



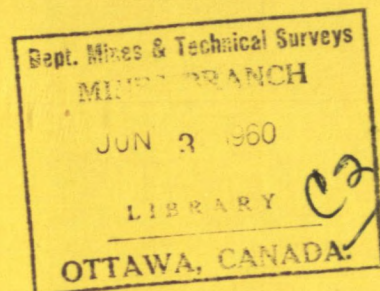
CANADA

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 61

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EXTRACTION METALLURGY DIVISION

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Isolation of the Rare Earth Elements

A Chlorination-Volatilization Procedure

J. BERNARD ZIMMERMAN* and JOHN C. INGLES**

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▶ A total chlorination treatment of radioactive ores and concentrates, with simultaneous volatilization at 900° C., eliminates most of the nonrare earth elements, including thorium and scandium. A subsequent ammonia precipitation removes the alkalies and alkaline earths and isolates the rare earths, including yttrium, in a pure concentrate suitable for weighing, spectrographic examination, or colorimetric determination. With materials consisting primarily of uranium and thorium compounds, preliminary extraction from nitric acid medium with a carbon tetrachloride solution of tributyl phosphate eliminates the bulk of these elements, permitting use of a larger sample and thus extending the range of the method. Over-all recoveries of the rare earth elements are 90% or better.

THE AMOUNT of rare earth minerals in many ores of radioactive materials is sufficient to be of economic interest and the rare earth elements must be determined as a major constituent. In the case of uranium concentrates to be used in the production of nuclear fuels, the maximum amount of rare earth elements (particularly samarium, europium, gadolinium, and dysprosium) that can be tolerated is set at a low level. Elements of this group are the most difficult to separate and determine, partly because of their chemical properties and partly because of the small amounts which must be determined.

Until 1948 (14) the most difficult step

in the isolation of the group was the removal of thorium. Recently, several improved procedures have included a solvent extraction using penta-ether (dibutoxy ethylene glycol) and 8-quinolinol-chloroform extraction steps (12), but the reagent penta-ether was not readily available commercially (it is now understood that this reagent is available from the Roberts Chemical Inc., Roberts Rd., Nitro, W. Va.) (13). A solvent extraction procedure employing tributyl phosphate-carbon tetrachloride and thenoyltrifluoroacetone extraction (22) (the thenoyltrifluoroacetone in the quantities used is expensive and requires troublesome pH adjustments), and a cellulose column method involving the use of 12.5% v./v. nitric acid in diethyl ether, followed by a double thenoyltrifluoroacetone extraction (6) (the use of 12.5% nitric acid in ether is hazardous) are also among those now used.

Moreover, the above methods were developed primarily for the determination of the rare earths in relatively pure thorium and uranium materials, and while they are capable of isolating microgram quantities of the rare earths, additional steps are needed to handle the many gross impurities found in ores and mill concentrates.

In a survey of chlorination methods for upgrading uranium and thorium concentrates, it was noted that the chlorides of the rare earths have very low vapor pressures at elevated temperatures, compared with the many elements which are normally difficult to separate from them. The literature data (Tables I and II) pointed to the feasibility of

using a high-temperature chlorination procedure to volatilize most of the foreign elements. The remaining non-volatile chlorides would apparently consist only of a few very easily separated elements. Of the reported chlorinating reagents and procedures (4), sulfuric chloride as a reducing and chlorinating agent in a chlorine atmosphere appeared best for the complete and rapid chlorination of the various metal oxides present. This procedure (19) has been employed for the separation of thorium and the rare earths, but it is tedious when more than milligram amounts of thorium are to be treated and results in rare earth losses (12).

In the present work, a technique has been evolved whereby the only losses are those resulting from volatilization and they are of the same order as in other procedures (6, 12, 22) (however, the solvent extraction procedures cited deal with microgram amounts of the rare earths, so that it is not strictly fair to compare the losses experienced with those found here).

The method is considerably faster and requires less manipulation with the relatively impure concentrates for which it was developed than the other methods. The purity of the rare earth concentrate (particularly freedom from thorium and scandium contamination) is such that it should be possible, if increased sensitivity is desired, to complete the determination by any of the colorimetric methods now available (2, 9). If this sensitivity is not desired, the concentrate can be weighed and reported with confidence in the knowledge that it is

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free from contamination with nonrare earth material, even though it is not possible to have it examined spectrographically.

APPARATUS AND REAGENTS

CHLORINATION APPARATUS (Figure 1). This consists of a quartz combustion tube 1 inch in inner diameter in a tube furnace capable of giving a temperature of 950° C. The furnace is equipped with a temperature-indicating device and is controlled by a variable resistance. A container fitted with a bypass controlled by a stopcock permits saturation of the entering gas with sulfur monochloride; either chlorine or nitrogen is directed into the combustion tube through a three-way stopcock, *B*, when required.

Chlorine, obtained from a lecture bottle or cylinder, is dispensed at low pressure from a polyethylene bag constructed from two plies of 2-mil polyethylene sheets. A three-way stopcock, *A*, allows one to refill the bag when it is empty. The gas pressure is regulated by flat lead weights laid on top of the bag. Connections are made

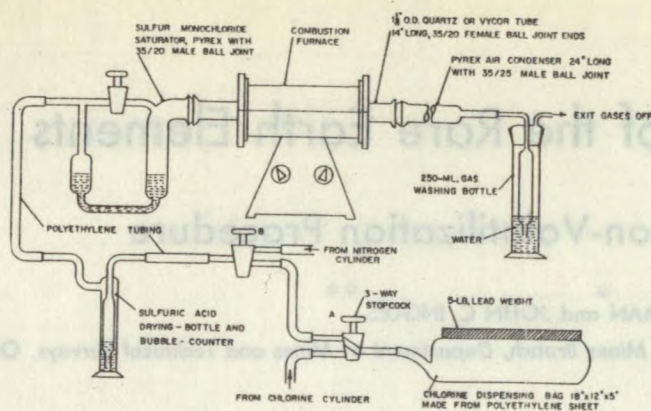


Figure 1. Chlorination apparatus

with polyethylene tubing, except at the combustion tube, where 35/20 $\frac{1}{4}$ ball joints are used. The entering gas is dried by passing it through a sulfuric acid bubbler, which also indicates the flow rate. A long air condenser condenses most of the volatile chlorides and the balance is trapped in a 250-ml. gas washing bottle containing water. This bottle also indicates the rate of flow of gas out of the combustion tube.

COMBUSTION BOATS. These are silica

boats 10 cm. long, 1.8 cm. wide, and 1.2 cm. deep.

SEA SAND, + 65 MESH. A bed of sea sand on the bottom of the boat increases the surface area and facilitates complete volatilization where a large amount of low-melting chlorides is formed.

TRIBUTYL PHOSPHATE SOLUTION. A solution of 40% v./v. reagent grade tri-*n*-butyl phosphate in reagent grade carbon tetrachloride is used for the preliminary solvent extraction step. It should be pre-equilibrated by shaking with an equal volume of 6*N* nitric acid. Collected and saved after use, it can be stripped with 0.05*N* nitric acid and used again after repeating the pre-equilibration step.

RARE EARTH MATERIALS. All the rare earths used were obtained from the Lindsay Chemical Co., West Chicago, Ill. These were: mixed rare earth oxides, Lindsay Code No. 330 (100%), and the oxides of yttrium (No. 1115, 99.9%), cerium (No. 216, 99.9%), neodymium (No. 629, 99%), gadolinium (No. 928, 99%), and erbium (No. 1305, 99.9%).

OTHER REAGENTS. Sulfur monochloride and chlorine.

PROCEDURE

Extraction with 40% Tributyl Phosphate (for chemical uranium and thorium concentrates only; omit for ores). Weigh a sample of the material containing at least 10 mg. of the rare earths. Dissolve the sample in acids, take to dryness, take up again in 100 ml. of 6*N* nitric acid (most uranium concentrates can be dissolved directly in dilute nitric acid), and boil. Cool, filter, and transfer the solution to a 500-ml. Squibb pear-shaped separatory funnel. Add 2 ml. of 30% hydrogen peroxide to the solution in the funnel and shake (this reduces ceric cerium which otherwise would be extracted by the tributyl phosphate).

Extract with three successive 60-ml. portions of tributyl phosphate-carbon tetrachloride solution, shaking at least 1 minute each time. After each shaking, allow the layers to separate and drain the lower (organic) layer into a second 500-ml. separatory funnel containing approximately 50 ml. of 6*N* nitric acid. This acid is used to back-

Table I. Melting and Boiling Points of the Rare Earth Chlorides

(Values in parentheses are estimated values)

Chloride	Melting Point, ° C. ^a	Boiling Point, ° C., 760 Mm. ^a	Volatilization Temp., ° C., 760 Mm. ^{b,c}	Chloride	Melting Point, ° C. ^a	Boiling Point, ° C., 760 Mm. ^a	Volatilization Temp., ° C., 760 Mm. ^{b,c}
LaCl ₃	852	1747	950	GdCl ₃	609	(1577)	865
CeCl ₃	802	1727	900	TbCl ₃	588	(1547)	730
PrCl ₃	776	1707	930	DyCl ₃	654	(1527)	780
NdCl ₃	760	1687	925	HoCl ₃	718	(1407)	...
PmCl ₃	737	1667	...	ErCl ₃	774	(1397)	925
SmCl ₃	740	2027	...	TmCl ₃	821	(1387)	...
SmCl ₂	678	Decomposed	895	YbCl ₂	727	(1927)	...
EuCl ₂	727	2027	...	YbCl ₃	854	Decomposed	930
EuCl ₃	623	Decomposed	...	LuCl ₃	892	(1477)	...

^a (17).

^b (20).

^c Temperature at which chloride was visually observed to volatilize and condense in a cooler part of apparatus.

Table II. Melting and Boiling Points of Some Elements Commonly Found Associated with Rare Earths in Ores and Concentrates^a

(Values in parentheses are estimated values)

Chloride	Melting Point, ° C.	Boiling Point, ° C., 760 Mm.	Chloride	Melting Point, ° C.	Boiling Point, ° C., 760 Mm.
Alkali chlorides	614-800	1300-1500	ThCl ₄	765	922
Alkaline earth chlorides	714-1000	1418-2027	UCl ₄	590	792
AlCl ₃	193	447	VCl ₄	-26	164
Al ₂ Cl ₆	193	180	NbCl ₅	212	243
ScCl ₃	960	967	TaCl ₅	207	234
YCl ₃	700	1507	CrCl ₂	815	1302
SiCl ₄	-67	57	CrCl ₃	1152	947
Si ₂ Cl ₆	-1	139	CrCl ₄	(-28)	(157)
TiCl ₄	-23	136	MoCl ₄	(312)	(317)
ZrCl ₄	437	331	MoCl ₅	194	268
HfCl ₄	432	317	FeCl ₂	677	1026
			Fe ₂ Cl ₆	304	319
			PbCl ₂	498	954
			PbCl ₄	-15	(137)

^a (11, 17).

wash the organic layer, the same 50-ml. portion being used for all three organic extracts. Combine the backwash solution with the original aqueous layer in a 400-ml. beaker and evaporate to about 25 ml. Dilute to 100 ml. with water and again bring to a boil.

Add concentrated ammonium hydroxide cautiously to the hot solution until the solution pH is 9. Digest on a hot plate to coagulate the precipitate and filter hot on a Munktell No. 1 F filter paper. If the calcium and magnesium contents are high, redissolve the precipitate in dilute hydrochloric acid and repeat the ammonia precipitation, filtering as before, and wash with hot water. Transfer the filter paper and precipitate to a 40-ml. platinum crucible. Dry and ignite at 900° C. in a muffle furnace.

Chlorination. Cover the bottom of a silica combustion boat with a thin layer of +65-mesh acid-washed sea sand. Transfer the precipitate from the previous step to this boat or, in the case of ores, weigh a portion of the ore sample containing not less than 10 mg. of rare earths directly into the boat.

Place the boat in the combustion tube and turn stopcock *B* so that the tube is connected to the nitrogen supply. Adjust the temperature of the furnace to 900° C. and pass nitrogen at the rate of 3 to 4 bubbles per second (indicated by the gas washing bottle) for 2 hours.

At the end of this period, stop the flow of nitrogen and turn stopcock *A* to permit chlorine from the weighted plastic bag to pass into the system. Close stopcock *C* so that the chlorine bubbles through the sulfur monochloride, and adjust the flow to provide 3 to 4 bubbles of chlorine per second. After 5 minutes, open stopcock *C* to permit the chlorine to bypass the sulfur monochloride saturator, and pass pure chlorine for 2 minutes. Close stopcock *C* again and pass the mixture of chlorine and sulfur monochloride for 2 minutes. Repeat this 4-minute cycle (2 minutes chlorine, 2 minutes chlorine-sulfur monochloride) twice more, giving a total chlorination time of 15 minutes.

When the chlorination has been completed, open stopcock *C*, leaving the system connected to the chlorine dispensing bag, and remove the weight from the bag. This prevents the contents of the last wash bottle from sucking back as the furnace cools. Allow the furnace to cool to 200° C. and remove the boat from the combustion tube.

Transfer the boat and contents to a 250-ml. beaker containing 100 ml. of 1% v./v. hydrochloric acid and bring to a boil. Remove and wash the boat with distilled water and filter the solution into a clean beaker. Wash the sand on the filter paper with hot 1% hydrochloric acid.

Warm the solution and add concentrated ammonium hydroxide until the solution pH is 9. Digest 15 minutes on a padded hot plate to coagulate the precipitate. Filter on a Whatman No. 41 filter paper. Transfer the filter paper and precipitate to a tared 30-ml.

Table III. Effect of Duration of Chlorination-Volatilization Step at 900° C. on Recovery of Gadolinium Oxide

Time, Minutes	Recovery, %
10	97
16	94
25	92
45	88

porcelain crucible. Dry, ignite at 1000° C., and cool in a desiccator. Weigh the ignited oxides and calculate and report as per cent rare earth oxides.

EXPERIMENTAL

Chlorination of Mixed Rare Earth Oxides. To test the chlorination technique, a 0.5-gram portion of the mixed rare earths was chlorinated by a procedure similar to that described above, except that a temperature of 665° C. and a chlorination time of 1.25 hours were used.

The sample was dissolved in water, filtered to remove the sand, and precipitated with ammonia, which gave 95% recovery of the mixed oxides. This established that conversion of the

Table IV. Recoveries of Added Individual Rare Earths from a Uranium Concentrate

(Using the complete extraction and chlorination-volatilization procedure)

Rare Earth Oxides in 20 Grams of Uranium Concentrate	Weight of Rare Earth Oxides, Mg.		Recovery, %
	Taken	Recovered	
Yttrium	114.6	106.1	93
Cerium	86.8	79.6	92
Neodymium	74.9	75.5	101
Gadolinium	133.8	125.8	94
Erbium	118.1	106.0	90

covery of rare earths through the over-all procedure, 100-mg. portions of the oxides of each of the following rare earths—cerium, neodymium, gadolinium, and erbium—were added to individual 20-gram portions of uranium concentrate which was known to be free of thorium and rare earths. Yttrium was also included in this series of tests. These 20-gram portions of uranium concentrate, each containing a different rare earth, were then carried through the whole procedure.

Table V. Recovery of Added Mixed Rare Earth Oxides from a Uranium Concentrate Containing Added Thorium

(Using the complete procedure)

Test No.	Weight of Uranium Concn., Grams	Weight of Added Thorium Nitrate, ^a Grams	Weight of Mixed Rare Earth-Oxide, Grams		Recovery, %
			Added	Recovered	
1	20.0	2.55	0.049	0.044	90
2	20.0	2.74	0.099	0.089	90

^a Th(NO₃)₄ · 4 H₂O.

rare earth oxides to chlorides is already complete at 665° C.

Effect of Chlorination Time on Rare Earth Recovery. The literature data (Table II) indicated that a temperature of 900° C. would be required to volatilize thorium chloride. It was therefore considered advisable to determine the loss of the more volatile rare earth chlorides at this temperature. Because, in so far as uranium refinery specifications are concerned, gadolinium is the most important of the rare earths that have low-boiling chlorides, tests were carried out using 100-mg. portions of gadolinium oxide and chlorination times varying from 10 to 45 minutes. The results of these tests, given in Table III, indicate that the chlorination-volatilization period at 900° C. should not exceed 30 minutes if a recovery of 90% or better is to be realized.

Recovery of Rare Earths by the Complete Procedure. INDIVIDUAL RARE EARTHS. To establish the re-

Table VI. Comparison of Composition of Mixed Rare Earth Oxides Recovered with That of Starting Material

(Semi-quantitative spectrographic analysis)

Element	Found in Sample, %		Content in Starting Material, %
	Test 1	Test 2	
Y	1	1.5	2
La	15	15	15
Ce	PC ^a	PC	PC
Sm	3	3	3
Gd	2	2	2
Dy	3	3	3
Yb	0.1	0.1	0.1
Si	0.2	0.1	0.3
Fe	0.3	0.07	0.2
Al	0.25	0.15	0.1
Mg	0.2	0.2	0.08
Cu	0.08	0.05	0.02
Ti	0.15	0.01	0.02
Bi	1.5	0.02	0.07
B	0.02	0.006	0.005
Mn	0.04	0.02	ND ^b
Pb	0.03	0.05	ND

^a Principal constituent, over 20%.

^b Not detected.

Table VII. Semiquantitative Spectrographic Analysis of Rare Earth Concentrates [Obtained by extraction chlorination and by the method of Carron *et al.* (5) from a Beaverlodge area carbonate leach concentrate]

Extraction-Chlorination Precipitate		Precipitate, Method of Carron <i>et al.</i>	
Element	%	Element	%
Y	PC ^a	Mg	1
La	2 ^b	Ca	0.9
Ce	PC ^a	Si	1.5
Sm	1.5 ^b	Ti	0.15
Eu	0.2 ^b	Cu	0.07
Gd	4 ^b	Ba	0.05
Dy	6 ^b	Al	0.15
Ho	0.5 ^c	Fe	0.15
Er	1.0 ^c	Pb	0.15
Tm	2 ^c	Mn	0.2
Yb	6 ^c	B	0.015
Lu	2 ^c		
Sc	...		

- ^a Principal constituent, over 20%.
- ^b Identification not positive.
- ^c Qualitative estimate.

The recoveries of the individual elements are given in Table IV.

MIXED RARE EARTHS. In a second series of tests, both thorium and the mixed rare earths were added to 20-gram portions of the same concentrate. This material was carried through the whole procedure. The recoveries are given in Table V. In Table VI, spectrographic analyses of the recovered rare earths are compared with the spectrographic analysis of the mixed rare earth starting material.

Analysis of Typical Concentrates.

URANIUM CHEMICAL PRECIPITATES. Two typical uranium chemical concentrates were carried through the whole procedure. One of these, the product from the carbonate leach process on an ore from the Beaverlodge area, was high in rare earths and low in thorium. The other, produced by acid leaching of a Blind River ore, followed by ion exchange upgrading and two-stage precipitation, contained moderate amounts of thorium but virtually no rare earths. These tests established that good recovery of the rare earths could be obtained and that thorium is completely volatilized, when authentic sample material was used.

In the first case, a rare earth content of 0.26% was found. This sample, analyzed by the method of Carron *et al.* (5), gave a precipitate corresponding to 0.42% of the sample weight; when this number was corrected for nonrare earths on the basis of the spectrographic analysis, it gave a value of 0.27% total rare earths plus yttrium. The spectrographic results on both samples are given in Table VII. This shows the extraction-chlorination precipitate to be free from all but traces of nonrare earth material. The absence of scandium in particular is noteworthy. The precipitate obtained by the method of Carron *et al.*, by contrast, contains about 25% of nonrare earths as the elements.

Table VIII. Composition of Euxenite Concentrate

Element	%	Element	%	Element	%
U ^a	4.5	Ba ^b	3	Y ^b	5
Th ^a	0.6	Al ^b	2	Gd ^b	0.2
Nb ^a	12	Ca ^b	2	Dy ^b	2
Ti ^b	12	Sr ^b	2	Yb ^b	1.5
Ta ^{b,c}	2	Pb ^b	1.5		
Si ^b	8	Mn ^b	0.2		
Fe ^b	4	Mg ^b	0.15		

- ^a Chemical.
- ^b Spectrographic (semiquantitative).
- ^c X-ray fluorescence.

Table IX. Composition of Rare Earth Oxides Obtained from Euxenite (Table VI) by Chlorination Procedure

(Spectrographic semiquantitative analysis)

Element	%	Element	%
Y	PC ^a	Si	0.8
Eu	0.2 ^b	Mg	0.25
Gd	4 ^b	Mn	0.2
Dy	6	Al	0.15
Ho	0.5 ^b	Ti	0.05
Er	10 ^c	B	0.01
Tm	2 ^c	Cu	0.08
Yb	15	Ca	0.4
Lu	2 ^c		

- ^a Principal constituent.
- ^b Identification not positive.
- ^c Qualitative estimate.

In the second sample no precipitate was obtained, showing again that the nonrare earth elements were completely removed. The method of Carron *et al.* gave a value of less than 0.003% on this sample.

CHLORINATION OF A EUXENITE CONCENTRATE. Many radioactive mineral occurrences in Canada consist basically of niobium-tantalum ores, containing minerals of the pyrochlore and samarskite series. These minerals are composed of rare earths, uranium, and thorium niobotantalates. They are not amenable to dilute sulfuric acid or

alkali carbonate leaching, but can sometimes be concentrated by physical means. Though they are usually low in uranium and thorium content, the concentrates are high in rare earths and the earth acids.

Conventionally, these materials are first treated with hydrofluoric acid, which dissolves the ore and converts the earth acids to soluble complex fluonobates and fluotantalates. The insoluble fluorides, which include thorium and the rare earth fluorides, are removed and treated by the oxalate-sebacate method. Though very insoluble, the rare earth fluorides are gelatinous and sometimes even colloidal, so that they are difficult to separate from the solution.

Accordingly, a test was carried out to determine whether the rare earths could be separated from a typical euxenite concentrate by the chlorination procedure. Direct chlorination without previous extraction was employed, because the extraction process would not upgrade the rare earth content significantly and the rare earths were known to be present in sufficient amounts to permit use of a sample which could be accommodated in the apparatus. A 1-gram sample was used, and the chlorination was carried out as described under Procedure.

The rare earth oxides obtained weighed 176 mg., indicating a rare earth content of 17.6%. The original composition of the mineral concentrate is given in Table VIII and the composition of the rare earth oxides is given in Table IX.

DISCUSSION

Large amounts of material cannot be successfully chlorinated by the technique employed. On the other hand, with most uranium concentrates, a sample of 10 to 20 grams is needed to provide the necessary 10 mg. of rare earths for the gravimetric finish and spectrographic examination. Removal of the bulk of uranium and thorium by a preliminary solvent extraction procedure effectively eliminates this difficulty.

The tributyl phosphate-carbon tetrachloride extraction step that is used is based on the procedure developed by Wray (22). Extraction coefficients for elements of interest in connection with the analysis of thorium and uranium concentrates are given in Table X. In some cases it has been necessary to extrapolate the literature data, and in other cases divergent results were found for values apparently obtained under similar conditions.

A point of particular importance, which is illustrated in the table, is that the extraction of the rare earths is suppressed while the extraction of uranium and thorium is occurring. Thus, if it is not necessary to remove these elements

completely (as is the case in the present method), extraction losses of the rare earths can be held at low levels. Two extractions will remove the bulk of the uranium from solutions of most uranium concentrates. With typical Canadian high-thorium products, a third extraction is desirable to remove the major part of the thorium and provide a rare earth concentrate of manageable size for the chlorination step. Sufficient thorium remains to prevent substantial extraction of the rare earths by the tributyl phosphate and to serve as a carrier for them in the subsequent precipitation with ammonia.

In the chlorination-volatilization step, the reaction between the metal oxides and sulfur monochloride was reported by Bourion (4) to be exothermic. This resulted in incandescence of the charge and premature melting, and led to the formation of nonvolatile thorium oxychloride. To avoid this, the technique of alternating between the chlorine-sulfur monochloride mixture and the pure chlorine was employed. By this procedure, the volatile chloride produced is volatilized progressively and a sudden rise in temperature due to the chlorination reaction is avoided.

The careful dehydration prior to the chlorination-volatilization step was also found to be necessary, to prevent formation of nonvolatile thorium oxychloride. Once formed, thorium oxychloride appears to resist vigorously any attempt at conversion to the volatile anhydrous chloride. As the principal aim of the method is to obtain rapid and complete separation of thorium, any reduction in over-all time for the analysis that leads to formation of the oxychloride must be avoided. While it is reasonably certain that with careful technique this dehydration time can be reduced, the pro-

cedure outlined here is the one that gave unfailingly good results.

In Table I are given the melting points, boiling points, and volatilization temperatures of the rare earth chlorides, and in Table II are given the melting points and boiling points of some of the elements commonly associated with the rare earths in ores and concentrates. An important observation is the proximity of the boiling point of scandium to that of thorium. This indicates that scandium should be volatilized along with the thorium. The results obtained with the Beaverlodge carbonate leach concentrate (Table VII) confirm this. On the other hand, the boiling point of yttrium is close to that of the rare earths and it is practically quantitatively recovered (Table IV). Some current

methods for rare earth determination give partial nonreproducible recoveries of both these elements.

A knowledge of the melting points is also of some value. The preferred mechanism is to have the chlorides sublime, because the solid material usually presents more surface for rapid volatilization. If the bulk of the constituents in the sample melt at a much lower temperature than that at which they volatilize, a pool of liquid forms and volatilization is slow. This slow volatilization can be partly overcome by using more sand in the combustion boat containing the sample.

In Table I the volatilization temperatures of the rare earths are given. These values were determined by Vickery (20) by visual observation of the

Table X. Partition Coefficients of Some Elements between 40% Tributyl Phosphate and 6N Nitric Acid Solution

Element	Concentration in Aqueous, Grams/Liter	Other Elements Present	E_2	Element	Concentration in Aqueous, Grams/Liter	E_2
U	5		50 (15)	La	Tracer	0.02 (18)
	50		10 (15)	Ce(IV)	Tracer, but see also reference (21)	0.2 (8)
	150		1 (15)			
Th	42		1.4 (22)	Ce(III)	Tracer	0.02 (18)
Zr	Tracer		18 (10)	Eu	Tracer	0.13 (18)
	Tracer		0.5 (1)	Sm	Tracer	0.05 (3)
		U-84 grams per liter in aqueous	0.08 (1)	Nb	Tracer	0.01 (8)
Sc	Tracer		0.05 (16)			
Y	Tracer		0.12 (18)			
	Tracer		0.02 (8)			
Total rare earths		Solvent 28% saturated with U	0.01 (7)			
Total rare earths		Solvent 62% saturated with U	0.002 (7)			

Table XI. Composition of Typical Uranium Concentrates from Major Producing Areas in Canada (Expressed as percentages)

Area	Process	U ₂ O ₅	ThO ₂	Fe	MgO	Na	CaO	V ₂ O ₅	TiO ₂	SiO ₂	Sc	Total Rare Earths
Bancroft	Acid leach, ion exchange, single-stage precipitation with MgO	75	1	2	8	1	0.5	0.002	0.07	2	0.001	0.05-0.15
Blind River	Acid leach, ion exchange, two-stage precipitation as sodium salt	80	0.7	0.2	0.1	2	2	0.01	0.1	0.5	0.001	0.00-0.02
Beaverlodge	Carbonate leach, caustic precipitation	75	0.1	1	0.2	6	0.5	2	0.1	4	0.02	0.1-0.3
Beaverlodge	Acid leach, ion exchange, single stage precipitation with MgO	70	0.02	0.5	8	2	0.5	0.05	0.003	0.5	0.004	0.00-0.02
Geat Bear Lake	Acid leach, solvent extraction, single stage precipitation from carbonate solution as sodium salt	75	<0.1	0.1	0.1	6	0.05	<0.002	<0.005	0.06	...	<0.005

Table XII. Distribution of Rare Earth Elements in Precipitates of Rare Earth Group from Typical Uranium Concentrates

Area	% Distribution												
	Y	La	Ce	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Lu	
Bancroft	14	25	50	2	...	2	3	3	...	
Blind River	25	15	30	3	...	5	10	5	...	
Beaverlodge, carbonate leach	30	5	30	3	0.2	3	5	0.5	10	2	8	2	
Beaverlodge, acid leach	15	12	...	5	6	2	2	

sublimation of rare earth chlorides, and are of more practical value than the actual boiling points in estimating the losses that may be expected at any particular temperature.

It has not been possible to analyze, by the new method, uranium concentrates from all the various producing areas. However, data on the composition of these materials are given in Tables XI and XII and these indicate that no elements are present which will cause interference in the proposed method. It is therefore considered that the method should be applicable to all the uranium refinery feed stocks being produced currently in this country.

SUMMARY AND CONCLUSIONS

A chlorination-volatilization procedure for the isolation of rare earths from the elements with which they are normally associated in uranium and thorium concentrates has been developed. In the case of concentrates containing a very large proportion of these two elements (such as uranium refinery feeds), a prior removal of part of the uranium and thorium is employed to permit use of a larger sample and to extend the range.

The purity of the rare earth concentrate is such that it need not be ex-

amined spectrographically for the presence of impurities, but can be weighed directly. The equipment required is simple, and the procedure can be carried out rapidly in the ordinary analytical laboratory.

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