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Selective Complexometric Determination of Palladium by Using L-Cystine as Releasing Agent

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A complexometric method for the determination of palladium in the presence of other metal ions based on the selective masking ability of L-Cystine towards palladium is described. Palladium(II) is complexed with excess of EDTA and the surplus EDTA is back titrated with standard lead nitrate solution at 5 to 6 pH by using hexamine and xylenol orange as an indicator. L-Cystine (0.02 M) solution is then added to release EDTA quantitatively from Pd-EDTA complex. The EDTA released is back titrated with standard lead nitrate solution as before. The method works well in the concentration range 2 to 34 mg of Pd with relative error ≤ 0.94 % and relative standard deviation ≤ 1.21 %. The method has been successfully applied to the determination of Pd in alloy composition and complexes.

Keywords: Palladium determination, Complexometry, L-Cystine, Releasing agent.

INTRODUCTION

The importance of speedy and reliable, accurate method for determining the palladium content in the samples is due to its wide spectrum of application. The high melting point 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. The alloys of palladium with rare earths are used as magnetic materials and palladium complexes like $Pd[(O_2Me)_2]_3$ are claimed to have antitumor properties[1]. Palladium is an element of increasing importance in today's industries. The annual production of palladium is estimated to be 195 tonnes; the majority of this is used in auto catalysts (55 %), with other uses including electronics (16 %), jewellery (11 %), dental (8 %), investment (5 %) and chemical (4 %)[2]. The most commonly used complexometric determination methods in the presence of diverse metal ions, using selective releasing agents to decompose Pd-EDTA complex are dimethyl glyoxime[3] and 1,2,3-benzotriazole[4], pyridine[5]. However these methods are found to be not rapid in spite of heating and extraction with chloroform are required.

4-Amino-5-mercapto-3-*n*-propyl-1,2,4-triazole[6], 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one[7], 1,3,4,6-tetrahydropyrimidine-2-thione[8] are time consuming in spite of requiring synthesis and also which are water insoluble. Thiosemicarbazide[9], 2-Imidazolidine[10], sodiumsulphite[11], sodium nitrite[12] and sodiummetabisulphite[13] were suffered by interference by various metal ions. Thiourea[14] and 1,10-phenanthroline[15] having the demerits like severe interference by Cu(II) and poor selectivity, respectively. This paper describes the method and advantages of L-cystine as a selective releasing agent.

EXPERIMENTAL

All chemicals used were analytical grade and their solutions being prepared by using double distilled water. Palladium(II) chloride solution was prepared by dissolving 0.1773 g of $PdCl_2$ in minimum volume of dilute KCl solution followed by dilution to known volume and standardised gravimetrically as palladium dimethyl glyoximate[16]. Lead nitrate solution (0.02 M) was standardized by chromate method[17]. 0.02 M solution of EDTA was prepared by dissolving disodium salt of EDTA in distilled water. Xylenol orange indicator was well mixed with KNO_3 in the ratio of 1:100. Solid hexamine was also used directly for maintaining desired pH. Solutions of various ions were also prepared by dissolving calculated amount of salt in distilled water or in diluted acids up to known volume.

To a solution containing 2-34 mg of palladium, an excess of 0.02 M EDTA solution was added and diluted to about 80-100 mL. To this solution hexamethylene tetramine (nearly up to 10 g) is added to bring the pH to 5-6, the surplus EDTA left behind is titrated with lead nitrate solution to the sharp colour change from yellow to red by using xylenol orange indicator. To this solution an excess of 0.02 M L-cystine is added and shaken well and EDTA released is titrated with standard lead

nitrate solution as before. The titre value of second titration is equivalent to palladium(II) present in aliquot. The results are given in the Table-1.

TABLE-1
DETERMINATION OF PALLADIUM IN PALLADIUM (II) CHLORIDE SOLUTION

Palladium (mg)		R.S.D	Relative	Student
Taken	Found	(n = 4)	error (%)	't' value
2.12	2.10	1.211	- 0.94	2.362
4.24	4.20	0.733	-0.94	2.597
6.36	6.31	0.909	-0.78	1.742
8.48	8.41	0.810	-0.82	2.052
16.96	16.87	0.152	-0.53	2.381
25.44	25.36	0.287	-0.31	2.185
29.68	29.57	0.253	-0.37	2.469
33.92	34.87	0.237	-0.15	1.245

Determination of palladium in complexes: Pd(II) with ligands such as thiocarbahydrazide, dimethyl glyoxime and thiophene-2-carboxaldehydethiosemicarbazone were prepared and purified as per the reported methods. A known weight of the complex was carefully decomposed by evaporating to near dryness with aqua regia. The residue was then dissolved in minimum amount of diluted HCl and diluted in volumetric flask. Aliquots of 10 mL were subjected to proposed procedure.

RESULTS AND DISCUSSION

L-Cystine selectively releases EDTA from Pd-EDTA complex at pH 5.0-6.0 EDTA at room temperature. The released palladium forms a soluble (1:2) stable complex with the reagent L-cystine. This fact is confirmed by the quantitative release EDTA from the Pd-EDTA complex due to soft metal ion Pd forms more stable complex with cystine as it is a sulphur containing ligand[18,19]. The precipitate free reaction mixture or soluble complex formation favours the detection of a sharp end point.

Effect of reagent concentration: To determine the amount of reagent required to release EDTA from Pd-EDTA complex quantitatively, titration were carried out with solution containing 4.25 mg of palladium and varying volume of 0.02 M L-cystine solutions. The plot of volume of reagent verses recovery of palladium shows that minimum of 1.2 mL of 0.02 M, L-cystine is required for each mg of Pd. Addition of excess reagent over the required volume has no effects on the experimental results.

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 8.5 mg of Pd(II) are summarized in Table-2. However severe interference of Hg(II) being observed and such an interference of mercury(II) can be obviated by premasking with 5 % alcoholic acetyl acetone (10 mL).

Precision and accuracy: To ascertain the precision and accuracy of the proposed method, determination of palladium in palladium(II) chloride solution, complexes and synthetic alloy composition samples were carried out by following the proposed procedure. Reproducible and accurate results were obtained in the concentration range 2-34 mg of palladium with relative error ≤ 0.94 % and relative standard deviation ≤ 1.21 %

TABLE-2
DETERMINATION OF PALLADIUM IN PRESENCE OF VARIOUS DIVERSE IONS (Pd(II) TAKEN IN SOLUTION IS 8.50 mg)

Diverse ions	Amount added (mg)	Pd found (mg)	Relative error (%)
Al(III)	46	8.42	+0.23
As(V)	34	8.38	-0.23
Ba(II)	66	8.37	-0.35
Bi(III)	40	8.40	0.00
Ca(II)	50	8.43	+0.35
Ce(III)	48	8.36	-0.47
Cd(II)	40	8.42	+0.23
Co(II)	44	8.38	-0.23
Cr(VI)	32	8.44	+0.47
Cu(II)	32	8.39	-0.11
Fe(III)	20	8.45	+0.59
Hg(II)*	10	8.48	+0.95
In(III)	54	8.36	-0.47
Ir(III)	38	8.34	-0.71
Mn(II)	30	8.38	-0.23
Mg(II)	60	8.46	+0.71
Mo(VI)	40	8.41	+0.11
Ni(II)	30	8.44	+0.47
Pb(II)	180	8.40	0.00
Sn(II)	20	8.42	+0.23
Sr(II)	25	8.41	+0.11
Ti(IV)	30	8.38	-0.23
Th(IV)	28	8.37	-0.35
Zr(IV)	40	8.43	+0.35
Acetate	160	8.42	+0.23
Bromide	140	8.38	-0.23
Citrate	130	8.39	-0.11
Chloride	140	8.41	+0.11
Fluoride	160	8.36	-0.47
Nitrate	160	8.42	+0.23
Oxalate	130	8.44	+0.47
Phosphate	170	8.43	+0.35
Sulphate	200	8.39	-0.11

Average of three determination, *using secondary masking agent

Analytical applications: In order to confirm the analytical suitability of the proposed method, it was applied for the analysis of palladium in complexes and in synthetic mixture of metal ions of alloy composition. The results obtained by this method being compared with determination of palladium content in the above mentioned samples analyzed by a reported spectrophotometric method using salicylaldehydethio semicarbazone[20]. The results of analysis of such samples are given in Tables 3 and 4. The experimental results of proposed method are in close agreement with that of reference method[20]. The main merits of the proposed method is that it does not require any stringent condition like heating, readjustment of pH or extraction. The method is also reasonably selective compared to other methods.

Conclusion

The proposed method is simple, rapid and reliable, as it does not require any extraction, readjustment of pH or heating. L-cystine is readily available, pleasant chemical and interference free from many of metal ions and anions, so it is convenient to use. This releasing agent does not form any

TABLE-3
DETERMINATION OF PALLADIUM(II) IN COMPLEXES

Complex	Pd present (%)	Present method			Reference method[20]		
		Pd found (%)	RSD (%) (n = 3)	RE (%)	Pd found (%)	RSD (%) (n = 3)	RE (%)
$Pd(C_4H_7O_2N_2)_2$ [a]	31.61	31.57	0.44	-0.13	31.57	0.48	- 0.19
$Pd(CH_6N_4S)Cl_2$ [b]	27.31	27.38	0.62	+0.26	27.37	0.54	0.22
$Pd(C_6H_7N_3S_2)_2Cl_2$ [c]	19.42	19.37	0.46	-0.26	19.30	0.58	-0.61

a, b, c = Pd complex with dimethyl glyoxime, thiocarbahydrazide, thiophene-2-carboxaldehyde thiosemicarbazone, respectively

TABLE-4
DETERMINATION OF PALLADIUM(II) IN SYNTHETIC MIXTURES WITH ALLOY COMPOSITION

Mixture	Composition	Present method			Reference method[20]		
		Pd found (%)	RSD (%) (n = 3)	RE (%)	Pd found (%)	RSD (%) (n = 3)	RE (%)
Dental alloy							
Pd-Pt-Cu-Zn	15 + 15 + 35 + 35	14.92	0.46	-0.53	15.08	0.60	+0.53
Jewellery alloy							
Pd-Cu	95+05	94.80	0.32	-0.21	94.92	0.32	-0.08

precipitate and unfavourable colour either with lead nitrate or with palladium, which made easy detection of a sharp end point. To summarize, the proposed method offers advantages of simplicity, rapidity and reasonable selectivity over the other reported complexometric methods.

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