Indian Journal of Chemical Technology
Vol. 16, May 2009, pp. 259-264

Selective complexometric determination of palladium with sodium metabisulphite as releasing agent

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Received 16 October 2008; revised 16 February 2009

Sodium metabisulphite has been proposed as a selective releasing agent for the rapid and selective complexometric determination of palladium. Pd(II) present in a given sample solution is first complexed with excess of EDTA and the surplus EDTA is back titrated with standard zinc sulphate solution at *p*H 5-5.5 (acetic acid-sodium acetate buffer) using xylenol orange as indicator. Sodium metabisulphite solution is then added to displace EDTA quantitatively from the Pd-EDTA complex. The released EDTA is back titrated with standard zinc sulphate solution as before. The method works well in the concentration range 2-20 mg of Pd with a relative error ≤ 0.40% and relative standard deviation ≤ 0.65%. The method has been applied to the determination of palladium in catalysts, alloys and complexes.

Keywords: Palladium determination, Complexometry, Sodium metabisulphite, Releasing agent

The importance of palladium as a transition metal lies in its wide spectrum of applications. The high melting temperature of palladium and its alloys provides high resistance to corrosion and hence, it is widely used in electrical contacts. Palladium and its alloys are also employed as dental restorative materials. Palladium–gold alloy is used in jewellary as a substitute for many gold alloys, which are difficult to obtain. In most of these applications, often it required a simple, speedy and accurate analytical method for determining the palladium content in the samples.

Complexometric determination of Pd(II) in the presence of diverse metal ions, using selective releasing agents enables the rapid analysis of such samples. The Pd-EDTA complex can be selectively decomposed using releasing agents such as dimethylglyoxime[1] and 1,2,3-benzotriazole[2]. These methods are not rapid as they involve heating and extraction of Pd-reagent complex using chloroform. The thiourea method[3] is not suitable for unknown samples of palladium in the presence of copper. The pyridine method[4] needs heating to 60ºC for 10 min. Many metal ions show interference in 1,10-phenanthroline[5], 4-amino-5-mercapto-3-propyl-1,2,4-triazole[6], thiosemicarbazide[7] and 4-amino-3-mercapto-1,2,4-triazine-5-one[8] method. Thiocyanate[9], hydroxylamine hydrochloride[10], *N*-(2-pyridyl) thiourea[11], DL–cystein[12], 3-mercaptopropane-1,2-diol[13], 2-mercapto propionyl glycine[14], 2-mercaptopropionic acid[15], and thioacetamide[16] were some of the other releasing agents used for palladium. However, some of these reagents require tedious and time consuming synthesis steps. Most of these releasing agents cannot be used for the determination of palladium in presence of copper.

The use of sodium metabisulphate for complexometric determination of Hg(II)[17] and Tl(III)[18] has been reported earlier. During the course of these investigations, it was observed that Pd(II) showed a severe interference giving positive errors. Hence, it was thought of investigating further the analytical usefulness of sodium metabisulphite in the complexometric determination of Pd(II) as well. This paper describes the applications and advantages of sodium metabisulphite as a selective releasing agent for the complexometric determination of Pd(II).

Experimental Procedure

Materials

All chemicals used were of analytical grade and

double distilled water was used throughout for dilution purpose. Palladium(II) chloride solution was prepared by dissolving 1.0 g of $PdCl_2$ (Merck) in minimum amount of conc. HCl followed by dilution to a known volume and standardized gravimetrically as palladium dimethylglyoximate[19]. Zinc sulphate solution (0.01 M) was standardized gravimetrically as zinc oxinate[19]. EDTA solution (0.01 M) was prepared by dissolving the disodium salt of EDTA (Merck) in distilled water. A freshly prepared 1% solution of sodium metabisulphite (BDH) in distilled water was used. A freshly prepared 0.5% aqueous solution of xylenol orange was used as indicator. Acetic acid-sodium acetate buffer (*p*H 5.3) was used as a mixture of 200 mL of acetic acid (0.2 M) and 800 mL of sodium acetate (0.2 M) solution. Solutions of various diverse ions were prepared by dissolving calculated amount of appropriate salts in distilled water or in suitable diluted acids and making up to a known volume.

Method

To a solution containing 2-20 mg of palladium and varying amounts of diverse ions, an excess of 0.01 M EDTA solution was added and diluted to about 70-80 mL. The *p*H of the solution was initially adjusted between 4 and 5 by the drop wise addition of diluted NaOH solution and finally to 5-5.5 by adding acetic acid-sodium acetate buffer. The excess of EDTA was back titrated against 0.01 M zinc sulphate solution using xylenol orange as indicator to a sharp colour change from yellow to red. To this solution 2-20 mL of sodium metabisulphite solution was added and mixed well by shaking. The released EDTA was then titrated with 0.01 M zinc sulphate solution as before. The second titre volume corresponds to the palladium content present in the aliquot.

Determination of palladium in catalysts

A known weight (0.2-0.3 g) of the palladium catalyst (Merck) was dissolved in aqua regia. The solution was evaporated to near dryness with addition of three 5 mL portion of con. HCl to remove the oxides of nitrogen and then treated with 10 mL diluted HCl. The solution was filtered, if necessary and diluted up to mark in a 100 mL standard flask. Suitable aliquots of this solution were taken and analyzed for palladium as per the recommended procedure.

Determination of palladium in complexes

Some palladium(II) complexes with ligands such as salicyloyl hydrazide, thiocarbohydrazide, thiosemicarbazide, thiophene-2-carboxaldehyde thiosemicarbazone, dimethylglyoxime, and 1,2,3-benzotriazole were prepared and purified as per the reported methods[20-23]. A known weight (0.3-0.4 g) of the complex was carefully decomposed by evaporating to near dryness with aqua regia. The residue was then cooled, dissolved in minimum amount of diluted HCl and made up to 100 mL with distilled water in a volumetric flask. Aliquots of 10 mL were used for titration as per the proposed procedure.

Results and Discussion

Sodium metabisulphite selectively decomposes Pd-EDTA complex at *p*H 5-5.5 and liberates EDTA quantitatively at room temperature. The released palladium forms a soluble and stable complex with the reagent. The fact that the reagent displaces EDTA instantaneously and quantitatively (*p*H 5-5.5) from the Pd-EDTA complex indicates that the Pd-reagent complex is more stable than Pd-EDTA complex. Being a sulphur containing ligand, sodium metabisulphite prefers to bond strongly with soft metal ions[24,25]. Therefore, it is reasonable to expect the formation of a stable complex between Pd(II) and the reagent. The absence of any precipitate in the reaction mixture favours the detection of a sharp end point.

Effect of reagent concentration

In order to determine the exact amount of reagent required to decompose Pd-EDTA complex quantitatively, titrations were carried out with solutions containing 10.40 mg of palladium and varying amounts of 1% sodium metabisulphite solution. The plot of volume reagent versus recovery of palladium (Fig. 1) shows that a minimum of 1 mL of 1% solution of sodium metabisulphite is required for each mg of Pd. Addition of excess reagent over the required amount has no adverse effects on the experimental result.

Precision and Accuracy

To ascertain the precision and accuracy of the proposed method, determination of palladium in palladium(II) chloride solution, catalysts, complexes and synthetic alloy samples were carried out

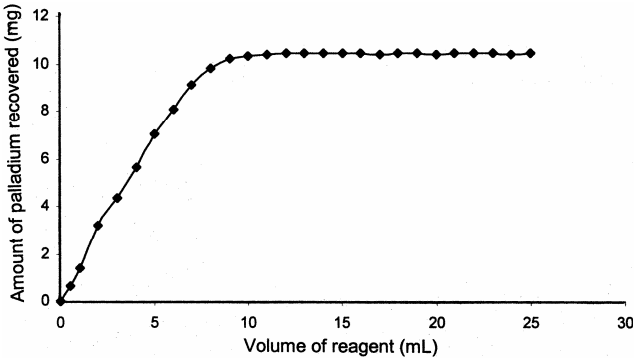

Fig. 1—Effect of reagent concentration on the recovery of Pd [Pd(II) taken=10.40 mg; Reagent=1% sodium metabisulphite]

Table 1—Determination of palladium in palladium(II) chloride solution

Palladium, mg		R.S.D, %	Relative
Taken	Found	(n=5)	error, %
1.56	1.56	0.28	0.00
2.60	2.60	0.20	0.00
3.64	3.65	0.10	+0.27
5.20	5.19	0.14	-0.20
10.40	10.39	0.09	-0.10
15.60	15.62	0.14	+0.13
20.80	20.84	0.11	+0.19

R.S.D. means relative standard deviation

according to the procedure described. Reproducible and accurate results (Tables 1, 3, 4 and 5) were obtained in the concentration range 2-20 mg of Pd with relative error ≤ 0.40% and relative standard deviation ≤0.65%.

Effect of diverse ions

The effect of various diverse ions was studied in the determination of palladium following the recommended procedure. The amounts (in mg) of diverse ions which do not cause any interference with 5.20 mg of Pd(II) are summarized in Table 2. However, Hg(II), Tl(III) and Sn(IV) interfere seriously. The interference of Hg(II)[17] and Tl(III)[18] is due to the simultaneous release of EDTA from their respective EDTA complexes along with Pd-EDTA complex by the reagent. However, the interference of Hg(II) (up to 24 mg) and Sn(IV) (20 mg) can be eliminated by premasking with acetyl acetone (5% acetyl acetone, 10 mL) and fluoride (5% NH_4F, 10 mL) respectively.

Table 2—Determination of palladium in presence of various diverse ions
[Pd(II) taken in solution = 5.20 mg]

Diverse ions	Amount added, mg	Pd found*, mg	Relative error, %
Pb(II)	200	5.19	-0.19
Zn(II)	200	5.20	0.00
Cd(II)	40	5.21	+0.19
Cu(II)	40	5.18	-0.39
Co(II)	36	5.17	-0.58
Ni(II)	30	5.22	+0.38
Ca(II)	40	5.21	+0.19
Mg(II)	50	5.18	-0.39
Hg(II)[#]	24	5.23	+0.58
Ba(II)	60	5.17	-0.58
Mn(II)	20	5.24	+0.77
Al(III)	30	5.22	+0.58
Bi(III)	40	5.18	-0.39
Fe(III)	28	5.22	+0.38
Ir(III)	16	5.17	-0.58
Ru(III)	18	5.23	+0.58
Rh(III)	20	5.21	+0.19
Au(III)	20	5.18	-0.39
Cr(III)	20	5.22	+0.38
Ce(III)	28	5.17	-0.58
Pt(IV)	20	5.21	+0.19
Ti(IV)	30	5.18	-0.39
Zr(IV)	30	5.22	+0.38
Sn(IV)[$]	20	5.24	+0.77
Th(IV)	24	5.17	-0.58
V(IV)	30	5.22	+0.38
As(V)	26	5.18	-0.39
Mo(VI)	30	5.23	+0.58
W(VI)	28	5.19	-0.19
U(VI)	20	5.22	+0.38
Os(VIII)	30	5.24	+0.77
Fluoride	200	5.18	-0.39
Chloride	150	5.23	+0.58
Bromide	150	5.18	-0.39
Nitrate	200	5.21	+0.19
Phosphate	180	5.22	+0.38
Sulphate	200	5.19	-0.19
Tartarate	160	5.17	-0.58
Citrate	150	5.19	-0.19
Oxalate	150	5.23	+0.58
Acetate	200	5.21	+0.19

*Average of five determinations; Premasked with acetyl acetone[#] and fluoride[$]

Analytical applications

In order to assess the analytical usefulness of the proposed method, it was employed for the analysis of palladium in its catalysts, complexes and synthetic mixtures of metal ions with alloy composition. To confirm the results obtained by the proposed method, the determination of palladium content in these samples were also carried out by a reported spectrophotometric method using salicylaldehyde thiosemicarbazone[26]. The results of analysis of some such samples are presented in Tables 3-5. The experimental results obtained by the proposed complexometric method are in close agreement with those obtained by the reference spectrophotometric method[26].

The proposed reagent, sodium metabisulphite is compared with some well known releasing agents for the complexometric determination of palladium (Table 6). The main advantage of the proposed method is that it does not require any stringent conditions like heating, readjustment of *p*H or extraction. The method is also fairly selective compared to other methods.

Table 3—Determination of palladium in catalysts

Catalyst	Palladium claimed, %	Present method			Reference method[26]		
		Pd found, %	R.S.D, % (n = 3)	Relative error, %	Pd found, %	R.S.D, % (n = 3)	Relative error, %
Pd-$CaCO_3$	5.00	4.98	0.65	-0.40	4.99	0.60	-0.20
Pd-activated charcoal	10.00	9.96	0.60	-0.40	9.96	0.58	-0.40

Table 4—Determination of palladium in complexes

Complex	Pd present, %	Present method			Reference method[26]		
		Pd found,%	R.S.D, % (n = 3)	Relative error, %	Pd found, %	R.S.D, % (n = 3)	Relative error, %
$Pd(C_7H_8O_2N_2)_2Cl_2$[a]	22.09	22.02	0.52	-0.32	22.05	0.40	-0.18
$Pd(CH_6N_4S)_2Cl_2$[b]	27.31	27.42	0.60	+0.40	27.38	0.54	+0.26
$Pd(CH_5N_3S)_2Cl_2$[c]	29.59	29.50	0.64	-0.30	29.54	0.62	-0.17
$Pd(C_6H_7N_3S_2)_2Cl_2$[d]	19.42	19.36	0.56	-0.31	19.32	0.58	-0.51
$Pd(C_4H_7O_2N_2)_2$[e]	31.61	31.54	0.42	-0.22	31.57	0.48	-0.13
$Pd(C_6H_5N_3)_2Cl_2$[f]	25.60	25.68	0.38	+0.31	25.70	0.42	+0.39

Pd complex with salicyloyl hydrazide[a], thiocarbohydrazide[b], thiosemicarbazide[c], thiophene-2-carboxaldehyde thiosemicarbazone[d], dimethylglyoxime[e], 1,2,3-benzotriazole[f]

Table 5—Determination of palladium in synthetic mixtures with alloy composition

Mixture	Composition, %	Present method			Reference method[26]		
		Pd found, %	R.S.D, % (n = 3)	Relative error, %	Pd found,%	R.S.D, % (n = 3)	Relative error, %
Dental alloys							
Pd-Pt-Cu-Zn	15+15+35+35	15.06	0.65	+0.40	15.08	0.60	+0.53
Pd-Au-Pt	20+40+40	20.05	0.58	+0.25	19.96	0.52	-0.20
Jewellary alloys							
Pd-Au	50+50	49.88	0.40	-0.24	50.05	0.50	+0.10
Pd-Cu	95+05	94.85	0.38	-0.16	94.92	0.32	-0.08
Pd-Ru-Rh	95+04+01	95.18	0.46	+0.19	95.12	0.48	+0.13

Table 6—Comparison of releasing agents for palladium determination

Releasing agent	Interfering ions	Comments	Ref.
Pyridine	Hg(II), Ir(III), Pt(IV), Mn(II)	Requires heating. Reagent is water insoluble	4
4-Amino-5-mercapto-3*n* propyl-1,2,3-triazole	Ag(I), Hg(II), Sn(II), Mn(II), Fe(II), Sb(III), Al(III), Tl(III)	Working range is 0.5-5 mg of Pd. Reagent is water insoluble and requires synthesis.	6
Thiosemicarbazide	Cu(II), Fe(II), Sn(II), Hg(II), Tl(III), Bi(III), Al(III),Cr(III)	-	7
4-Amino-3-mercapto -1,2,4-triazine-(4H)-5-one	Ag(I), Hg(II), Sn(II), Mn(II), Fe(II), Sb(III), Al(III), Tl(III)	Working range is 0.5-5 mg of Pd. Reagent is water insoluble and requires synthesis.	8
Thiocynate	Hg(II), Ir(III), Tl(III), Mn(II), Sn(IV)	-	9
Hydroxylamine hydrochloride	Hg(II), Cd(II), Cr(III), Al(III), Tl(III)	Requires readjustment of *p*H	10
N-(2-pyridyl) thiourea	Hg(II), Cr(III), Tl(III), Mn(II)	Reagent is water insoluble and requires synthesis	11
DL-Cystein	Cu(II), Hg(II), Tl(III),Zr(IV), Sn(IV)	-	12
3-Mercapto propane-1,2-diol	Hg(II), Tl(III),Cr(III), Bi(III), Sn (IV), Mn(II)	-	13
2-Mercapto propionyl glycine	Cu(II), Hg(II), Tl(III),Cr(III), Sn(IV)	-	14
2-Mercaptopropionic acid	Cu(II), Hg(II), Tl(III), Sn(IV)	-	15
Thioacetamide	Hg(II), Tl(III), Cr(III),Sn(IV)	-	16
Sodium metabisulphite	Hg(II), Tl(III), Sn(IV). Interference from Hg(II) & Sn(IV) can be suitably avoided by premasking.	Reagent is readily soluble in water. Stringent conditions like heating, readjustment of *p*H or extraction are not required	Present method

Conclusion

The proposed method is simple and rapid, as it does not require any extraction, readjustment of *p*H or heating steps or very expensive facilities. Sodium metabisulphite is a cheap, readily available and water soluble material, so it is of convenient use. The releasing reagent does not form any precipitate either with zinc sulphate (the titrant) or with palladium (the analyte) under the experimental conditions, which helps in the detection of a sharp end point. Since many metal ions including Cu(II) do not show any interference, the method is most suitable for the rapid and selective determination of palladium in various samples such as catalysts, alloys and complexes. To sum up, the proposed method offers advantages of simplicity, rapidity and reasonable selectivity over other reported complexometric methods.

Acknowledgement

The authors are grateful to Manipal University, Manipal, for providing the laboratory facilities.

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