The Extraction and Purification of Scandium.

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The extraction of scandium from wolframite residues and thortveitite is described. Final purification is effected by ion-exchange techniques which are approached by phase-distribution and acid–base-titration data. Hydrazine-*NN'*-diacetate solutions rapidly remove scandium from mixtures with the rare earths and thorium, and the separation thus achieved is superior to that with citrate or ethylenediamine-*NNN'N'*-tetra-acetate solutions.

THE extraction of scandium from its natural sources is hindered by the dearth of knowledge of scandium compounds and their reactions. Because of this lack there is little doubt that techniques used by early workers for the extraction and purification of scandium gave low recoveries of this relatively rare element.

Operations commonly recommended in the treatment of scandium-containing materials involve precipitation of the oxalate or hydroxide. The inefficiency of these procedures and the complications arising from their use are demonstrated in the two following papers.

The scandium employed in these studies was extracted from wolframite residues and thortveitite, being finally purified by ion-exchange techniques. This first paper records these initial operations.

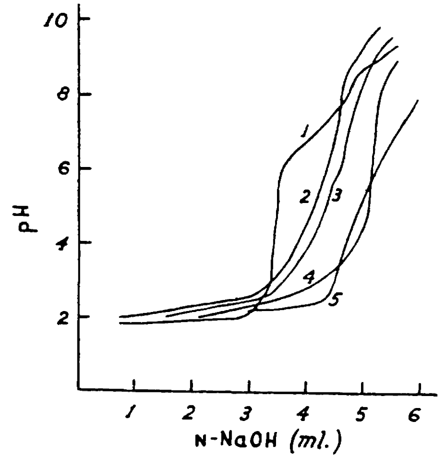
Preliminary Extractions.—Meyer (*Z. anorg. Chem.*, 1907, **60**, 134) and Sterba-Bohm (*Z. Elektrochem.*, 1914, **20**, 289) surveyed the extraction of scandium from ores, but, by use of radioactive scandium and monitoring the progress of extractions by the usual techniques (Vickery, unpublished work), several of the procedures recommended by the earlier workers have been found neither as complete nor as efficient as was once considered.

Conventional methods of decomposing siliceous ores generally involve attack by hydrochloric, sulphuric, or hydrofluoric acid. Attack by either of the first two acids generally yields a gelatinous residue of silica which occludes much scandium. This is avoided by using hydrofluoric acid, and the resulting fluorides are readily metathesised by alkali. However, as indicated in the following paper, alkali hydroxides effect at least partial dissolution of scandium and their use is preferably avoided. Acid attack on siliceous ores is generally an untidy procedure however, and Iya (*Compt. rend.*, 1953, **236**, 608) decomposed thortveitite by roasting the finely comminuted mineral with charcoal at 1800° to form carbides which were readily decomposed by dilute hydrochloric acid. Hartley and Wylie (*J. Soc. Chem. Ind.*, 1950, **69**, 1) and Hartley (*J. Appl. Chem.*, 1952, **2**, 24) recently prepared lanthanon chlorides from monazite by chlorination at 700—900° in the presence of carbon, and the possible application of a similar process to thortveitite possessed several attractive features. Scandium chloride sublimes at *ca.* 970° (Klemm *et al.*, *Z. anorg. Chem.*, 1923, **131**, 22 *et seq.*; Fischer *et al.*, *ibid.*, 1939, **242**, 161), and chlorination of thortveitite might well provide a rapid means of decomposing the ore and simultaneously concentrating the scandium by volatilisation. In the present work, however, it was sufficient to provide for the decomposition of thortveitite with the production of scandium in a soluble form. Details of the procedure adopted are given in the Experimental section; insufficient thortveitite was available for determination of the optimum conditions, and the attractive results obtained must be considered as fortuitous rather than designed.

After the commercial extraction of tungsten from some wolframites, the ferruginous residues may contain as much as 0·3% of Sc_2O_3 and it was from residues of this type that Meyer (*loc. cit.*) extracted the scandium on which was based his subsequent work on the element. Such wolframite residues are usually readily soluble in hydrochloric acid, but the presence of much iron in the resulting solution hinders recovery of the scandium. Precipitation of scandium oxalate from such solutions should never be attempted; it is never quantitative and, with iron, vanadium, manganese, and, possibly, uranium present, soluble oxalato-complexes are formed which further inhibit the precipitation of scandium. From such solutions, scandium is best precipitated as silicofluoride or by hydrofluoric acid after the addition, if necessary, of calcium or lanthanon salts to act as " carriers." Precipitated from hot solutions, the fluorides of the carrier and scandium settle well and are easily filtered or centrifuged off. The wet fluorides are readily decomposed with a minimum of concentrated sulphuric acid, and the sulphates thus obtained are ignited and the residues redissolved in hydrochloric acid for further purification.

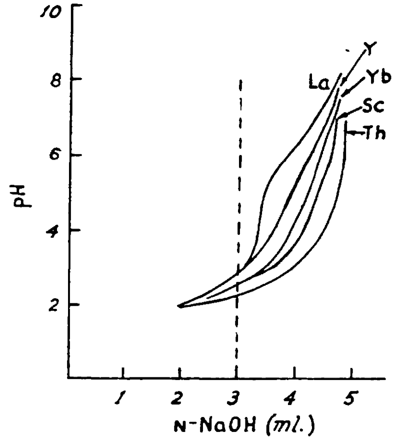
Preliminary Concentration.—Not infrequently, the chloride solutions obtained by the foregoing methods contain varying quantities of, *e.g.*, magnesium, aluminium, iron, calcium, barium, manganese, etc. The individual proportions of these elements may not be high, but the aggregate amount may be sufficient to affect adversely further operations unless their amounts are appreciably diminished. For this purpose precipitation of scandium as double tartrate is as effective as any other method and, although the procedure adopted here was not precisely that of Fischer *et al.* (*Z. analyt. Chem.*, 1951, **133**, 57) it gives excellent yields of scandium when the element is present in concentrations of >3 mg./ml. The double tartrate is readily decomposed by acids, so that a concentrated solution of scandium of *ca.* 80—90% purity was readily obtained.

FIG. 1. *Titration of scandium in polycarboxylate systems.*



1. Imda. 2, Trilo. 3, Enta. 4, Citrate. 5, Hyda. 2 × 10^{-6}M-Sc. 10^{-3}M-Acid.

FIG. 2. *Titration of rare earths and thorium in citrate systems.*



10^{-6}M-Rare earth. 10^{-3}M-Citrate.

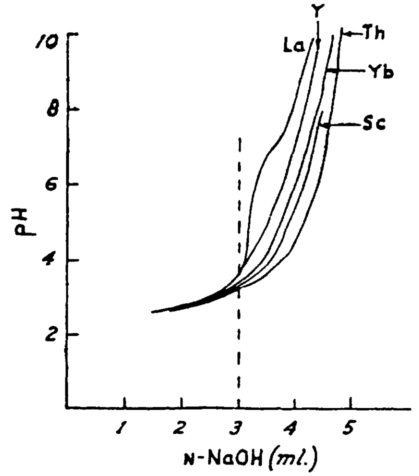
Purification by Ion-exchange.—Because of the known geogenetic association of scandium with the lanthanons, yttrium, and thorium, and the great similarities in the chemistry of these elements, it is inevitable that the final purification of scandium should be more closely concerned with systems containing these elements. Ion-exchange techniques would appear admirably suited for the treatment of such scandium-containing mixtures, but this application has been studied only by Radhakrishnar (*Analyt. Chim. Acta*, 1953, **8**, 140), Iya (*loc. cit.*), and Iya and Loriers (*Compt. rend.*, 1953, **237**, 1413).

Recent tendencies in ion-exchange studies are towards the use of eluants containing complex-forming anions other than citrate. Hydrazine-*NN'*-diacetic (hyda), nitrilotriacetic (trilo), and ethylenediamine-*NNN'N'*-tetra-acetic (enta) acid have been effectively employed in the ion-exchange separation of the lanthanons (Higgins and Baldwin, ORNL, 1951, 894; Fitch and Russell, *Canad. J. Chem.*, 1951, **29**, 363; *Analyt. Chem.*, 1951, **23**, 1469; Vickery *J.*, 1952, 4357; 1954, 1181; Spedding *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 612, 2557), and their use has now been examined in the separation and purification of scandium from thorium and the lanthanons.

Titration and Distribution Studies.—pH titrations of systems containing metal and complex-forming anions yield information of much application to ion-exchange separations. Titration curves are given in Fig. 1 for scandium solutions containing the acids citric, iminodiacetic (imda), hyda, trilo, and enta. Similar curves are given in Figs. 2 and 3 for systems of thorium, lanthanum, yttrium, ytterbium, and scandium with citric and enta acid.

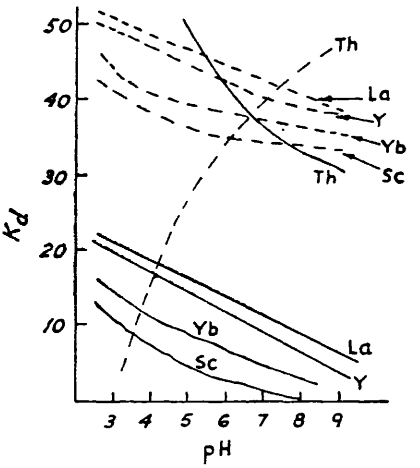
Qualitatively, the titration curves show that complex stability increases in the order La < Y < Yb < Sc < Th for the systems studied. Although stability constants for the complexes formed can be derived from the titration data, these are often less significant than the pH values at which the titration curves show greatest divergence from each other. These values of greatest divergence (symbolised here as ∂pH) represent the loci of greatest stability of the complexes formed, and hence are those at which ion exchange should be most selective in the systems studied. ∂pH values obtained are given in the Table. The narrow range between maximum and minimum values for each acid system shows the complexes formed by the metal ions and any one acid to be derived from similar anionic species. With the tervalent ions studied therefore, any variation in behaviour of the

FIG. 3. *Titration of rare earths and thorium in enta systems.*



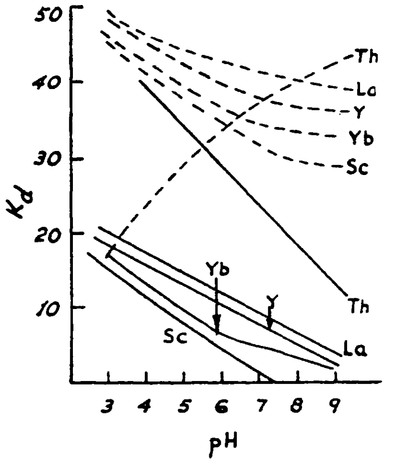
10^{-4}M-Rare earth. 10^{-3}M-Citrate.

FIG. 4. *Distribution coefficients* (K_d) *for enta systems.*



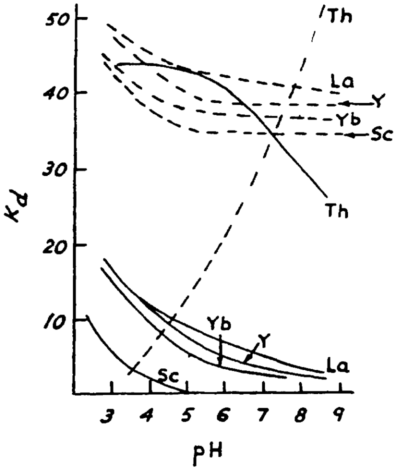
---- 0·1% Enta. ——— 1·0% Enta.

FIG. 5. *Distribution coefficients* (K_d) *for hyda systems.*



---- 0·1% Hyda. ——— 1·0% Hyda.

FIG. 6. *Distribution coefficients* (K_d) *for citrate systems.*



---- 0·1% Citrate. ——— 1·0% Citrate.

complexes formed must be attributed to variations in stability of the complexes and not to the formation of different anionic species. Variation of ionic species in solution is of great influence in ion-exchange studies but this point of variance does not here appear to arise, so that observations on phase distribution should yield very pertinent data.

Differential pH *values* (∂pH).

System	Citrate	Hyda	Enta
La–Y	5·3	7·5	6·5
Y–Yb	3·9	6·8	4·1
Yb–Sc	4·5	7·3	5·6
Sc–Th	4·5	6·9	5·3

Distribution coefficients for metal ions–Zeokarb 225 resin–eluant systems were determined at, and in the neighbourhood of, the ∂pH values. Plots of these K_d values against pH are shown in Figs. 4, 5, and 6 for enta, hyda, and citrate systems (for definitition of K_d see p. 250). Since distribution of an element between resin and eluant phases must be largely proportional to the degree of complex formation between metal ions and the eluant, it was reasonable to expect that maximum differences in K_d values would occur close to, or at, the ∂pH values, and except for the thorium–scandium values it was generally found to be so.

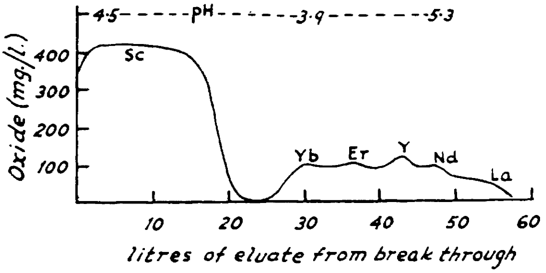


FIG. 7. *Elution with citrate.*

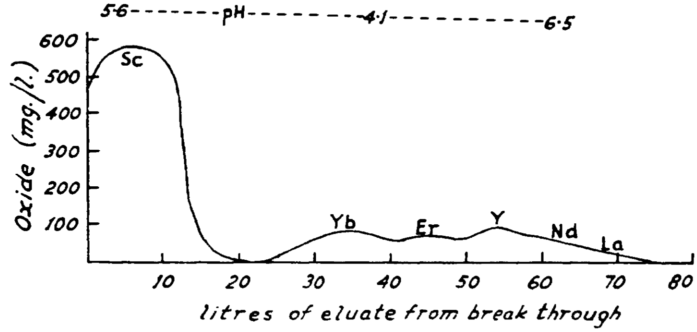


FIG. 8. *Elution with enta.*

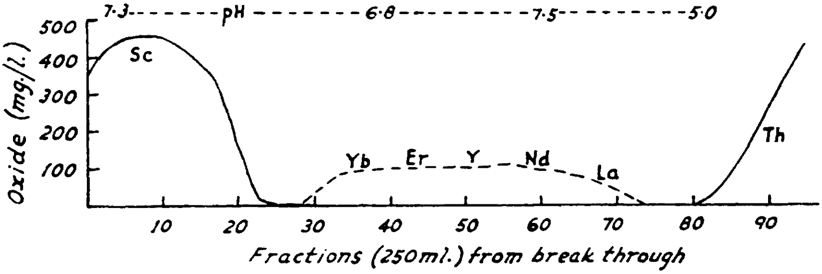
Distribution coefficients for the scandium–hyda systems appeared anomalous, but they were consistently confirmed and indicated that the stability of the scandium–hyda complex was much greater than those of the lanthanon complexes. This apparently anomalous behaviour of the scandium–hyda system has now been successfully exploited (see below).

Individual divergencies of K_d values in hyda and enta systems increased with the concentration of acid. In citrate systems this was reversed, so elution should be with 0·1% citrate or 1·0% amino-acid. Since however the sequential position of thorium at the lower eluant concentrations was the reverse of that at the higher, the latter were employed throughout at the possible sacrifice of a certain separational efficiency.

Resin Column Separations.—The influence upon resin-column operations of factors such as eluant flow rate, resin particle size, temperature, etc., have been fully studied by Spedding *et al.* (*J. Amer. Chem. Soc.*, 1947, **69**, 2769 *et seq.*) and require no further consideration here. If solely a result of simple metal-ion size and charge, the sequence of elution of a thorium–rare earth system from a resin column should be Sc, Yb, Y, La, Th. This has been confirmed now and in the work of Iya and Loriers (*loc. cit.*). Figs. 7, 8, and 9 illustrate the separations achieved with citrate, enta, and hyda eluants respectively. Eluant acidities were adjusted throughout the runs to the ∂pH values appropriate to the elements breaking through from the column. Flow rates of citrate and hyda eluants were chosen somewhat arbitrarily but, as previous (unpublished) work had shown high flow rates to be advantageous with enta eluants, separations with this reagent were conducted at the maximum flow rate possible. Enta eluants again appeared superior to those containing citrate, although the higher flow rates rendered the elution curves less steep. The anomalous behaviour of scandium–hyda complexes shown in titration and phase-distribution data is emphasised in elutions with hyda solutions. Whereas with this eluant no exceptional separations were obtained within the lanthanon series scandium was readily and cleanly removed from the system.

In large-scale work on lanthanon systems containing scandium the latter tends to collect, together with ytterbium and thorium, at the tail of fractionated systems. Scandium and thorium are then eliminated from the ytterbium either during separation of the latter with sodium amalgam or during the prior preparation of the acetates, scandium and thorium forming insoluble basic salts. The ion-exchange separation of a simple thorium–scandium system was therefore examined. It is accomplished very easily by using citrate, hyda (Fig. 10), or enta eluants.

FIG. 9. *Elution with hyda.*



Recovery of Scandium.—Insufficient was known about how quantitative was precipitation of scandium by alkali hydroxide, fluoride, phosphate, etc., in the presence of complex-forming anions. Unpublished radiochemical studies indicated, however, that precipitation by these ions was rarely complete, so the procedure adopted for recovery of scandium from the eluted fractions simply involved evaporation to dryness twice in the presence of nitric acid, followed by ignition of the residue at *ca.* 900°.

EXPERIMENTAL

Norwegian thortveitite (200 g.) was obtained in small hand-picked lumps. After being ground to 200 mesh, a portion gave analyses Ln_2O_3 12·1% and Sc_2O_3 33·8%, *i.e.*, close to the most recent results for Norwegian thortveitite by Marble and Glass (*Amer. Mineral.*, 1942, **27**, 696). The wolframite residues (4 kg. available) were of unknown, but possible Nigerian, origin and had been found to contain 0·08% of Sc_2O_3.

The individual lanthanons employed had been derived from various sources during past years and had been purified by various methods to >99% purity. The thorium was of B.D.H. laboratory reagent grade, and the scandium employed for the titration and distribution studies was "Specpure." Other general chemicals were of "AnalaR" grade. Enta acid was the "Sequestrene" material supplied by the Geigy Co. Trilo acid was kindly supplied by Dr. J. K. Marsh. Hyda acid was prepared and purified as recorded by Vickery (*J.*, 1954, 385). Imda acid was prepared from hyda acid by Bailey and Read's method (*J. Amer. Chem. Soc.*, 1914, **36**, 1747).

pH titrations were followed through a glass–calomel electrode system on a Cambridge electrometer. Distribution coefficients were determined by equilibrating the exchange resin

(Zeo-Karb 225; Permutit Co.) with the appropriate solutions during 24—48 hr. with continuous shaking, then evaporating the mother-liquors to dryness, and igniting and weighing the residue. The resin was also ignited and the ash weighed for check data. K_d values were then obtained from the equation $K_d = (M_s/M_L)(V/M)$, where M_s and M_L are fractions of the cation in the resin and liquid phases respectively, V = volume of solution, and M = mass of resin.

Chlorination of Thortveitite.—The simple furnace employed for chlorination was arranged horizontally and rotated on its axis. A Vitreosil tube (18″ × 1¼″) was fitted with internal baffles of ⅛″-diam. silica rod fused to the main tube 1″ from each end. The tube was mounted inside a platinum-wound tube-furnace, with inlet and outlet tubes for chlorine provided by silica tubing penetrating rubber bungs at each end of the main tube. The entry tube for chlorine was fitted with a rotating adaptor, and the main tube was rotated at 8 r.p.m. by the friction drive of a rubber band encircling the rubber bung at the entry end and attached to a small, geared-down, electric motor.

The finely comminuted thortveitite was thoroghly mixed with an equal weight of wood charcoal and hand-granulated with the addition of a small volume of 10% dextrin solution. 75-g. quantities of the granules thus obtained were charged into the furnace tube and chlorinated for 4 hr. at 800—850° with 250 ml. of chlorine per hr. Insufficient material was available for a critical survey of factors influencing efficienty but, in the six charges treated, temperature was varied from 800° to 850°, chlorine flow-rate from 150 to 250 ml./min. (*ca.* 0·45—0·75 g./min.), *i.e.*, 2·2—3·3 times the theoretical quantity, and the time of reaction was reduced from 4½ to 3 hr., all without manifestly affecting the quantity of scandium chloride produced. Each charge, after chlorination, was separately leached with 200 ml. of 1% hydrochloric acid, filtered from carbon, silica, etc., evaporated to a syrup, and diluted to 250 ml. 10 ml. of each extract were taken for determination of scandium and lanthanon contents which, with the mild variations introduced in treatment, remained remarkably constant. Each extraction of the equivalent of 37 g. of thortveitite yielded Sc_2O_3 12·3 ± 0·1 g. and Ln_2O_3 4·3 ± 0·1 g., *i.e.*, average recoveries of 98·3 and 95·9% respectively. After analysis the solutions were combined and retained for further treatment.

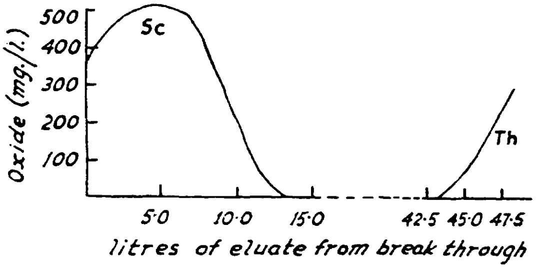


FIG. 10. *Elution of scandium–thorium with hyda at* pH 7·0.

The wolframite residues were received in a fine state of sub-division and required no further comminution. Treated in 800-g. quantities, these residues were sifted into 2·5 l. of 50% v/v hydrochloric acid at *ca.* 75° with continuous stirring. Digestion was carried out for 90 min., whereafter the slurry was allowed to settle and was then centrifuged. The mother-liquor was first decanted, then filtered off. The extracted solutions were individually evaporated to *ca.* 500 ml., combined, and then further evaporated to *ca.* 1500 ml. Lanthanum chloride (equiv. to 10 g. of La_2O_3) was added to the solution, and sulphur dioxide was passed in to reduce tervalent iron. The pH of the solution was adjusted to 5·2 and concentrated hydrofluoric acid was slowly added with constant stirring until no further precipitate appeared. The pH was then 3·4 and some 35 ml. of acid had been added. After the mixture had been kept overnight the mother-liquor was first decanted, then filtered, from the precipitated fluorides which, after being washed twice by decantation, were digested with boiling 30% sulphuric acid (200 ml.) for 30 min. and the solution was then evaporated. The residue was ignited to oxide at 1000°.

The final weight of mixed oxides was 14·4 g., so that, with allowance for the 10 g. of La_2O_3 added, a recovery of 4·4 g. from the wolframite had been obtained. This is greater than expected from the original analysis, but the final oxide was grossly impure and undoubtedly recovery of scandium had not been complete. An optimistic approximation of scandium recovery would be *ca.* 2·5 g., *i.e.*, 75—80%. The recovered oxides were redissolved in dilute hydrochloric acid, and the solution obtained added to that from the thortveitite.

To the mixed solutions (derived from thortveitite and wolframite) was added tartaric acid (250 g.), the whole was warmed to *ca.* 60°, and precipitation effected by the addition of ammonia solution to increase the pH to *ca.* 7.

The thick slurry was immediately filtered off at the pump and washed with 5% ammonium tartrate solution (1 l.). After drying, the double tartrate was ignited at 900° in varying portions. The final combined oxides (85 g.) were obviously impure, and their solution in hydrochloric acid showed strong spectral absorption lines of the lanthanons when examined with a hand-spectroscope. This chloride solution was then purified by ion-exchange.

Except for the change in resin from Dowex 50 to Zeo-Karb 225, the resin columns used were identical in construction with those previously described (Vickery, *loc. cit.*). Fractions eluted by citrate and hyda were collected at 250 ml./hr., and those eluted by enta at 1 l./hr. Each eluted fraction was evaporated to dryness, and when a mineral residue appeared it was redissolved in hydrochloric acid and held for further examination. The first fractions were treated with ammonium tartrate for detection and determination of scandium. Elution of the lanthanons and yttrium was followed spectrophotometrically as far as possible.

Initial elutions were carried out on 30 ml. of the impure scandium solution containing 5 g. of solids, *i.e.*, *ca.* 3·5 g. of Sc_2O_3. When the efficiency of hyda elution and applicability of the K_d and pH data had been confirmed, three resin columns were allocated for elutions with hyda, and one each retained for comparative citrate and enta elutions. In all cases the aliquot part taken of initial solutions was increased to 60 ml., *i.e.*, 10 g. of solids equiv. to *ca.* 7·0 g. of Sc_2O_3.

For observation of the ease of separating thorium from scandium, the final 20 ml. of the impure scandium solution were mixed with 40 ml. of 20% thorium chloride solution, and the mixture eluted from the resin bed with 1% hyda solution. All fractions were examined for thorium by additions of iodate. The results obtained are shown in Fig. 9. To confirm this ease of separation in simple scandium–thorium systems 5 g. of pure scandium oxide from the final hyda elutions were converted into chloride and mixed with 10 g. of thorium chloride, and the whole was eluted from a resin column with 1% hyda solution at pH 7. Fig. 10 records the results.

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