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ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (4): 1921-1928

(International Peer Reviewed Journal)

Thermal Decomposition of 8-Hydroxyquinoline Complexes with Ca, Ni, Zn, Pb, Fe, La, Ti and W

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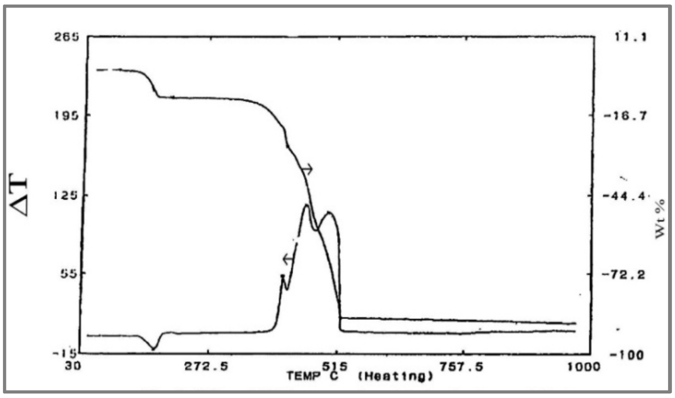
Accepted on 29th May, 2019

ABSTRACT

8-Hydroxyquinoline forms complexes with more than forty metal ions. Present study is concerned with preparation and thermal decomposition of 8-Hydroxyquinoline complexes with Ca, Ni, Zn, Pb, Fe, La, Ti and W using Thermo gravimetric and Differential thermal analysis techniques. The study established temperature regions useful for possible gravimetric determinations of Ca, Ni, Zn, Pb and W either as corresponding 8-Hydoxyquinolines or as oxides.La can be determined either as 8-Hydoxyquinoline complex of La, or as $La_2O_3CO_2$ *whileTi cannot be determined as 8-Hydoxyquinoline complex but can be determined as* TiO_2*only.*

Graphical Abstract



TG and DTA cures fro nickel oxinate precipitate.

Keywords: 8-Hydroxyquinoline, Metal oxinates, Thermal decomposition.

INTRODUCTION

Binary, ternary and quaternary metal oxides have become extremely important in various fields of technological relevance namely semiconductors, ferroelectrics, magnetic materials, super conductors, fast ion conductors, phosphors, optoelectronics and heterogeneous photo catalysis. Preparation of simple and mixed metaloxides have been reported in terms of several synthesis methods such as solid-state reactions [1], solid-state metathesis [2], precipitation [3], thermal decomposition of complex precursors [4], sol-gel [5], hydrothermal [6], microwave [7], spraypyrolysis [8] and self propagation [9]. Thermal decomposition of metal carbonates, hydroxides, oxalates, citrates and tartrates has been reported to yield nano metal oxide particles [10]. Nevertheless, as compared to studies on metal hydroxides, oxalates, citrates and tartrates, reports on thermal decomposition ofmetal8-Hydroxy quinoline complexes are relatively less.8-hydroxyquinoline, a bi dentate chelating ligand also known as oxine is very interesting because of its diverse bioactivities, therapeutic potentials, and preservating efficiency in textile, wood & paper industries and fungicidal ability in agriculture [11]. Several metal ions form sparingly soluble derivatives with 8-hydroxyquinoline at room temperature with general formula $M(C_9H_6ON)_n$ where n is the valence of the metal M. Early studies on synthesis and stoichiometry of some metal oxinate complexes and their associated stabilities were due to thermo gravimetric studies of Borrel and Paris[12-14] and differential thermal analysis studies of Wendlandt [15-16] and, Gore and Wendlandt [17]. Subsequently, PartliKokkonese *et al.*, [18] reported thermal decomposition of oxine complexes with Al, Co, Mn and Ni. Nag Pure et al[19] reported synthesis, thermal and spectroscopic characterization of Ca oxinate organic phosphor. Long Liu and coworkers [20] investigated preparation of Co and Ni complexes of oxine with nanobelt structure via one step, low heating solid- state reactions. Mehmood and co workers [21]studied surface layer by layer chemical deposition for thin film formation of nano sized metal oxinate complexes of Fe, Co, Ni, Cu and Zn. Patel and coworkers [22] reported synthesis, spectroscopic characterization and thermal studies of some divalent transition metal complexes of oxine. Marisa Crespi *et al.*, [23] reported preparation and thermal decomposition of Cu, Zn, and Cd chelates with oxine. Gravimetric determinations of Al [24], trace amounts of Cd in micellar medium [25] Mg and W [26] have also been reported. Present paper describes synthesis and thermal decomposition studies relatingto8-Hydroxyquinoline complexes of Ca, Ni, Zn, Pb, Fe, La, Ti and W precipitated under specified conditions of pH, using thermo gravimetric and differential thermal analysis techniques.

MATERIALS AND METHODS

Materials: Calcium chloride, Nickel sulphate, Zinc sulphate, Ferricnitrate, Lead nitrate, Lanthanum nitrate, Potassiumtitanyloxalate, sodiumtungstate and 8-hydroxyquinoline of AR grade Merck/BDH/Sd-fine Chemicals were used.

Oxine reagent: 0.2 moxine reagent was prepared by dissolving 2.9032 gm of 8-hydroxyquinolinein 1000 mL of 2N acetic acid and 1:1 ammonia solution was added dropwise until turbidity begins to form. This was cleared by the addition of a little amount of acetic acid and the solution was stored in an amber colored bottle.

Oxinates of Ca, Ni, Zn, Pb, Fe, La, Ti and W: Metal complexes were prepared by the reaction between aqueous solutions of metal ions with excess acetic acid solution of oxine at respective pH values as specified in Vogel (26). To 20ml of 0.1M solution of metal ion suitable amount of oxine

Table1. Experimental conditions used for synthesis of metal/mixed metal oxinates

Volume of 0.1M metal ion solution taken	Volume of 0.2M Oxine reagent added mL	pH maintained	Precipitate obtained
20 mL of Ca^{2+}	30	9.4	$Ca\ (C_9H_6ON)_2\ xH_2O$
20 mL of Ni^{2+}	30	5.0	$Ni\ (C_9H_6ON)_{2.}\ xH_2O$
20 mL of Zn^{2+}	30	5.0	$Zn\ (C_9H_6ON)_{2.}\ xH_2O$
20 mL of Pb^{2+}	30	9.4	$Pb\ (C_9H_6ON)_2$
20 mL of Fe^{3+}	100	4.6	$Fe\ (C_9H_6ON)_3$
20 mL of La^{3+}	100	4.6	$La\ (C_9H_6ON)_3$
20 mL of TiO^{2+}	60	5.4	$TiO\ (C_9H_6ON)_{2.}\ xH_2O$
20 mL of WO_2^{2+}	60	5.4	$WO_2\ (C_9H_6ON)_2$

reagent was added slowly while stirring until yellow / orange yellow color appears in the supernatant liquid. The precipitate was digested for 2 h, at a temperature not exceeding 70°C after adjusting the required pH. The precipitate was filtered through Whatman-42 filter paper and washed with water adjusted to the same pH used for precipitation and dried at room temperature. Amounts of metal ions taken, oxine reagent added and pH maintained for precipitation of different metal ions are given in the table1. Phase identifications of residues obtained after suitable heat treatment of respective precipitates of Ca, Ni, Zn, Pb, Fe and Ti were carried out by X-ray diffraction technique using Ni filtered Cu K_α radiation with four degrees per minute scanning rate.XRD patterns of heat treated residues Ca, Ni, Zn, Pb, Fe, Ti, and W oxinates indicated to resultant solids as corresponding oxides.

RESULTS AND DISCUSSION

Thermogravimetric (TG) and Differential thermal analysis (DTA) curves for oxinates of Ca, Ni, Zn, Pb, Fe, La, Ti and W in the temperature range of 30-950°C are shown in figures 1to 9. Figure 1 shows TG and DTA curves for calcium oxinate precipitate. TG curve indicates three weight losses which can be ascribed to the following dehydration and decomposition reactions based on the corresponding weight losses observed.

$$Ca(C_9H_6ON)_2\ 2H_2O \rightarrow Ca(C_9H_6ON)_2 + 2H_2O \qquad \ldots 1(a)$$

$$Ca\ (C_9H_6ON)_2 + 11O_2 \rightarrow CaCO_3 + 2NH_3 + 3H_2O + 16CO + CO_2 \qquad \ldots 1(b)$$

$$Ca\ CO3 \rightarrow CaO + CO_2 \qquad \ldots 1(c)$$

Formation of CaO starts at 825°C. Theoretical and experimental weight losses for the above reactions as shown in the table 2 are in good agreement. DTA curve shows one endothermic and two exothermic peaks which lie in the three weight loss regions of TG curve respectively. Endothermic peak is due to dehydration while exothermic peaks are due to decomposition. Figure 2 shows TG and DTA curves for Ni-oxinate precipitate. TG curve indicates two weight losses during 50 to 150 and 300 to 520°C. Based on the experimental weight losses observed, the first loss is assigned to dehydration while the second loss is ascribed to decomposition leadingto formation of NiO as shown below.

$$Ni\ (C_9H_6ON)_2 3H_2O \rightarrow Ni\ (C_9H_6ON)_2 + 3H_2O \qquad \ldots 2(a)$$

$$Ni(C_9H_6ON)_2 + 11O_2 \rightarrow NiO + 2NH_3 + 3H_2O + 16CO + 2CO_2 \qquad \ldots 2(b)$$

Table 2. Theoretical and experimental weight losses for thermal decomposition reactions of different metaloxinates studied

S.No.	Reaction	%Weight loss	
		Theoretical	Experimental
1	$Ca\ (C_9H_6ON)_2\ 2H_2O \rightarrow Ca\ (C_9H_6ON)_2$	9.89	11.0
2	$Ca\ (C_9H_6ON)_2\ 2H_2O \rightarrow CaCO_3$	73.5	74.8
3	$Ca\ (C_9H_6ON)_2\ 2H_2O \rightarrow CaO$	84.6	87.0
4	$Ni\ (C_9H_6ON)_2\ 3H_2O \rightarrow Ni\ (C_9H_6ON)_2$	13.5	14.0
5	$Ni\ (C_9H_6ON)_2\ 3H_2O \rightarrow NiO$	81.4	80.9
6	$Zn\ (C_9H_6ON)_2\ 2H_2O \rightarrow Zn\ (C_9H_6ON)_2$	9.24	9.3
7	$Zn\ (C_9H_6ON)_2\ 2H_2O \rightarrow ZnO$	79.1	81.5
8	$Pb\ (C_9H_6ON)_2 \rightarrow PbO$	54.9	54.4
9	$2Fe\ (C_9H_6ON)_3 \rightarrow Fe_2O_3$	81.7	83.7
10	$TiO\ (C_9H_6ON)_2\ 2H_2O \rightarrow TiO_2$	79.4	82.0
11	$La\ (C_9H_6ON)_3 \rightarrow La_2O_3CO_2$	67.6	68.0
12	$WO_2\ (C_9H_6ON)_2 \rightarrow WO_2C_2O_4CO_2$	31.0	31.0
13	$WO_2\ (C_9H_6ON)_2 \rightarrow WO_3$	53.9	55.0

Corresponding theoretical and experimental weight losses for the above reactions are in good agreement as shown in table 2. TG and DTA curves of zinc oxinate precipitate shown in figure 3 indicate that the hydrated sample is stable upto115°C and thereafter looses water. Dehydrated sample is stable upto320°C above which it undergoes weight loss up to 620°C. Plateau between 630 to 950°C corresponds to formation of ZnO. Theoretical and experimental weight losses corresponding to the following dehydration and decomposition reactions of Zinc oxinate are given in table 2.

$$Zn\,(C_9H_6ON)_2 2H_2O \rightarrow Zn\,(C_9H_6ON)_2 + 2H_2O \quad \ldots 3(a)$$

$$Zn\,(C_9H_6ON)_2 + 11O_2 \rightarrow ZnO + 2NH_3 + 3H_2O + 16CO + 2CO_2 \quad \ldots 3(b)$$

DTA curve shows two endothermic peaks and one exothermic peak at temperatures which overlap with weight loss regions in TG curve. First endothermic peak is due to dehydration while the remaining two peaks are due to decomposition as they fall within weight loss regions of TG curve.

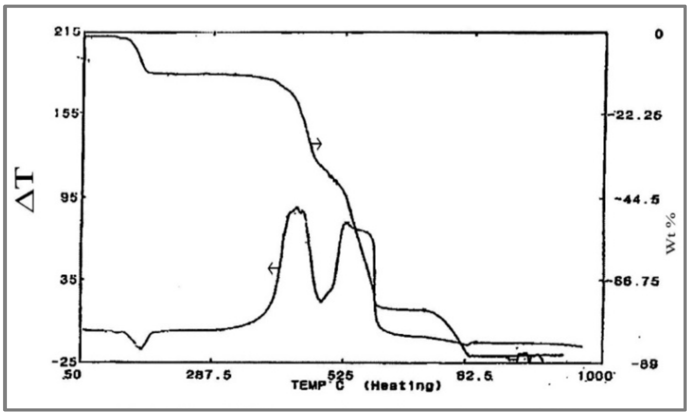


Figure 1. TG and DTA cures for calcium oxinate precipitate.

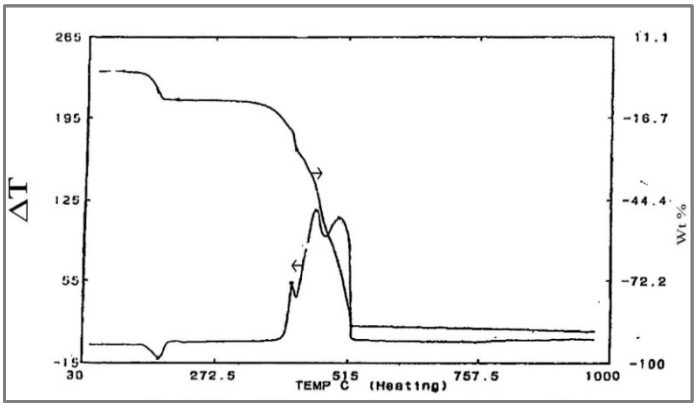


Figure 2. TG and DTA cures fro nickel oxinate precipitate.

Figure 4 depicts TG and DTA curves for lead oxinate precipitate. As seen from TG curve, lead oxinate is stable up to 250°C and undergoes decomposition from 250–625°C leading to formation of PbO. The net reaction is given below:

$$Pb(C_9H_6ON)_2 + 11O_2 \rightarrow PbO + 2NH_3 + 3H_2O + 16CO + 2CO_2 \quad ---4$$

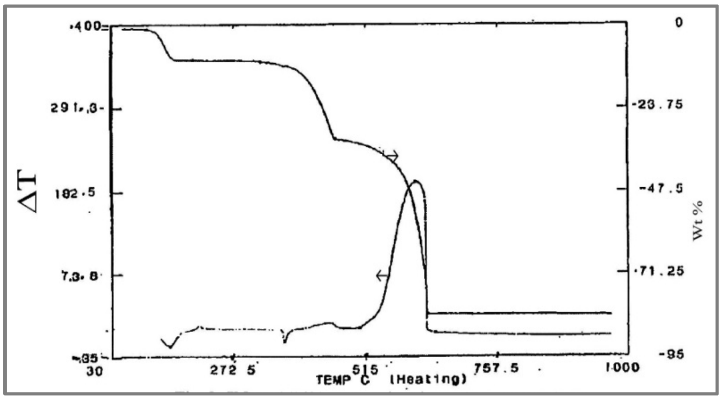


Figure 3. TG and DTA curves for zinc oxinate precipitate.

Theoretical and experimental weight losses for the above reaction shown in table 2 are in good agreement. DTA curve shows peaks within the weight loss regions observed in TG curve.

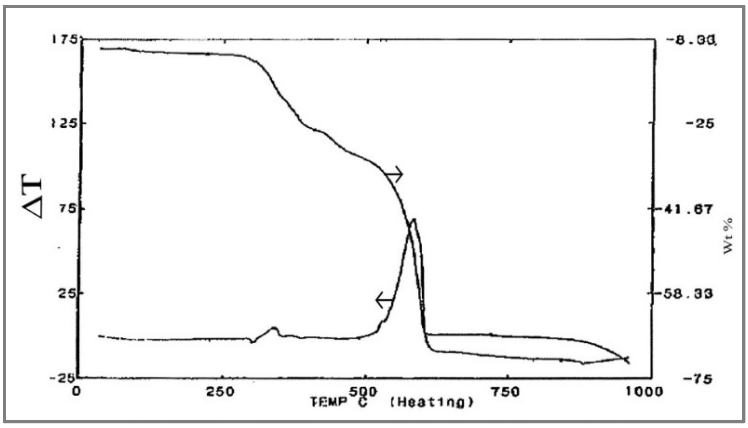


Figure 4. TG and DTA cures for lead oxinate precipitate.

Figure 5 shows TG and DTA curves for iron oxinate precipitate. From the figure, it is apparent that iron oxinate is stable between 50–250°C and thereafter slowly undergoes thermal decomposition up to 520°C followed by no significant weight change up to 950°C. Observed weight loss can be assigned to the following reaction:

$$2Fe(C_9H_6ON)_3 + 32O_2 \rightarrow Fe_2O_3 + 6NH_3 + 9H_2O + 50CO + 4CO_2 \qquad \ldots 5$$

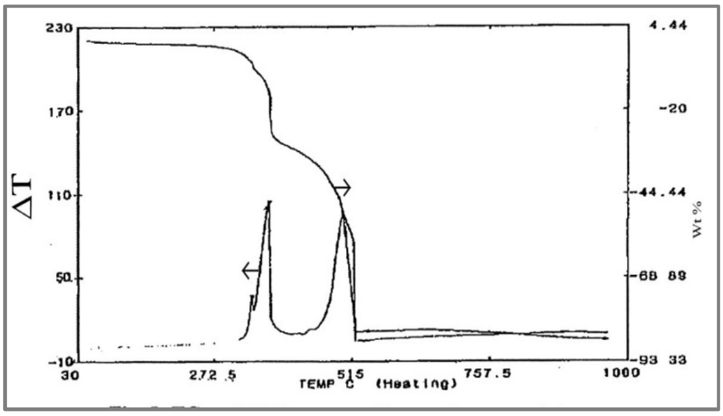


Figure 5. TG and DTA cures of iron oxinate precipitate.

Theoretical and experimental weight losses for the above reaction shown in table 2 are in good agreement.DTA curve shows two exothermic peaks in the temperature region of 250-520°C which coincides with the weight loss region in TG curveand hence both peaks are ascribed to decomposition. Figure 6 shows TG and DTA curves for Ti-oxinate precipitate. From the TG curve, it may be noted that Ti–oxinatelooses weight from50°C up to 600°C. Absence of clear plateau indicates no intermediate formation. Based on the experimental weight loss observed, the decomposition may be assigned to the following reaction:

$$TiO(C_9H_6ON)_2\ 2H_2O + 11O_2 \rightarrow TiO_2 + 2NH_3 + 5H_2O + 16CO + 2CO_2 \qquad \ldots 6$$

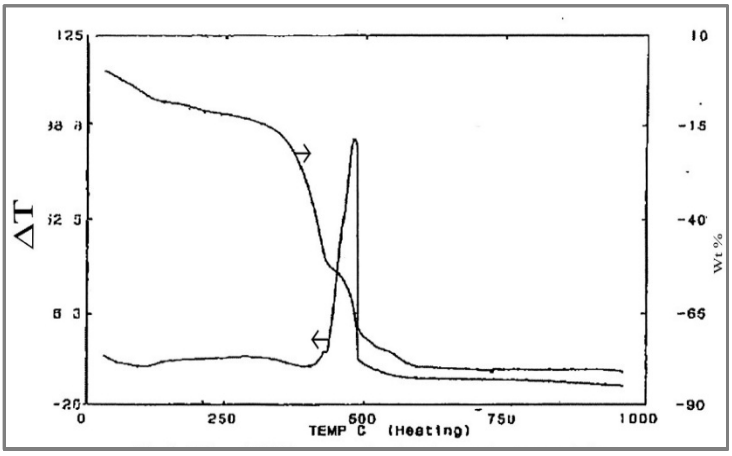


Figure 6. TG and DTA cures for titanium oxinate precipitate.

DTA curve shows one broad endothermic peak around 100^{o}C and a sharp exothermic peak in the temperature range between 450-500°C and since both peaks lie within the weight loss region they can be ascribed to thermal decomposition of Fe-oxinate. Figure 7 shows TG and DTA curves for La-oxinate precipitate. From the TG curve it can be seen that La-oxinate is stable upto 350°C and above this temperature weight loss is observed up to 750°C. Based on the weight loss observed, the decomposition may be represented by the reaction given below following the report of $La_2O_3CO_2$ by Duval [27].

$$2La(C_9H_6ON)_3 + 31O_2 \text{--->} La_2O_3CO_2 + 6NH_3 + 9H_2O + 52CO + CO_2 \qquad \ldots 7$$

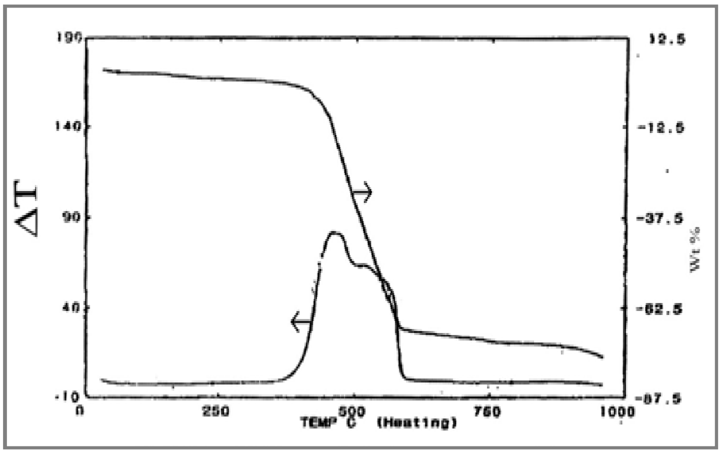


Figure 7. TG and DTA curves for lanthanum oxinate precipitate.

Theoretical and experimental weight losses correspondingto the above reaction shown in table 2 are in good agreement. DTA curve shows the decomposition is exothermic in nature. Figure 8 denotes TG and DTA curves for W oxinate precipitate. From TG curve it can be seen that W-oxinate is stable upto 250°C and forms an intermediate around 400°C. This further disassociates to give a stable compound from 600°C onwards. Based on the experimental weight losses observed, the following reactions are proposed.

$$WO_2(C_9H_6ON)_2 + 12O_2 \rightarrow WO_2C_2O_4CO_2 + 2NH_3 + 3H_2O + 13CO + 2CO_2 \quad \ldots 8(a)$$

$$WO_2(C_9H_6ON)_2 + 12O_2 \rightarrow WO_3 + 2NH_3 + 3H_2O + 14CO + 4CO_2 \quad \ldots 8(b)$$

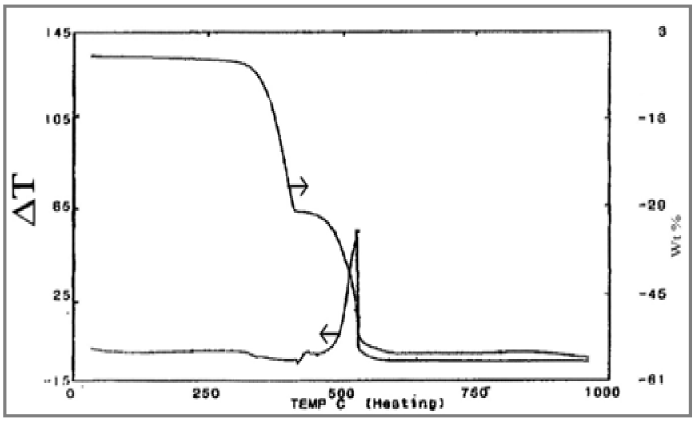


Figure 8. TG and DTA curves for tungsten oxinate precipitate.

DTA curve of this compound denotes one broad endothermic peak immediately followed by a sharp exothermic peak. Since both of them fall in the weight loss region of TG curve, these peaks are attributed to the above decomposition reactions. The above study concludes that besides earlier literature reports (2.2) for gravimetric determination of Al and W only as metal oxinates with drying temperatures confined to narrow temperature regions of 100 to 110°C, quantitative determinations of other metal ions like Ca, Ni, Zn, Pb, Fe, La, Ti and W can also be performed with oxine by heat treating the corresponding metal oxinates to yield stable residues of fixed compositions as per respective thermal decomposition temperatures indicated below.

Ca as CaO between 850-950°C or as Ca $(C_9H_6ON)_2$ between 150-250°C

Ni as NiO between 550-950°C or as $Ni(C_9H_6ON)_2$ between 150-300°C

Zn as ZnO between 650-950°C or as $Zn(C_9H_6ON)_2$ between 100-110°C

Pb as PbO between 600-650°C or as $Pb(C_9H_6ON)_2$ between 50-200°C

Fe as Fe_2O_3 between 650-950°C or as Fe $(C_9H_6ON)_3$ between 100-250°C

La as La $(C_9H_6ON)_3$ between 100-250°C or as $La_2O_3CO_2$ between 700-850°C

Ti as TiO_2 between 650-950°C

W as WO_3 between 600-900°C or as $WO_2(C_9H_6ON)_2$ between 100-300°C

APPLICATION

The study established suitable heat treatment temperatures for quantitative determinations of the given metal ions.

CONCLUSION

Thermal decompositions of 8-hydroxyquinoline complexes with Ca, Ni, Zn, Pb, Ca, Fe, La, Ti and W have been studied. From the corresponding TG and DTA curves it is observed that Fe, W and Ni complexes form oxides at 500°C while Zn, Pb and Ti complexes form oxides at 600°C and 8-hydroxyquinoline complex of Ca yields Cao at 850°C. The study established suitable heat treatment temperatures for quantitative determinations of the above metal ions. Ca, Ni, Zn, Pb, Fe and W can be quantitatively determined either as respective metal 8-hydroxyquinoline complexes or as corresponding oxides, while Ti can be determined only as TiO_2, and La can be determined either as La 8-hydroxyquinoline or as $La_2O_3CO_2$ and not as La_2O_3.

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