601. *Some Reactions of Scandium.*

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The efficiency of several precipitation and extraction reactions of scandium has been investigated by radioactive-isotope techniques. The lack of a specific, quantitative precipitant is manifest.

The solubilities of scandium hydroxide and oxalate, and the influence thereon of ammonium salts have been confirmed. The ineffectiveness of both precipitations for recovery of scandium is also confirmed. Precipitation of scandium as the potassium double fluoride or by disodium hydrogen phosphate is shown to give good recoveries of scandium but the suggested value of precipitation as pyrophosphate has not been fully confirmed.

The solubility of potassium scandium sulphate has been determined radiometrically, and precipitation of scandium as organic basic found to be an inefficient mode of recovery. Precipitation of scandium as the ammonium double tartrate is quantitative at scandium concentrations greater than 50 mg. of Sc_2O_3 per ml. Precipitation of thorium as iodate successfully separates this element from scandium even in the presence of high concentrations of lanthanons.

Solvent-extraction of scandium complexes has been briefly examined and extraction of the oxine chelate by chloroform or the acetylacetone chelate by ethyl acetate gives quantitative recovery in one operation. Such extractions are, however, less specific than that of scandium thiocyanate by ether which, in four extractions, gives 98·5% recovery.

The application of the reactions studied to extraction of scandium from ores, and its purification, are briefly considered.

Excellent separations of scandium from thorium and the lanthanons have been obtained by ion-exchange techniques [1,2,3] but difficulty was encountered in recovering the purified scandium from the eluted fractions. Methods commonly accepted as affording quantitative recovery of scandium were found to give, in fact, only incomplete precipitation under optimum conditions which were themselves sometimes very critical (cf. Fischer and Bock [4]). This incomplete recovery, and the dearth of chemical information on scandium, are greatly emphasized when attempts are made to extract scandium from such minerals as davidite [5] in which the low scandium content and the complexity of the mineral render recovery of the scandium almost fortuitous.

In an attempt to find a firmer basis for investigations on scandium chemistry, simple precipitation reactions have been studied by radiochemical techniques. This work now shows, not only the lack of a specific, quantitative precipitant for scandium, but also the dubious quality of any analytical data for scandium based on conventional gravimetric

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[1] Vickery, *J.*, 1955, 245.

[2] Rhadhakrishnar, *Analyt. Chim. Acta*, 1953, **8**, 140.

[3] Iya and Lorier, *Compt. rend.*, 1953, **236**, 608; **237**, 1413.

[4] Fischer and Bock, *Z. anorg. Chem.*, 1942, **249**, 146.

[5] Vickery, *Austral. J. Sci.*, 1953, **16**, 113.

procedures. In the present experiments the distribution of scandium between the various phases has been determined by the isotope dilution technique with the β–γ-active ^{46}Sc isotope as tracer. Table 1 gives the figures for percentage precipitation based on radiometric comparison of the original solution and the mother-liquor.

TABLE 1. *Scandium (%) precipitated under optimum conditions.*

Precipitant	Mg. of Sc_2O_3 per ml.					
	1	5	10	50	75	100
NaOH	80	90	—	98	98	—
KOH	80	—	100	—	—	—
NH_4OH	60	69	—	82	—	85
Na_2CO_3	Nil	Nil	10	—	—	16
K_2CO_3	50	—	72	—	85	—
$(NH_4)_2CO_3$	Nil	Nil	Nil	10	—	12
$H_2C_2O_4$	Nil	12·5	27	—	37	52
$Na_2C_2O_4$	Nil	—	—	25	—	61
$K_2C_2O_4$	Nil	—	20	—	—	43
$(NH_4)_2C_2O_4$	Nil	Nil	Nil	—	16	—
HF	90·5	—	95	94	—	96
NaF	35	42	—	55	—	72
KF	86	—	—	90	92	92
NH_4F	Nil	Nil	Nil	—	—	—
H_3PO_4	Nil	—	—	—	—	Nil
NaH_2PO_4	90	90	—	95	—	97
Na_2HPO_4	99	—	100	100	—	100
Na_3PO_4	53	—	76	—	82	84
$K_2H_2P_2O_7$	95	—	97	—	99	—
$Na_2H_2P_2O_7$	96	—	—	98	—	99
Cocarboxylase	93	93	—	98	—	99
Phytin	99	100	—	100	—	100
Na_2SO_4	Nil	—	—	—	Nil	—*
K_2SO_4	66	—	73	—	81	—*
$(NH_4)_2SO_4$	Nil	Nil	—	Nil	—	Nil*
AcOH	Nil	Nil	32	—	—	63
NaOAc	66	70	—	74	—	72
NH_4OAc	Nil	—	Nil	—	Nil	—
Tartaric acid	Nil	—	50	—	63	—
Na K tartrate	Nil	—	—	Nil	—	—
$(NH_4)_2$ tartrate	81	92	—	96	99	—
Citric acid	—	30	—	39	—	42
KIO_3	Nil	Nil	—	—	—	Nil
$Na_2B_4O_7$	93·5	—	—	99	—	99
Tannin	85	—	86	—	90	—
Oxine	85	93	—	99·3	—	—
Alizarin	89	91	99	—	—	100

* In the presence of mixed lanthanons.

TABLE 2. *Precipitation of* $Sc(OH)_3$ *in presence of* NH_4Cl (*concn.*, 50 *mg. of* Sc_2O_3 *per ml.*).

NH_4Cl concn. (mg./ml.)	5	15	25	50
Pptn. (%) by NaOH	96	85	79	63
,, KOH	95	87	75	60
,, aq. NH_3	89	75	62	45

TABLE 3. *Inhibition of* $Sc(OH)_3$ *precipitation* (50 *mg. of* Sc_2O_3 *per ml.*).

Hydroxy-acid concn. (%)	1	5	15	30
Pptn. (%) by NaOH (citrate)	80	52	27	15
,, ,, (tartrate)	86	49	22	19

Hydroxide Precipitation.—Earlier work[6] showed that, because of the formation of scandate ions, precipitation of scandium from solutions of its salts by hydroxyl ions was very incomplete. This has been confirmed and more precise determination made of the extent

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[6] Vickery, *J.*, 1955, 251.

of precipitation under the optimum conditions previously found. Results are incorporated in Table 1. The influence of ammonium ions on precipitation of scandium hydroxide by alkali hydroxides has again been examined and has yielded the data given in Table 2.

The extent to which citric and tartaric acid inhibit precipitation of scandium hydroxide is shown in Table **3**. With increasing concentration of hydroxy-acid, the scandium precipitate became less gelatinous and more granular. This indication of the formation of basic precipitates renders unlikely the prevention, by citric or tartaric acid, of the precipitation of scandium by alkali hydroxides. The special case of precipitation by ammonia solution in the presence of tartaric acid is considered below.

Carbonate Precipitation.—Meyer and Speter [7] claimed quantitative precipitation of scandium as the double carbonate, but this was disputed by Sterba-Bohm [8] and by Fischer and Bock.[4] The present results show conclusively the incompleteness of this precipitation. Little [9] quoted Crookes as having prepared $Sc_2(CO_3)_3,12H_2O$ by direct precipitation with alkali carbonate, but Sterba-Bohm [8] was unable to confirm this. More recently, Pokras [10] was likewise unable to prepare the normal carbonate by simple precipitation, or further by hydrolysis of the trichloroacetate. Indeed, by analogy with the lanthanons and aluminium, scandium could not be precipitated from solution as a simple carbonate on the addition of alkali carbonate.

Turbidimetric titrations employed in the hydroxide systems [6] were not carried out on these carbonate systems, but some evidence for dissolution of the precipitates in excess of precipitant was obtained by adding a large excess of alkali carbonate, filtering the mixture, and gradually acidifying the filtrate. Only where sodium or ammonium carbonate was used was any dissolution found; double carbonate formation must be expected to some extent, but then the behaviour of systems containing potassium carbonate becomes anomalous. Yet similar anomalous behaviour is found in sulphate systems (see below). The use of carbonate-free ammonia to precipitate scandium hydroxide has shown that the presence of ammonium carbonate cannot be the sole reason for incomplete precipitation of the hydroxide. This is emphasized by the low degree of precipitation by sodium carbonate. Since the carbonate compounds of yttrium and the heavy lanthanons are readily hydrolysed, scandium carbonate compounds should be expected to be similarly unstable. Fischer and Bock [4] have shown that scandium hydroxide is quite soluble in carbonate solutions, so that the rapid hydrolysis of a scandium carbonato-compound could well be the reason for the solubility of such a precipitate in excess of carbonate used as precipitant.

Oxalate Precipitations.—Meyer and Wirth [11] early observed the incomplete precipitation of scandium by alkali oxalates and this was, to a large extent, confirmed by Sterba-Bohm and Skramovsky [12] and by Fischer and Bock.[4] Complex formation in scandium–oxalate systems was shown by Vickery [13] to account for this incomplete precipitation and the deleterious effect of ammonium ions on precipitation of scandium oxalate was demonstrated. In addition, current studies have confirmed the water solubilities reported for scandium oxalate. Klein (personal communication) obtained 194 mg./l. for the solubility of freshly prepared scandium oxalate hexahydrate in water but found the solubility to decrease when the moist salt was equilibrated with a fresh sample of water: hydrolysis to a less soluble basic salt may thus be possible. In spite of this absolute solubility of scandium oxalate, we have consistently been unable to detect, by oxalate precipitation, scandium at a concentration of less than 1·5 g./l. As shown in Table 1 recovery of scandium by oxalate precipitation is always poor and the influence of the ammonium ion on recovery is clear.

Although recovery of scandium by simple precipitation as oxalate must be considered of dubious value, the use of the lanthanons as " carriers " considerably aids recovery when relatively large amounts are present. The following results show the precipitation of

[7] Meyer and Winter, with Speter, *Z. anorg. Chem.*, 1910, **67**, 398.

[8] Sterba-Bohm, *Casopis Ceskoslov. Lekarn*, 1937, **17**, 301.

[9] Little, in Newton Friend's " Textbook of Inorganic Chemistry," Chas. Griffin, London, 1921, Vol. IV, p. 213.

[10] Pokras, Thesis, Illinois, 1952.

[11] Meyer and Wirth, *Z. anorg. Chem.*, 1914, **86**, 287; **87**, 2.

[12] Sterba-Bohm and Skramovsky, *Coll. Czech. Chem. Comm.*, 1929, **1**, 1.

[13] Vickery, *J.*, 1955, 255.

scandium by oxalic acid at pH 5 in the presence of increasing quantities of lanthanon oxides:

Ratio, $Ln_2O_3 : Sc_2O_3$	0·5 : 1	1 : 1	5 : 1	10 : 1	50 : 1	100 : 1	500 : 1
Recovery (%) of Sc_2O_3	30	31	35	57	72	89	99

(Initial concn. of Sc_2O_3: 50 mg./ml.)

On the other hand, precipitation of scandium oxalate may be reduced or even prohibited by the use of calcium as a "hold-back carrier." A smaller amount of calcium is required to inhibit precipitation of scandium than of lanthanon to expedite it:

Ratio, $CaO : Sc_2O_3$	0·3 : 1	0·5 : 1	1 : 1	6 : 1	10 : 1
Recovery (%) of Sc_2O_3	16	10	3	Nil *	Nil *

* In these experiments a precipitate of calcium oxalate was obtained which contained no scandium.

Fluoride Precipitation.—The solubility of scandium fluoride in ammonium fluoride solutions was first observed qualitatively by Meyer and Hauser.[14] Fischer and Bock[4] have since found ammonium fluoride to be of dubious value in separating scandium from thorium and the lanthanons. The lack of precipitation from simple scandium solutions by ammonium fluoride is confirmed by the data in Table 1. Sodium and potassium fluoride yield precipitates with scandium solutions, the potassium salt, as in carbonate and sulphate systems, affording the higher yields.

Freshly precipitated fluorides appear somewhat soluble in excess of hydrofluoric acid. The influence upon fluoride precipitation of pH and concentration of alkali fluoride is shown by the figures for recovery from a cold solution initially containing 50 mg. of Sc_2O_3 per ml.:

pH	5·0	4·2	3·5	3·0	2·4	1·8
Recovery (%)	90	82	61	56	49	36

pH was adjusted by the addition of potassium hydroxide, and precipitation was effected by the addition of hydrofluoric acid (105% theor.). The precipitates were not analysed, but it is considered probable that those obtained at pH $>3·5$ were largely double fluorides.

Although lanthanum fluoride is much used as a "carrier" in radiochemical studies, the work of Fischer and Bock[4] indicated that thorium and the heavy lanthanon fluorides would be only partially successful as such agents in systems containing scandium. It is now found that lanthanum fluoride is not very effective as a carrier for scandium and does not greatly increase recoveries above those normally encountered. Calcium, however, is extremely useful in this respect:

Ratio, CaO(or La_2O_3) : Sc_2O_3	1 : 5	1 : 2	1 : 1	2 : 1	5 : 1
Recovery (%) with La_2O_3	94	93	95	96	98
Recovery (%) with CaO	100	100	—	100	—

(Initial Sc_2O_3 concn.: 50 mg./ml. at pH 5)

Phosphate Precipitation.—The precipitation of scandium as a phosphate cannot be considered specific, but it is apparent from Table 1 that disodium hydrogen phosphate gives more complete recovery than any of the other precipitants examined except phytin. The degree of precipitation may well be related to the pH attained by the phosphate solutions: thus, orthophosphoric acid at pH $<3·0$ gave no precipitate; the monosodium salt solution had pH 4·0 and gave approximately 90% recovery of scandium; the disodium salt gave 100% recovery at pH 7·5; the trisodium salt at pH 9·5 gave only 60% recovery. This decrease in precipitation at high pH may be due to sequestration since it is difficult to consider the disodium salt as having special properties specific towards scandium.

Beck[15] has shown the pyrophosphate ion, particularly in association with an organic

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[14] Meyer and Hauser, "Die Analyse der seltenen Erden," F. Enke, Stuttgart, 1912.

[15] Beck, *Mikrochem. Mikrochim. Acta*, 1948, **34**, 62; 1949, **34**, 282; 1951, **36/37**, 790; *Analyt. Chim. Acta*, 1950, **4**, 21.

moiety such as inositol or aneurine, to be of particular value for the precipitation of scandium. Strong claims were made for the insolubility of the scandium complexes with these compounds but we have been unable fully to confirm Beck's work. The pyrophosphates do not afford as complete precipitation as disodium hydrogen phosphate, and the pyrophosphate precipitates are much affected by conditions of precipitation. They are soluble in excess of precipitant, ammonia solution, and hydrochloric acid. Optimum pH of pyrophosphate precipitation appears to be *ca.* 6·5, but even then the precipitate is readily hydrolysed, since, when it is shaken with water, phosphate but no scandium appears in solution. Precipitation of scandium with phytin gives recoveries equivalent to those obtained with disodium phosphate.

Double-sulphate Precipitation.—The insolubility of potassium scandium sulphate (cf. the double sulphates with sodium and ammonium) is well shown in Table 1. Despite this anomalous similarity in behaviour of the double potassium salt to that of the lighter lanthanons, potassium scandium sulphate is precipitated more completely in the presence of heavy lanthanons than in that of the lighter group:

50 mg. Sc_2O_3 + 10 mg. La_2O_3–Sm_2O_3 in 5 ml.: 75% pptn. by K_2SO_4
50 mg. Sc_2O_3 + 100 mg. Y_2O_3–Yb_2O_3 in 5 ml.: 87% pptn. by K_2SO_4

Recalculating the data of Crookes,[16] Fischer and Bock[4] obtained a value of 1·5 g. of Sc_2O_3 per l. for the equivalent solubility of potassium scandium sulphate in saturated potassium sulphate solution. Radiometric determinations of solubility have now given the much lower value 116 mg. More work appears necessary in this field since our results on the *precipitation* of potassium scandium sulphate indicate *ca.* 20 g. of Sc_2O_3 per l. to remain in solution. However, much supersaturation and possibly hydrolysis must be expected in such systems.

Precipitation of Basic Carboxylates.—Precipitation of scandium as basic acetate and tartrate has been studied, the former more specifically as a technique of thorium separation. In acid solutions basic scandium acetate is not precipitated at a concentration less than *ca.* 7 mg. of Sc_2O_3 per ml. The reason for this is obscure since hydrolysis would be expected to occur more readily at low concentrations. The basic acetate is not precipitated from solutions containing *ca.* 20% of ammonium acetate: this is a further example of the influence of ammonium ions on scandium precipitation. By comparison, however, precipitation of scandium by hydrolysis with sodium acetate is as ineffective as precipitation as oxalate. Although thorium may not itself be completely precipitated by the basic acetate method[17] it acts as an effective carrier for scandium. In an experiment in which 25 mg. of Sc_2O_3 and 50 mg. of ThO_2 were hydrolysed in 25 ml. by boiling with sodium acetate, 98·5% of the scandium was precipitated within 10 minutes, while at a similar concentration in the absence of thorium only 66% of the scandium was precipitated after 30 minutes' boiling.

Precipitation as basic tartrate appears of little value for quantitative recovery of scandium although higher recoveries are obtained than by the basic acetate process. The addition of Rochelle salt to scandium solutions yields no precipitate, but the efficiency of scandium precipitation as the double ammonium tartrate affords some confirmation of the enthusiasm of Fischer and Bock[4] and Fischer *et al.*[18] for this mode of scandium recovery. With strict adherence to the conditions specified by Fischer *et al.* recovery of scandium from solutions more concentrated than *ca.* 50 mg./ml. may be considered excellent. Below this concentration recovery deteriorates somewhat. Generally, precipitation of scandium by ammonium tartrate may be considered almost as effective as precipitation as hydroxide or phosphate and certainly more selective.

Scandium salts are hydrolysed in citrate solutions but the degree of precipitation is lower than for acetate or tartrate solutions.

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[16] Crookes, *Z. anorg. Chem.*, 1909, **61**, 361.
[17] Moeller, Schweitzer, and Starr, *Chem. Rev.*, 1948, **42**, 63.
[18] Fischer, Steinhauser and Hohmann, with Bock and Borchers, *Z. analyt. Chem.*, 1951, **133**, 57.

Iodate Precipitations.—Scandium is not precipitated from its simple solutions by potassium iodate, and even in the presence of large amounts of thorium scandium remains wholly in solution when the thorium is precipitated by the iodate procedure. When lanthanons are also present in a solution containing scandium and thorium, much lanthanon accompanies the thorium iodate precipitate, but scandium is not co-precipitated until a $Ln_2O_3 : Sc_2O_3$ ratio of 750 : 1 is reached:

$ThO_2 : Sc_2O_3$	2	10	100	5	10	10	20	100
$Ln_2O_3 : Sc_2O_3$	—	—	—	1	70	100	750	1000
Sc_2O_3 pptd. (%) ...	Nil	Nil	Nil	Nil	Nil	Nil	4	10

For the separation of thorium and scandium, iodate precipitation appears to be one of the best procedures available.

Borate Precipitation.—Rankama and Sahama [19] considered that precipitation of scandium as borate might explain its occurrence in certain marine sediments. The insolubility of scandium borate is certainly well marked but the precipitation is unlikely to be specific.

Tannin Precipitation.—This does not occur below pH 5 and attains its maximum in the pH range 6·5—8·0. Even at high concentrations, however, precipitation is incomplete.

Oxine Precipitation.—Pokras and Bernays [20] commented favourably on the completeness of precipitation of scandium with oxine, but radiometric studies have not completely confirmed this. Maximum recoveries of only 99·3% have been obtained by precipitation under the conditions specified by the American workers. The solvent extraction of oxine chelates has been practised by several workers and we have found that, while only 85% of the scandium is precipitated by oxine at low concentrations, all of it can be extracted as the chelate compound by chloroform. Neither precipitation nor extraction can be considered specific, but the latter might well be valuable for the reclamation of small quantities of scandium from simple solutions.

Alizarin Precipitation.—The reaction between scandium and sodium alizarin-3-sulphonate was first reported by Beck [21] who recommended its analytical use. The reaction and precipitation were not claimed to be specific, scandium being accompanied by any thorium present. Since the reaction is carried out in the presence of ammonium acetate and acetic acid at *ca.* 95° the precipitation of some basic acetate may occur. This is to some extent indicated by the diminution of recoveries when the Sc_2O_3 concentration is below *ca.* 7 mg./ml., the concentration below which basic scandium acetate is not precipitated (see above).

Liquid–liquid Extraction Methods.—Four extraction procedures only have been examined. Chloroform extraction of the oxine complex has already been referred to. None of the other three is always entirely specific for scandium.

Extraction of thiocyanate. Fischer and Bock [4] introduced the ethereal extraction of scandium thiocyanate and considered it a method by which the maximum separational effect could be obtained with a minimum of effort. Losses of scandium of the order of 5—10% were recorded for single extractions. We have now found somewhat higher losses in single extraction, and overall recovery after four extractions is still less than is attained by some gravimetric methods. However, the near-specificity of the extraction makes amends for the slight overall loss. One concentration only of scandium was examined (50 mg./ml.) but Fischer and Bock's results show extraction to diminish only slightly at low concentrations of scandium. The pH of the scandium solution was 4·5 and extraction was with an equal volume of ether, 3 minutes' shaking being taken as standard. The following results are the average of four series of experiments under the same conditions. An ethereal solution (E^1) was shaken with water, giving an aqueous

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[19] Rankama and Sahama, "Geochemistry," Univ. Chicago Press, Chicago, 1950.

[20] Pokras and Bernays, *J. Amer. Chem. Soc.*, 1951, **73**, 7; 1953, **75**, 1254; *Analyt. Chem.*, 1951, **23**, 757.

[21] Beck, *Mikrochem.*, 1939, **27**, 47.

phase (A^1); shaking A^1 with ether gives the solution E^2, which with water gives A^2, etc.:

Solution:	$E^1 \rightarrow$	$A^1 \rightarrow$	$E^2 \rightarrow$	$A^2 \rightarrow$	$E^3 \rightarrow$	$A^3 \rightarrow$	$E^4 \rightarrow$	A^4
Proportional activity:	81	19	11	8	3·8	4·2	2·7	1·3

The overall recovery in the ether was 98·5%.

Extraction of quinalizarin complex. That scandium, like beryllium, magnesium, and the lanthanons, gives a blue lake with quinalizarin was noted by Komarovsky and Korenmann [22] and Beck.[23] Beck also found [15] that this lake could be extracted with *iso*pentyl alcohol or pentyl acetate. Photometry of the extracted lake was claimed to permit determination of as little as 0·1 μg. of Sc_2O_3. While confirming the lake formation we have been unable to obtain, in one operation, more than *ca.* 3% extraction of scandium quinalizarin derivative into either solvent. After five extractions with an equal volume of the alcohol of a scandium solution at a concentration of 50 mg. of Sc_2O_3 per ml., only 8% extraction was obtained.

Extraction of acetylacetone complexes. Except possibly by adjustment of the pH of the solution acetylacetone can be expected to exhibit little selectivity towards chelation of scandium. Nevertheless, for comparison with extractions of the oxine, thiocyanate, and quinalizarin methods, the scandium acetylacetone complex was extracted by ethyl and pentyl acetate and light petroleum with the following results: Ethyl acetate, 100% extraction; pentyl acetate, 51%; light petroleum, 95%; all for one extraction by an equal volume of solvent of a solution containing 50 mg. of Sc_2O_3 per ml. at pH 4·5. In spite of its lack of specificity, ethyl acetate extraction of the scandium acetylacetone complex clearly attains more effective recovery of scandium than any other solvent extraction procedure examined.

Extraction and Recovery of Scandium.—From the foregoing studies, several conclusions can be drawn relating to the extraction of scandium from ores and its purification. The solubility of scandium in alkali hydroxide and carbonate solution is of significance in the extraction of the tungsten ores and residues normally regarded as potential sources of scandium.[1, 24] Treatment of such materials involves, at some stage, extraction of tungsten as an alkali tungstate. It is now clear that unless the extraction is done at pH $<$*ca.* 8·0, much scandium will be extracted with the tungsten and lost. Again, where silicate ores are decomposed by hydrofluoric acid, scandium will be found in both the solution and the insoluble fluoride residue unless the pH is adjusted to near neutrality with potassium hydroxide.

If scandium is reclaimed from solutions, the absence of ammonium salts is essential, and oxalate precipitation should rarely be used. Non-specificity renders double fluoride precipitation, or precipitation with disodium hydrogen phosphate, applicable only to relatively pure solutions for which purpose their use might well become standard procedure. The last traces of phosphate can be easily removed from scandium only by ion-exchange techniques.

The difficulties encountered with fluoride and phosphate precipitations in highly ferruginous systems are not, however, met when scandium can be precipitated as the double tartrate. Although this precipitation is less efficient at low concentrations, its application to ferruginous systems would be as effective as precipitation by potassium sulphate in the presence of lanthanons. The alternative use of potassium and sodium or ammonium sulphate is indicated as a suitable means of concentrating scandium from the lanthanons and thorium. For final elimination of thorium and the lanthanons, ion-exchange techniques are admirable but, where they are not applied, the precipitation of thorium as iodate and reclamation of scandium from the filtrate with disodium hydrogen phosphate or ammonium tartrate appears the most adequate procedure.

While solvent extraction of the oxine or acetylacetone compounds requires essentially pure solutions, ethereal extraction of the thiocyanate is of wide application in the absence

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[22] Komarovsky and Korenmann, *Z. analyt. Chem.*, 1933, **94**, 247.
[23] Beck, *Mikrochim. Acta*, 1937, **2**, 9.
[24] Meyer, *Z. anorg. Chem.*, 1907, **60**, 134.

of iron. In mildly ferruginous systems much iron may be initially removed by the Rothe ether-extraction technique, thiocyanate added, and the scandium extracted by a second ether-treatment.

EXPERIMENTAL

The progress and efficiency of all the procedures examined was determined radiometrically. The ^{46}Sc isotope was monitored through a Dekatron tube scaler. The general procedure of monitoring, after determination of background radiation, was to obtain an initial, liquid, count on 10 ml. of the (Sc + Sc*) solution, add the precipitant under the appropriate conditions, centrifuge the precipitate, and obtain a proportionate count on the mother-liquor. Results are given to the nearest whole number. Sufficient radioactive scandium was included in each experiment to give an initial activity of *ca.* 3000 counts min.$^{-1}$ per 10 ml. Counting periods of 3—5 min. were employed on initial solutions; for supernatant liquids, etc., the counting time was prolonged where necessary to give at least 8000 counts.

The inactive scandium employed had been extracted from wolframite residues and thortveitite and purified by ion exchange to >99·9% purity.[1]

Other reagents were of analytical reagent purity. Except where otherwise indicated, precipitations were carried out with dilute reagent added to the scandium solution at *ca.* 95° for 10—15 min., which was allowed to cool to room temperature, and centrifuged. 10 ml. of the supernatant liquor were taken for counting.

Hydroxide precipitation was effected by the slow addition at 95° of 10% alkali hydroxide to pH 8·0—8·5. Subsequent operations were as above.

Although the oxalate precipitations reported were carried out at 95° some secondary precipitations were made at room temperatures. There was no significant variation in the recoveries. Precipitation at low temperatures did, however, affect the degree of hydration of the oxalate obtained.[13]

For oxalate co-precipitation, mixed lanthanons were employed rather than individuals in order more closely to simulate the conditions of occurrence of scandium. The lanthanon mixture was a synthetic one with the approximate percentage composition in terms of oxides: La 15; Ce 20; Pr 9; Nd 21; Y 15; Er 9; Yb 8.

Double-sulphate precipitations were carried out at 95° by the addition of solid alkali sulphate. Attempts to overcome the solubilities of the sodium and ammomium salts by adding sodium chloride [25] were unsuccessful. In the sodium sulphate systems at the highest concentrations of scandium the solution was concentrated to the formation of sodium sulphate crystals in the hot solution but scandium was not precipitated. The solubility of scandium sodium sulphate is at least greater than the equivalent of 200 g. of Sc_2O_3 per l. Solubility determinations on the double potassium salt were made by equilibrating the dried salt with water by shaking for 24—36 hr. The determinations were made in duplicate and approach to equilibrium was followed radiometrically. Final determinations of solubility were made through radiometry of the final supernatant liquor after centrifugation.

Precipitation of thorium iodate was at *ca.* 50° on solutions containing 30% of concentrated nitric acid, by the addition of an equal volume of 15% aqueous potassium iodate in 50% (v/v) nitric acid. The solution and precipitate were set aside for 45 min., then centrifuged, and an aliquot part of the supernatant liquor pipetted for radiometry. It is known that the degree of lanthanon occlusion with the $Th(IO_3)_4$ precipitate can be readily reduced by washing with iodate solution and undoubtedly such washing would remove much of the scandium occluded at the higher lanthanon ratios. The lanthanon mixture employed was also used in oxalate studies.

In the solvent extraction experiments, equal volumes of organic and aqueous phases were shaken together for at least 3 min. The phases were then carefully separated, the organic phase evaporated to dryness, and the residue dissolved in dilute acid for radiometry.

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[25] Marsh, *Nature*, 1949, **163**, 998.