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SUMMARY

A thermometric method is presented for the redox titration of uranium(IV) with dichromate. The investigation was made primarily to determine the applicability of the thermometric method to redox titrations in solutions that contain ions deleterious to electrodes used in electrometric methods. A relative standard error of ±1% is attainable in the titration of quantities of uranium(IV) of the order of 5 mg. Less than 15 min is required to complete a titration. Fluoride ion can be tolerated in the solution provided that sufficient aluminum(III) is added to complex all the fluoride.

RÉSUMÉ

Une méthode thermométrique est proposée pour le titrage redox de l'uranium(IV) au moyen de dichromate. En présence d'ion fluorure, il est nécessaire d'ajouter de l'aluminium(III) en quantité suffisante pour le complexer totalement.

ZUSAMMENFASSUNG

Es wird eine thermometrische Methode zur Redox-Titration von Uran(IV) mit Dichromat beschrieben. Fluor-Ionen stören nicht, wenn sie durch Zugabe einer genügend grossen Menge von Aluminium(III) in die Komplexverbindung übergeführt werden.

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THERMAL DECOMPOSITION OF SOME RARE EARTH METAL CUPFERRATES AND NEOCUPFERRATES

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Cupferron (ammonium salt of *N*-nitrosophenylhydroxylamine) and neocupferron (ammonium salt of *N*-nitrosonaphthylhydroxylamine) have been proposed as organic precipitants for the gravimetric determination of the lighter rare earth elements[1]. Previous thermobalance studies have shown that reagent is coprecipitated with the metal cupferrates, making it necessary to ignite and weigh as the metal oxides[2]. The metal neocupferrates required the same procedure[3].

As was anticipated, the heavier rare earth ions, those from europium to ytterbium, are also precipitated by these reagents. With the objective in mind that these two

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reagents may prove useful as analytical precipitants for the heavier rare earth metal ions, the metal cupferrates and neocupferrates were prepared and subjected to thermal decomposition on the thermobalance. Such information, as with the lighter rare earth metal chelates, is needed in order to determine the weighing form of the precipitates.

EXPERIMENTAL

Reagents

Cupferron and neocupferron were obtained from the Matheson, Coleman, and Bell Co., East Rutherford, N. J. They were used without further purification.

The rare earth samples were obtained as the oxides of 99.9% purity from Research Lab., Inc., Newtown, Ohio. The purity was that listed by the supplier.

All other reagents were of analytical reagent-grade quality.

Thermobalance

An automatic recording thermobalance which has previously been described was used[4]. The sample sizes ranged in weight from 60 to 90 mg and were run in duplicate or triplicate. A linear heating rate of 5.4° was used on all of the samples. During the pyrolysis of the samples, a slow stream of air was passed through the furnace to remove the decomposition products.

Preparation of chelates

The rare earth metal cupferrates and neocupferrates were prepared by the same general procedure as previously described[1]. The precipitates were air dried at room temperature for 24 h before being pyrolyzed on the thermobalance.

DISCUSSION

The thermograms of the rare earth metal cupferrates and neocupferrates are given in Figs. 1 and 2 with the composition data given in Table I.

Europium cupferrate

(Fig. 1F) The compound began to lose weight slowly beginning at 85°. At 150° the first break, but not a horizontal weight level, was found in the curve, followed by a very rapid weight loss above 170°. A second break in the curve was observed at 265° followed by further weight loss above 320°. An almost horizontal weight level was then found beginning at 415°, resulting in the formation of the oxide level, Eu_2O_3, at 570°.

TABLE I

COMPOSITION DATA FOR RARE EARTH CUPFERRATES AND NEOCUPFERRATES

Rare earth	*% Metal oxide*			
	Cupferrate		*Neocupferrate*	
	Theoretical	*Found*	*Theoretical*	*Found*
Europium	31.24	31.4	24.66	24.0
		31.9		24.0
Terbium	32.78	32.8	25.94	25.2
		32.6		25.3
Dysprosium	32.49	32.3	25.75	26.4
		32.6		26.6
Holmium	32.78	29.6	26.00	24.9
		29.6		24.9
Erbium	33.04	28.8	26.24	25.8
		28.4		25.8
Ytterbium	32.71	33.4	26.82	24.8
		33.1		24.8

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Terbium cupferrate

(Fig. 1E) From the composition data, the air-dried chelate corresponded exactly to that expected for $TbCup_3$; where Cup is the cupferron ion. The first weight loss began at 85°, slowly at first, but becoming very rapid above 205°. A break in the curve was observed at 265° with further weight loss above 325°, resulting in the Tb_4O_7 level at 540°.

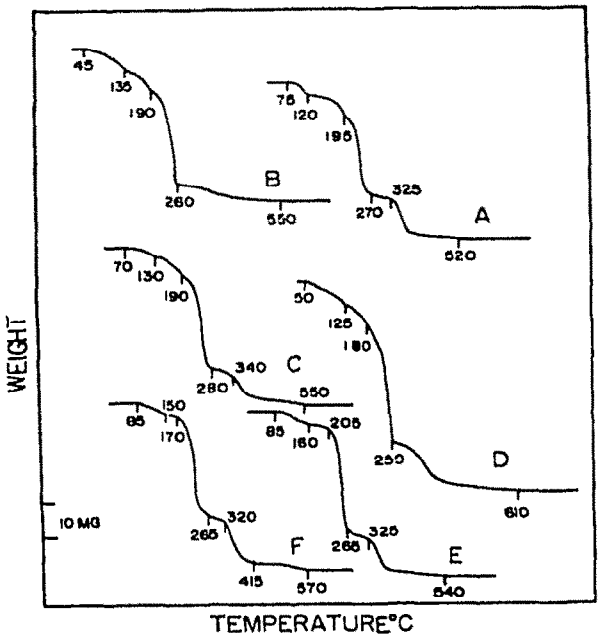

Fig. 1. Thermograms of the metal cupferrates. A. ytterbium, B. erbium, C. dysprosium, D. holmium, E. terbium, F. europium.

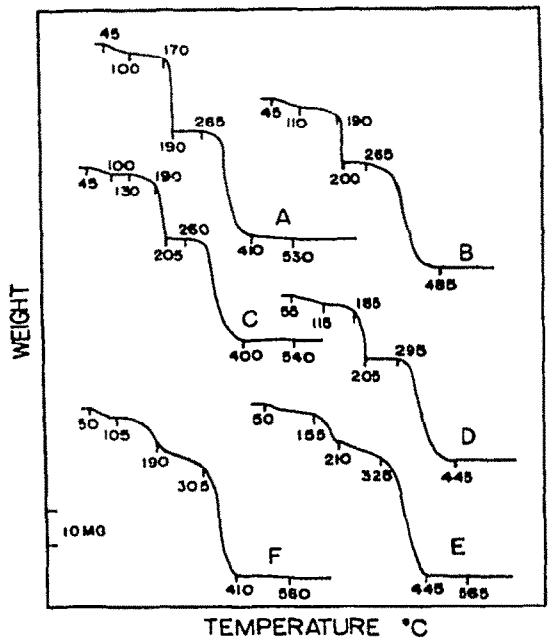

Fig. 2. Thermograms of the metal neocupferrates. A. erbium, B. ytterbium, C. dysprosium, D. holmium, E. terbium, F. europium.

Dysprosium cupferrate

(Fig. 1C) The composition of the chelate corresponded to the formula, $DyCup_3$, when air dried at room temperature. The first weight loss began at 70°, somewhat less than that found for $TbCup_3$. Breaks were observed in the curve at 130°, 190°, and 280°. The final oxidation of the organic matter began at about 340°, resulting in the Dy_2O_3 level at 550°.

Holmium cupferrate.

(Fig. 1D) This chelate began to lose weight at a low temperature, probably because of coprecipitated cupferron. The composition data shows a smaller percentage of oxide than the theoretical amount, indicating coprecipitation of reagent.

After the first weight loss at 50°, breaks in the curve were observed at 125°, 180°, and 250°. The final oxidation of the organic matter began at 250°, resulting in the Ho_2O_3 level at 610°.

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Erbium cupferrate

(Fig. 1B) This chelate was the least stable of all of the metal cupferrates studied. Again, as in the case of $HoCup_3$, this was probably due to coprecipitated reagent. The first weight loss began at 45°, with breaks in the curve at 135°, 160°, and 260°. The Er_2O_3 level began at 550°.

Ytterbium cupferrate

(Fig. 1A) The first weight loss was observed at 75°, with breaks in the curve at 120°, 195°, and 270°. Final oxidation of the organic matter began at 325°, resulting in the Yb_2O_3 level at 520°.

Europium neocupferrate

(Fig. 2F) The composition of the air-dried metal chelate corresponded approximately to the formula, $Eu(Neocup)_3$; where Neocup is the neocupferron ion. The first weight loss was observed at 50°, with breaks in the curve at 105° and 190°. The initial weight loss did not correspond to the evolution of an entity of molecular weight 18 as was found in the lighter rare earth neocupferrates[3]. A horizontal weight level was not observed in the curve after this initial weight loss as was previously found. Beyond 305° the weight loss was quite rapid, resulting in the Eu_2O_3 level at 560°.

Terbium neocupferrate

(Fig. 2E) The composition of the air-dried chelate corresponded closely to the formula, $Tb(Neocup)_3$. The first weight loss began at 50°, slowly at first, but becoming quite rapid above 155°. A break in the curve was observed at 210°, with further rapid weight loss above 325°. The Tb_4O_7 level began at 505°.

Dysprosium neocupferrate

(Fig. 2C) The first weight loss began at 45° with a horizontal weight level being observed from 100° to 130°. The composition of the curve in this region is not known. Beyond 190° the chelate decomposed very rapidly, forming another horizontal weight level from 205° to 260°. This same general thermogram pattern is different from the previous two chelates but similar to the neocupferrates of Ho, Yb, and Er. Above 260° the chelate decomposed rapidly, resulting in the Dy_2O_3 level at 540°.

Holmium cupferrate

(Fig. 2D) The first weight loss began at 55° with a break in the curve, but not a horizontal weight level, at 115°. Beyond 185° the chelate decomposed rapidly, resulting in a horizontal weight level extending from 205 to 295°. The composition of the curve in this level is not known. Beyond 295° the organic matter began to oxidize rapidly, resulting in the Ho_2O_3 level at 445°.

Erbium neocupferrate

(Fig. 2A) The air-dried chelate began to lose weight at 45°. After a break in the curve at 100°, the weight loss was quite slow until 170°. Above this temperature, the chelate lost weight rapidly, giving a horizontal weight level from 190 to 265°.

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Beyond 265° the remaining organic matter oxidized rapidly, resulting in the Er_2O_3 level at 530°.

Ytterbium neocupferrate

(Fig. 2B) The first weight loss began at 45°, giving a break in the curve at 110°. Above this temperature the weight loss was slow until about 190°, where the weight loss became quite rapid. A horizontal weight level was then observed from 200 to 265° with additional rapid weight loss about 265°. The Yb_2O_3 level began at 485°.

General

In general, the heavier rare earth metal cupferrates and neocupferrates were less stable thermally than the corresponding lighter rare earth compounds. However, the minimum oxide level temperatures were in the same general temperature range.

The thermograms show that it is not possible to dry the precipitated complexes to constant weight and then weigh as the stoichiometric metal chelates. In several cases, the amount of metal oxide found for the metal chelates was less than the theoretical amount, indicating coprecipitation of the reagent. This phenomena was found even if a stoichiometrical amount of reagent was used to precipitate the rare earth metal ions.

The exact decomposition mechanism of the metal complexes is not known so it is difficult to assign definite compositions to all parts of the thermal decomposition curve. However, from the first weight loss temperature to the minimum oxide level temperature, the curve probably represents the resultant of a mixture of two or more different compounds. It appears fairly certain that the metal complexes are not hydrated so that the first weight losses are not due to the loss of hydrate-bound water.

SUMMARY

The thermal decomposition of the cupferrates and neocupferrates of europium, terbium, dysprosium, holmium, erbium, and ytterbium was studied on the thermobalance. The metal chelates possessed poor thermal stability as well as a pronounced tendency to coprecipitate reagent. The minimum oxide level temperatures for the metal cupferrates were: Eu, 570°; Tb, 540°; Dy, 550°; Ho, 610°; Er, 550°; and Yb, 520°. The minimum oxide level temperatures for the metal neocupferrates were: Eu, 560°; Tb, 565°; Dy, 540°; Ho, 445°; Er, 530°; and Yb, 485°.

RÉSUMÉ

On a examiné la décomposition thermique des cupferrates et néocupferrates d'europium, de terbium, de dysprosium, d'holmium, d'erbium et d'ytterbium sur la thermobalance. Ces composés présentent une faible stabilité thermique.

ZUSAMMENFASSUNG

Es wurde die thermische Zersetzung der Kupferron-und Neokupferron-Komplexe von Europium, Terbium, Dysprosium, Holmium, Erbium und Ytterbium auf der Thermowage untersucht. Diese Verbindungen besitzen nur eine geringe Wärmestabilität.

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