for which ΔF is 1.7 kcal.,[18-20] we find ΔF equal to 15.0 kcal. for the reaction

$$U^{+4} + 2H_2O = UO_2^{+2} + 2H^+ + H_2 \quad (23)$$

Fontana[21] has determined the heat of reaction (23) to be 32.9 kcal.; whence ΔS is 60 cal./deg. Assuming the same entropy change for the reaction

$$2UO_2^+ + H_2 = 6H^+ + 2U^{+4} + 4H_2O \quad (24)$$

as for the analogous neptunium reaction and adding to (23), we obtain ΔS for reaction (20) equal to -62 cal./deg. From the data of Kritchevsky and Hindman[18] and Fontana[21] for the reaction

$$U^{+3} + H^+ = U^{+4} + {}^1/_2H_2 \quad (25)$$

ΔF is -14.5 kcal. and ΔH is -23.7 kcal. Combining these values with the entropy changes for reactions (20) and (24) we obtain ΔS equal to -32 cal./deg. for reaction (21). Combination of (20) and (21) yields 122 cal./deg. for the entropy change of the reaction

$$3U^{+4} + 2H_2O = 2U^{+3} + UO_2^{+2} + 4H^+ \quad (26)$$

The reaction entropies are summarized in Table VI. More recent determinations[7,10,21,22] of some of the heats of reactions measured by Evans[14] suggest that the ΔH of reaction (11) may be larger than 77.8 kcal. A larger value for the heat of the reaction would shift the calculated plutonium entropy changes in the direction of those for the uranium and neptunium reactions. Comparison of results for the disproportionation of the +4 states indicates that the assumption of equal entropy changes for analogous reactions is an approximation. The entropy differences appear to occur mainly in the oxygenated ions of the +6 state. From the relation

$$(\partial \Delta F/\partial T)_{P,N} = -\Delta S \quad (27)$$

and the approximate entropy changes of Table VI, we may predict with respect to disproportionation that the stability of the X^{+4} ion will decrease and the stability of the XO_2^+ ion will increase with increasing temperature. The predicted trends agree with an observation that Pu(V) appeared to be more stable at higher temperature.[23]

TABLE VI

SUMMARY OF ENTROPY CHANGES FOR DISPROPORTIONATION REACTIONS IN 1 MOLAL PERCHLORATE SOLUTIONS AT 25°

Values in parentheses calculated by assuming ΔS equal to -61 cal./deg. for the reaction $XO_2^+ + {}^1/_2H_2 + 3H^+ = X^{+4} + 2H_2O$.

Reaction	ΔS, cal./deg. U	Np	Pu
$3X^{+4} + 2H_2O = 2X^{+3} + XO_2^{+2} + 4H^+$	122	130	116
$2XO_2^+ + 4H^+ = XO_2^{+2} + X^{+4} + 2H_2O$	(−62)	−55	(−67)
$3XO_2^+ + 4H^+ = 2XO_2^{+2} + X^{+3} + 2H_2O$	(−32)	−17	(−43)

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Separation of Carrier-free Scandium from a Calcium Target

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Scandium can be separated carrier-free from calcium by filtration of a solution containing Sc of the order 10^{-9} M or less and calcium about 10^{-3} M. The effects of a number of variables on the adsorption of Sc by filter paper have been determined. Eighty per cent. of the Sc present can be recovered in one hour.

Introduction

A sample which is to be used in the measurement of the β-spectrum of a positron or negatron emitter must have a high specific activity in order that the results be accurate. The presence of stable atoms produces questionable data because these atoms absorb part of the energy of the β-particle before it emerges from the surface of the sample. If the isotope to be studied is separated with the addition of an isotopic carrier, the sample will necessarily contain many stable atoms and will have a relatively low specific activity, whereas when a carrier-free separation is performed, the specific activity of the sample will be relatively high.

It has been known that when a solution is filtered through filter paper some of the ions present are adsorbed by the paper in considerable quantity. When a solution with a scandium concentration of the order of 10^{-9} gram atom/liter, or less, and calcium about 10^{-3} gram atom/liter is filtered, an appreciable amount of scandium is adsorbed by the paper, while the calcium passes through with the filtrate. Many factors, *e.g.*, *p*H, salt concentration, etc., affect the per cent. scandium adsorbed. The effects of a number of variables on the adsorption have been determined, and a procedure for separating scandium carrier-free in quantities of 10^{-9} gram atom or less from a calcium target has been devised.

Procedure.—Several samples of commercially pure calcium carbonate, each containing 25–50 mg., were bombarded with protons in The Ohio State University cyclotron for one hour periods. The target material was picked out of the holder, covered with triple distilled water in a 50-ml. beaker, dissolved by the addition of 10 drops of concentrated hydrochloric acid and evaporated to dryness. Solution in hydrochloric acid and evaporation to dryness were repeated twice more to ensure the removal of radioactive fluorine. A tracer solution was prepared by dissolving the residue, which included scandium and calcium chloride from the target material, in 0.01 *N* hydrochloric acid.

Samples were prepared, composed of known amounts of tracer solution, triple distilled water and hydrochloric acid. These were titrated to desired *p*H values with 0.1 *N* ammonium hydroxide and filtered through Schleicher and Schuell Blue Ribbon filter paper, except for one sample which was filtered through White Ribbon paper. The diameters of the papers were 4.8 cm. or 6 cm., the same size being used throughout an experiment. Each paper was washed before the filtration with boiling triple distilled water and dilute ammonium chloride solution (about 10^{-4} *M*) of the same *p*H as that of the solution to be filtered. The papers were washed with 20 ml. of dilute ammonium chloride solution of the same *p*H as the samples which had been filtered. The amount of scandium adsorbed by the papers was determined by holding papers and funnels under a mica end-window Geiger–Müller tube and counting or by removing the scandium from the papers with hot 6 *N* hydrochloric acid, evaporating to dryness, and counting.

Results and Discussion

The effect of *p*H on the amount of scandium retained by filter paper is shown in Fig. 1 and Table I. The per cent. scandium adsorbed, given by curves A and B, was calculated from the initial activity of the sample and the amount remaining on the filter paper, as determined by holding papers and funnels under a Geiger tube window and counting. The per cent. scandium adsorbed, indicated by curve C, was obtained from the initial activity of the sample and the amount removed from the paper with hot 6 *N* hydrochloric acid. Correction was made for the adsorption of scandium by glassware. Curve C is the most accurate and curves A and B are to be considered preliminary results. Maximum adsorption occurs at about *p*H 8.5.

TABLE I

EFFECT OF *p*H ON PER CENT. SCANDIUM RETAINED BY FILTER PAPER

A		B		C	
*p*H	Retained, %	*p*H	Retained, %	*p*H	Retained, %
4.02	13.1	4.00	38.4	6.05	64.3
5.02	16.6	7.18	39.9	7.00	77.6
6.62	28.2	7.55	41.0	7.40	78.3
7.26	39.3	7.87	52.2	7.70	83.5
7.50	62.4	8.30	62.2	8.50	85.7
7.52	55.6	9.16	17.4	9.00	81.1
8.00	38.0				

The influence of "coagulation time," *i.e.*, the time between titration and filtration, was determined by titrating two samples to *p*H 8.01 and filtering one within five minutes and the other 4.3 hours later. The per cent. scandium adsorbed was 67.4% in the former case and 63.5% in the latter. Apparently the coagulation time has little influence on the adsorption, up to 4.3 hours.

Two samples of *p*H 7.8 were filtered through 6 cm. papers. One paper was washed with 20 ml. of wash solution and the other with 100 ml. The amounts of scandium retained after the washing were 53.2 and 37.5%, respectively, and it is evident that prolonged washing removes scandium from the paper.

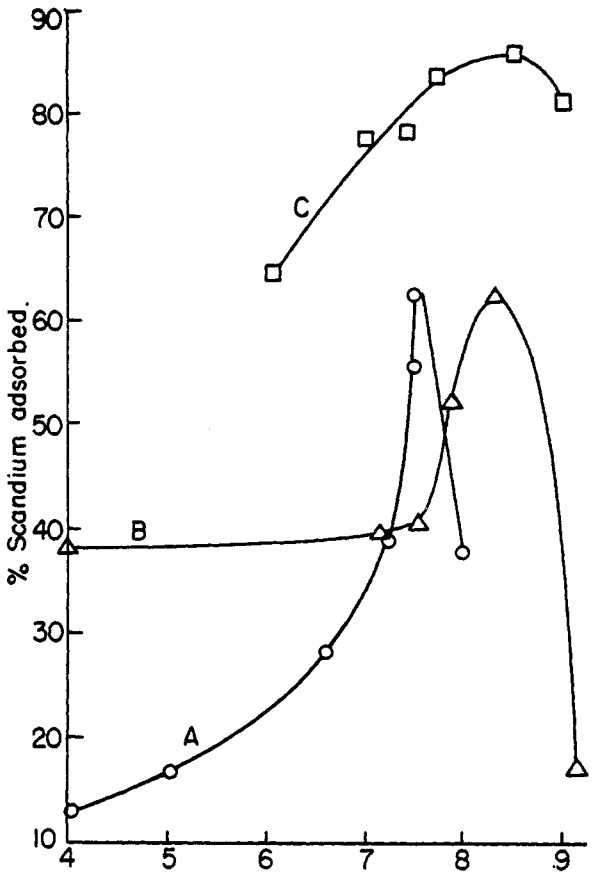

Fig. 1.—Effect of *p*H on adsorption of scandium by filter paper.

A sample of *p*H 8.50 was filtered through three 6 cm. filter papers held in funnels one above the other, and the papers were washed. The *p*H of the solution changed during filtration from 8.50 to 8.31. The scandium adhering to the papers was removed with hot 6 *N* hydrochloric acid, and after these solutions were evaporated to dryness, the activities were measured. The percentages adsorbed by the top, middle and bottom papers were 69.0, 21.6 and 4.3%, respectively. Corrections have been made for losses on glassware. It is to be noted that practically all the scandium can be removed in two filtrations.

Three samples which contained tracer in the ratio 1:2:3 were titrated to *p*H 8.50 and filtered. The amounts of scandium adsorbed were 72.9, 76.3 and 75.5%, respectively, after correction for loss on glassware. There is apparently very little effect caused by the concentration of the scandium within the range studied. This experiment shows also that the tracer solution is of high chemical purity, because if other trivalent ions were present, their interference would result in a noticeable change in the per cent. scandium adsorbed as the concentration of tracer increases.

The influence of ammonium chloride on the adsorption of scandium by filter paper is illus-

trated in Table II. The data imply that the presence of ammonium chloride in a tracer solution, which contains the target material and hydrochloric acid, does not have a great effect on the per cent. scandium adsorbed, within the range studied.

TABLE II

EFFECT OF AMMONIUM CHLORIDE ON ADSORPTION OF SCANDIUM BY FILTER PAPER

NH_4Cl, M	Sc adsorbed, %	NH_4Cl, M	Sc adsorbed, %
0.003	65.0	0.101	69.4
.009	72.9	.168	69.3

One sample of pH 8.50 was filtered through a Schleicher and Schuell White Ribbon filter paper instead of a Blue Ribbon paper. The scandium adsorbed was 25.0%, a markedly lower value than that adsorbed by Blue Ribbon paper. This probably occurs because the White Ribbon paper permits a greater speed of filtration, thus allowing a shorter time for adsorption to take place. The time required for filtration of 25 ml. of distilled water through Blue Ribbon paper is 2.5 times that required for filtration through White Ribbon paper.

Summary

The carrier-free separation of tracer amounts of scandium from calcium by filtration of a solution of their ions through filter paper has been studied. The influences of a number of variables on the per cent. scandium retained by the paper are as follows. Greatest adsorption occurs between pH 7 and 9 with a maximum at about 8.5. An increase in the time between titration and filtration of a sample, up to 4 hours, does not result in a greater percentage removal of scandium from solution. Excessive washing of the filter paper to which scandium has adhered lowers the per cent. scandium retained. Two filtrations of a sample are all that are necessary to separate over 90% of the scandium passing through the filter papers. The concentration of scandium in the tracer solution has little effect on the percentage adsorbed by filter paper, within the range studied. All scandium concentrations were of the order of 10^{-9} M or less. When a scandium tracer solution contains the original target material in 0.01 N hydrochloric acid, the effect of additional ammonium chloride, up to 0.168 M on the per cent. scandium adsorbed is negligible.

The following procedure for separation of carrier-free scandium from a calcium carbonate target is proposed:

"Cover target material with distilled water in a small beaker, and dissolve the material in a minimum amount of hydrochloric acid. Evaporate to dryness, and repeat the solution and evaporation twice more to remove radioactive fluorine. Dissolve residue in 25–35 ml. of 0.001–0.01 N hydrochloric acid, and titrate to pH 8.5 with 0.1 N ammonium hydroxide. Filter the solution through two 6 cm. Schleicher and Schuell Blue Ribbon filter papers in separate funnels one above the other, the pH of the papers having been adjusted previously to 8.5. Wash papers with 20–30 ml. of dilute ammonium chloride solution, the pH of which is 8.5. Remove the scandium from the filter papers separately by treating each with two 10-ml. portions of 3–6 N hydrochloric acid. The fraction of scandium recovered from the target solution is about 80%. Time required for separation is 1 hr."

This scheme has been used with success in the preparation of calcium-free, carrier-free samples of scandium for use in the β-spectrometer. As an example of the radioactive purity obtained, see Fig. 2. It shows the decay of scandium which was separated from a common calcium carbonate target that had been bombarded with α-particles in the cyclotron. The predominant activity is scandium-43, and the minor activity is scandium-47. No other activities were observed. The decay was followed until the sample had only 8 counts/min. above background.

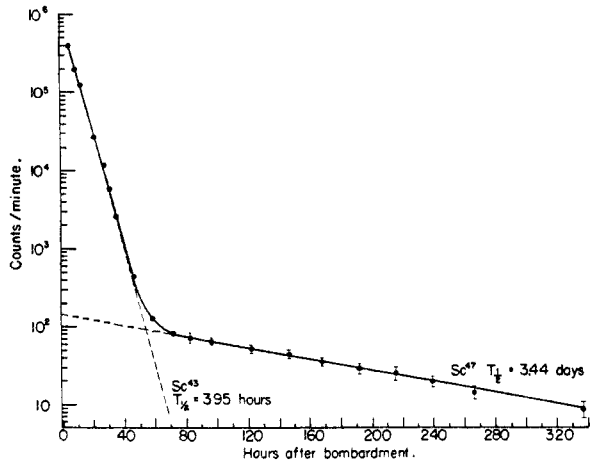

Fig. 2.—Decay of $Sc^{43,47}$.

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