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*THE DETERMINATION OF  
RARE EARTHS IN CANADIAN ORES  
PART I: CHEMICAL ISOLATION AND  
GRAVIMETRIC DETERMINATION OF  
TOTAL RARE EARTHS*

D. BARKLEY

EXTRACTION METALLURGY DIVISION

JULY 1970

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THE DETERMINATION OF RARE EARTHS  
IN CANADIAN ORES

Part 1: Chemical Isolation and Gravimetric  
Determination of Total Rare Earths

by

D. Barkley\*

SUMMARY

A procedure is described for the chemical isolation and gravimetric determination of total rare earths, including yttrium, in Canadian ores and related products.

The method involves a combination of two or more separation procedures, depending on the sample matrix. Precipitation processes are used to disengage the rare earths from macro amounts of interfering ions, while an 8-quinolinol solvent extraction procedure is instrumental in removing low-level impurities.

The recovery and the purity of the rare earths are both very good, so that the method provides accurate values for the total rare-earth content. The average relative standard deviation for ores with an average content of 0.17 per cent is  $\pm 1.9$  per cent, and for chemical rare-earth concentrate products, with an average content of 39 per cent, the precision is  $\pm 0.2$  per cent. The high rejection of non-rare-earth elements also greatly simplifies the subsequent determination of individual rare earths by X-ray emission spectrometry.

One sample in duplicate can be processed in about 3 days, while 6 samples can be analyzed within a 5-day period.

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Direction des mines

Bulletin technique TB 125

LA DÉTERMINATION DE LA TENEUR EN TERRES RARES  
DES MINÉRAIS CANADIENS

Partie I: Isolation chimique et mesure gravimétrique  
des terres rares

par

D. Barkley\*

RÉSUMÉ

L'auteur décrit une méthode que permet d'isoler chimiquement et de mesurer gravimétriquement la teneur totale en terres rares (y compris l'yttrium) des minerais canadiens et autres produits similaires.

Cette méthode comprend une combinaison de deux modes de séparation ou plus, suivant le type de gangue analysée. On utilise la précipitation pour séparer les terres rares des quantités macroscopiques d'ions interférants, et un solvant à l'hydroxyquinoléine-8 pour extraire les impuretés plus fines.

La récupération et la pureté des terres rares sont toutes deux excellentes, de sorte que cette méthode donne une évaluation précise de la teneur totale en terres rares. L'erreur moyenne relative normale pour les minerais contenant en moyenne 0.17 p. 100 de terres rares est de  $\pm 1.19$  p. 100, tandis que pour les produits chimiques concentrés contenant 39 p. 100 en moyenne de terres rares, elle est de  $\pm 0.2$  p. 100. L'élimination massive des corps étrangers facilite également la mesure ultérieure des terres rares individuelles par spectrométrie d'émission de rayons X.

Il faut environ trois jours pour traiter un double échantillon, alors que six échantillons peuvent être analysés en cinq jours.

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## INTRODUCTION

The initiation of a hydrometallurgical investigation into processes for the recovery of rare earths from the waste liquors from Canadian uranium mines necessitated the development of procedures for the determination of these rare earths in ores, residues, concentrates and solutions covering a wide range of concentrations and compositions. In addition to the necessity of obtaining an accurate total rare-earth value, there was a requirement that the rare-earth precipitate from the gravimetric method be suitable for examination by X-ray emission spectrometry in order to obtain values for the individual rare earths.

In view of the already complex spectrum which results when even a pure rare-earth concentrate is examined by X-ray emission, it was essential that all extraneous non-rare-earth elements be absent. Concentration and separation methods to ensure the purity of the precipitate were therefore required\*.

A literature survey revealed that previously reported procedures were developed for specific problems and, particularly in the case of the low-grade ores and products, were not applicable. Also, few data are available on the behaviour of rare earths in the form of different compounds, e.g. fluorides, oxalates and hydroxides, under conditions for concentrating them from different ore matrices.

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\*This report is the first of a two-part series. The second part will describe details of the X-ray spectrometric methods for the determination of the individual rare earths.



This report describes the studies carried out to establish optimum conditions for separations to isolate rare earths quantitatively. A number of tests illustrating the application of the separations to the individual rare earths and to actual samples are presented to indicate the accuracy and reproducibility of the method developed.

## EXPERIMENTAL

### Decomposition

The requirements of the method - to determine total rare earths, and to provide a concentrate containing 25-50 mg of purified rare earth oxides for the subsequent analysis of the individual rare earths by X-ray emission - necessitated decomposing a 25-g sample of those materials containing an estimated 0.1% of rare earth oxides. Therefore, the initial use of a flux was not feasible. Difficulty was experienced in obtaining complete solution of an ore or residue when the sample was treated with either sulphuric or perchloric acid, and the remaining undecomposed sample fused with either sodium carbonate or sodium peroxide.

Decomposition by repeated treatments with hydrofluoric and nitric acids proved to be advantageous. The samples high in silica were readily attacked and simultaneously gave a fluoride precipitate in which the rare earths were quantitatively

retained. The precipitated fluorides were separated, decomposed by boiling with a potassium hydroxide solution, and the subsequent hydroxides, along with any remaining undecomposed material, were treated with perchloric and nitric acids. Material not attacked during the hydrofluoric acid evaporations was found to yield to refluxing with perchloric acid\*.

This mode of attack has been used successfully on a number of ores from the Elliot Lake, Ontario, area, as well as on pyrochlore samples from deposits at Oka, Que.

#### Fluoride Separation

A preliminary precipitation of the rare earths as fluorides has been recommended in solutions containing iron, aluminum and uranium (1), but with the high iron-to-rare-earth ratio encountered in the samples in question, precipitation would be incomplete (2). Sandell (3) has suggested the use of calcium as a carrier in the precipitation of small amounts of rare earths as fluorides or oxalates. Use of thorium as a carrier for the precipitation of rare earth fluorides has also been recommended (4,5).

Quantitative information on the solubility of rare earth fluorides in the presence of other ions was not available; comparative tests were therefore made on methods recorded in the literature

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\*The amount of residue remaining after the hydrofluoric acid attack and the additional treatment with perchloric acid on a typical Elliot Lake ore is as follows: (a) 1.2 mg from a 20-g feed sample, and (b) 1.6 mg from a 20-g leached residue sample. Spectrochemical analysis indicated that the principal constituent of these residues is titanium.

for precipitation of rare earths as fluorides. These methods were applied to actual samples of Elliot Lake area ores and residues. The tests included: [A] the use of calcium as a carrier and hydrofluoric acid as the precipitating agent (6), [B] the fluoride precipitation method involving thorium as a carrier and ammonium fluoride as precipitant (4,5), and an additional test, [C], the effect of using calcium as a carrier and ammonium fluoride as a precipitant.

The gelatinous nature of the calcium fluoride precipitates, which contained the co-precipitated rare earths, hindered filtering and centrifuging, and made final decomposition of the solids difficult. Results of the tests showed low recoveries of the rare earths.

The results of test [B], however, were superior to those of tests [A] and [C] with respect to the initial recoveries obtained and to the ease of handling of the thorium fluoride precipitate; also, the chemical similarity of the rare earths and thorium in Test [B] led to the development of a separation based on the procedure of Bornong and Moriarty (5). In this procedure, 2 g of ammonium fluoride is added to the fluoride suspension of thorium and rare earths. After heating, the gelatinous thorium fluoride changes to a dense white precipitate that can be easily centrifuged and separated.

An investigation was made to determine, by the Bornong and Moriarty procedure, the effect of hydrofluoric acid and mineral acid concentration on the completeness of precipitation of the rare

earths present in ores from the Elliot Lake area. A variation of the hydrofluoric acid concentration from 2 to 10% v/v, and of the mineral acid concentration (both hydrochloric and nitric acids were tested) from 2 to 10% v/v, had no detrimental effect on the recovery of the rare earths in the proposed separation.

Under the conditions of precipitating the rare earths with hydrofluoric acid, and the addition of 2 g of ammonium fluoride, the presence of 100 mg of thorium (added as thorium nitrate tetrahydrate dissolved in water) led to essentially complete recovery with each type of sample investigated.

Tantalum, niobium, zirconium, titanium, iron, aluminum, uranium, tin, and tungsten, which form soluble fluoride complexes, are eliminated. There is also a separation of rare earths from large amounts of phosphate (1). Tetravalent uranium, which would be precipitated, is oxidized to the uranyl state with nitric acid during decomposition.

Tests on determining rare earths in 25 g of Elliot Lake area ore showed that two fluoride precipitations were necessary to reduce the amount of interferences (0.65 g Fe present; an Fe-to- $RE_2O_3$  weight ratio of 16:1) to less than 100-mg quantities, where a further purification step, namely an oxalate precipitation, could be used. Tests on uranium-barren effluent solutions (100-ml samples were used, containing 0.36 g of Fe; an Fe-to- $RE_2O_3$  weight ratio of 5:1)

showed that one fluoride separation was sufficient to reduce the amount of iron along with other interfering elements present - aluminum, titanium, and zirconium - to less than 50 mg, where the 8-quinolinol extraction separation could be applied.

In those samples where there was a high concentration of calcium present, along with iron, aluminum and other metals that form soluble fluoride complexes, it was found advantageous to do an ammonia separation to remove calcium after the initial fluoride precipitation. The presence of the calcium impeded the separation of soluble fluoride complexes from the rare earths and thorium. A second fluoride separation was then carried out to remove interferences.

#### Decomposition of the Thorium-Rare Earth Fluoride Precipitate

Methods were investigated for the decomposition of the rare earth and thorium fluoride precipitate. These included the treatment of the precipitate with: [A] sulphuric acid (1); [B] perchloric acid (6); [C] nitric acid and boric acid (4); and [D] potassium hydroxide (1). Procedures [A] and [B] were found suitable for small quantities of fluorides, i.e., resulting from less than 25 mg of rare earths, but not the amounts resulting from 25 g of Elliot Lake area ore plus 100 mg of thorium. Low results were obtained for rare earths when method [C] was used. In method [D], it was found possible to decompose the fluoride precipitate by boiling it in a 20% w/v potassium hydroxide solution for  $\frac{1}{2}$  hour.

The hydroxide precipitates obtained in method [D], containing thorium and rare earths, were treated with nitric and perchloric acids, and then evaporated to dryness. This step performed the following functions: to solubilize the hydroxide precipitates, to dissolve any remaining undecomposed material, to ensure that all fluorides had been destroyed, and to facilitate the adjustment of the acidity of the resultant solution for subsequent operations. This procedure would separate the elements, such as vanadium, tungsten, molybdenum, arsenic, aluminum and zinc, which form soluble anionic compounds with hydroxide, together with phosphate from the thorium and rare-earth precipitates.

#### Oxalate Separation

In chemical analysis, oxalate precipitation methods have been used to separate rare earths from a number of accompanying elements such as Fe, Al, Ni, Cr, Mg, Zr, U, and, to a lesser extent, phosphates, Co, Cu, Zn, Ag, Cd, Sn and Bi. However, since this procedure gave poor recovery in rare earths from Elliot Lake leach solutions, a literature survey was made to determine the qualitative factors which affect rare-earth oxalate precipitation.

The governing condition is oxalate ion concentration, i.e. oxalate ion activity. A high oxalate ion concentration reduces solubility because of common-ion effect, but the rare

earths of high atomic number and yttrium form soluble complexes at high oxalate ion concentration. Proper conditions for quantitative precipitation are obtained by controlling the oxalic acid concentration and pH or acidity (1).

In the proposed procedure the final pH is adjusted to 2-2.5 and a three- to five-fold stoichiometric excess of oxalic acid is used. The volume of solution is adjusted so that the rare earth concentration is greater than 0.005 M.

Mechanical stirring for two minutes immediately after adding oxalic acid at room temperature, and digestion of the precipitate at 10°C overnight as recommended by Broadhead and Heady (7), were found to prevent rare earth oxalates from escaping through the filter paper and precipitating out later in the filtrate. This phenomenon, which has been attributed to formation of super-saturated solutions (2), proved to be a problem with some of the procedures recorded in the literature that were tested.

Under these conditions, recovery was more than 98% for the individual rare earths tested: cerium, europium, erbium and yttrium, at concentrations from 10 to 150 mg as the oxide. Thorium was found not to accompany the rare earths quantitatively through the oxalate precipitation under the above chosen conditions.

The influence of the presence of iron on the completeness of precipitation of rare earth oxalates was also

investigated. The rare earths were precipitated as oxalates from 100 ml of an actual sample\* containing 0.36 g of Fe and 0.69 mg of  $RE_2O_3$ , by the foregoing procedure, using a five-fold excess of oxalic acid; the iron was present in the ferrous state. The results given in Table 1, Test A, show that low recovery was obtained. The influence of thorium as a carrier on the completeness of precipitation in the presence of foreign ions was then investigated. Tests were carried out as described above, on the same sample, but with the addition of a solution of thorium nitrate containing 100 mg of thorium. Results given in Table 1, Test B, show that a quantitative recovery of the rare earths was not obtained.

The influence of organic solvents, such as acetone and methanol, to increase the recovery of the rare earths in the presence of other ions was looked at briefly. From 100-ml aliquots of the above sample, the rare earths were precipitated by the oxalate separation step described previously; methanol, or acetone, was then added in a ratio of 1:1 to the initial volume. There was an increase in the amount of rare earths precipitated, but there was also an increase in the contamination of the precipitate.

#### 8-Quinolinol Extraction of Thorium and Low-Level Impurities

The importance of solvent extraction methods in rare earth analysis lies not in the extraction of the rare earths but

---

\*Denison Mines Ltd. uranium barren effluent solution.



TABLE 1

The Recovery of Rare Earths as Oxalates in the Presence of Iron (with and without thorium as a carrier)

Test #	Rare Earths Present, mg RE <sub>2</sub> O <sub>3</sub>	Iron Present, mg Fe <sup>II</sup>	Thorium Added, mg ThO <sub>2</sub>	Rare Earths Recovered, mg RE <sub>2</sub> O <sub>3</sub>
A	0.69	360	-	47
B	0.69	360	100	44

rather in the removal of other elements in both large and small amounts in order to permit isolation of small amounts of the rare earths in the aqueous phase.

The following extractants were considered for removing up to 150 mg of thorium from milligram quantities of rare earths:

[A] 2-thenoyl trifluoroacetone (TTA). Use of this reagent has been limited to the removal of small amounts of thorium (<10 mg) because of the low solubility of the TTA chelate in an organic solvent (8).

[B] Dibutoxytetraethyleneglycol. Lerner and Petretic (9) obtained only 90 to 96% of recovery of rare earths.

[C] Tributyl phosphate. This reagent has a smaller separation factor for the rare earths than the other reagents noted above (1).

8-quinolinol has been used by Lerner and Pinto (4) to separate thorium from rare earths and by Onishi and Banks (6) for removal of small amounts (1 mg) of iron and aluminum from rare earths. The quantitative aspects of 8-quinolinol as an

extracting agent for the separation of thorium and low-level impurities remaining with the rare earths after a fluoride or oxalate precipitation were examined. According to the literature, the  $pH_{\frac{1}{2}}$  value for thorium is lower than those values recorded for the individual rare earths at the corresponding concentration of 8-quinolinol in chloroform\*; the extraction constant for the thorium 8-quinolinolate-chloroform system is relatively large, indicating that a separation of thorium from the rare earths is possible. There are, however, few experimental data available concerning the quantities of thorium that can be extracted and the optimum conditions for quantitative recovery of the various individual rare earths from lanthanum to lutetium, including yttrium.

The distribution of the metals should mainly be a function of two experimental variables, the pH and the concentration of the chelating agent in the organic phase, but the usual buffer solution of ammonium acetate that is used to maintain pH in an 8-quinolinol extraction has a masking effect on thorium (12,13) and, as a result, the distribution ratio of thorium is diminished (10). There is no quantitative information as to the effect of acetate concentration on pH and 8-quinolinol concentration. Hence the dependence of the pH and the 8-quinolinol concentration on the presence of the acetate ion concentration for the extraction of thorium 8-quinolinolate into chloroform was determined.

---

\* $pH_{\frac{1}{2}}$  is defined as the pH value of 50% extraction of the metal at a stated molar concentration of the extracting reagent in the organic phase. The  $pH_{\frac{1}{2}}$  value of thorium for 0.1 M 8-quinolinol in  $CHCl_3$ ,  $(pH_{\frac{1}{2}})_{0.1}$ , is 3, while the values recorded for the rare earths are  $La(pH_{\frac{1}{2}})_{0.1} = 6.5$ ;  $Y(pH_{\frac{1}{2}})_{0.2} \sim 5$ , and  $Ho(pH_{\frac{1}{2}})_{0.1} \sim 5$  (10,11).

In the initial experiments, the following procedure was used: To solutions of thorium chloride containing 100 mg of  $\text{ThO}_2$  were added different amounts of acetic acid and 2 g of 8-quinolinol. The samples were diluted to 75 ml and the pH adjusted with ammonium hydroxide to a value where the thorium 8-quinolinolate precipitated. The contents were then transferred to a separatory funnel, diluted to 100 ml, and each sample was extracted with three 25-ml portions of a solution of 8-quinolinol in chloroform. The extraction of the 8-quinolinol resulted in a drop in the pH of the aqueous phase, and therefore the acidity was readjusted to the initial value between each extraction. The thorium remaining in the aqueous phase was determined by precipitating with ammonium hydroxide. Results given in Table 2 show that, under the conditions employed, 100 mg of  $\text{ThO}_2$  can be quantitatively extracted from a 1 M acetate solution with a 0.5 M solution of 8-quinolinol in chloroform at a pH of 4.1, while a pH of 4.4 and a 1 M 8-quinolinol solution are required to quantitatively separate 100 mg of  $\text{ThO}_2$  from a 2 M acetate solution.

The extraction procedure was later modified, for ease of operation (to eliminate transferring the bulky 8-quinolinates) and to obtain a more accurate pH adjustment. The required amounts of hydrochloric and acetic acids were added to the solution containing the metal ions. (The hydrochloric acid was fixed at 5 ml, which was sufficient to dissolve the rare earths after a fluoride or oxalate separation.) The pH was adjusted with ammonium hydroxide (1:1) to a pH of 4.2-4.3, transferred to a separatory funnel, diluted to 100 ml, and extracted with four 35-ml portions of a chloroform solution of

TABLE 2

The Effect of Acetate Concentration on 8-Quinolinol Concentration and pH Needed for the Quantitative Extraction of Thorium 8-Quinolinolate into Chloroform

ThO <sub>2</sub> Added, mg	Concentration of Acetic Acid	pH of Aqueous Phase	Concentration of 8-Quinolinol in Chloroform	ThO <sub>2</sub> Left in Aqueous Phase, mg
100	1 M	4.1	0.1 M	19.2
100	1 M	4.1	0.5 M	0.0
100	1 M	4.1	1 M	0.0
100	2 M	4.4	0.1 M	39.3
100	2 M	4.4	0.5 M	4.0
100	2 M	4.4	1 M	0.0

8-quinolinol. With this procedure, an initial acetic acid concentration of 1 M, i.e. prior to pH adjustment, was found to maintain the initial pH adjustment to  $\pm 0.1$  pH unit throughout the extraction, while 0.5 M 8-quinolinol in chloroform gave a convenient rate of extraction for thorium. Under the optimum conditions employed, up to 150 mg of thorium can be quantitatively separated from the aqueous phase.

The extraction behaviour of several of the individual rare earths in the presence of 100 mg of thorium, as a function of the equilibrium pH for the system 0.5 M 8-quinolinol in chloroform and 1 M acetic acid, was determined by the above procedure. The rare earths were precipitated as their hydroxides from the aqueous raffinate and determined gravimetrically. The results obtained are shown in

Table 3. At a pH of  $4.2 \pm 0.1$ , the recovery was quantitative for the rare earths tested, except ytterbium for which it was 97% and lutetium for which it was 94%.

TABLE 3

The Extraction Behaviour of Several Rare Earths  
as a Function of the Equilibrium pH for the System:  
0.5 M 8-Quinolinol in Chloroform, and 1 M Acetic Acid

Rare Earth Present	RE <sub>2</sub> O <sub>3</sub> Added, mg	RE <sub>2</sub> O <sub>3</sub> Recovered, mg			
		Equilibrium pH ( $\pm 0.1$ )			
		4.2	4.5	5.0	5.5
La <sub>2</sub> O <sub>3</sub>	24.0	23.8	23.9	24.3	23.2
CeO <sub>2</sub>	25.0	24.8	24.7	24.9	25.2
Eu <sub>2</sub> O <sub>3</sub>	24.0	23.8	23.8	23.8	23.9
Dy <sub>2</sub> O <sub>3</sub>	29.9	29.5	29.3	29.3	28.1
Ho <sub>2</sub> O <sub>3</sub>	25.1	25.0	25.4	24.6	13.2
Yb <sub>2</sub> O <sub>3</sub>	25.1	-	23.6	17.2	1.4
	38.2	37.0	35.5	-	-
Lu <sub>2</sub> O <sub>3</sub>	25.5	24.2	21.2	-	-
Y <sub>2</sub> O <sub>3</sub>	24.4	24.5	24.2	24.1	23.5

Metals that will be quantitatively extracted into the organic phase along with thorium at the stated pH and concentration of 8-quinolinol are indicated by their respective pH<sub>1/2</sub> values. These include: Al, Fe, Cu, Mo, Zr, Ti, U, and V. Because of the appreciable amounts of Fe, Al, U, Ti and Zr that may still be present in the samples (e.g. Elliot Lake area products) which have undergone a fluoride separation and an oxalate separation, the quantities of these elements that could be extracted from rare earths in the presence of 100 mg of the thorium carrier, under the optimum conditions selected, were experimentally investigated. These

results are given in Table 4 and show that up to 50 mg of iron, aluminum, uranium and up to 25 mg of zirconium can be removed along with 100 mg of  $\text{ThO}_2$ .

TABLE 4

The Extraction Behaviour of Some Non-Rare Earth Metals at a Equilibrium pH of 4.2 for the System: 0.5 M 8-Quinolinol in Chloroform, and 1 M Acetic Acid

(100 mg  $\text{ThO}_2$  present in all cases)

Metal Taken, mg		Metal Recovered, mg
Fe(III)	100	2.5
Fe(III)	50	0.2
Al(III)	50	0.0
Zr(IV)	43	12.2
Zr(IV)	21.7	0.1
U(VI)	50	0.1

#### Ammonium Hydroxide Separation

The precipitation of the rare earths as hydroxides serves for the separation of rare earths from calcium and magnesium (also, from manganese and zinc more or less effectively), and for collecting the rare earths for their gravimetric determination.

A quantitative recovery of the rare earths can be obtained at a pH of 10 or greater (1). The precipitation was carried out at room temperature to improve the separation from calcium (14).

To ensure the complete recovery of lanthanum, it was found necessary to maintain a pH of greater than 10 throughout the precipitation procedure. This was accomplished by adopting the following method: The pH of the solution of rare earths was adjusted to 8-9 with 1:1 ammonium hydroxide. Ten ml of concentrated ammonium hydroxide was added. The sample was transferred to a hot plate and brought to a boil and boiled for 3 minutes. It was then removed from the hot plate and allowed to cool somewhat before an additional 5 ml of concentrated ammonium hydroxide was added. The precipitate was digested for 5 minutes before filtering.

The acetate ion remaining in the solution from the 8-quinolinol extraction was found to have no effect on the rare earth recovery. Teflon beakers for carrying out the precipitation with 10 to 15% v/v ammonium hydroxide solution were used to prevent silica contamination of the rare earth precipitate\*.

Quantitative recovery of the rare earths as their hydroxides was obtained by the procedure recommended in this report. The following individual rare earths were tested: La, Ce, Nd, Eu, Dy, HO, Er, Yb, Lu, and Y.

#### Mercury Cathode Separation

Mercury cathode electrolysis could provide a convenient separation step, particularly for the removal of iron from feed and barren effluent solutions containing rare earths. The efficiency of recovery of some of the light rare earths, i.e. lanthanum,

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\*There was an increase of some 2 mg in the weight of the calcined rare-earth hydroxides due to silica, as a result of conducting the precipitation in Pyrex beakers.

cerium, neodymium, and praesodymium, has been reported (15,16), but not that of the heavy rare earths. Accordingly, synthetic solutions of dysprosium, erbium and yttrium, containing added iron in 100 ml of 1 M perchloric acid, were electrolyzed at the mercury cathode for 0.5 hr at 10 amperes. An 8-quinolinol extraction was then carried out on the electrolyzed solutions, to remove any remaining iron; the rare earths were precipitated from the aqueous raffinate as hydroxides, and calcined to oxides. The results are given in Table 5, and show a quantitative recovery of all three rare earths was obtained.

TABLE 5

Recovery of Rare Earths from a Mercury Cathode  
Electrolysis for the Removal of Iron

Rare Earth Taken, mg		Fe Present, mg	RE <sub>2</sub> O <sub>3</sub> Recovered, mg
Yttrium	25.0	250	25.8
			26.2
Dysprosium	30.0	250	30.7
			30.1
Erbium	30.0	250	29.3
			29.1

Cinnamic Acid Separation

Manganese and zinc, if present in more than nominal amounts, can survive the procedure sequence of a fluoride, an oxalate, an 8-quinolinol, and an ammonia separation. Accordingly, the use of cinnamic acid (C<sub>6</sub>H<sub>5</sub>.CH = CH.COOH) (17), which precipitates the rare earths and separates them from manganese, nickel, cobalt,



zinc, calcium and magnesium, was evaluated, and the conditions for quantitative recovery, i.e. pH, reagent concentration, digestion time, and the effect of ammonium acetate (present from the prior 8-quinolinol separation), were investigated.

Six ml of glacial acetic acid and five ml of concentrated hydrochloric acid were added to a solution of the individual rare earth. The sample was diluted to 75 ml with water and then neutralized to a pH of  $4 \pm 0.2$  with ammonium hydroxide (1:1). (This solution simulated an aqueous raffinate from a 8-quinolinol extraction.) The sample was then heated to  $70^{\circ}$ - $80^{\circ}$ , and 25 ml of an ammonium cinnamate solution (5% cinnamic acid) was added with vigorous stirring. The beaker was transferred to a position near the hot plate to digest the precipitate for 45 min at about  $85^{\circ}$ . The precipitate was filtered, washed five times with a hot solution of ammonium cinnamate (3% cinnamic acid), and calcined at  $950^{\circ}$ .

It was found that the heavy rare earths europium, dysprosium, erbium and yttrium could be recovered quantitatively at a pH of 4 from solutions 1 M in ammonium acetate. Recovery of cerium was 93%, but that of lanthanum was only 54% (see Table 6). It was postulated that the high concentration of ammonium ions decreased the dissociation of the ligand, so the effect of increasing the ammonium cinnamate concentration was examined. There was an improvement but quantitative recovery of lanthanum was still not obtained (75%).

Lanthanum, cerium, and yttrium were precipitated as cinnamates by the above procedure, but without the addition of acetic acid. The results (Table 6) show that cerium and yttrium were recovered quantitatively, and that 90% of the lanthanum can

TABLE 6

The Effect of Acetate Ion Concentration  
on the Precipitation of Individual Rare Earths  
with Cinnamic Acid

RE <sub>2</sub> O <sub>3</sub> Taken, mg		Acetate Ion Concentration, M	RE <sub>2</sub> O <sub>3</sub> Recovered	
			mg	%
La <sub>2</sub> O <sub>3</sub>	37.5	1.0	20.3	54
La <sub>2</sub> O <sub>3</sub>	37.5	-	33.6	90
CeO <sub>2</sub>	37.5	1.0	35.0	93
CeO <sub>2</sub>	37.5	-	37.1	99
Eu <sub>2</sub> O <sub>3</sub>	37.5	1.0	37.1	99
Dy <sub>2</sub> O <sub>3</sub>	30.0	1.0	29.1	97
Er <sub>2</sub> O <sub>3</sub>	30.0	1.0	29.0	97
Y <sub>2</sub> O <sub>3</sub>	37.5	1.0	37.5	100
Y <sub>2</sub> O <sub>3</sub>	37.5	-	37.8	101

be recovered. Therefore, acetate ions should be removed from the aqueous raffinate from the 8-quinolinol extraction, prior to the precipitation of rare earths with cinnamic acid. This can be done by adding concentrated nitric acid and evaporating to dryness at low temperature.

RECOMMENDED METHOD

Reagents

Thorium nitrate solution: Dissolve 5.3 g of Th(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in distilled water and 5 ml of hydrochloric acid, and dilute to 250 ml; 1 ml = 10 mg ThO<sub>2</sub>.

Ammonium fluoride ( $\text{NH}_4\text{F}$ ), reagent grade.

Hydrofluoric acid, 48%, reagent grade.

Ammonium fluoride wash solution: Dissolve 10 g of ammonium fluoride in distilled water, add 20 ml of 48% hydrofluoric acid, and dilute to 1 litre. Store in a plastic bottle.

Potassium hydroxide, pellets, reagent grade.

Nitric acid, reagent grade.

Perchloric acid, 70%, reagent grade.

Hydrochloric acid, reagent grade.

Oxalic acid solution, 10% w/v: Dissolve 25 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in distilled water and dilute to 250 ml.

Chloroform, reagent grade.

8-Quinolinol solution, 0.5 M: Dissolve 35 g of reagent-grade 8-quinolinol in 500 ml of chloroform.

Acetic acid, glacial, reagent grade.

Ammonium hydroxide, reagent grade.

Ammonium chloride wash solution: Dissolve 20 g of ammonium chloride in distilled water, add 100 ml of concentrated ammonium hydroxide, and dilute to 1 litre.

Potassium hydroxide wash solution, 2%: Dissolve 20 g of potassium hydroxide pellets in distilled water and dilute to 1 litre.

Ammonium cinnamate solution, 5% w/v cinnamic acid: Add 25.0 g of cinnamic acid to 200 ml of distilled water. Neutralize with ammonium hydroxide (1:1), add two to three ml in excess, heat, and stir to dissolve. Dilute to 500 ml.

Ammonium cinnamate wash solution, 3% w/v cinnamic acid: Dilute 300 ml of the 5% w/v cinnamic acid solution to 500 ml with distilled water.

### Apparatus

Beakers, Teflon and Pyrex: 250 ml.

Centrifuge bottles, Nalgene: 250 ml.

Funnels, Nalgene.

Stirring rods, Teflon.

Centrifuge: For 250-ml bottles.

Mechanical stirring apparatus.

Separatory funnels: 250 ml, equipped with Teflon plugs.

pH meter.

Crucibles, porcelain: Coors No. 00.

### Procedure

#### Initial Attack and Dissolution of Ores and Residues

Weigh out a sample to contain 15 to 50 mg of rare earth oxides. (For Elliot Lake area ores this will be a 20 to 25 g sample.) If carbonaceous matter is present, heat the sample in a platinum dish at 650°C for 20-30 minutes; cool and transfer to a 250-ml Teflon beaker. Moisten the sample with about 25 ml of distilled water, add 10 ml of concentrated nitric and 50 ml of

48% hydrofluoric acid. Break up any lumps with a Teflon stirring rod, and evaporate at low heat to about 20 ml. Watch for excessive frothing, and do not allow contents to go to dryness. Cool, add 25 ml of 48% hydrofluoric acid, break up any lumps, and loosen any sample adhering to bottom; evaporate to low volume as noted above. Repeat the hydrofluoric acid treatment if required, i.e. until the iron colour is discharged, or nearly so. Then evaporate to near dryness on a steam bath or on a hot plate set at low heat.

#### Fluoride Separation

Moisten the contents of the beaker from the above treatment with water, and break up any residue with a Teflon stirring rod.

In the case of solutions, transfer an aliquot containing 15 to 50 mg of rare earth oxides to a 250-ml Teflon beaker. Continue with the following procedure for both solid and solution samples.

Adjust the volume to about 85 ml with distilled water, add 3 to 4 ml of nitric acid, 10 ml of the thorium solution, and mix. Add 5 ml of 48% hydrofluoric acid, stir contents, then add 2 g of ammonium fluoride; stir well. Cover the beaker and boil at low heat for 30 minutes, and then digest below boiling (at the side of the hot plate) for one hour.

Cool, transfer the contents of the beaker to a 250-ml plastic centrifuge bottle, using the fluoride wash solution (reserve the Teflon beakers). Balance the bottles, and centrifuge for 10 min at 1500 r.p.m. Decant into a clear plastic bottle to check clarity of the liquor. Wash the precipitate twice, by centrifuging, using about 50 ml of the fluoride wash solution each time.

#### Decomposition of Fluorides and Potassium Hydroxide Separation

To the precipitate in the centrifuge bottle, add 15 to 20 ml of water and 15 g of potassium hydroxide pellets. Swirl to dissolve the pellets and to break up the fluoride precipitate. Transfer the contents back into the original Teflon beaker with water. (Reserve the centrifuge bottle.) Adjust the volume to 75 ml; cover, and boil for 30 min. Dilute with water to 175-200 ml and boil for 10 min, then digest beside the hot plate for 15-20 min. Filter, using plastic funnels, through a No. 52 Whatman paper. Wash the precipitate three times with hot 2% KOH solution.

Transfer the paper and precipitate to a 250-ml Pyrex beaker. Wash out the reserved centrifuge bottle with 50 ml of concentrated nitric acid; transfer the washings to the reserved Teflon beaker, and heat to dissolve any precipitate adhering to the beaker. Transfer the nitric acid solution into the Pyrex beaker, and add 10 ml of 70% perchloric acid. Evaporate carefully to fumes of perchloric acid, cool somewhat, and rinse down the sides with water; then evaporate to near dryness.

To the beaker, add 5 ml HCl, 20 ml water, and 2-4 drops of hydrogen peroxide (30% v/v); cover, and warm to dissolve.

#### Fluoride Reprecipitation

Carry out a second fluoride separation on Elliot Lake area ores and residues, and on material with high iron, niobium, tantalum, zirconium or titanium content.

#### Oxalate Separation

Cool the sample solution from the potassium hydroxide separation (containing 5 ml of hydrochloric acid) to room temperature and dilute to 90 ml with water. Adjust the acidity to a pH between 2.0 and 2.5 with ammonium hydroxide (1:1), using a pH meter. If the cerium content is high, adjust solution to a pH no greater than 1.5 (to prevent ceric ions from hydrolyzing). Add 10 ml of a 10% w/v oxalic acid solution, and mix.

Readjust the pH to between 2.0 and 2.5. Using a mechanical stirrer, stir fairly vigorously for 2 minutes. Digest at about 10°C for four hours, preferably overnight. Filter through a Whatman No. 42 paper, and wash 5 times with a 0.5% w/v oxalic acid solution.

Return the paper and precipitate to the precipitation beaker, add 30 ml of concentrated nitric acid and 5 ml of 70% perchloric acid, and evaporate carefully to near dryness. Dissolve the residue by heating with 5 ml of hydrochloric acid, 25 ml of water, and a couple of

drops of hydrogen peroxide (30%). Filter off any silica or undissolved residue and wash it three times with a 1% hydrochloric acid solution. Collect the filtrate in a 250-ml Pyrex beaker and discard the residue.

#### 8-Quinolinol Extraction of Thorium and Low-Level Impurities

Boil the solution to eliminate peroxide, otherwise a third phase forms (a honeycomb effect) on extraction and difficulty will be experienced in separating the organic from the aqueous phase. Cool, and dilute the volume up to 75 ml. Add 6.0 ml of glacial acetic acid. Adjust the pH with 1:1 ammonium hydroxide to 4.2-4.3. Cool the solution and transfer it to a 250-ml separatory funnel with two washings of 10 ml each, i.e., the final volume should be 100 ml. Extract by shaking for one minute with 35 ml of 0.5 M 8-quinolinol in chloroform. Allow the phases to separate for 2 to 3 min, and then drain off the chloroform layer and discard it. Extract with three more 35-ml portions of 8-quinolinol in chloroform by shaking for 1 minute each time. Wash the aqueous phase with two 25-ml portions of pure chloroform, shaking for 0.5 minute each time. Transfer the aqueous layer to a 250-ml Teflon beaker and evaporate to about 90 ml.

#### Ammonium Hydroxide Precipitation

Cool to room temperature and add 2-3 drops of hydrogen peroxide (30% v/v). Adjust the pH to between 8 and 9 by adding



ammonium hydroxide (1:1) dropwise, with stirring; then, while continuing to stir, add 10 ml of fresh concentrated ammonium hydroxide. Transfer the sample to a hot plate and bring to a boil and continue to boil for 3-5 min. Remove from hot plate and allow sample to cool somewhat, then add carefully, with stirring, 5 ml of concentrated ammonium hydroxide. Digest near the hot plate for 5 minutes.

Transfer the precipitate to a Whatman No. 40 paper, using a warm fresh solution of 2% w/v ammonium chloride and 10% v/v ammonium hydroxide. Wash the precipitated rare earth hydroxides four or five times with this solution.

Place the paper containing the precipitate in a tared crucible (Coors No. 0 or No. 00), dry and char the paper, and calcine at 950-975° for 30 min. Cool in desiccator, and weigh the rare earth oxides.

#### Cinnamic Acid Separation

When a cinnamic acid precipitation is to be done instead of an ammonium hydroxide precipitation, after the 8-quinolinol extraction, pretreat the aqueous raffinate to eliminate acetate ions as follows: Add 30 ml of concentrated nitric acid to the sample and evaporate to dryness at low temperature. Add 5 ml of hydrochloric acid and 50 ml of water, and warm to dissolve. Neutralize the solution to a pH of 3.5-3.8 with ammonium hydroxide (1:1), using indicator paper, and dilute to about 90 ml with water. Heat the

solution to boiling and, with vigorous stirring, add 25 ml of an ammonium cinnamate solution (5% cinnamic acid). Move the beaker to a position near the hot plate to digest the precipitate for 1 hr at about 90°. Filter the precipitate onto a No. 40 Whatman paper and wash the precipitate four or five times with a hot ammonium-cinnamate solution (3% cinnamic acid). Transfer the filter paper plus precipitate to a tared Coors crucible, dry, ash, and then calcine at 950°. Weigh the total rare earth oxides.

#### RESULTS OF RECOMMENDED METHOD

##### Analysis of Typical Ores and Products from the Elliot Lake Area by the Recommended Method

As an indication of the reliability of the developed analytical separations, samples of products from Denison Mines Ltd. - a feed material, a leached residue, a washed residue, a pregnant liquor, and a uranium barren effluent - were analyzed for total rare earths by the "Recommended Method". For these samples the Recommended Method consisted of two fluoride separations (one fluoride separation only on the barren effluent sample), an oxalate, an 8-quinolinol, and an ammonium hydroxide separation. The cinnamate separation step was not considered necessary for these samples, because zinc and manganese were not present in appreciable amounts.

These results are given in Table 7, and show that the reproducibility of the results is excellent.

TABLE 7

Recovery of Rare Earths from Samples  
of Products from Denison Mines Ltd.

Product	Sample Taken	RE <sub>2</sub> O <sub>3</sub> Found		RE <sub>2</sub> O <sub>3</sub> Found, Avg.	Range*	Standard Deviation*
Feed	20.00g	41.2 mg	0.206%	0.21%	0.006	± 0.003
	20.00	42.1	0.210			
	25.00	51.4	0.206			
	25.00	51.1	0.204			
Leached Residue	25.00g	41.2 mg	0.165%	0.17%	0.009	± 0.004
	"	42.0	0.168			
	"	42.4	0.169			
	"	40.6	0.162			
	"	40.0	0.159			
Leached Washed Residue	20.00g	31.5 mg	0.157%	0.16	0.003	± .003
	"	32.0	0.160			
Uranium Barren Effluent	100.0 ml	69.7 mg	0.697g/l	0.69g/l	0.013	± 0.006
	"	69.2	0.692			
	"	68.8	0.688			
Pregnant Liquor	100.0 ml	15.9 mg	0.159g/l	0.16g/l	0.005	± 0.004
	"	16.4	0.164			

To illustrate the quantitative recovery of the rare earths, samples of products from Denison Mines Ltd., whose rare earth content had been determined previously (see Table 7), were treated with hydrofluoric and nitric acids (as described in the procedure) to decompose the samples. Known amounts of yttrium (solution of yttrium chloride) were then added to each sample, and the rare earth content of the spiked samples was determined by the "Recommended Procedure", i.e.

\*The range of the observations is the difference between the greatest and least value, and the range is converted to a measure of dispersion independent of the number of observations (18).

TABLE 8

Recovery of Added Yttrium from Samples  
of Products from Denison Mines Ltd.

Product	Sample Taken	Mg of RE <sub>2</sub> O <sub>3</sub> Present Initially	Mg Y <sub>2</sub> O <sub>3</sub> Added	Mg RE <sub>2</sub> O <sub>3</sub> Found	% Y <sub>2</sub> O <sub>3</sub> Recovered, Avg.
Feed	20.00 g	42.0	24.4	65.5	96
	20.00	42.0	24.4	64.8	
Leached Residue	25.00 g	42.5	24.4	64.3	95
	25.00	42.5	24.4	66.2	
Washed Residue	20.00 g	32.0	24.4	56.2	97
	20.00	32.0	24.4	55.3	
Uranium Barren Effluent	150 ml	103.5	24.4	124.8	94

using the fluoride, oxalate, 8-quinolinol and ammonium hydroxide separation steps. These results are shown in Table 8 and confirm that good recovery can be obtained for low concentrations of rare earths in ores and products.

Some typical chemical rare-earth concentrates were analyzed for total rare earths. The samples were calcined and dissolved with hydrochloric acid (1:1) and hydrogen peroxide. The solutions were evaporated to dryness, and the silica was dehydrated and filtered off. An oxalate (using the recommended 5:1 stoichiometric ratio of oxalic acid to rare earths), an 8-quinolinol, and an ammonium hydroxide separation were applied to recover the rare earths from the filtrates. The results are shown in Table 9 and illustrate the reproducibility that can be obtained when the proposed analytical separations are used.

TABLE 9

Recoveries of Rare Earths from Some Typical  
Chemical Rare-Earth Concentrates

Product	g Sample Taken	Mg RE <sub>2</sub> O <sub>3</sub> Found	% RE <sub>2</sub> O <sub>3</sub> Found	% Avg. RE <sub>2</sub> O <sub>3</sub> Found	Range*	Standard* Deviation
Stanrock Concentrate	2.0084	0.5592	27.84	27.87	0.15	± 0.064
	2.0105	0.5616	27.93			
	2.0177	0.5610	27.80			
	1.5141	0.4214	27.83			
	1.5177	0.4242	27.95			
Denison X-ray Standard	1.0074	0.4471	44.38	44.37	0.04	± 0.024
	1.0110	0.4483	44.34			
	1.0110	0.4487	44.38			
Rio Algom Concentrate	1.0129	0.4588	45.30	45.40	.29	± 0.17
	1.0116	0.4582	45.30			
	1.0095	0.4602	45.59			

\*See page 28.

DISCUSSION

The selection of analytical separations to be used in isolating and determining total rare earths will depend, of course, on the sample matrices. A procedure consisting of a fluoride, an oxalate, an 8-quinolinol and an ammonium hydroxide separation provides for the elimination of most of the interfering elements in Canadian rare-earth-containing ores.

The fluoride separation was found to be valuable in reducing the concentration of large quantities of iron, niobium, tantalum, zirconium and titanium in a sample while still giving

a quantitative recovery of rare earths. The situations in which the oxalate separation can be used initially are limited. It was found that the heavy concentration of the ions that form soluble complex compounds with the oxalate ion has to be reduced to a moderate concentration, i.e. about a 3:1 ratio to the rare earths. The 8-quinolinol extraction provides an excellent quantitative separation of rare earths from small amounts of a number of elements, and is valuable in producing a pure product.

It was desirable to implement the cinnamic acid separation as the final step in the procedure for the removal of calcium and magnesium, and of manganese and zinc (which if present in more than nominal amounts in a sample would possibly not have been completely removed by earlier separations); the rare-earth cinnamates could then be calcined to oxides and determined. However, because of the difficulties that were experienced in transferring and washing the bulky rare-earth cinnamate precipitate, the ammonium hydroxide separation is preferred for removal of calcium and magnesium, and for collecting the rare earths for calcining, when manganese and zinc are not present in significant amounts.

To illustrate the purity of the rare-earth concentrate obtained by the "Recommended Method", three calcined rare-earth precipitates from a Denison Mines Ltd. feed sample were combined and submitted for spectrochemical analysis. The only extraneous elements detected were Si (0.8%), Mn (0.02%), and Pb (0.3%).

To determine rare earths in chemical rare-earth concentrates, techniques were adopted to ensure a high level of accuracy. A particular effort was made to use a minimum number of separation steps on the sample in order to lessen solubility losses and to reduce the overall analyzing time. The number of separation steps required is dependent on the number and nature of the contaminants (estimated from spectrochemical analysis). A sample weight was taken to give a final rare-earth-oxide weight of 0.3 to 0.5 g. Some of the products were air-dried hydroxide precipitates, and their moisture content varied with atmospheric conditions; the percentage of rare earths should therefore be based on the calcined weight of the sample to obtain reproducible values.

The final rare-earth-oxide product that is obtained in a state of high purity is more suitable for subsequent examination by X-ray emission spectrometry than the original concentrate, because of the elimination of impurities that could contribute to a matrix effect in the X-ray technique.

#### CONCLUSIONS

The proposed method permits the determination of total rare earths, over a wide range of concentrations, with good selectivity and precision. It is applicable to the various types of products obtainable from Canadian rare-earth ores. The rare-earth concentrate from the "Recommended Method" is suitable for the determination of the individual rare earths by X-ray emission spectrometry.

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