



4,5-DIMETHYL-2-HYDROXYACETOPHENONE OXIME AS AN ANALYTICAL REAGENT: GRAVIMETRIC ESTIMATION OF PALLADIUM(II), COPPER(II), NICKEL(II), COBALT(II) AND TITANIUM(IV)

4,5-Dimethyl-2-Hydroxyacetophenone oxime is found to be good reagent for the gravimetric estimation of palladium(II), copper(II), nickel(II), cobalt(II) and titanium(IV). By suitable adjustment of pH and using appropriate masking agent, wherever necessary, these metal ions are estimated in the presence of large number of foreign ions. Composition of the complexes is 1:2 (metal:ligand) for Pd(II), Cu(II), Ni(II) and Co(II), and 1:1 (metal:ligand) for Ti(IV) as determined by elemental analyses and by modified continuous variation method.

1 — INTRODUCTION

The survey of literature reveals that 4,5-dimethyl-2-hydroxyacetophenone oxime (DMHAO) has not been used as a gravimetric reagent. During the present studies, DMHAO is successfully employed for the gravimetric determination of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) ions and their separation from one another. Interference due to several foreign ions is also studied.

2 — EXPERIMENTAL

The reagent DMHAO was synthesised as reported earlier [1]. Standard stock solution of metal ions were prepared by dissolving AnalaR grade samples of the corresponding metal salt (palladium chloride, copper sulphate, nickel ammonium sulphate, cobalt chloride and potassium titanyl oxalate). The solution of titanium was prepared by digesting pure potassium titanyl oxalate in concentrated sulphuric acid and then diluted with distilled water. The metal ions were standardised gravimetrically [2] (Nickel and palladium as dimethylglyoximate, Copper as cuprous thiocyanate, Cobalt as anthranilate and Titanium as 5,7-dibromo-8-hydroxyquinolate). The solutions of all the foreign ions were prepared from B.D.H. reagents. Buffers of different pH values were prepared by mixing suitable amounts of $\text{NH}_4\text{Cl-NH}_4\text{OH}$ and $\text{CH}_3\text{COOH-CH}_3\text{COONa}$.

2.1 — PROCEDURE

A known quantity of standard solution of Pd(II), Cu(II), Ni(II), Co(II) or Ti(IV) ion was taken in 400 ml beaker separately, diluted to 150-200 ml. The pH of the solution was adjusted between 2.0-4.5, 2.5-9.0, 5.0-8.5, 8.0-9.0 and 6.5-8.5 for Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) respectively by using suitable buffers. The alcoholic solution of the reagent (1%) was then added to the hot solution ($\sim 70^\circ\text{C}$) with constant stirring (the solution of the reagent was added according to the metal ion taken for example, for ~ 6 mg 5 ml, ~ 10 mg 10 ml and ~ 40 mg 40 ml of the reagent was added. The coloured precipitate (yellow, buff, green, pink and orange of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) complexes respectively) was digested on the water bath for about 30 minutes. The precipitate was filtered through sintered glass crucible G-4,

washed 4-6 times with warm water followed by two washings with aqueous ethanol (20-30 %) and dried to constant weight at 100-120°C in an oven. The conversion factor (metal/metal complex) is 0.2301, 0.1514, 0.1415, 0.1420 and 0.1850 for (Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) ions respectively. The results are reported in Table 1.

Table 1
Gravimetric Estimation of Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV)

Metal taken (mg)	Precipitate (mg)	Metal found (mg)	Error (%)
<i>Pd(II)</i> (pH 2.4—4.5; 3.0*; C.F. 0.2301)			
6.00	26.2	6.02	+0.32
10.00	43.6	10.03	+0.30
20.00	86.8	19.97	-0.15
30.00	131.0	30.14	+0.50
40.00	174.2	40.08	+0.20
<i>Cu(II)</i> (pH 2.5—9.0; 3.0*; C.F. 0.1514)			
6.35	42.2	6.39	+0.60
9.53	63.0	9.54	+0.10
19.06	126.2	19.11	+0.30
25.40	167.6	25.37	-0.10
31.80	211.4	31.85	+0.10
<i>Ni(II)</i> (pH 5.0—8.5; 6.0*; C.F. 0.1415)			
5.85	41.2	5.83	-0.30
11.70	82.6	11.69	-0.10
23.40	165.6	23.43	+0.15
31.20	220.6	31.21	+0.03
46.80	331.4	46.89	+0.20
<i>Co(II)</i> (pH 8.0—9.0; 8.5*; C.F. 0.1420)			
7.32	51.8	7.36	+0.60
14.64	103.8	14.74	+0.60
21.96	155.4	22.07	+0.50
29.28	206.0	29.25	-0.10
36.60	259.4	36.84	+0.60
<i>Ti(IV)</i> (pH 6.5—8.5; 7.0*; C.F. 0.1850)			
6.03	32.4	5.99	-0.60
14.07	75.8	14.02	-0.40
18.09	97.8	18.09	±0.00
24.12	130.8	24.20	+0.30
32.16	174.0	32.19	+0.10
* pH for Estimation C.F. Conversion Factor			

2.1.1 — DETERMINATION OF METAL IONS IN A MIXTURE

There is a marked difference in the pH value for precipitation of these cations. Hence this property was used for the precipitation of the two metal ions in the same solution. The different mixtures of Cu(II)/Pd(II) and Ni(II), Co(II) or Ti(IV) were prepared. The Cu(II) or Pd(II) was precipitated first at pH 2.5 or 3.0 respectively and from the filtrate Ni(II), Co(II) or Ti(IV) was precipitated by the addition of more reagent and adjusting the pH at 6.0, 8.0 or 6.5 respectively as above. The values obtained are well within the experimental error. Generally 0.5 % error is exempted in gravimetric estimations, which is written here as experimental error.

3 — INTERFERENCE

Interference due to foreign ions in the estimation of these metal ions with DMHAO was studied. The procedure followed was the same as in the absence of foreign ions with some modifications.

In the case of palladium(II), the interference due to Cu(II) and Fe(II) was removed by using EDTA and tartaric acid (about four-six times excess w.r.t. metal ion conc. of the masking agent was added) respectively. Excess (10-15 times) of cations like, Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Mn(II), Bi(III), Sb(III), As(III), Mo(VI), U(VI) and sufficiently large excess of anions like, Cl^- , Br^- , I^- , NO_2^- , NO_3^- , $\text{C}_2\text{O}_4^{2-}$, SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-} , citrate and tartrate do not interfere at pH 2.5. In the case of copper(II), the interference of the foreign ions was removed by suitable adjustment of the pH. Excess of the cations (10-15 times) such as Fe(II), Fe(III), Bi(III), Sb(III), As(III) at pH 3.0, Ni(II), Co(II) at pH 3.5 and Zn(II), Cd(II), Hg(II), Mn(II), Mg(II), W(VI), Mo(VI) and U(VI) at pH 4.0 and sufficiently large excess (about 100 times) of several anions Cl^- , Br^- , I^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , BO_3^{3-} , PO_4^{3-} , citrate and tartrate could be tolerated at pH 4.0.

In the estimation of nickel(II), the interfering ions Fe(III), Sb(III), Bi(III) were masked by adding tartaric acid. In some cases the interference was removed by changing the pH of the mixed solution e.g. Zn(II), Mn(II) (at pH 5.5); Cd(II), Hg(II), Mg(II), W(VI), Mo(VI), U(VI) (at pH 6.0) and sufficiently large excess of anions such as Cl^- , Br^- , I^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , PO_4^{3-} , BO_3^{3-} , citrate and tartrate (at pH 6.0).

In the case of cobalt(II) and titanium(IV) the cations such as Zn(II), Mn(II), Mg(II), Cd(II), Mo(VI), U(VI), W(VI) (5-7 times) and excess of the anions as Cl^- , Br^- , I^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , PO_4^{3-} , citrate and tartrate do not interfere in the determination of cobalt(II) at pH 8.0 and titanium(IV) at pH 6.5.

4 — DETERMINATION OF METAL IONS IN ALLOYS

Copper was successfully estimated in the alloys like brass (Cu 61.24 %, Zn 38.76 %), (Cu 70.8 %, Zn 24.2 %, Sn 1.85 %, Pb 2.52 %, Fe 0.31 %, P 0.61 %, Mn 0.12 %, Ni 0.17 %); bronze (Cu 87.32 %, Sn

estimated at 3.0 followed by nickel after raising the pH of the filtrate to 6.0-8.0.

5 — COMPOSITION OF THE COMPLEXES

The complexes were analysed for nitrogen (estimated by the micro Dumas method) and metal (estimated as given above). The analyses of the complexes show 1:2 (metal:ligand) composition in case of Pd(II), Cu(II), Ni(II) and Co(II); and 1:1 (metal:ligand) for Ti(IV) (Table 2). The composition of the complexes as determined by modified continuous variation method [3] is also 1:2 for the metal ions under study except Ti(IV) of which composition is 1:1.

Table 2
Characteristics and Elemental Analyses of DMHAO and its Metal Complexes

Compound	Colour of the ppt.	Dec. Temp. (°C)	Analyses (%)			
			N		Metal	
			Found	Cald.	Found	Cald.
DMHAO	Light yellow	—	7.86	7.82	—	—
PdL ₂	Yellow	280	6.00	6.05	23.03	23.01
CuL ₂	Buff	240	6.71	6.67	15.10	15.14
NiL ₂	Green	280	6.72	6.78	14.20	14.15
CoL ₂	Pink	200	6.72	6.75	14.16	14.20
TiO(OH)L	Orange	200	5.35	5.40	18.53	18.50
DMHAO = C ₁₀ H ₁₃ NO ₂ ; L = C ₁₀ H ₁₂ NO ₂						

8.46 %, Pb 1.98 %, Zn 1.2 %) and white metal (Cu 4.2 %, Sb 9.3 %, Pb 2.25 %, Sn 84.25 %). About 0.5 gm of the alloy was dissolved in concentrated nitric acid, digested on a water bath for one hour and evaporated to dryness and treated with water. If the sample contained tin, metastannic acid was filtered off and washed with dilute nitric acid. The filtrate and washings were collected and made up to 250 ml. 10 ml of this solution was used to determine the copper content at pH 4.0. The results are in good agreement with the reported values.

Nickel was also successfully estimated in german silver (Cu 64.3 %, Ni 25.2 %, Zn 9.2 %, Mn 0.2 %) and cupro nickel tubing (Cu 68.16 %, Ni 30.45 %, Fe 0.12 %). The solution of about 0.5 gm of the alloy was prepared as above in concentrated nitric acid. Tartaric acid was added in case the sample contained iron, 10-15 ml of this solution was used for the determination of nickel, copper was first

6 — ACCURACY OF THE ESTIMATION

The analytical data in Table 1, indicate that ligand can be effectively used as a promising gravimetric reagent for the Pd(II), Cu(II), Ni(II), Co(II) and Ti(IV) in macro and semi micro quantities. It is easy to isolate the precipitate and bring it to constant weight within a period of half an hour. The precision was fair and the accuracy was within the permissible limits (*i.e.* 0.5 %).

7 — THERMAL STABILITY

The metal complexes of DMHAO under study are thermally more stable than those of salicylaldoxime [4,5] nioxime [4,5], 2-hydroxy-5-methylpropionophenone oxime [6] (Table 3). These metal complexes are less soluble in common organic solvents. This may be due to the introduction of two methyl groups (electron releasing) at the position 4 and 5 in the benzene ring which tends to increase the above properties.

Table 3

Ligand	Decomposition Temp. (°C)		
	Pd(II)	Cu(II)	Ni(II)
DMHAO	280	240	280
Salicylaldoxime	197	170	240
Nioxime	170	130	240
2-Hydroxy-5-methylpropiophenone oxime	220	220	270

Therefore it is concluded that DMHAO is a better gravimetric reagent than other *o*-hydroxy- aldoximes or ketoximes.

REFERENCES

- [1] M. MITTAL, K. LAL, S.P. GUPTA, *N M L Tech. J.*, **21**, 37 (1979); *J. Indian Chem. Soc.*, **57**, 46 (1980).
- [2] A.I. VOGEL, «A Text Book of Quantitative Inorganic Analysis» Longmans Green & Co., London (1971).
- [3] J. FENGER, K.E. SIEKIESKA, B.S. JENSEN, *J. Inorg. Nucl. Chem.*, **33**, 4366 (1971).
- [4] G. LIPTAY, E.P. MOLNAR, K. BURGER, *J. Inorg. Nucl. Chem.*, **31**, 247 (1969).
- [5] C. DUVAL, «Inorganic Thermogravimetric Analysis» Elsevier, London (1953).
- [6] S. PRAKASH, Ph. D. Thesis, Delhi University, Delhi (1969).

ABSTRACT

4,5-Dimetil-2-hidroxiacetofenona é estudada como reagente para doseamento gravimétrico de Pd(II), Cu(II), Ni(II), Co(II) e Ti(IV).

Mediante uma escolha adequada de pH e agentes sequestrantes estes iões metálicos podem ser doseados sem interferência de outros iões.

A composição dos complexos é 1:2 (metal:ligando) para Pd(II), Cu(II), Ni(II) e Co(II). e 1:1 para Ti(IV) o que é verificado por análise elemental e pelo método das variações contínuas.