



CANADA

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# THE DETERMINATION OF TOTAL RARE EARTHS IN HIGH GRADE URANIUM PRODUCTS



DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA

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EXTRACTION METALLURGY DIVISION

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THE DETERMINATION OF TOTAL RARE EARTHS  
IN HIGH GRADE URANIUM PRODUCTS

by

R.J. Guest\*

SYNOPSIS

A procedure is described for the determination of total rare earth oxides in high grade uranium products, based on the use of solvent extraction with long-chain alkyl amines. Extraction with tri-isooctylamine from strong hydrochloric acid medium removes uranium, zirconium, and a number of other ions. This is followed by a second extraction from sulphate solution, employing di(tridecyl P) amine to remove thorium. Following further conventional purification steps, mixed rare earth oxides are determined by ignition to the oxides, or by a suitable colorimetric method.

To establish the completeness of the separations, extraction coefficients for tri-isooctylamine have been determined for rare earths, uranium, zirconium, titanium and thorium in hydrochloric acid solutions of various strengths. The extent of rare earth pick-up by di(tridecyl P) amine and tri-isooctylamine from sulphate solutions at various pH values is also shown. Application of the procedure to synthetic high grade uranium samples and actual high grade uranium products indicates that reliable analyses can be obtained on a variety of sample material.

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Direction des mines

Rapport de recherche R 67

DÉTERMINATION DE LA TENEUR TOTALE EN TERRES RARES  
DANS LES CONCENTRÉS D'URANIUM

par

R. J. Guest\*

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## RÉSUMÉ

La présente étude décrit un procédé utilisé pour déterminer la teneur en oxydes de terres rares dans les concentrés d'uranium; ce procédé a recours à l'extraction par solvant à l'aide d'amines alcoyles à longues chaînes. L'extraction à l'aide de tri-isooctylamine à partir d'un milieu riche en acide chlorhydrique élimine l'uranium, le zirconium et un certain nombre d'autres éléments. Par une seconde extraction en milieu sulfaté, à l'aide de di(tri-decyl P) amine, on enlève le thorium. Après les autres étapes classiques de purification, les mélanges d'oxydes de terres rares sont déterminés par gravimétrie, ou par un procédé colorimétrique approprié.

Afin de s'assurer que les séparations sont parfaites, les coefficients d'extraction du tri-isooctylamine ont été déterminés pour les terres rares, l'uranium, le zirconium, le titane et le thorium, en présence de solutions plus ou moins fortes en acide chlorhydrique. On a également déterminé les quantités de terres rares extraites par le di(tridecyl P) amine et le tri-isooctylamine à partir de solutions sulfatées à divers pH. L'application de ce procédé à des concentrés synthétiques d'uranium ainsi qu'à des produits naturels d'uranium de haute teneur indique qu'on peut en arriver à des analyses sûres dans le cas d'une foule d'échantillons.

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1. Extraction Coefficients of Uranium, Zirconium, Mixed Rare Earths and Titanium from Hydrochloric Acid Solution with Tri-isooctylamine in Methyl Isobutyl Ketone and Carbon Tetrachloride.....	14
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## INTRODUCTION

As a result of their strong neutron absorption characteristics, the amount of certain rare earths that can be tolerated in uranium intended for nuclear applications is very low. For this reason a stringent specification is set on the rare earth content of mill concentrates; and the determination of the rare earths at such low concentrations presents considerable difficulty. The method now in use in this Division (1) is long and involved. Separations included in the procedure are: a) ion exchange, b) two oxalate precipitations, c) an ammonium hydroxide precipitation, and d) two sebacate precipitations. This procedure does not eliminate all non-rare earth materials, so the gravimetric finish gives high results. As a result, a spectrographic examination of the final rare earth precipitate is necessary to permit a correction for the interfering elements.

A chlorination-volatilization technique (2) which has also been developed here uses special apparatus, the cost of which might not be justified where a rare earth determination is only occasionally required. It was therefore felt that there was a need for a simpler method for the determination of rare earths, employing equipment readily available in a control laboratory.

Previous work in this Division (3) had led to the belief that a solvent extraction technique might be of value in developing a

rapid and accurate procedure for rare earth determination. It had been found that uranium, zirconium and molybdenum could be separated from the rare earths by the extraction of the former three ions from sulphate solution with tri-isooctylamine. Thorium could then be extracted with di(tridecyl P) amine, or amine 9D-178, from sulphate solution. Extraction of the rare earths was low with tri-isooctylamine, but not quite so low with di(tridecyl P) amine or amine 9D-178, and required the use of a scrub solution and/or a lower pH to reduce rare earth loss in these cases.

It was found by Moore<sup>(4)</sup> that extraction with tri-isooctylamine from hydrochloric acid solution will separate uranium and plutonium from thorium and the rare earths. This paper also showed that by varying the acidity in hydrochloric acid, some additional separations were feasible. A separation of such ions as iron III, cobalt<sup>II</sup>, zinc<sup>II</sup>, vanadium<sup>V</sup> and molybdenum<sup>VI</sup> would be expected.

The work described in this report, then, is an attempt to evaluate the use of tri-isooctylamine and di(tridecyl P) amine as extractants of contaminants in acid media, before final rare earth determination. It is hoped to obtain a purer rare earth oxide concentrate for weighing or for colorimetric finish, and to improve the rare earth recovery and speed of the analyses compared with other methods.

## REAGENTS AND APPARATUS

Reagents5% Amine 9D-178 in Carbon Tetrachloride

Mix 50 ml of amine 9D-178 (Rohm and Haas Company, Washington Square, Philadelphia 5, Pa., U.S.A.) with 950 ml of carbon tetrachloride. Equilibrate as described under "Procedure" on page 5.

5% Di(tridecyl P) Amine (DTDA) in Carbon Tetrachloride

Mix 50 ml of di(tridecyl P) amine (Carbide Chemicals Company, Division of Union Carbide Canada Limited, Montreal, Canada) with 950 ml of carbon tetrachloride. Equilibrate as described under "Procedure".

5% Di(tridecyl P) Amine in Varsol

Mix 50 ml of di(tridecyl P) amine with 940 ml of Varsol and 10 ml of decyl alcohol. Equilibrate as described under "Procedure".

15% Tri-isooctylamine (TIOA) in Carbon Tetrachloride

Mix 150 ml of tri-isooctylamine with 850 ml of carbon tetrachloride. Equilibrate as described under "Procedure".

20% Tri-isooctylamine in 15% Methyl Isobutyl Ketone (MIBK) and 65% Carbon Tetrachloride

Mix 200 ml of tri-isooctylamine with 150 ml of methyl isobutyl ketone and 650 ml of carbon tetrachloride.

Mixed Rare Earths in Sulphuric Acid Solution

Add mixed rare earths (Lindsay Chemical Co., West Chicago, Illinois, U.S.A., Code 330) to dilute sulphuric acid, take to sulphuric acid fumes, and dilute with distilled water to a desired volume. If necessary, add a little hydrogen peroxide or ascorbic acid to aid



solution. Standardize by means of an ammonia or oxalate precipitation; ignite and weigh.

Lanthanum in Sulphuric Acid Solution

Add lanthanum oxide to a dilute sulphuric acid solution, take to sulphuric acid fumes, and dilute with distilled water to a desired volume. Standardize by means of an ammonia or oxalate precipitation; ignite and weigh.

Lanthanum in Hydrochloric Acid Solution

Dissolve lanthanum oxide or lanthanum chloride in concentrated hydrochloric acid, and dilute to a desired volume. Standardize by means of an ammonia or oxalate precipitation; ignite and weigh.

Mixed Rare Earths in Hydrochloric Acid Solution

Dissolve mixed rare earths (Lindsay Chemical Co., West Chicago, Illinois, U.S.A., Code 330) in concentrated hydrochloric acid and dilute to a desired volume with concentrated hydrochloric acid. Standardize by means of an ammonia or oxalate precipitation; ignite and weigh.

Uranium, Zirconium, Titanium and Thorium in Hydrochloric Acid Solution

Dissolve, individually, appropriate amounts of uranium, zirconium, titanium and thorium, as the oxide or chloride, in concentrated hydrochloric acid and dilute to a desired volume with concentrated hydrochloric acid.

### Apparatus

Beckman pH meter, model "H".

Beckman "B" or "DU" spectrophotometer.

250 ml separatory funnels.

## PROCEDURE

### General

#### Determination of the Extraction Coefficient

The general procedure used for determining the extraction coefficient was as described in Research Report R 43, (3) and the extraction coefficient was calculated from:

$$\frac{\text{Concentration of ion in organic}}{\text{Concentration of ion in aqueous}} = E_a^o$$

#### Equilibration of the Amine

For extraction from sulphuric acid medium, shake the amine-diluent mixture with a solution of 2.5% sulphuric acid. Draw off and discard the aqueous fraction, and wash the organic fraction with portions of 0.5% sulphuric acid solution until the pH of the aqueous fraction remains at about pH 1.

### Main Procedure

#### Sample Dissolution

Weigh a 20 g sample of the high grade concentrate into a 250 ml beaker. Treat with 30 ml concentrated hydrochloric acid, warming and stirring as required. Transfer to a 50 ml centrifuge tube and

centrifuge 15 minutes to remove insoluble matter. Decant the supernatant solution into a clean 250 ml beaker. Rinse the original beaker into the centrifuge tube with a 25 ml portion of concentrated hydrochloric acid. Repulp the insoluble residue with the acid, centrifuge again, and decant the wash into the same beaker as the initial supernatant solution. Rinse the beaker into the centrifuge tube with 25 ml of concentrated hydrochloric acid, repulp the residue again, and centrifuge as before. Decant the acid wash into the beaker.

Transfer the insoluble residue to a 50 ml platinum dish with water. Add 5 ml of hydrofluoric acid and take to dryness. Repeat with 5 ml more of hydrofluoric acid. Add perchloric acid, fume to dryness twice with 5 ml portions, and, finally, fuse the residue remaining with 5 g of sodium carbonate, take up in water, and filter. Discard the filtrate. Dissolve the residue in a minimum of concentrated hydrochloric acid. Dilute to 100 ml, boil, and precipitate with ammonia. Filter and discard the filtrate. Dissolve the precipitate in about 5 ml of concentrated hydrochloric acid and add to the main solutions, using about 15 ml of water for rinsing.

#### Solvent Extraction

Rinse the sample solution into a 250 ml separatory funnel with concentrated hydrochloric acid and add 2-3 ml of 30% hydrogen peroxide. At this point the sample solution should have a volume of about 100 ml, and should be approximately 10 molar in hydrochloric acid. Add 100 ml of the 20% TIOA-15% MIBK-65%  $\text{CCl}_4$  solution, and

shake the mixture for about 2 minutes. Allow the layers to separate, and discard the bottom(organic)layer. Add 100 ml of the TIOA solution and repeat the extraction. Extract once more with 50 ml of TIOA solution. If the formerly deeply coloured aqueous fraction is now colourless or virtually so, it may be assumed that this step is complete. If titanium is present, however, this colour will not disappear and the expected uranium content of the sample must serve as the indication of how much TIOA solution should be used. The above procedure should be adequate to remove at least 10 g of uranium.

Evaporate the aqueous fraction to dryness. Add about 5 ml of concentrated nitric acid and 10 ml of 1:1 sulphuric acid, and take to sulphuric acid fumes. Cool, and add 5-10 ml of concentrated nitric acid and 1-2 ml of perchloric acid to complete the destruction of organic matter. Take to sulphuric acid fumes, wash down the sides of the beaker, and repeat the fuming step. Cool. Cautiously add 50-100 ml of distilled water, warm to dissolve the salts, and cool again. Adjust the pH to 0.6 with ammonia, using a pH meter.

Transfer the sample solution (about 100 ml) to a 250 ml separatory funnel; add 1-2 ml of 30% hydrogen peroxide and 100 ml of 5% DTDA in Varsol. Shake for 2 minutes. Transfer the aqueous (lower) fraction to a second separatory funnel, add 50 ml of DTDA solution, and repeat the extraction.

Carry out a spot test for thorium, using Thoron reagent, and continue to extract with DTDA solution until the test indicates thorium is completely removed. As a precautionary step, extract once more with a small portion of DTDA solution. Combine the last two extraction fractions and scrub them once with 0.5 N sulphuric acid solution. Add the scrub solution to the aqueous fraction containing the rare earths. Discard all organic fractions. Evaporate the aqueous solution to dryness, destroy organic matter, and redissolve the salts, as described previously.

Precipitate with ammonia and filter to remove sulphates, dissolve the precipitate, and destroy the paper, using a 2-1 mixture of nitric-perchloric acid. After evaporating the sample to dryness, take up soluble salts with a few ml of concentrated nitric acid and about 5 ml of 30% hydrogen peroxide, and dilute the solution to 100 ml. Add sufficient solution of calcium nitrate to give 100 mg of calcium oxide, and adjust the pH to about 2.0 with ammonia, using a pH meter. Heat the solution to boiling and add about 5 g of solid oxalic acid per 100 ml of sample solution. Boil with stirring for 15-20 minutes, or until precipitation seems to be complete. Allow the precipitate to stand for several hours or preferably overnight, filter on Whatman No. 42 paper, and wash with a 1% oxalic acid solution of about pH 2. If titanium is high, repeat the oxalate precipitation step. Discard the filtrate. Finally, dissolve the precipitate and destroy the paper with nitric-perchloric mixture as described above.

Take up the soluble salts in dilute hydrochloric acid and filter the solution through Whatman No. 42 paper to remove any silica which remains. Carry out a double ammonia precipitation in the presence of about 1 g of ammonium chloride. Finally ignite the paper and precipitate at 950°C, weigh, and have the ignited precipitate examined spectrographically for contaminants. Alternatively, dissolve the ammonia precipitate in acid and assay colorimetrically by the arsenazo colorimetric method.<sup>(5)</sup>

#### EXPERIMENTAL

##### Determination of Extraction Coefficients of Rare Earths from Sulphate Solutions with 5% Di(tridecyl P) Amine, Amine 9D-178 and Tri-isooctylamine in Various Solvents

In an earlier report,<sup>(3)</sup> a number of tests were described which established that separation of rare earths could be obtained from gross amounts of certain contaminants by extraction of the contaminants from sulphate solutions with DTDA, amine 9D-178 and TIOA, leaving the rare earths behind. A number of the extraction coefficients of rare earths found at that time, together with certain information obtained since, are tabulated in Table 1. It seems clear from a study of these data that although extraction coefficients of rare earths with TIOA were satisfactorily low at pH 1, with DTDA it would be desirable to lower the pH to about 0.6 to avoid loss of rare earths to the organic phase. Although previous work has shown that extraction of thorium using DTDA is good at a pH of 0.6, it was difficult to extract thorium efficiently with amine 9D-178 at this pH.

TABLE 1

Determination of Extraction Coefficients of Rare Earths from Sulphate Solutions with 5% Di(tridecyl P) Amine, Amine 9D-178 and Tri-isooctylamine in Various Solvents

Rare earths present	Found in organic fraction	Found in aqueous fraction	pH of aqueous fraction	Volume, ml, org./aq.	Organic phase composition	Extraction coefficient, $E_a$	Remarks
58.6 mg $\text{La}_2\text{O}_3$	38.5 mg $\text{La}_2\text{O}_3$	20.1 mg $\text{La}_2\text{O}_3$ calculated	1.5	40/40	5% DTDA-95% $\text{CCl}_4$	1.9	Very cloudy layers
50 mg $\text{Re}_2\text{O}_3$	25.2 mg $\text{Re}_2\text{O}_3$	24.5 mg $\text{Re}_2\text{O}_3$ calculated	1.0	25/25	5% DTDA-95% $\text{CCl}_4$	1.0	10 g/l ascorbic acid added
50 mg $\text{Re}_2\text{O}_3$	2.30 mg $\text{Re}_2\text{O}_3$	47.7 mg $\text{Re}_2\text{O}_3$ calculated	0.6	25/25	5% DTDA-95% $\text{CCl}_4$	0.048	10 g/l ascorbic acid added
50 mg $\text{Re}_2\text{O}_3$	1.01 mg $\text{Re}_2\text{O}_3$	49.0 mg $\text{Re}_2\text{O}_3$ calculated	0.6	25/25	5% DTDA-95% $\text{CCl}_4$	0.021	10 g/l ascorbic acid + 40 g/l $\text{Na}_2\text{SO}_4$ added
50 mg $\text{Re}_2\text{O}_3$	11.4 mg $\text{Re}_2\text{O}_3$	38.6 mg $\text{Re}_2\text{O}_3$ calculated	1.0	25/25	5% DTDA in 95% Varsol-1% decyl alc.	0.30	10 g/l ascorbic acid added
50 mg $\text{Re}_2\text{O}_3$	1.33 mg $\text{Re}_2\text{O}_3$	48.7 mg $\text{Re}_2\text{O}_3$ calculated	0.6	25/25	5% DTDA in 95% Varsol-1% decyl alc.	0.027	10 g/l ascorbic acid added
50 mg $\text{Re}_2\text{O}_3$	1.35 mg $\text{Re}_2\text{O}_3$	48.6 mg $\text{Re}_2\text{O}_3$ calculated	0.6	25/25	5% DTDA in 95% Varsol-1% decyl alc.	0.028	10 g/l ascorbic acid + 40 g/l $\text{Na}_2\text{SO}_4$ added
100 mg $\text{Re}_2\text{O}_3$	1.06 mg $\text{Re}_2\text{O}_3$	98.9 mg $\text{Re}_2\text{O}_3$ calculated*	1.0	55/55	15% TIOA-85% $\text{CCl}_4$	0.011	1 ml of 30% $\text{H}_2\text{O}_2$ added
58.6 mg $\text{La}_2\text{O}_3$	0.53 mg $\text{La}_2\text{O}_3$	58.1 mg $\text{La}_2\text{O}_3$ calculated	1.0	40/40	15% TIOA-85% $\text{CCl}_4$	0.009	
58.6 mg $\text{La}_2\text{O}_3$	0.80 mg $\text{La}_2\text{O}_3$	57.8 mg $\text{La}_2\text{O}_3$ calculated	1.5	40/40	15% TIOA-85% $\text{CCl}_4$	0.014	
100 mg $\text{Re}_2\text{O}_3$	5.75 mg $\text{Re}_2\text{O}_3$	94.2 mg $\text{Re}_2\text{O}_3$ calculated*	1.0	55/55	5% 9D-178 in $\text{CCl}_4$	0.061	Excess of $\text{H}_2\text{O}_2$ added

Extraction of Uranium from Hydrochloric Acid Solution with Tri-isooctylamine in Various Solvent Combinations

Recent work by Moore<sup>(4)</sup> had indicated that a large number of elements, including uranium and zirconium, could be extracted from strong hydrochloric acid solution by TIOA in various solvents. The prospect of using such a technique in the analysis of high grade uranium precipitate is attractive, as the precipitate is readily amenable to hydrochloric acid treatment. A number of tests were carried out to evaluate solutions of TIOA in various solvents, as uranium extractants. Moore has indicated that methyl isobutyl ketone (MIBK) was a suitable solvent, and that a 20% concentration of TIOA was satisfactory. As it was desirable to have the organic layer heavier than the aqueous layer and thus obtain uranium loading in the bottom layer, combinations of TIOA and MIBK with carbon tetrachloride (CCl<sub>4</sub>) were tested. As shown in Table 2, four mixtures were tried. Of these mixtures, a combination of 20% TIOA-15% MIBK-65% CCl<sub>4</sub> was chosen.

Extraction of Various Ions from Hydrochloric Acid Solution with 20% Tri-isooctylamine-15% Methyl Isobutyl Ketone-65% Carbon Tetrachloride

The extraction coefficients of uranium, zirconium, lanthanum, mixed rare earths, titanium and thorium in hydrochloric acid medium were determined, using a 20% TIOA-15% MIBK-65% CCl<sub>4</sub> mixture. The results obtained, as shown in Table 3 and Figure 1, are in general agreement with the findings of Moore.<sup>(4)</sup> Uranium was extracted over a fairly wide range of acidity, whereas zirconium required a



TABLE 2

Extraction of Uranium from Hydrochloric Acid Solution with  
Tri-isooctylamine in Various Solvent Combinations

Test No.	Uranium added, mg U <sub>3</sub> O <sub>8</sub>	Uranium found in aqueous phase, mg U <sub>3</sub> O <sub>8</sub>	Phase ratio for extr., ml, org./aq.	HCl strength	Extraction coefficient, * E <sub>a</sub> <sup>o</sup>	Composition of organic extractant
1	1000	1.62	50/25	Conc.	308	20% TIOA - 80% MIBK
2	1000	4.44	50/25	Conc.	112	20% TIOA - 5% MIBK - 75% CCl <sub>4</sub>
3	1000	1.82	50/25	Conc.	274	20% TIOA - 15% MIBK - 65% CCl <sub>4</sub>
4	1000	1.90	50/25	Conc.	263	20% TIOA - 30% MIBK - 50% CCl <sub>4</sub>

\*.uranium content of organic phase calculated

TABLE 3

Extraction of Various Ions from Hydrochloric Acid Solution with 20%  
Tri-isooctylamine-15% Methyl Isobutyl Ketone-65% Carbon Tetrachloride

Test No.	Ion added	Ion found in organic phase	Ion found in aqueous phase	Molarity in hydrochloric acid	Extraction ** coefficient, $E_a$
1	204 mg $U_3O_8$	200 mg $U_3O_8$ calcd	4.0 mg $U_3O_8$	11.8	50.
2	204 mg $U_3O_8$	203 mg $U_3O_8$ calcd	0.75 mg $U_3O_8$	9.9	271..
3	204 mg $U_3O_8$	203 mg $U_3O_8$ calcd	0.54 mg $U_3O_8$	7.0	377.
4	125.5 mg $ZrO_2$	124.3 mg $ZrO_2$ calcd	1.2 mg $ZrO_2$	11.8	104.
5	125.5 mg $ZrO_2$	110.2 mg $ZrO_2$ calcd	15.3 mg $ZrO_2$	9.9	7.2
6	125.5 mg $ZrO_2$	1.7 mg $ZrO_2$	138. mg $ZrO_2$	7.0	0.01
7*	169. mg La	1.23 mg La	171. mg La	9.0	0.007
8*	44.7 mg $Re_2O_3$	1.09 mg $Re_2O_3$	43.6 mg $Re_2O_3$ calcd	10.9	0.025
9*	44.7 mg $Re_2O_3$	1.34 mg $Re_2O_3$	43.4 mg $Re_2O_3$ calcd	10.9	0.031
10*	44.7 mg $Re_2O_3$	1.13 mg $Re_2O_3$	43.6 mg $Re_2O_3$ calcd	9.6	0.026
11*	44.7 mg $Re_2O_3$	1.57 mg $Re_2O_3$	43.1 mg $Re_2O_3$ calcd	9.6	0.036
12*	44.7 mg $Re_2O_3$	1.63 mg $Re_2O_3$	43.1 mg $Re_2O_3$ calcd	6.7	0.038
13*	44.7 mg $Re_2O_3$	1.56 mg $Re_2O_3$	43.1 mg $Re_2O_3$ calcd	6.7	0.036
14*	89.3 mg $Re_2O_3$	1.51 mg $Re_2O_3$	90.0 mg $Re_2O_3$	9.0	0.017
15	139 mg Ti	6.75 mg Ti	132.2 mg Ti calcd	11.5	0.051
16	139 mg Ti	1.42 mg Ti	137.6 mg Ti calcd	9.6	0.010
17	139 mg Ti	0.33 mg Ti	138.7 mg Ti calcd	6.7	0.002
18	121 mg $ThO_2$	<0.03 mg $ThO_2$	121 mg $ThO_2$ calcd	11.8	<0.001
19	121 mg $ThO_2$	<0.03 mg $ThO_2$	121 mg $ThO_2$ calcd	9.9	<0.001
20	121 mg $ThO_2$	<0.03 mg $ThO_2$	121 mg $ThO_2$ calcd	7.0	<0.001

\* 1 ml of 30% hydrogen peroxide added before extraction

\*\* Phase ratio for extraction, 1:1

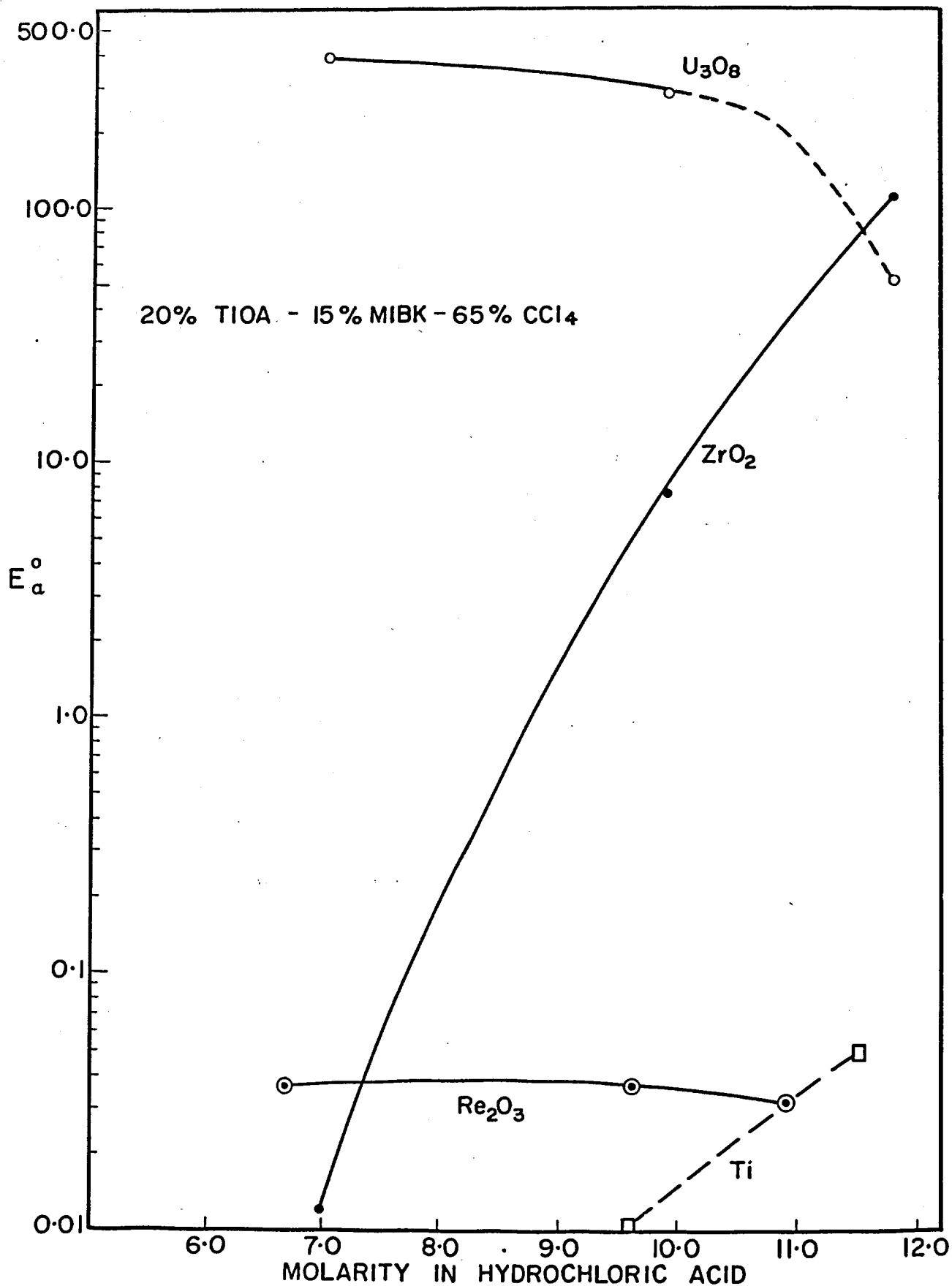


FIGURE 1

EXTRACTION COEFFICIENTS OF URANIUM, ZIRCONIUM, MIXED RARE EARTHS AND TITANIUM FROM HYDROCHLORIC ACID SOLUTION WITH TRI-ISOOCTYLAMINE IN METHYL ISOBUTYL KETONE AND CARBON TETRACHLORIDE

strongly acid solution; and rare earths, thorium and titanium were not extracted appreciably at any acidity tried. This established that a second extraction process, to separate thorium from the rare earths, would be necessary. A logical separation would be an extraction of thorium from sulphate medium with DTDA or amine 9D-178. Titanium would then have to be removed by an oxalate separation, as the solvent extraction procedures tried were only partially successful in separating it from the rare earths.

Application of Solvent Extraction Procedures for Removal of Contaminants Before Rare Earth Determination in Synthetic High Grade Uranium Products

A comparison of two general procedures was then made on synthetic high grade uranium samples containing thorium and rare earths. One procedure employed extraction of uranium from sulphate solution at pH 1.0 by means of 15% TIOA in carbon tetrachloride, followed by extraction of thorium with 5% 9D-178 in carbon tetrachloride. It was thought advisable to use 9D-178 here, rather than DTDA, because of its lower rare earth extraction (Table 1). Thus, in this procedure both extractions could be carried out on the same solution without pH adjustment. Results shown for synthetics No. 1 and No. 2 (Table 4) indicated that a separation was feasible.

A second procedure utilized extraction of uranium by means of a 20% TIOA-15% MIBK-65% CCl<sub>4</sub> mixture at 10 M acidity in hydrochloric acid. This step was followed by addition of sulphuric

TABLE 4

Application of Solvent Extraction Procedures for Removal of Contaminants  
Before Rare Earth Determination in Synthetic High Grade Uranium Products

Sample	Composition of sample	Acidity	Extractant	Rare Earths Present		Rare Earths Found	
				as mg Re <sub>2</sub> O <sub>3</sub>	% Re <sub>2</sub> O <sub>3</sub> **	as mg Re <sub>2</sub> O <sub>3</sub>	% Re <sub>2</sub> O <sub>3</sub> **
Synthetic No. 1	1.00 g U <sub>3</sub> O <sub>8</sub> 0.0430 g ThO <sub>2</sub> 0.009 g La <sub>2</sub> O <sub>3</sub>	pH 1.0 sulphate solution	15% TIOA in CCl <sub>4</sub> + 5% 9D-178 in CCl <sub>4</sub>	9.31	0.05	12.6*	0.06
Synthetic No. 2	10.2 g U <sub>3</sub> O <sub>8</sub> 0.215 g ThO <sub>2</sub> 0.0279 g La <sub>2</sub> O <sub>3</sub>	pH 1.0 sulphate solution	15% TIOA in CCl <sub>4</sub> + 5% 9D-178 in CCl <sub>4</sub>	27.9	0.14	26.6	0.13
Synthetic No. 3	10.2 g U <sub>3</sub> O <sub>8</sub> 0.24 g ThO <sub>2</sub> 0.0264 g Re <sub>2</sub> O <sub>3</sub>	10 M hydrochloric acid solution, and pH 0.6 sulphate solution	20% TIOA -15% MIBK -65% CCl <sub>4</sub> , and 5% DTDA in Varsol	26.4	0.13	26.4	0.13
Synthetic No. 4	10.2 g U <sub>3</sub> O <sub>8</sub> 0.24 g ThO <sub>2</sub> 0.0264 g Re <sub>2</sub> O <sub>3</sub>	10 M hydrochloric acid solution, and pH 0.6 sulphate solution	20% TIOA-15% MIBK -65% CCl <sub>4</sub> , and 5% DTDA in Varsol	26.4	0.13	26.2	0.13

\* Removal of thorium not checked by a spot test, and thorium subsequently found to be only 84% removed. Lanthanum analysis carried out colorimetrically.

\*\* % Re<sub>2</sub>O<sub>3</sub> calculated on the basis of mg Re<sub>2</sub>O<sub>3</sub> present in 20 g sample material.

acid and evaporation of the aqueous solution to sulphuric fumes, then by adjustment of the pH to 0.6 and extraction of thorium by means of 5% DTDA in Varsol. Under these conditions, low rare earth losses would be expected.<sup>(3)</sup> This procedure (synthetics No. 3 and No. 4) gave satisfactory recovery of rare earths. In both procedures, the rare earths were given a double ammonia precipitation, and an oxalate separation, in order to duplicate conditions expected to be required on actual samples. Final rare earth determination, except where noted, was by weighing as rare earth oxides.

#### Comparison of Procedures for Analysis of Mixed Rare Earth Oxides in High Grade Uranium Products

The next step in the investigation was to test both of the procedures described under the previous heading on actual high grade uranium products, and on these products with added mixed rare earth oxides. Results were then compared with analyses obtained by the regular laboratory procedure as described in detail in the Manual.<sup>(1)</sup> All final rare earth precipitates were subjected to spectrographic examination, and appropriate corrections were made.

The results, as shown in Table 5, were obtained by only one of the two solvent extraction procedures. Under practical conditions the solvent extraction procedure for removing uranium from sulphate medium was found to be very clumsy and was not completed. The sample was found to be soluble in sulphuric acid medium only with

TABLE 5

The Determination of Total Rare Earths in High Grade  
Uranium Products

Sample	Treatment	Rare earths found % $\text{Re}_2\text{O}_3$ (Corrected for all impurities after spectrographic analysis)			
		Ignited precipitate	including	except	except
			$\text{SiO}_2 + \text{Y}_2\text{O}_3$	$\text{SiO}_2$	$\text{Y}_2\text{O}_3 + \text{SiO}_2$
RE 3151*** (Bicroft uranium conc.)	Regular procedure	0.56, 0.55	0.47	0.48	0.53
RE 3151	Solvent extraction procedure	0.58, 0.56	0.44	0.49	0.54
RE 3151 (with 0.25% mixed $\text{Re}_2\text{O}_3$ added)*	Solvent extraction procedure	0.81, 0.84 av. minus $\text{Re}_2\text{O}_3=0.57$	0.48	0.49	0.51
RE 3152*** (Pronto uranium conc.)	Regular procedure	0.08, 0.05	0.03**	-	-
RE 3152	Solvent extraction procedure	0.05, 0.05	0.02**	-	-
RE 3152 (with 0.25% mixed $\text{Re}_2\text{O}_3$ added)*	Solvent extraction procedure	0.29, 0.28 av. minus $\text{Re}_2\text{O}_3=0.03$	0.05	0.05	0.03
Mixed $\text{Re}_2\text{O}_3$ standard	Double oxalate + ammonia precipitation	0.26, 0.25	0.22	0.22	0.25

\* Silica filtered off before final ammonia precipitation and ignition.

\*\* Calculated from percentage of rare earths estimated in ignited precipitate, since total rare earths were less than 50% of the final product.

\*\*\* Other analyses on RE 3151 and RE 3152 were:

RE 3151 - 54.5%  $\text{U}_3\text{O}_8$ , 0.70%  $\text{ThO}_2$ , 4.3% Fe, 10.2% Mg, 0.32% Ti, 0.8% CaO, and 4.0%  $\text{SiO}_2$ .

RE 3152 - 56.0%  $\text{U}_3\text{O}_8$ , 1.10%  $\text{ThO}_2$ , 5.0% Fe, 5.7% Mg, 0.24% Ti, 1.1% CaO, and 4.0%  $\text{SiO}_2$ .

great difficulty. Further, the quantity of liquid with which it was necessary to work in order to remove all the uranium was found to be considerably higher than with hydrochloric acid medium. In general, then, the procedure employing TIOA extraction from hydrochloric acid medium, followed by DTDA extraction from sulphuric acid medium, is considered to be by far the more satisfactory of the two procedures tested. Additional steps, such as two ammonia precipitations, an oxalate separation to remove titanium, and a filtration before the final ammonia precipitation to remove silica, were found necessary.

Spectrographic analyses (semi-quantitative) were made on the products and are shown in Table 6. It will be noted that yttrium, silica and lead are almost always contaminants, although the extra filtration step removes most of the silica.

#### SUMMARY AND DISCUSSION

The most satisfactory of the solvent extraction procedures tried for removal of uranium was extraction from hydrochloric acid medium with 20% TIOA-15% MIBK-65%  $\text{CCl}_4$ . When this step was followed by extraction from sulphuric acid solution with 5% DTDA in Varsol, it was found that complete separation of uranium and thorium from rare earths was obtained and that recovery of rare earths was virtually complete. It was necessary to include further separation steps in the procedure, to remove titanium and residual silica (which



TABLE 6

## Spectrographic Analysis of Ignited Precipitates Following Chemical Separation

Sample	Treatment	% Element in Precipitate (c)																		
		Ce	La	Y	Gd	Dy	Yb	Sm	Sc	Pb	Si	Fe	Al	Mg	Ca	Ba	Ti	Mn	U	Th
Synthetic No. 2: 10.2 g U <sub>3</sub> O <sub>8</sub> , 0.215 g ThO <sub>2</sub> , 0.0279 g La <sub>2</sub> O <sub>3</sub>	Extraction from sulphate solution with TIOA and 9D-178 - plus oxalate and ammonia precipitations.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<0.2	<0.2
Composite of Synthetics Nos. 3 and 4: 10.2 g U <sub>3</sub> O <sub>8</sub> , 0.24 g ThO <sub>2</sub> 0.0264 g Re <sub>2</sub> O <sub>3</sub>	Extraction from hydrochloric solution with TIOA - extraction from sulphate solution with DTDA - plus oxalate and ammonia precipitations.	P.C.	P.C.	2	3	1	0.1	3(a)	-	0.7	6	0.4(a)	0.4(b)	0.1(a)	0.5	<0.1	<0.1	-	0.9-N.D.	0.8(a)
Synthetic No. 5: 0.0264 g Re <sub>2</sub> O <sub>3</sub>	Oxalate and ammonia precipitations.	P.C.	P.C.	2	3	1	0.1	3(a)	-	0.7	4	0.4(a)	0.4(b)	0.2(a)	0.7	0.1	<0.1	-	N.D.	0.9(a)
Synthetic No. 6: 0.0279 g La <sub>2</sub> O <sub>3</sub>	Oxalate and ammonia precipitations.	-	P.C.	-	-	-	-	-	-	0.3	5	0.3	0.4	0.2	0.6	0.1	<0.1	<0.1	1	0.2
RE 3151 (Bicroft precipitate)	Regular procedure <sup>(1)</sup>	P.C.	15	7	5	2.5	2	3(a)	0.2	2	0.6	1	0.5	<0.1	-	<0.1	<0.1	-	-	-
RE 3151	Extraction from hydrochloric solution with TIOA - extraction from sulphate solution with DTDA - plus oxalate and ammonia precipitations	P.C.	15	7	3	3	1.5	2(a)	0.2	2.5	4	0.4(a)	0.4	<0.1	0.1	<0.1	0.15	<0.1	-	N.D.
RE 3151 (with mixed Re <sub>2</sub> O <sub>3</sub> added)	Extraction from hydrochloric solution with TIOA - extraction from sulphate solution with DTDA - plus oxalate and ammonia precipitations	P.C.	15	4	2.5	2	0.14	3	1	3	1(d)	0.7	0.4	0.1	-	0.1	0.9	-	-	-
RE 3152 (Pronto precipitate)	Regular procedure <sup>(1)</sup>	7.5	1.8	7.5	5	4	1	2(a)	3	8	3	12	15	0.4	0.4	0.5	N.D.	0.1	-	0.6(a)
RE 3152	Extraction from hydrochloric solution with TIOA - extraction from sulphate solution with DTDA - plus oxalate and ammonia precipitations	N.D.	6	9	3	5	2	N.D.	3	15	P.C.	2(a)	3	0.6	2	N.D.	2	0.15	-	N.D.
RE 3152 C (with mixed Re <sub>2</sub> O <sub>3</sub> added)	Extraction from hydrochloric solution with TIOA - extraction from sulphate solution with DTDA - plus oxalate and ammonia precipitations	P.C.	20	2	2.5	1.5	0.15	3	N.D.	0.6	1.5(d)	0.8	0.5	0.15	-	0.1	0.03	-	-	-

N.D. = Not detected. P.C. = Principal constituent. All results were semi-quantitative.

- Notes: (a) Identification not positive.  
 (b) Interference; results probably high.  
 (c) Indicated quantity of any other element was less than 0.1% of the precipitate.  
 (d) Relatively lower silica was found to be due to extra filtration before ammonia precipitation.

has a tendency to appear in the rare earth precipitate).

Recently, an arsenazo colorimetric procedure for the determination of rare earths has been applied in this Division in other work, (5) and it could considerably simplify the procedure. Yttrium will contribute to the rare earth colour with arsenazo and would be included as a rare earth by the procedure. A considerable amount of calcium and some magnesium could be tolerated in the colorimetric finish. The effect of titanium has not been tested here, but it would be expected to interfere. However, if titanium is absent, direct colorimetric determination of the rare earths plus yttrium, after the solvent extraction step, is feasible.

The chosen acidity for the TIOA extraction represents a level at which it is convenient to work, but conditions can be varied to meet particular requirements. Three obvious advantages of extracting with TIOA in hydrochloric acid medium, rather than sulphuric acid medium, are: 1) ease of sample solution; 2) elimination of the amine equilibration step for TIOA; and 3) separation from the rare earths of a number of additional contaminants, such as zirconium, iron, vanadium, and molybdenum.

It was thought desirable to use the amine DTDA rather than amine 9D-178 for thorium extraction, as the former amine gave higher extraction coefficients for thorium. Because of the danger of rare earth loss with DTDA, however, it was necessary to work at higher

concentrations of sulphuric acid than would be required with amine

9D-178.

### CONCLUSIONS

The procedure described in this report has been found to be satisfactory for the determination of small amounts of rare earths in high grade uranium products. It gives adequate elimination of many troublesome impurities, and produces a final rare earth precipitate in a reasonable time, requiring three days as compared with the five days of the regular procedure. Although the chlorination procedure is faster for individual samples, the simple apparatus of the outlined procedure is more suitable for handling a large number of samples.

### REFERENCES

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