p*H of the solution was initially adjusted between 4-5 by the 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 0.1% solution of ethanethiol was added in required amount (3-5 mL, 1:12 M:L ratio). 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) ions present in the aliquot.

Analysis of palladium complexes

Palladium(II) complexes with some sulphur-donor ligands were prepared and purified as per the reported methods[24-27]. 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 100 mL standard flask with distilled water. Aliquots [3-5 mL, 1.0-10.0 mg of palladium as Pd(II) ions] of this solution were used for estimation as per the proposed procedure.

Analysis of the palladium catalysts

A known weight (1.0-2.0 g) of the catalysts such as palladium-charcoal and palladium-asbestos (S.D.fine Chemicals) was digested with aqua regia to nearly dryness. The residue was treated with 2 N HCl filtered, if necessary, and made up to a 100 mL in a standard flask with distilled water. Aliquots [3-5 mL, 1.0 – 10.0 mg of palladium as Pd(II) ions] of this solution were used for the estimation of palladium as per the proposed procedure.

Results and Discussion

Masking property of the reagent

Ethanethiol acts as a mono-dentate ligand and forms a 1:12 (M:L) complex with palladium(II)[28]. According to HSAB theory[29,30], 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, which results in the formation of a stable complex[28]. The quantitative release of EDTA from Pd-EDTA complex by ethanethiol indicates that $Pd(SR)_2$ ($R = -C_2H_5$) complex is more stable than Pd-EDTA complex under the experimental conditions employed. The release of EDTA is quantitative and instantaneous at 25-30°C itself. The $Pd(SR)_2$ complex formed is soluble in the aqueous medium under the experimental conditions and the detection of the end point is very sharp.

Effect of reagent concentration

The addition of ethanethiol in the molar ratio of 1:12 (M:L) was found to be sufficient for the instantaneous and quantitative release of EDTA from the Pd-EDTA complex. Further, it was noticed that the addition of excess ethanethiol, as much as 20-fold excess over the required molar ratio did not have adverse effect on the results obtained. In all subsequent determinations, the concentration of ethanethiol was maintained at slight excess over the 1:12 (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 was carried out under the optimized experimental conditions. The results are presented in Table 1. The results obtained are reproducible and accurate in the concentration range 0.5-14.26 mg of Pd(II), with relative error and coefficient of variation

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

Palladium (mg) Taken	Palladium (mg) Found	Relative error (%)	Standard deviation	Coefficient of variation(%)
0.581	0.580	-0.17	0.002	0.34
1.162	1.160	-0.17	0.004	0.34
1.711	1.714	+0.17	0.005	0.29
2.852	2.848	-0.14	0.005	0.17
5.704	5.700	-0.07	0.005	0.08
11.41	11.42	+0.01	0.010	0.08
14.26	14.26	0.00	0.012	0.08

Table 2 – Analysis of palladium complexes and catalysts (n=6)

Complex	Pd(II) calculated (%)	Pd(II) found (%)	Relative error (%)
$Pd(C_4H_7O_2N_2)_2$[a]	31.63	31.58	-0.16
$Pd(CH_5N_3S)_2Cl_2$[b]	29.59	29.53	-0.20
$Pd(C_6H_5N_3)_2Cl_2$[c]	25.60	25.56	-0.16
$Pd(CH_6N_4S)_2Cl_2$[d]	27.31	27.25	-0.21
Pd – Charcoal catalyst	5	4.99	-0.20
Pd – Asbestos catalyst	5	4.98	-0.40

[a]Palladium complex with dimethylglyoxime, [b]thiosemicarbazide, [c]1,2,3-benzotriazole, [d]thiocarbohydrazide.

(n=6) not more than ±0.40% and ±0.34%, respectively.

Effect of foreign ions

The effect of various cations and anions on the quantitative determination of Pd(II) was studied by estimating 1.71 mg of Pd(II) in the presence of different metal ions. No interference was observed in the presence of following ions at the amounts shown in mg: Mg(II) (50.10), Ba(II) (20.00), Pb(II) (80.20), Zn(II) (80.08), Cu(II) (10.00), Co(II) (50.00), Ni(II) (60.25), Cd(II) (15.00), Mn(II) (5.00), Sb(III) (15.00), Al(III), La(III) (50.10), Y(III) (100.0), Bi(III) (10.00), Rh(III) (50.01), Ru(III) (5.00), Fe(III), Zr(III), Au(III) (5.00), Se(IV) (50.52), Pt(IV) (25.00), W(VI), U(VI) (15.00), acetate (60.22), chloride (100.00), sulphate (50.00), oxalate (30.00), tartarate (50.00), citrate (30.00), phosphate (50.00). Metal ions such as Hg(II), Tl(III) and Sn(IV) show severe interference with a positive error. This is due to the simultaneous release of EDTA from their respective EDTA complexes by the reagent. 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.

Table 3 – Determination of palladium(II) in synthetic mixtures of metal ions (n=6)

Mixture	Pd(II) present (%)	Pd(II) found (%)	Relative error (%)
Pd + Ru	47.78 + 52.22	47.76	-0.04
Pd + Rh	3.00 + 97.00	3.01	+0.33
Pd + Cu + Au	3.46 + 94.64 + 1.90	3.45	-0.28
Pd + Pt + Au	3.54 + 57.88 + 38.58	3.54	0.00
Pd + Co + Ni	4.38 + 23.90 + 71.72	4.38	0.00
Pd + Cu + Ni	5.58 + 91.38 + 3.04	5.57	-0.17

Applications

In order to explore the practical applications of the proposed method, it was extended for the determination of palladium in its complexes and in synthetic mixtures 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 analysis of such samples.

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