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Complexometric determination of palladium(II) using 2-mercapto propionyl glycine as demasking agent

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A simple, rapid and accurate complexometric method for the determination of palladium(II) is proposed, based on the selective demasking property of 2-mercapto propionyl glycine ($MPGH_2$) 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 *p*H 5-5.5 (acetic acid-acetate buffer) with standard zinc sulphate solution using xylenol orange as indicator. An excess of a 0.2% aqueous solution of $MPGH_2$ 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 2-22 mg of palladium with relative error of ±0.36% and coefficient of variation (n=6) not exceeding 0.31%. The effect of diverse ions are studied. The method is used for the determination of palladium in its complexes, catalysts and synthetic alloy mixtures.

A complexometric method for the determination of palladium(II) in the presence of diverse metal ions using selective demasking 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[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 1,10-phenanthroline method[3] does not work for Pd(II) in the presence of common metal ions. Thiourea[4] is free from these limitations. The quantitative release of EDTA by pyridine[5] requires heating of the solution to 60°C for 10 min and the reagent is unpleasant to use because of its smell. Many metals interfere in thiosemicarbazide method[6]. Other reported reagents such as 4-amino-5-mercapto-3-propyl-1,2,4-triazole[7], thiocyanate[8], thiosulphate[9], 4-amino-3-mercapto-1,2,4-triazine(4H)-5-one[10], hydroxylamine hydrochloride[11], N-(2-pyridyl)thiourea[12], DL-methionine[13] and 3-mercapto propane-1,2-diol[14] were found to be reliable besides being convenient. However, some of the reagents require tedious and time-consuming preparation methods.

In this paper, the application of $MPGH_2$ as a selective demasking reagent in the complexometric determina-tion of Pd(II) has been reported.

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Experimental Procedure

All chemicals used were of A.R. or chemically pure grade. Palladium(II) chloride solution was prepared by dissolving $PdCl_2$ in minimum amount of conc. HCl and making up to a known volume with distilled water. The stock solution was standardised gravimetrically as palladium dimethylglyoximate[15]. Zinc sulphate solution (0.01M) was prepared in distilled water and standardised gravimetrically as zinc oxinate[15]. EDTA solution (~ 0.01M) was prepared from the disodium salt by dissolving in distilled water. A freshly prepared 0.2% aqueous solution of 2-mercapto propionyl glycine ($MPGH_2$) (kindly supplied by Santen, Japan) in distilled water was used. A freshly prepared 0.5% aqueous solution of xylenol orange indicator was used.

To an aliquot of solution containing 2-22 mg of palladium(II) and varying amounts of diverse metal ions, an excess of ~0.01M EDTA solution was added and diluted with 20 mL of distilled water. The *p*H of the solution was initially adjusted between 4 and 5 by the dropwise addition of dilute sodium hydroxide solution and finally to 5-5.5 by adding acetic acid-sodium acetate buffer. The uncomplexed EDTA was backtitrated with standard zinc sulphate solution using xylenol orange as indicator to the sharp colour change from yellow to red. To this, a freshly prepared 0.2% solution of $MPGH_2$ was added in required amounts and the contents were mixed well. The liberated EDTA was again titrated with the same standard zinc

sulphate solution as before. The second titre value corresponds to the palladium content in the aliquot.

Analysis of palladium complexes and catalysts

Palladium(II) complexes with salicyloyl hydrazide, thiocarbohydrazide, thiosemicarbazide, thiophene-2-carboxaldehyde thiosemicarbazone, dimethylglyoxime and 1,2,3-benzotriazole were prepared and purified as per the reported methods[16-19]. 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 2 N HCl and made up to a known volume with distilled water. Aliquots of this solution were used for estimation as per the above procedure. A known weight of the catalyst (supplied by MERCK) 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. Aliquots of the solution were used for estimation as per the procedure.

Results and Discussion

Masking property of the reagent

2-Mercapto propionyl glycine is a ligand with three donor sites, namely, sulphur of thiol group, oxygen of carbonyl group and nitrogen of amide group. Therefore, it is expected to behave as a bidentate ligand in general and a tridentate ligand if required. According to HSAB theory[20,21], soft 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 and oxygen of amide group, which results in the formation of a stable five membered chelate. The quantitative release of EDTA from Pd-EDTA complex by $MPGH_2$ indicates that $Pd(MPGH)_2$ 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 $Pd(MPGH)_2$ complex formed is soluble under the experimental conditions and so, the end-point is very sharp.

Effect of reagent concentration

The addition of $MPGH_2$ in the molar ratio 1:2 (M:L) is sufficient for the instantaneous and quantitative release of EDTA from Pd-EDTA complex. However, in all the determinations, a slight excess of $MPGH_2$, over the 1:2 molar ratio was maintained. A large excess of the reagent did not have any adverse effect on the determination.

Table 1—Precision and accuracy in the determination of palldium(II)

Palladium,mg		Recovery	Coefficient of Variation
Taken	Found*	(%)	(%)
1.65	1.65	100.00	0.26
2.75	2.75	100.00	0.31
3.85	3.84	99.74	0.28
5.50	5.52	100.36	0.24
8.25	8.26	100.12	0.21
11.00	11.02	100.18	0.12
16.50	16.51	100.06	0.13
22.00	22.05	100.22	0.14

*Average of six determinations.

Precision and accuracy

In order to check the accuracy and precision of the method, determinations of palladium in the concentration range 2-22 mg were carried out under optimised experimental conditions. These results are presented in Table 1. The results show that the maximum mean error and coefficient of variation (n=6) of the method are 0.36% and 0.31% respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of diverse ions

The effect of various metal ions on the quantitative determination of Pd(II) was studied by estimating 5.50mg of Pd(II) in the presence of different metal ions. No interference was observed for the following ions at the amounts shown in mg: Pb(II) (40 mg), Zn(II) (46), Bi(III) (36), Cd(II) (32), Co(II) (26), Fe(III) (22), Mo(IV) (22), Ni(II) (24), Al(III) (18), Ti(IV) (18), V(V) (18), Ce(III) (20), Rh(III) (8), Ir(III) (8), Pt(IV) (14), Zr(IV) (16), Ru(III) (10) and Mn(II) (5). Metal ions like Tl(III), Hg(II), Cu(II), Sn(IV) and Cr(III) show severe interferences. The interference of Tl(III), Hg(II), Cu(II) and Sn(IV) is attributed to demasking of these metal ions from their respective M-EDTA complexes and thereby releasing EDTA. 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.

Applications

In order to explore the practical applications of the proposed method, it was extended for the determination of palladium in its complexes, catalysts

Table 2—Analysis of palladium complexes and catalysts (n=3)

Complex	Pd Calculated (%)	Pd Found (%)	Relative Error (%)
$Pd(C_7H_8O_2N_2)_2Cl_2$[a]	22.09	21.97	-0.54
$Pd(CH_6N_4S)_2Cl_2$[b]	27.31	27.10	-0.77
$Pd(CH_5N_3S)_2Cl_2$[c]	29.59	29.38	-0.71
$Pd(C_6H_7N_3S_2)_2Cl_2$[d]	19.42	19.44	+0.10
$Pd(C_4H_7O_2N_2)_2$[e]	31.61	31.52	-0.28
$Pd(C_6H_5N_3)_2Cl_2$[f]	25.60	25.44	-0.62
Pd-$CaCO_3$ catalyst	9.94	10.01	+0.70
Pd-charcoal catalyst	10.02	9.98	-0.40

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

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

Mixture	Composition (%)	Pd Found* (%)	Relative Error (%)
Pd(II) + Ni(II)	60.0 + 40.0	59.85	-0.25
Pd(II) + Ru(III)	95.5 + 04.5	95.75	+0.26
Pd(II) + Pt(IV)	50.0 + 50.0	49.75	-0.50
Pd(II) + Co(II)	65.0 + 35.0	65.08	+0.12
Pd(II) + Ni(II) + Co(II)	20.0 + 60.0 + 20.0	20.05	+0.25

and synthetic mixtures of metal ions with compositions of alloy samples. The experimental results pertaining to the analysis of some such samples are presented in Tables 2 and 3, respectively. It is evident from these results that the method can be conveniently employed in the analysis of palladium in its complexes and alloys with fair degree of accuracy.

Conclusion

The proposed method is simple and rapid as it requires no heating for the quantitative release of EDTA. The absence of any precipitate during the titration facilitates an 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 alloys. The proposed procedure does not require any adjustment of *p*H after the addition of the reagent.

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